UNIVERSITY OF SOUTHERN QUEENSLAND

A FOUNDATIONAL INVESTIGATION OF VINYL ESTER / CENOSPHERE COMPOSITE MATERIALS FOR CIVIL AND STRUCTURAL ENGINEERING

A Dissertation Submitted by

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ABSTRACT

With the increasing use of fibre reinforced polymer (FRP) composites in civil engineering structures, there is a growing realisation of the need to develop new structural systems which can utilise the unique characteristics of these materials in a more efficient and economical manner. In many instances this will require the development of new materials tailored to address the unique performance and economic parameters of mainstream construction.

Over recent years, researchers at the University of Southern Queensland have pioneered the use of a new type of particulate filled polymer core material which greatly improves the robustness and cost effectiveness of FRP structural systems. These composite materials are composed of small hollow spherical fillers (microspheres) in a thermosetting polymer matrix. Initial research into these materials, including their feasibility in prototype structural elements, have shown these materials to have major potential for widespread application in structural composite systems.

One of the most promising classes of these materials investigated to date are vinyl ester / cenosphere composites, which utilise cenospheres derived from fly ash in a vinyl ester matrix. Previously reported studies into these materials have been restricted to initial surveys of material behaviour which sought to identify key parameters in achieving desired performance outcomes in the composite.

This dissertation presents the first in-depth investigation of these materials specifically as a core material option for civil infrastructure applications. The particular focus of this work is on the relationship of the vinyl ester matrix to the characteristics of the resulting composite. Several key matrix parameters were identified and assessed as to their influence on cure characteristics, fabrication operations, mechanical properties and the retention of such properties under elevated service temperatures.

The outcomes of this work have significantly improved the understanding of matrix influences on the behaviour of these composite systems and have been drawn together to provide a number of recommendations on the application of this new technology to new structural systems.

CERTIFICATION OF DISSERTATION

I certify that the ideas, experimental work, results, analyses, software and conclusions reported in this dissertation are entirely my own effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any other award, except where otherwise acknowledged.

Signature of Candidate Date

Endorsement

Signature of Supervisor Date

Signature of Supervisor Date

Signature of Supervisor Date

ASSOCIATED PUBLICATIONS

Davey, S.W., **Van Erp, G.M.** and **Marsh, R.**, 2001, Fibre Composite Bridge Decks – An Alternative Approach. *Composites Part A*, Vol 3A, No 9, pp. 1339-1343.

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"*That Which Does Not Kill Us Makes Us Stronger*"

- Friedrich Nietzsche

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CHAPTER 1.

INTRODUCTION

1.1. INTRODUCTION

The focus of this PhD thesis is the investigation of vinyl ester / cenosphere composite materials for civil and structural engineering applications. This research builds on earlier preliminary investigations into particulate composite materials made at the University of Southern Queensland (USQ). This study is the first specifically directed at examining the behaviour of vinyl ester / cenosphere composite systems in terms of both their processing characteristics and end performance.

1.2. BACKGROUND

While fibre reinforced polymer (FRP) composites offer significant potential for application in civil engineering structures, their widespread acceptance into this industry continues to be hampered by their high cost relative to traditional building materials. In order to offset the high cost of FRPs, it is necessary to utilise these materials in unique ways that extract maximum performance while minimising fabrication costs.

In 1998 researchers at the University of Southern Queensland developed a new type of structural beam concept which used high performance FRP laminate flanges placed on either side of a new type of particulate filled resin (PFR) core [1]. This modified version of traditional sandwich construction allows for more efficient use of the FRP laminates by increasing their distance from the neutral axis of the section. The use of what is normally a lower cost core material (compared to the laminates) for the majority of the cross-section helps to reduce the overall cost of the section.

The PFR core material was developed as an alternative to tradition core material options which were seen to be either too expensive or lack the robustness required in civil engineering applications [2]. This stems from the fact that most traditional core materials have historically been designed for use in the marine or aerospace industries where cost considerations are secondary to weight reduction. Sometimes referred to as syntactic foam, the new PFR materials can provide significantly higher structural and functional performance compared to traditional polymeric foams, whilst retaining a competitive cost structure [2].

These materials can also be designed to give good flow characteristics in their uncured form, enabling mass casting fabrication techniques [3]. The potential of mass casting both in terms of freedom-of-form and cost have been well demonstrated in concrete construction and it is thought that these types of benefits may also be seen in composite structures constructed using casting techniques.

Since the development of the initial beam concept, researchers at USQ have investigated their application in a range of additional structural elements including:

- Girders [4]
- Floor slabs [5]
- Bridges [6], and
- Trusses [7].

Testing of these elements has confirmed the strong potential for application of particulate composite core materials in primary structural elements. Development of these element concepts is ongoing.

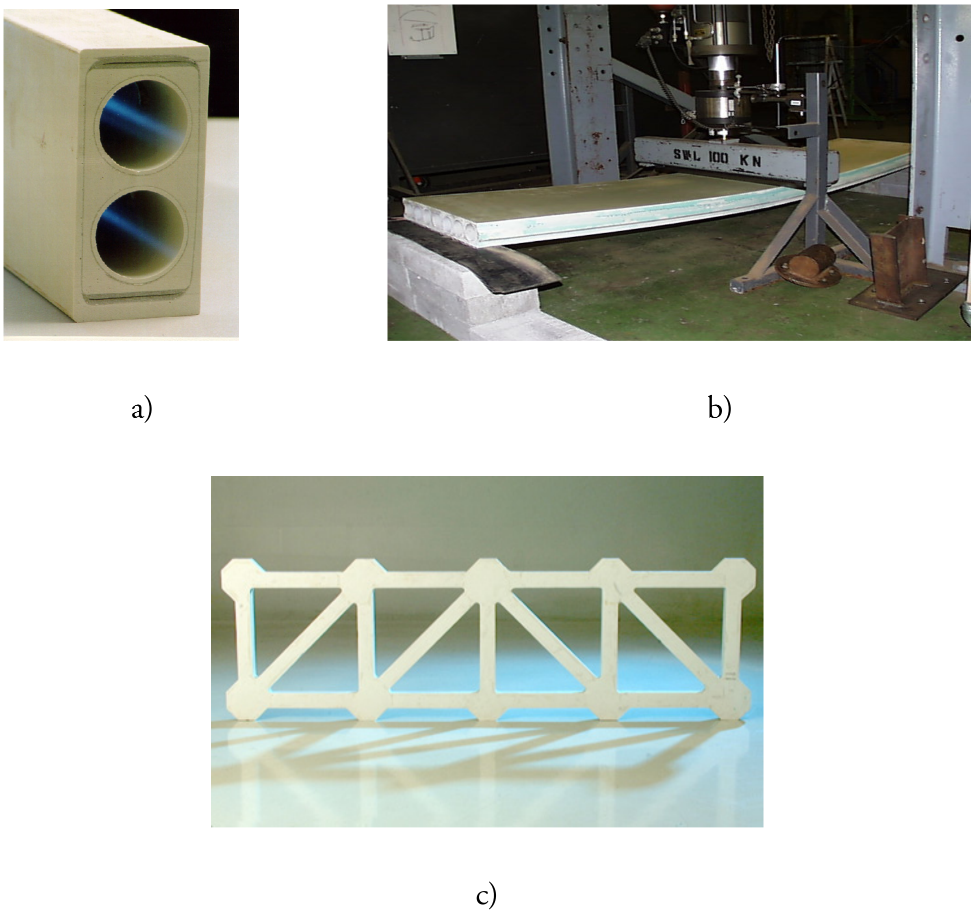

Figure 1.1 Prototype structural elements fabricated utilising resin / cenosphere composite materials: a) beam, b) bridge deck and c) truss.

While initial developments in these new core materials appear extremely promising, there is need to develop a more comprehensive understanding of their behaviour to properly develop the technology for the mainstream civil engineering industry. In particular, there is a need to improve understanding of constituent influences on the behaviour of a resulting composite.

1.3. AIMS AND OBJECTIVES

It is the broad aim of this project to improve understanding of the behaviour of vinyl ester / cenosphere composites as applicable to civil and structural engineering applications. Within this aim the following specific objectives were adopted:

1. Review the current status of particulate composite research and the constituent material options for vinyl ester / cenosphere composite systems as core materials for civil and structural engineering applications.

2. Identify key parameters to aid in the evaluation of constituent materials for vinyl ester / cenosphere composites for civil and structural engineering applications.

3. Develop a fundamental understanding of the relationships between constituent materials and the behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites.

4. Improve the understanding of the relationships between the processing characteristics of the materials and performance of the end-product vinyl ester / cenosphere composites.

1.4. SCOPE AND LIMITATIONS

Limited previous research on these topics means that this investigation had to be constrained to the most prominent outstanding issues that could be identified by the author. The established objectives were therefore constrained by the following:

- The experimental components of this research are quite involved, with the planning, preparation and testing stages requiring a considerable investment of time, effort and capital. With all of these investments at a premium, generally only single sample sets were used for experiments to identify key behaviours with conclusions based on these experiments.
- The foundational nature of this PhD study means that the focus was on determining the existence (or lack) of relationships rather than their precise nature. Over 500 individual tests were completed examining only a limited number of parameters. This strategic investigation provides the platform to undertake a large number of subsequent detailed investigations. Consequently caution has been exercised in the analysis and interpretation of data because much more testing will be required to establish and verify detailed relationships.
- The experimental techniques applied within this dissertation have been restricted to those permitted by the facilities available at the University of Southern Queensland.

It is noted that the utilisation of some techniques (eg: Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA)) only became possible late in the research.

1.5. STRUCTURE OF DISSERTATION

Chapter 2 reviews the current status of particulate composite research and examines in detail the formulation options for vinyl ester / cenosphere composite systems. It identifies a range of constituent parameters, and evaluates their potential for application based on manufacturer-supplied data and research previously reported in the literature. At its conclusion, the study draws together several of the most promising constituent material options as recommended systems for further study.

Using constituent materials based on the recommendations made in Chapter 2, Chapter 3 investigates the cure behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites. Thermal analysis techniques were utilised to examine the influences of the constituents on the cure kinetics and network properties.

The processing characteristics of vinyl ester / cenosphere composites are examined in Chapter 4. The viscosity and shrinkage behaviour of the composite systems were identified as important parameters influencing the processing of particulate composite systems. The relative influences of the constituent materials on these properties are investigated.

Chapter 5 assesses the mechanical properties of vinyl ester / cenosphere composites through an experimental characterisation program examining capacity and stiffness behaviour.

The transition behaviour is investigated in Chapter 6, examining the mechanical performance of vinyl ester matrix systems and vinyl ester / cenosphere composites under elevated temperatures. An alternative approach to characterising the temperature performance is suggested.

Chapter 7 provides a summary of the results of the previous chapters, presenting the major findings of the completed research. A number of key areas identified for further research are also presented.

1.6. REFERENCES

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CHAPTER 2.

A REVIEW OF CONSTITUENT OPTIONS FOR VINYL ESTER / CENOSPHERE COMPOSITES

2.1. INTRODUCTION

There are a plethora of materials available that can be combined to produce particulate composite systems. This wide range of materials offers considerable flexibility to the engineer to optimise material combinations for the requirements of a specific application, service environment or available fabrication technique. All of the alternative types of constituent materials have their own specific properties that in some way contribute to the characteristics of the resultant composite. Developing an understanding of the issues relating to the relative constituents, properties of the range of material options and their subsequent impact on the characteristics of a particulate composite is of considerable importance.

This Chapter firstly introduces the basics of particulate composite systems and assesses the status of research in this field. The focus then shifts to a review of constituent material options for vinyl ester / cenosphere composite systems, the subject of this dissertation. Vinyl ester (VE) resins are detailed including modifications to basic grades which offer improved performance in response to industry requirements. The materials for curing vinyl ester resins and cenosphere fillers are also outlined. The Chapter concludes with a discussion on the selection of appropriate constituent material combinations for vinyl ester / cenosphere composites, culminating in the recommendation of materials for subsequent experimental investigations discussed in the remainder of this dissertation.

2.2. COMPOSITION BASICS

Particulate composite systems are formed by the combination of a series of discrete particles and a continuous binder phase referred to as the matrix. The discontinuous particle phase may be formed by the combination of one or more particulate materials.

For the composite systems considered in this current study, the particles are small, hollow spheres (microspheres) of either glass or ceramic material. The ceramic spheres, which are the primary focus of this study, are derived from fly ash and are commonly referred to as cenospheres. Cenospheres are comprised largely of silica and alumina and are a naturally occurring by-product of the burning process at coal-fired power stations [1].

The matrix materials considered in this current study are thermosetting polymer systems. These materials are typically two-part chemical systems which react when mixed to form the final thermoset polymer network. The primary matrix chemistry considered is that of vinyl esters, which feature an acrylated epoxy oligomer crosslinked with styrene monomer.

2.3. REVIEW OF PREVIOUS RESEARCH

Initial research at USQ into the characteristics of particulate composite core materials was reported by Ayers and Van Erp [2,3,4]. These preliminary studies examined a range of different composite formulations based on epoxy and vinyl ester resins with glass and ceramic microspheres. The aim of this work was to identify basic relationships between the constituent materials and resulting characteristics of the particulate composite.

Parameters studied included the volumetric ratio of microspheres to matrix resin, the type and size of microsphere particles, and the mechanical properties of the matrix.

A subsequent study by Ayers and Van Erp [5] built on the outcomes of this original work, presenting a more detailed examination of constituent influences on the stiffness characteristics of microsphere composite systems. The study included experimental work with several different epoxy and vinyl ester resins and included both glass and ceramic microspheres. The outcomes of this work indicated that the use of cenospheres (ceramic microspheres) in these systems provided beneficial increases in particulate composite stiffness, while offering a more advantageous cost structure compared with glass microspheres. It was also concluded that due to an apparent convergence in properties at high filler loadings, the use of high performance matrix systems may be unwarranted at the type of loading levels considered cost effective for civil engineering applications. A consequence of this finding is that vinyl ester / cenosphere composites would appear to present a more viable combination for civil engineering applications.

Recently, Ayers and Van Erp [6] have published a further study on constituent influences, this time on the specific characteristics of vinyl ester / cenosphere systems. The vinyl ester resins used in this study were standard commercial grades commonly used within the Australian composites industry. The study examined several matrix parameters and the flexural properties of the resulting composites. While highlighting several key trends observed in experimental work the primary conclusion of the study was that further work was needed to improve the understanding of constituent influences.

A number of other authors have reported studies on the behaviour of particulate composite systems using hollow microspheres [7,8,9]. However, most of these have only considered glass microspheres and have examined systems with filler loadings under 25% by volume.

Kim and Khamis [10] have reported on the behaviour of glass microsphere composite systems at filler loadings up to 65%. While limited to a single matrix / microsphere combination, the reported flexural properties were consistent with those reported earlier by Ayers and Van Erp [2] for lightweight glass microspheres. This study also examined the influence of particulate volume fraction on impact characteristics, highlighting improvements in energy dissipation characteristics gained with increased loadings. Subsequent work by Kim and co-researchers [11,12] has extended the original findings with Kim and Oh [11] suggesting a model for impact force and stress as a function of specimen diameter.

While the work of Kim and co-researchers provides valuable insight into the failure mechanisms of lightweight glass microsystems, the direct applicability of these results to cenosphere systems is questionable due to differences in the physical structure of the two types of filler. The glass microspheres used by Kim were very thin walled, flexible spheres whereas cenospheres typically have much thicker walls yielding a more rigid particle with higher compression strength. This difference in structure has been shown to cause significant differences in the failure strains obtained from resulting composites [3].

More recently, a number of investigations into the behaviour of cenospheres / polymer systems have been reported by Shukla and co-authors [13,14,15]. Of particular interest to this current study is the work of Cardoso, Shukla and Bose [14], who investigated the behaviour of cenospheres in a thermosetting polyester matrix. The study investigated the effect of particle size and surface treatments on a range of mechanical properties including elastic modulus, compressive strength and fracture toughness. Results indicated that both tensile modulus and compressive strength increase with decreasing particle diameter, which is consistent with the earlier work of Ayers [16]. It was also found that the cenosphere composite yielded improved toughness compared to the neat matrix. This toughness was shown to increase as the sphere diameter decreased.

From the data presented, it would appear that the mechanism of failure varies with the size of particle used. Samples with larger particle diameters were reported to exhibit significant sphere fracture while samples with smaller diameters showed greater sphere pop out on the failure surface. Efforts to improve sphere/matrix adhesion in samples with smaller spheres through silane treatment displayed only modest improvements in properties. It was not reported whether the silane treatments resulted in a reduced rate of sphere pop out and greater sphere fracture. If this is the case, it would appear to suggest that the failure of cenosphere composites is largely limited by the sphere themselves and not the matrix. It is thought that further investigation of this theory should be undertaken in developing a sound strategy for optimising performance of these materials.

Like many of the other studies previously reported in the literature, the work of Cardoso *et al.* [14] is limited to the investigation of a single composite formulation, with a set 25% mass fraction of a single cenosphere grade in the nominated polyester matrix system. This situation is characteristic of most published studies in the literature, with few authors providing a justification for the particular formulations investigated.

From the various studies reported it would appear that interactions between factors such as the particle and matrix mechanics, mix ratio, and particle/matrix adhesion are key factors in the performance of microsphere (or more specifically cenosphere) polymer composites. Understanding of these interactions is vitally important in developing a thorough knowledge of the behaviour of these materials. There is therefore seen to be a need for a more comprehensive study of these materials which expands upon the range of previously reported formulations and examines the effect of constituent interactions on composite behaviour.

2.4. VINYL ESTER POLYMERS

2.4.1. BASIC CHEMISTRY

Vinyl ester (VE) matrix systems bear a strong similarity to conventional unsaturated polyester (UP) systems. Both utilise a base oligomer and reactive monomer which react via a free-radical cross-linking cure mechanism to form the final thermoset polymer network. Like UP systems, both the VE oligomers and the reactive monomers contain unsaturation sites through which covalent bonds are established.

The vinyl ester oligomers are formed by the reaction of an unsaturated carboxylic acid (eg: methacrylic or acrylic acid) with a base epoxide. The most widely used epoxide for commercial VE systems is common diglycidal ether of bisphenol A (DGEBA) epoxy, however other epoxy chemistries (eg: novolacs) are also used for specialised VE formulations.

DGEBA epoxy only possesses terminal epoxy functional groups, which are reacted with the carboxylic acid to yield a molecule with terminal unsaturation (see Figure 2.1). This is considerably different to conventional UP oligomers where unsaturation exists at multiple points along the molecule. The lower ester content and lower unsaturation of the VE oligomer leads to greater chemical and hydrolysis resistance compared with UP systems [17] . It also leads to reduced exothermic heat generation during cure, which may be beneficial in the production of thicker parts. The shrinkage exhibited by these materials is less than that found for UP systems, however this shrinkage is still high when compared to epoxy systems [18].

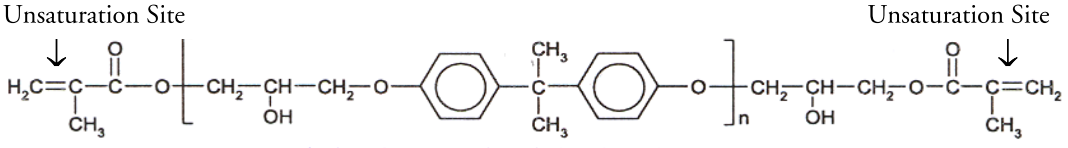


Figure 2.1 Bisphenol-A epoxy-based dimethacrylate (vinyl ester) oligomer. Source [19]

One of the commonly reported benefits of vinyl esters compared with epoxy systems is their lower cost. Though the cost of the VE oligomer is higher than a standard DGEBA epoxy due to the extra process step required to convert the DGEBA to VE, this is normally offset through the addition of the reactive monomer. Monomeric styrene, the most widely used monomer, is significantly cheaper than DGEBA epoxy even before its conversion to VE [20]. With typical addition levels from between 35% to 50% of the final volume, any cost increase in the oligomer is more than offset.

2.4.2. GRADES OF BASE VINYL ESTER RESIN

Proposals for the synthesis of VE resin appear in the literature from the early 1960's [21,22]. However the vinyl esters on today's market trace their roots back to vinyl esters developed in the late 1960's by Shell Oil Co. [23,24,25,26], and The Dow Chemical

Company [27]. These formulations used a basic methacrylated DGEBA backbone in styrene monomer. Several companies now produce resins based on this type of formulation (see Table 2.1). These products are normally sold within the marketplace as equivalent products and are often regarded as "standard" grade VE resins. Over the years these products have established a good performance reputation, particularly in areas requiring high chemical and/or environmental resistance [28].

Table 2.1 Types of vinyl ester resin and resin properties.

Product Name	Manufacturer	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)	Styrene Content (%)	HDT (°C)	Reference
Derakane 411-350	Dow Chemical Company	86	3.2	5.5	45	105	[29]
Hetron 922	Huntsman Chemical Company (Australia) Pty Ltd	86	3.4	6.5	45	100	[30]
Dion VER 9100	Reichhold Chemicals, Inc.	83	3.2	5.2	44	105	[31]
Vipel F010	AOC Resins	88	3.2	6.2	39	120	[32]

In recent years, both Ashland Chemical Company (Hetron 922) and Dow Chemical Company (Derakane 411) have made alterations to their resin formulation process to alter the processing characteristics of their respective resin systems [33,34]. The resulting products are still marketed as being equivalent in their end performance, however these claims would appear to warrant further investigation. Given the lack of reported comparative studies on the various "standard" grades, the equivalence of any two products should not be assumed and should be the subject of appropriate analysis and verification.

2.4.3. MODIFIED VINYL ESTER GRADES

Equivalence issues aside, the “standard” VE grades have demonstrated successful performance in a wide range of application areas over the years. However, instances may arise where these products do not meet the processing or performance specifications of a particular application. For example, standard resins may need to be modified to provide:

1. Greater toughness
2. Reduced emissions during processing
3. Improved performance at elevated or low temperatures
4. Improved chemical resistance

In some instances, it may be possible to modify the formulation of the VE resin to accommodate these needs. Such modifications may be separated into two primary techniques:

- Modification of the VE oligomer or reactive monomer chemistry.
- Introduction of other additives to the resin solution.

The following sections discuss ways in which these two techniques may be applied to achieve some of the aforementioned performance modifications.

2.4.4. MODIFICATION OF TOUGHNESS

The usage and maintenance strategy of many civil engineering structures requires that they are relatively robust, being able to withstand moderate impacts or other damage events. One method of achieving this robustness is to have good toughness and impact dissipation characteristics. For polymer composites, the toughness characteristics of the matrix play a primary role in the resulting system toughness [35].

Toughness can be defined as the ability of the matrix to resist crack propagation. All polymers develop micro level cracks in service. The key issue is preventing the propagation and growth of these defects into macro level failures. In rigid glassy materials, an initial crack rapidly develops into a larger crack. In tough materials, the crack energy can be dissipated into the surrounding material and the crack front pinned either through the inherent properties of the polymer network or by the addition of non-matrix inclusions such as fibres within the network.

In considering improvement to the inherent properties of the polymer network, two potential paths emerge. The first is through simple modifications to the VE oligomer or the reactive monomer. Li [36] and co-authors [37], Shan *et al.* [38] and Burts [39] have reported on the influence of crosslink density on the toughness of VE resins. The mechanisms studied were the molecular weight of the VE oligomer and the addition rate of styrene monomer. As vinyl esters possess only terminal unsaturation, increasing the molecular weight of the oligomer pushes the crosslink sites further apart, resulting in a lower crosslink density. Reported results indicate that increased oligomer molecular weight (and hence decreased crosslink density) leads to increased fracture toughness.

It has been widely reported [36,37,38,39] that the fracture toughness of a fully cured VE matrix system decreases as styrene addition levels increase. Li *et al.* [37] attributed these observed decreases to the VE backbone providing greater toughness compared to the styrene. However, the majority of commercial VE resins contain much greater styrene levels than that required for a straight stoichiometric cross-link formation. While a percentage of this excess monomer is lost as atmospheric emissions during processing and cure, a portion homopolymerises to form polystyrene segments within the final matrix network. As polystyrene is a rather brittle material, it is thought that higher styrene additions may result in higher polystyrene contents within the cured matrix and this may be the mechanism which causes reduced matrix toughness. Further experimental investigation is required to verify this behaviour.

Whatever the underlying mechanism, the reported data indicates that toughness can be improved through reducing the level of styrene monomer in VE resins. However, reducing styrene monomer levels causes an increase in the VE resin viscosity and lowers the workability of the resin. Therefore there needs to be a compromise made with regard to styrene levels which are high enough to maintain good resin workability but low enough to improve resin toughness.

Over recent years, some manufacturers have begun to investigate the use of alternative monomer systems (eg: Hetron HP35, Ashland Specialty Chemical Co. [40]). However, investigation of such systems to date has focussed on emission issues. Further investigation is required to establish the toughness alterations resulting from such monomer substitutions.

An alternative path to modifying the intrinsic characteristics of the resin chemistry is through the grafting of elastomer segments onto the VE oligomer. A notable example of this approach is the Derakane 8084 resin produced by the Dow Chemical Company [41]. While the exact formulation of the VE backbone in this resin is proprietary, literature indicates that this product has an elastomer grafted directly onto the resin backbone [42]. Several studies have shown that this elastomeric modification results in improved resin toughness [35,43,44].

As mentioned earlier, modification of the VE or reactive monomer chemistry is one of the methods used for toughness modification. The other method is through use of non-matrix additives, the most common of which are liquid butadiene nitrile rubbers. These materials, which contain reactive terminal groups tailored to a specific resin chemistry, are added to the resin solution in liquid form. During the cure process prior to gelation, phase-separation occurs providing a dispersion of rubbery domains within the final (relatively brittle) thermoset network.

A number of authors have reported on this technique. Pham and Burchill [43] and Dreerman *et al.* [44] both reported on the use of butadiene nitrile rubber additives in commercial VE resin systems, while Auad and co-authors [45,46] utilised VE resins synthesised in-house.

Dreerman *et al.* [44] utilised commercially available butadiene nitrile rubber additives with vinyl (VTBN) and epoxy (ETBN) terminal functionality in their study. The study noted that the compatibility of the studied vinyl esters and rubbers was poor, however fracture toughness improvements of between 30 to 70% were still possible at low loading rates. Under impact conditions fracture toughness was not improved. Furthermore it was found that the addition of the rubbers resulted in decreases to both the flexural modulus and yield stress of the matrix.

Pham and Burchill [43] also examined the behaviour of hydroxy terminated (HTBN) and vinyl terminated (VTBN) rubbers in VE resins. In an effort to overcome observed incompatibilities of the rubbers with the VE resin, they also investigated the use of hydroxy terminated polybutadiene (HTPB) modified with isocyanate end-caps. Reported results from the modified HTPBs indicate improvements of 200 – 300% in the stress intensity factor K_{1C} and a ten-fold increase in G_{1C} fracture energy with addition levels of 5%. Toughness of the tested resins was seen to improve with increased length and polarity in the end-caps of the HTPB. Loss of elastic modulus due to the rubber additives was relatively low at a 5% addition level, however modulus losses increased to between 30 – 50% at 10% addition levels. This would suggest use of this technique should be limited to low addition levels.

From the reported data it would appear that the addition of liquid butadiene nitrile rubbers is a valid strategy for the toughening of VE matrix systems. While the rubbers are immiscible with the resin solution, the fine dispersion of rubbery particles which results during gelation appears to work in harmony with other crosslinked material to create an effective toughening mechanism. Due to the phase separation observed in this material, dispersion of the rubber within the resin solution would need to occur shortly before manufacturing and would likely need to be done by the fabricator. While this is not an entirely satisfactory scenario from a manufacturing perspective the performance improvements afforded by this approach may justify its use.

If this path is to be pursued care should be taken to minimise the loss of other important mechanical properties of the matrix. Reported data indicates that elastic modulus and yield and break stresses of the matrix are adversely affected by addition of the liquid rubbers. Care should be taken to balance toughness improvements with adequate retention of other properties.

2.4.5. REDUCED EMISSIONS DURING PROCESSING

In response to increasing regulatory actions aimed at decreasing volatile organic compounds (VOCs) from manufacturing operations (eg: California's South Coast Air Quality Management District Rule 1162, National Emission Standards for Hazardous Air Pollutants [47], Maximum Achievable Control Technology (MACT) standards [48]), many resin manufactures have sought to modify the formulation of their VE resins to limit the VOC emissions during fabrication operations. The primary target of regulatory controls to date has been styrene, the most widely used monomer in VE resin systems.

The reasons for the focus on styrene are complex but extend well beyond the composites industry. Styrene is a major commodity chemical used in vast quantities across a wide array of industries. Styrene emissions are also distinctive and easily detectable with an aromatic odour at low concentrations and a sharp, penetrating disagreeable odour at higher levels with a human detection threshold of around 0.1ppm [49]. The effect of styrene on humans is currently the subject of significant international debate and different regulatory bodies have adopted different stances on the issue. For example, while the official US Environmental Protection Agency (EPA) position is that the carcinogenic potential of styrene is still under review, the EPA Office of Research and Development has suggested that styrene be listed as a Group C carcinogen [50]. In 1987 the International Agency for Research on Cancer (IARC) upgraded the classification of styrene from "not carcinogenic" to "possibly carcinogenic to humans" [50]. This finding was upheld in two subsequent reviews in 1994 [51] and 2002 [52].

The uncertain status of styrene and the threat of increasing restrictions on emissions has resulted in a rethink on styrene usage by the composites industry, the sector identified by IARC as having highest styrene exposures [52]. Over the past few years a number of companies have introduced products aimed at providing the end-user with reduced emissions during fabrication operations. As with the toughening of matrix systems, styrene emission levels can be modified by two different paths:

- Modification of the resin chemistry.
- Incorporation of additional compounds to the resin solution.

The primary techniques used in modification of the resin chemistry involve reductions in the amount of styrene blended into the resin solution. This can be achieved through a reduction in the overall reactive monomer content of the solution or by substitution of another reactive monomer in place of styrene. As mentioned previously, the styrene addition level required to achieve a stoichiometric balance with the VE oligomers is well below the 40 to 50% addition levels used in typical vinyl ester resins. The theory is that by reducing the disparity between required and available styrene, the amount of styrene available for emission is reduced.

The most obvious path to reduce the amount of excess styrene in a system is to simply reduce the percentage added at manufacture. Some manufacturers have pursued this path with their vinyl ester resins, offering a range of products with the same oligomer but different styrene contents. Table 2.2 shows three such vinyl ester products from the Dow Chemical Company. This table highlights one of the inherent problems in limiting formulation changes to a simple reduction in styrene content. As can be seen from the figures, when the styrene content is decreased there is a corresponding increase in the resin viscosity. With most formulators seeking to achieve low viscosity levels to facilitate high filler or fibre loadings, this viscosity increase can be an undesirable side effect of styrene reduction strategies. Even the 45% styrene level of the 411-350 resin would be regarded as a relatively high styrene content. For styrene contents to be reduced to the 30 - 35% typically regarded as necessary for meeting new legislation, greater formulation changes are required to retain workable resin solutions.

Table 2.2 Styrene content and viscosity of VE resins by the Dow Chemical Company.

Product Name	**Styrene Content (%)**	**Viscosity (cP)**	**Reference**
Derakane Momentum 411-100	52	100	[53]
Derakane Momentum 411-200	48	200	[53]
Derakane Momentum 411-350	45	370	[54]

As previously mentioned, styrene content has been shown to influence a number of properties of a VE resin [36,37,38,39]. A lower styrene content increases the crosslink density with a lower portion of brittle polystyrene segments forming leaving the matrix dominated by the VE structure. This leads to improved mechanical performance which is supported by published manufacturer data. However with a lower styrene content, the greater oligomer content will increase the cost of the VE resin [20] and increase the viscosity, adversely affecting processing.

One alternative to simply reducing the level of styrene in a resin solution is the substitution of another reactive monomer in place of styrene. Some manufacturers have approached the new legislation by using alternative monomer systems to manage styrene emission issues. An example is the previously mentioned Hetron HP35 which is styrene free, using an acrylate monomer instead of styrene [40].

As noted earlier, styrene is used in a broad range of applications and produced in very high volumes. With its associated health issues still being debated, this high profile has potentially contributed to movements directed at regulating styrene emissions. Acrylates and methacrylates are not as widely used and their use does not currently appear to attract the same attention. Additionally, acrylates and methacrylates are not considered to be carcinogenic by the U.S. EPA [55] and methyl methacrylate has been deemed "not classifiable as to its carcinogenicity to humans (Group 3)" by IARC [56].

Costin and Bailey [57] investigated the use of acrylic monomers as additives in UP resins and found that both acrylate and methacrylate monomers reduced emissions and lowered odours. The use of these alternative monomers was found to reduce gel times, improve tensile strength and elongation but reduce tensile modulus. Complete replacement of styrene with methacrylate was found to reduce emissions by approximately 80%. However, complete replacement was not regarded as being a viable option due to the higher cost of the alternative monomers and the resulting increased resin viscosity. Agrawal *et al.* [58] studied the curing behaviour of VE resins with methyl methacrylate and styrene monomers, with reported results indicating that combinations of styrene and methyl methacrylate were more reactive than each on their own.

Lowering the styrene content or replacing the styrene with an alternative addresses the styrene emission issue but in doing so, can increase the cost of the VE and the viscosity. The combination of these two techniques appears a promising option which may maintain the resin viscosity at a workable level appropriate for processing, however the cost increases may still hinder the adoption of these methods.

In addition to changing the reactive monomer in a resin formulation, it is possible to make modifications to the VE oligomer so as to reduce styrene addition levels while maintaining an acceptable viscosity. As will be discussed in more detail later, a reduction in the molecular weight of the oligomer yields a corresponding drop in viscosity [36]. This could permit a reduction in styrene addition rates without sacrificing formulation viscosity.

Another approach to reducing emissions is by sealing the exposed surfaces of parts during fabrication, limiting the escape of styrene and reducing emissions. An example of a commercial product that applies this theory is the Derakane LSE (Low Styrene Emission) resin series by the Dow Chemical Company [28]. Emission levels are reportedly the same as standard grades during fabrication with the low styrene mechanism activating after the resin surface becomes static, preventing further styrene emissions. These resins reportedly handle and cure and possess similar properties to the standard resins.

The “sealing” of resin surfaces to prevent emissions may be achieved in a variety of ways. One of the most common ways is through the addition of a paraffin wax to the resin which blooms to the surface forming a barrier layer of wax that limits the emission of styrene [18,28]. These mixtures however have been known to phase separate over time and the strength of secondary bonds to the surface may be lowered due to the wax concentration.

It is also possible to utilise specially formulated additives which are designed to reduce emissions by sealing the surface through forming a barrier film. An example is BYK-S 750 produced by BYK Chemie that, when combined with the resin prior to the addition of other components is reported to suppress styrene emissions without adversely effecting secondary bonds, however phase separation of the system over time is still a concern [59].

More recently, some authors have suggested techniques which essentially seal volatile monomers into the system by partially curing the surface of the resin. McCartney [60] reported on "UV Cocooning" where a photo-initiated ultraviolet (UV) curing process is applied to cure the resin surface, reducing monomer evaporation, before completing the ambient cure of the product.

While each of these methods is reported to reduce emissions, the selection of an appropriate method must take into consideration the fabricated product and the adopted manufacturing processes.

2.4.6. ELEVATED TEMPERATURE PERFORMANCE

Thermosetting resins are amorphous polymers, possessing networks which consist of random arrangements of polymer chains, as opposed to a crystalline polymer where the network consists of an ordered arrangement of chains. Although most crystalline polymers contain portions of both amorphous and crystalline material, the distinction between the two classes is important as it determines the behaviour of a polymer when exposed to heat at elevated temperatures.

When exposed to heat, crystalline polymers melt at a certain temperature changing from a solid to a liquid phase. Amorphous polymers on the other hand do not melt, instead they exhibit a softening transition where they pass from a glassy state to rubbery state. This temperature of this transition is known as the glass transition temperature or T_g. When cooled below the T_g a polymer is rigid and brittle but heated above the T_g the polymer is soft and flexible. The T_g of a resin is dependant on the mobility of the chains within the network. The more mobile the chains are, the less heat is required to instigate molecular movement, resulting in a lower glass transition temperature. Similarly the less mobile the chains are the more heat is required to instigate movement, resulting in a higher glass transition temperature.

The glass transition temperature is a key factor in determining the suitability of a polymer to various service conditions. While in some situations it may be advantageous to operate a material above its glass transition to achieve tough, elastomeric properties, the cenosphere composites examined in this dissertation are most commonly applied as structural core materials [61,62,63,64] and in these instances it is seen as more desirable to operate the material below its glass transition to provide maximum rigidity.

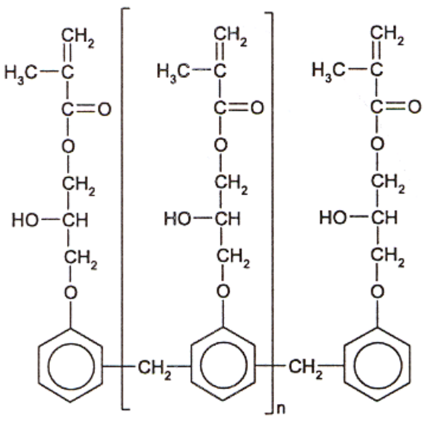
One of the reported advantages of VE resins is that they possess high transition temperatures that approach 90°C without a post-cure [18]. This characteristic may be particularly beneficial in the fabrication of large civil engineering components where it is difficult to post cure products at elevated temperatures. Given that the high thermal insulation characteristics of the VE / cenosphere composites would generally slow temperature ramps and prolong soak times to achieve uniform part temperature during post-cure, the ability to achieve high T_g values without post-cure may be particularly attractive.

Another measure of the softening transition of an amorphous polymer is the heat distortion temperature (HDT or temperature of deflection under load). Evaluation of the HDT involves the measurement of deflection in a constantly loaded flexural specimen with increasing temperature. The HDT is the temperature at which the deflection equals a predetermined level specified in the relevant testing standard [65,66]. The test essentially measures the loss of modulus in the specimen which occurs when the material passes through is glass transition. While the T_g and HDT are not exactly the same they are related. Initial HDT testing of cenosphere composites by FCDD staff has indicated a strong correlation between the HDT of the matrix and the HDT of the resulting composite. It is therefore thought that the glass transition characteristics of the matrix will be an important parameter in temperature performance of the vinyl ester / cenosphere composites.

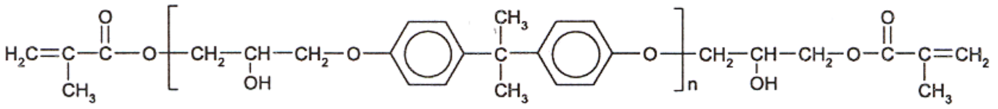
Unlike most of the other performance modifications discussed previously, the elevated temperature performance of a matrix can generally only be improved through modification of the chemical structure of the polymer network. Most additives used with vinyl ester systems tend to reduce the glass transition temperature of the polymer rather than improve it. The current discussion will therefore be limited to chemical structure modifications which aid in elevated temperature performance.

The primary factor in the glass transition temperature of a thermosetting polymer is the crosslink density of the network. The T_g is determined by the inherent mobility of the molecules within the network. The more mobile the structure, the lower the glass transition temperature. The crosslinking of a thermoset network significantly reduces the mobility of the various molecules within the network and thus raises the glass transition temperature. A number of authors [36,37,38,39] have reported on the relationship between the crosslink density of the cured polymer network and the resulting glass transition temperatures in VE resins. These studies indicate that an increased crosslink density due to the use of lower molecular weight oligomers leads to increased glass transition temperatures. Conversely, the addition of increasing amounts of styrene, which effectively reduces the crosslink density, was found to lower the T_g of systems with lower molecular weight oligomers. However, the studies [37,38] showed the addition of styrene to higher molecular weight oligomers had only a minor effect on glass transition temperatures.

The crosslink density can also be increased by increasing the number of sites available for crosslinking. This can be achieved by utilising a novolac epoxy as opposed to the DGEBA epoxy as the chemical backbone for the VE resin (eg: Derakane 470-300, The Dow Chemical Company [67]). The DGEBA epoxide with its terminal epoxy groups yields a vinyl ester which only possesses terminal unsaturation. However, the novolac epoxide is a branched molecule with an epoxy reactive group terminating each "branch". When the novolac is reacted to form the vinyl ester oligomer each of these epoxide groups is converted to provide terminal unsaturation on each "branch" (see Figure 2.2). The number of unsaturation points on a novolac vinyl ester is always three or more, allowing crosslinks to form along the length of the molecule rather than just on the ends. This results in a network with increased crosslink density.



Novolac Vinyl Ester



Standard Vinyl Ester

Figure 2.2 Chemical structure of alternative VE resin oligomers. Source: [19]

Investigations by Scott *et al.* [19] found improvements in T_g were achieved by use of a novolac based oligomer. T_g improvements of 17 to 27°C compared to standard grade vinyl esters have been reported for novolac vinyl ester systems [17]. One manufacturer has even reported improvements of up to 45°C [67]. Manufacturer literature shows novolac based VE resins generally maintain comparable mechanical properties to standard grades but have reduced elongation [67], which would be a direct influence of the increased crosslink density. Literature also indicates that novolac based VEs are typically formulated to have a lower styrene content compared to their standard grade counterparts. It is reasonable to conclude that the lower styrene content also contributes to the increases in T_g, perhaps explaining the disparity between the aforementioned values. At similar levels of styrene content however, Scott *et al.* [19] found approximately a 20°C improvement in T_g with a novolac based oligomer.

While improvements in glass transition temperature can be achieved by increasing crosslink density, there are additional side effects which should be considered. As was reported earlier, lower crosslink densities lead to increased fracture toughness and highly crosslinked novolac vinyl esters typically display lower toughness characteristics compared to standard grade products. Manufacturer data of elastomer modified VE resins indicates the toughening process led to a lower T_g [41]. Other conflicts in performance expectations exist where higher styrene concentrations provide improved processing characteristics yet can lower the T_g and influence other properties. It would therefore appear that desired temperature performance characteristics cannot be considered in isolation but must be evaluated concurrently with other details of the proposed application to provide a suitable matrix system.

2.4.7. IMPROVED CHEMICAL RESISTANCE

Many industries utilise corrosive and hazardous materials which require processing, storage and handling facilities capable of withstanding these aggressive surroundings. Vinyl ester resins have been reported to provide good resistance to a wide range of aggressive chemical environments [28]. The good chemical resistance of VE resins is a result of their reduced number of ester linkages and the epoxy resin backbone [17]. Vinyl ester resins with higher styrene concentrations offer improved resistance to acids and alkalis while those with lower styrene concentrations offer better resistance to solvents [36].

Compared to DGEBA based VE resins, the higher crosslink density of novolac based VE resins tends to provide improved chemical resistance due to the higher density of crosslinks in the network limiting the infiltration of aggressive agents. The increased crosslink density of novolac epoxy based VE resins combines corrosion resistance with elevated temperature performance [68].

Improved corrosion resistance and high temperature performance may also be achieved by altering the resin chemistry through a urethane-modification [69]. An example of a commercial resin using this technique is Atlac 580-05 by Reichhold Chemicals Inc. Manufacturer data indicates the incorporation of a urethane onto the backbone creates a tough and resilient polymer which provides superior corrosion resistance and elevated temperature strength retention [70]. However by comparison, the temperature performance did not reach that of other high temperature performance resins. Atlac 580-05 is free radically cured, with Martin *et al.* [71] investigating the influences of initiator concentration and promotion level on gel and vitrification times. Similar to other resin grades, the desired performances must be prioritised to determine a suitable resin system.

2.5. CURING VINYL ESTER POLYMERS

Vinyl ester resins cure through a free radical initiated, copolymerisation reaction. The cure process commences with the addition of a chemical initiator to the resin solution. The initiator decomposes under heat or radiation to provide the free radicals required for the cure. The free radicals start the polymerisation reaction by breaking the unsaturation (double carbon) bonds of the oligomer end groups and the reactive monomer. These sites then link to create the three dimensional crosslinked thermoset network. A more detailed discussion of the reaction mechanisms is provided in Chapter 3.

The most common types of initiators used for VE resins are organic peroxides, however other initiators such as UV activated photo-initiators may also be used. Due to their inherent instability, the organic peroxides used for VE resin curing are blended products containing a proportion of the particular peroxide in some form of carrier medium. The carrier can be water, a solvent or some other liquid with which the peroxide does not react. The reactivity of the initiator is determined by the type of peroxide used and its concentration within the particular product. The active oxygen content of an initiator is a quantitative descriptor of the product's reactivity addressing both the type and concentration of peroxide, with higher active oxygen contents translating to more reactive systems.

At ambient temperature the decomposition rate of most peroxide initiators is too low for viable composites production so an accelerator is used to speed up the decomposition rate. The accelerator is added to the resin solution at relatively low levels (typically 0.1 to

0.8%) prior to introduction of the peroxide initiator. When the initiator is added to the resin, the accelerator causes the peroxide to decompose at a much increased rate. It should be noted that accelerators should never be directly combined with peroxide initiators as this will result in a violent decomposition reaction. However, when combined in the appropriate manner, accelerators can be used to increase decomposition of the peroxide to a viable rate for ambient temperature fabrication.

Methyl ethyl ketone peroxides (MEKP) are probably the most widely used type of organic peroxide initiator used for ambient temperature curing. MEKP solutions appear as clear, colourless liquids and are normally used in combination with metal salt (cobalt) accelerators. The MEKP is dissolved in a phthalate plasticiser or phlegmatiser such as dimethyl phthalate (DMP) forming a solution typically containing 30 - 40% peroxide with the balance predominantly DMP with a small quantity of methyl ethyl ketone (MEK) and water. A number of MEKP based initiators of varying reactivity manufactured by Akzo Nobel are shown in Table 2.3. The relative concentrations of components and the active oxygen contents of each solution are also shown, highlighting the general lowering of reactivity of the solutions with decreasing active oxygen content.

Table 2.3 Composition and reactivity of MEKP based organic peroxide initiators.

Product	**Description**	**Active Oxygen Content (%)**	**Peroxide Content (%)**	**Reference**
Butanox M-60	Medium reactive MEKP	9.9	36	[72]
Butanox M-50	Medium reactive MEKP	8.9	33	[73]
Butanox LA	Low reactive MEKP	8.7	34.5	[74]
Butanox LPT	Very low reactive MEKP	8.5	35	[75]

Manufacturer supplied MEKP product data sheets generally recommend an initiator addition level of between 1 and 4%. Addition levels lower than the recommended minimum will potentially result in an undercure of the resin, while levels greater than the maximum will increase costs with only minimal increases in cure speed [76].

One of the disadvantages of using MEKP initiators is the presence of hydrogen peroxide within the peroxide blend. Hydrogen peroxide is used in the production of MEKP and small residual quantities are found in all end products. In unsaturated polyester reaction the H_2O_2 can provide a beneficial initial "kick" to the cure reaction due to its high reactivity and a similar effect can be observed with vinyl esters. In vinyl esters however, the decomposition of the H_2O_2 will yield oxygen which will exhibit itself in the formation of bubbles within the resin. This phenomena known as "fizzing" can result in voids in the cured matrix which may adversely affect performance and durability.

The relatively high concentration of phlegmatiser used in MEKP solutions also requires care. This non-reactive material will remain as an inclusion within the cured network and tends to act as a plasticiser. When high initiator addition levels are used, this plasticising material can begin to exhibit detrimental effects on the mechanical and thermal characteristics of the cured network.

Use of an accelerator is necessary for ambient temperature curing with MEKP initiators. The most common accelerators used are cobalt complexes such as cobalt napthenate and cobalt octoate. Like the peroxide initiators, cobalt accelerators are formulated solutions containing the active cobalt component in a non-reactive carrier. The percentage of active cobalt in a formulation varies with the particular cobalt complex used and its addition level. Examples of commercially available cobalt accelerators with relative cobalt concentrations are shown in Table 2.4. The lower limit for cobalt accelerator addition is probably only determined by the ability to achieve a desired minimum reactivity at a given processing temperature. However, work by Abadie *et al.* [77] and Cook *et al.* [78] has suggested that there may be an upper limit for the addition of cobalt accelerators. Published test results indicate a drop off in system reactivity above certain addition levels, with the conclusion that the cobalt accelerator actually retards the reaction. Further investigation would be needed to assess whether it is the cobalt itself which retards the reaction or whether this effect is due to the other components of the accelerator solution.

Table 2.4 Composition of cobalt accelerators.

Product	Description	Cobalt Complex (%)	Active Cobalt (%)	Reference
Accelerator NL-48P	Cobalt octoate in plasticiser	3	0.5	[79]
Accelerator NL-49P	Cobalt octoate in plasticiser	6	1	[80]
Accelerator NL-51P	Cobalt octoate in plasticiser	35	6	[81]
Accelerator NL-53	Cobalt octoate in solvent	55	10	[82]

In some instances the cobalt accelerator will not provide the reactivity levels for a particular production scenario. In such instances it is possible to further increase the reactivity of the initiated system by using an amine accelerator such as dimethylaniline (DMA). For MEKP these accelerators must be used in conjunction with the cobalt accelerator. Addition levels for the amine are much lower than for the cobalt accelerator, typically only being in the order of 0.05 to 0.1% [83].

An alternative to the ketone peroxides are the hydroperoxides. These materials, generally cumyl hydroperoxides (CHP), are slower reacting than MEKP and subsequently cure occurs over a longer period. CHP solutions appear as a clear, colourless to pale yellow liquid. They are commonly used with vinyl esters instead of ketone peroxides due to the absence of "fizzing" and can still be used with cobalt accelerators. The CHP is dissolved in a solvent mixture and can contain from 40 - 90% peroxide, less than 10% cumene and water with the balance formed by the solvent. Again a number of formulations are available with degrees of reactivity achieved by altering the peroxide content and active oxygen content. The CHP based Trigonox 239 initiator manufactured by Akzo Nobel also contains an accelerator in its formulation to increase the reactivity [84]. Initiator addition levels are typically from 1-3% but depend on the reactivity of the CHP solution with higher minimum concentrations required for those of lower reactivity.

To effect curing at moderately elevated temperatures, diacyl peroxides are often utilised. Benzoyl peroxide (BPO), the most widely used form, is used extensively for heated, closed mould production methods such as resin transfer moulding. For midly elevated temperature production, BPO is normally used in conjunction with amine accelerators such as dimethylaniline (DMA), diethylaniline (DEA) or dimethyl paratoluidine (DMPT). For high temperature curing the BPO is often sufficiently active such that accelerators are not required. BPO is available in a number of forms that offer improved handling characteristics including free flowing powders and thixotropic pastes. The peroxide content of these formulations can vary from 20 to 50% with the balance in pastes comprised of water and plasticisers and in powders, an inert filler (eg: calcium sulphate). Examples are shown in Table 2.5.

Table 2.5 Composition and reactivity of BPO based organic peroxide initiators.

Product	Description	Active Oxygen Content (%)	Peroxide Content (%)	Reference
Perkadox BT-50	Standard BPO paste	3.3	50	[85]
Perkadox CH-50	Standard BPO powder	3.3	50	[86]
Perkadox 20S	BPO on filler	1.3	20	[87]

Formulations have been developed where ultraviolet (UV) light from lamps or natural light is used to initiate the cure of adhesives and resins. The UV curing of resins has advantages of extended resin pot-life and working time, when kept protected from UV light and not being affected by heat sources that can potentially lead to ambient temperature cure. The cure kinetics of VE resins cured with UV light has been studied by Scott *et al.* [88,89]. A UV curing system would not be an option to effectively cure particulate reinforced composites. The filler suspended within the matrix would obstruct the penetration of light into the material leading to a non-homogeneous cure throughout the cross-section with only the exposed external surfaces hardening.

The reactivity of the cure system can also be adjusted through the use of inhibitors. An inhibitor which is combined into the resin formulation before use, consumes the first free radicals as they are formed thus delaying the onset of the cure reaction at ambient and elevated temperatures. Delaying the onset of the cure can aid processing procedures by lengthening the gel time of the resin. Examples of inhibitors are hydroquinone, p-benzoquinone and t-butyl catechol [18] with some commercial varieties produced by Akzo Nobel shown in Table 2.6. Inhibitors can have an inhibitor content of 1 to 20% in a solution with the balance formed from plasticiser or styrene with an inhibitor of lower concentration requiring higher addition levels.

Table 2.6 Composition of inhibitors. Source: [90]

Product	Description	Inhibitor Content (%)
Inhibitor NLC-1	p-tert-Butyl catechol in styrene	1
InhibitorNLC-10	p-tert-Butyl catechol in plasticiser	10
Inhibitor NLD-20	Di-tert-butyl-p-cresol in styrene	20

Commercial resin grades are often supplied with the option of being “pre-promoted”, containing accelerators, promoters, inhibitors and other additives to meet specific requirements. An advantage of these grades is that the resin is supplied in a condition that can be used immediately, not requiring an on-site promotion process. However there are associated disadvantages due to the exact details of the formulation being proprietary knowledge and not available, the flexibility of promoting the resin to suit on-site processes and conditions is lost and the resins generally have a limited shelf-life.

There is a considerable variety of cure system components available to cure VE resins. While advantageous in the fact that systems can be tailored, care must be taken to select constituents to optimise the cure process to suit the fabrication materials, available processing techniques, operating conditions and the desired properties of the final product.

2.6. CENOSPHERES

Particulate reinforcements for composite systems are available in numerous different forms including spherical, cubic, platelet or any other regular or irregular geometry [91,92]. Each type and form imparts their own specific properties to the composite. Particulate reinforced composites have been reported to offer many advantages over neat resin matrices including [93]:

- increased stiffness, strength and dimensional stability,
- increased toughness or impact strength,
- increased heat distortion temperature,
- increased mechanical damping,
- reduced permeability to gases and liquids,
- modified electrical properties, and
- reduced costs.

Of particular interest to this current study are cenospheres (see Figure 2.3) which are a type of hollow ceramic microsphere found in the fly ash by-product created through the burning of coal at power stations [94,95]. When fly ash is placed in the storage ponds normally used by power stations, the lightweight cenospheres (SG $\approx$ 0.7) float to the surface and can be collected for re-use. With the current low global utilisation of ash by-products, cenospheres are seen to offer some significant environmental benefits.

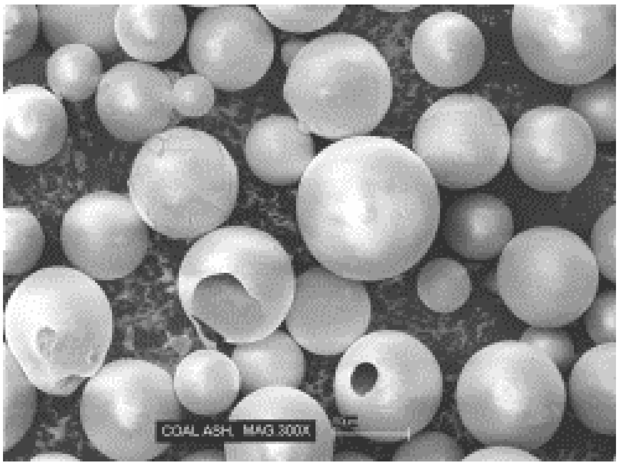


Figure 2.3 Cenosphere particles, a fly ash derivative used as a particulate reinforcement. Source: [96]

The concentration of cenospheres in coal combustion ash is typically less than 1% however they can constitute up to 80% of some fly ashes. Gurupira *et al.* [97] cited an example of a fly ash from one coal type having a cenosphere concentration of 9% whereas another type had a cenosphere concentration of 87%. The chemical and physical composition of a fly ash is a function of many factors including coal rank, coal source and the burning plant characteristics and processes [98]. The amount of ash generated by a plant is directly related to the grade of coal being burnt, with higher grades having less ash than lower grades. The ASTM Coal Classification Index defines coal grades including:

- Anthracite
- Bituminous
- Subbituminous
- Lignite

The chemical properties of coal ash with respect to coal rank are shown in Table 2.7.

Table 2.7 Typically chemical properties of coal ash with respect to coal rank. Source: [98]

	Anthracite	Bituminous	Subbituminous	Lignite
Silicone, SiO_2	48 - 68%	7 - 68%	17 - 58%	6 - 40%
Aluminium, Al_2O_3	25 - 44%	4 - 39%	4 - 35%	4 - 26%
Calcium, CaO	0.2 - 4%	0.7 - 36%	2.2 - 52%	12.4 - 52%
Potassium, K_2O	-	0.2 - 4%	-	0.1 - 1.3%
Iron, Fe_2O_3	2 - 10%	2 - 44%	3 - 19%	1 - 34%
Titanium, TiO_2	1 - 2%	0.5 - 4%	0.6 - 2%	0 - 0.8%
Magnesium, MgO	0.2 - 1%	0.1 - 4%	0.5 - 8%	2.8 - 14%
Sulphur, SO_3	0.1 - 1%	0.1 - 32%	3 - 16%	8.3 - 32%
Sodium, Na_2O	-	0.2 - 3%	-	0.2 - 28%
Ash	4 - 19%	3 - 32%	3 - 16%	4 - 19%

The cenosphere component of fly ash will take on similar properties to the coal it is formed from. Between current commercial suppliers, the chemical and physical properties of cenospheres appear similar with only small percentages differences in key components [1,99,100,101]. Typical chemical composition properties are summarised in Table 2.8. Comparing the chemical composition of the cenospheres to the composition of each coal rank gives an indication from which coal type the cenospheres may have been sourced.

Table 2.8 Typical chemical properties of cenospheres. Source: [1]

	Concentration
Silicone, SiO_2	53%
Aluminium, Al_2O_3	38%
Calcium, CaO	3.6%
Potassium, K_2O	1.5%
Iron, Fe_2O_3	1.3%
Titanium, TiO_2	1.3%
Magnesium, MgO	0.7%
Phosphorous, P_2O_5	0.4%
Sodium, Na_2O	0.1%
Manganese, Mn_2O_3	0.1%

The implications of the chemical properties with regard to potential applications of cenospheres and the characteristics of final products is not clearly defined. Trelleborg Fillite Ltd, a supplier of cenosphere products, supply a specialty grade of cenospheres marketed as being specifically developed for high temperature applications [102]. This grade has a high alumina content of 40 - 44% as opposed to the usual 34 - 37%. In general the chemical composition primarily relates to resistance to acids and alkalis. With their neutral pH, cenospheres generally do not interfere with the reaction of the matrix materials [1]. Typical physical properties of cenospheres are summarised in Table 2.9.

Table 2.9 Typical physical properties of cenospheres. Source: [1]

	Description
Specific Gravity	0.68 - 0.72 g/cm^3
Loose Bulk Density	350 - 450 kg/m^3
Mohs Hardness	5 - 6
Compressive Strength	180 - 280 kg/cm^2 (18 – 28 MPa)
Shape	Spherical
Colour	Off-white
Shell Thickness	1/10 d, nominal
Melting Point	1250 °C
Thermal Conductivity	0.11 W/mK
pH in water	7.0 - 8.0
Moisture Content	0.2% max

Due to their low density, cenospheres can be used to produce composites of low weight. Their hard surface also provides good resistance to erosion and weather, with the glassy shell being impermeable to liquids and gases [1].

The spherical shape of cenospheres also has many advantages as it provides the lowest particle surface area compared to volume. This shape requires less resin to wet the particle surface, permitting higher filler loadings which aid in reducing shrinkage and lowering costs. The shape also leads to good flow characteristics, improving workability and handling characteristics. Furthermore, the spherical shape provides a uniform stress distribution on its surface, avoiding localised high stress concentrations and premature failure initiation of the matrix, often associated with sharp edged particles [91].

Cenospheres are supplied in the form of a free flowing, white to grey coloured powder, available in different grades generally classed by particle size. The colour of cenospheres appears to be a reflection of the severity of cleaning processes applied with the lighter colours often preferred for use in paints and decorative applications. An example of cenosphere grades and the associated particle sizes are shown in Table 2.10.

Table 2.10 Available product grades of cenospheres from Envirospheres Pty Ltd. Source: [101]

E-Spheres SL Series	Nominal Particle Size (μm)	Approximate Particle Mean (μm)	Description
E-Spheres SLG	20 – 300	130	General multi-purpose
E-Spheres SL500	250 – 500	300	Coarsest
E-Spheres SL350	250 – 350	270	Coarse
E-Spheres SL300	150 – 300	150	Mid range coarse
E-Spheres SL180	20 – 180	115	Mid range fine
E-Spheres SL150	20 – 150	100	General purpose fine
E-Spheres SL125	12 – 125	80	Very fine
E-Spheres SL75	12 – 75	45	Finest specialist

By using particles of different sizes, higher packing densities are possible due to the finer particles filling the voids between the larger particles. With regard to suspensions containing coarse and fine particles, Shenoy [103] concluded that smaller particles interposed between larger particles causes a reduction in the interparticle impact resulting in a decrease in the viscosity. Generally by altering the particle size distribution from a sharp monomodal type to a broad distribution, the filler content can be increased without increasing the viscosity of the system [103]. This suggests a graded particle distribution containing a range of particle sizes may be the most appropriate to facilitate high filler concentrations while maintaining a workable viscosity.

2.7. DISCUSSION

The above review has shown there are a wide range of constituent material options available for vinyl ester / cenosphere particulate composites. Through the review process it has become apparent that complex relationships exist within each material group. In the case of a composite where several constituents must be combined into a unified structural system, thorough understanding of these relationships and their interactions with each other is essential to achieve desired physical, mechanical and durability requirements. These relationships must be considered concurrently to select the most appropriate constituents for a particulate composite core material in a given application.

This also implies evaluating the materials not entirely on the merits of their chemical structure and performance but how these merits apply in meeting the engineering requirements of an application. Currently of interest to this study are civil infrastructure applications comprised of elements which lend themselves to open casting techniques completed in ambient conditions [61,62,63,104].

In considering the options for a given end application, a number of parameters have been identified to aid in the selection of constituent materials. These parameters address the characteristics of the final composite and include:

- mechanical performance,
- processing characteristics, and
- cost.

The sensitivity of the construction industry to up-front costs has been well documented [105] and often influences the selection of any construction material to some degree. As detailed by earlier research by the author into particulate composite core materials, one of the primary aims of these new materials is to offset some of the cost disparity between FRP laminates and traditional core materials [61,104]. Thus the mechanical performance and processing characteristics must be considered with respect to their associated cost ramifications. For the purposes of this study, costs are explained using supplier list prices for materials with the prices in $AUD on the dates as detailed in the appropriate references.

The cost savings associated with using a filled system are achieved through the replacement of more expensive resin with a less expensive filler. It follows that the more resin that is replaced by filler, the more cost effective the composite becomes. However the actual savings are dependent on the relative cost differences between the resin and filler. Limits on the filler volume fraction do apply. It is obvious that a 100% filler volume fraction is not feasible, and the imposed constraints due to processing limitations must still be considered. Drawing on previous related research by the author [61,104], the potential filler volume fraction is restricted to a maximum of around 50% by volume.

Standard vinyl ester resins offer a good balance of physical and mechanical properties but for some applications their performance (eg: glass transition temperature, toughness) may be inadequate. It is a considerable advantage of VE resins that a variety of different types exist and as detailed earlier, their properties can be modified using a number of methods to meet specific performance expectations. There are commercially available grades of resin which utilise these techniques to provide improved performance in various applications. Examples of selected grades produced by The Dow Chemical Company with associated costs are shown in Table 2.11.

Table 2.11 Commercial resin grades and associated costs.

Performance	Resin Grade	Cost ($/kg)
Standard	Derakane 411-350	8.30
Improved Toughness	Derakane 8084	13.54
Reduced Emissions	Derakane 441-400 LSE	8.91
Improved Temperature Performance	Derakane 470-300	11.10

Source: Pricing [106]

This indicates that enhanced performance comes at significantly higher cost which suggests that the use of these modified resin grades would be limited to specialised applications where the extra cost may be justified. The cost issue is relative, requiring the consideration of all materials in the system. If the use of a resin that is twice the cost of another doubles the performance of the overall composite system, then the added resin cost may be appropriate. However in many instances such performance increases may not be adequate to warrant the extra expenditure.

In some instances, broader policies may significantly negate the types of considerations discussed above, for example emissions policy. Although not currently in place in Australia, many countries have imposed regulations that restrict volatile emissions. Thus the available options for VE resins may be constrained to those that meet emission requirements, limiting the range of material and processing options available. It would therefore appear reasonable to include the influence of styrene levels in any study of constituent influences.

Ambient temperature cure appears to offer the greatest flexibility for the fabrication of vinyl ester / cenosphere composite products, implicating the use of MEKP or CHP based initiators to effect cure. Generally MEKP initiators would be the standard selection but CHP initiators may provide better exotherm control when fabricating large products. Elevated temperature curing may have some benefits for specific applications but the ambient cure option is more generally appropriate and has been chosen for this investigation.

As mentioned previously, there are a number of suppliers of cenospheres who generally supply grades classed by particle size. The finer grade particles typically attract a higher cost due to extra grading processes (see Table 2.12). A product with a range of particle sizes over a broad distribution would appear to be the most promising with regard to maintaining processing characteristics at higher filler volume fractions where cost effectiveness is highest. Table 2.12 also shows that the graded product is lowest in cost.

Table 2.12 Grades of E-Spheres cenospheres with associated costs.

Product Grade	Nominal Particle Size (μm)	Cost ($/kg)
E-Spheres SLG	20 – 300	1.50
E-Spheres SL150	20 – 150	1.80
E-Spheres SL125	12 – 125	1.90
E-Spheres SL75	12 – 75	4.89

Source: Grades and sizes [101]; Pricing [107]

Again while a specific application may warrant the use of finer particles, for general applications the graded distribution appears appropriate and has been chosen for this investigation.

2.8. CONCLUSIONS

This Chapter has reviewed the status of particulate composite research and the range of constituent material options available to optimise the performance of vinyl ester / cenosphere composite systems. The review indicated that research in the field is at a relatively early stage suggesting that before specialised performances are explored, it is logical to develop an understanding of the fundamentals of material behaviour. This implies the investigation of systems based on standard materials should be prioritised to develop a base-line of knowledge for system behaviour that subsequent research can be built from.

From this review, the following types of constituent materials were identified to meet these requirements:

- A standard grade vinyl ester resin that offers a good balance of mechanical and physical performance while remaining cost-effective.
- Alternative grade of vinyl ester resin with a basic oligomer type modification which may possess improved performances.
- An ambient temperature cure system that offers considerable flexibility to cure VE resins using standard equipment in a range of conditions.
- A class of cenospheres with a graded particle distribution and a range of particle sizes.

The aforementioned criteria will form the basis for the selection of materials in the subsequent work of this PhD study.

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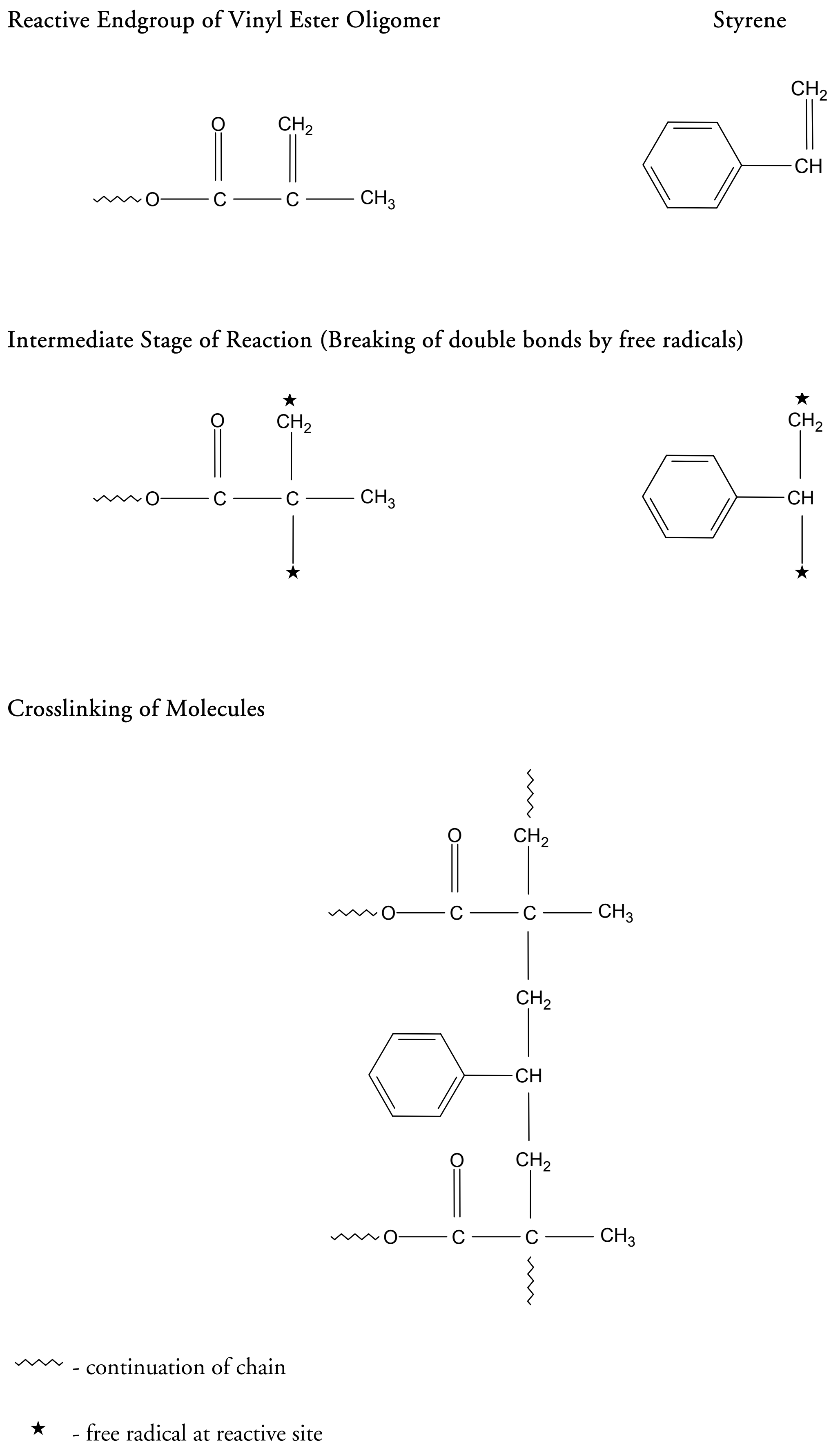
CHAPTER 3.

THE CURE BEHAVIOUR OF VINYL ESTER / CENOSPHERE COMPOSITES

3.1. INTRODUCTION

Having reviewed the various constituent options available for vinyl ester / cenosphere composites in the previous chapter, the next step in developing a more complete understanding of such systems is to examine their production from the constituents options identified. Creation of a functional composite system requires that the various constituents be blended together while the vinyl ester is in an uncured state and that this blend then be chemically cured to form the final thermoset composite. It is therefore important to understand the curing mechanisms of the vinyl ester resin and the various parameters which influence this cure in a cenosphere composite system.

As discussed in the previous Chapter, vinyl ester resins are generally cured through a free-radical-initiated copolymerisation reaction. In this reaction, the double-bond endgroups of the oligomer are crosslinked with the double-bond of the styrene monomer to form a three-dimensional network. The cure process is shown schematically in Figure 3.1. The free radicals will normally be generated through the decomposition of an organic peroxide initiator aided by heat and/or an accelerator. The cure can be achieved at ambient or elevated temperatures depending on the adopted cure system and its elements.



Reactive Endgroup of Vinyl Ester Oligomer

Styrene

Intermediate Stage of Reaction (Breaking of double bonds by free radicals)

Crosslinking of Molecules

∿∿∿ - continuation of chain

★ - free radical at reactive site

Figure 3.1 Schematic of free radical crosslinking reaction of VE oligomer with styrene.

It is important here to note the difference between a resin changing from liquid to solid state and the attainment of full cure. The term "cured" refers to a state in which all possible network linkages have been formed through the conversion of unsaturation sites in the oligomer and reactive monomer. However, a resin will typically change from liquid to solid state when only a small portion of these bonds have been formed. The cure reaction must then continue within the new solid for full conversion to be achieved.

For a crosslink to occur, it is necessary for two unsaturation points and two free radicals to be in sufficient proximity for the reaction to initiate. The mobility of the oligomer and reactive monomer will significantly influence their ability to achieve this required proximity and hence will be a determining factor in the progress of a given cure reaction. The mobility of the oligomer and reactive monomer is a function of their respective molecular weights and temperature.

The molecular weight also influences the inherent proximity of unsaturation points in the resin solution. As VE oligomers are only terminally unsaturated, a shortening of the chain length (corresponding to a reduction in molecular weight) will result in more molecules within a given volume and thus increasing the number of unsaturation points within that volume.

The reactive monomer is normally of significantly lower molecular weight than the oligomer to achieve desired viscosity reduction of the resin solution. Additional monomer into a resin formulation will therefore introduce a greater number of monomer molecules into a given volume. This will in turn result in a higher concentration of unsaturation sites within that volume. Examination of molecular weight and monomer content influences would therefore appear to be an important part of any experimental investigation of cure behaviour.

In addition to the proximity to reactive unsaturation sites, the progression of the cure process is heavily influenced by the presence of free radicals near these sites. As mentioned previously the free radicals required to initiate a crosslink reaction are provided through the decomposition of an organic peroxide. When added to a resin solution which is properly promoted for the given processing temperature, the organic peroxide breaks down to form a pair of free radicals. During the cure reaction each free radical may participate in a large number of crosslink formations, being temporarily taken up by a VE oligomer or styrene molecule during the breaking of the unsaturated double bond and then coming free again as the VE and styrene react with each other to create the thermoset network. The number of crosslink formations that a given radical can participate in is generally limited by the decreasing mobility of the molecule as network formation progresses. It may also be consumed in a side reaction with other substances such as inhibitors. Successful polymerisation therefore requires the generation of an adequate distribution of radicals over a prescribed timeframe to affect all the necessary crosslinks before the growing network can restrict further movement.

Based on this scenario, it would appear that two factors will play a primary role in the progression of the cure process. Firstly, the initiator addition rate will largely determine the rate distribution of peroxide and thus radical creation throughout the resin solution. This assumes of course that the peroxide is properly dispersed within the solution through adequate mixing procedures. In such instances, higher addition rates will result in a greater number of peroxide molecules within a given volume, leading to greater radical density as the peroxide decomposes. Secondly, the rate at which the peroxide decomposes will obviously determine the profile of the radical distribution with respect to time. Given the need for a degree of molecular mobility in achieving optimum cure, it is probably preferable to have the free radical generation spread over a time period. This would allow for some redistribution of the oligomer, reactive monomer and radical before crosslink formation fully retards molecular movements. The rate of decomposition of the peroxide is influenced by three principal factors, namely

- the type of peroxide,
- the temperature of the system, and
- the presence of accelerators within the system.

The aim of this current experimental investigation is to develop an improved understanding of vinyl ester curing and the impact of the cure profile on vinyl ester / cenosphere composite systems. To achieve this end, the study will first examine the cure characteristics of neat vinyl ester resin systems and utilise these findings in characterising cenosphere composite systems. Based on the observations outlined already, the study of neat resin curing will examine the following parameters:

- The concentration of initiator.
- The type of peroxide initiator.
- The promotion regime.
- The molecular weight of the oligomer.
- The reactive monomer concentration.
- The filler addition level.

The influence of each parameter is studied using differential scanning calorimetry (DSC), an analytical technique which measures changes in the heat flow characteristics of a material. This technique utilises the exothermic nature of the crosslinking reaction to assess cure behaviour.

Following the study of the neat resin matrix, the parameters will be examined for their influence on cenosphere composite systems. In this instance however, experimentation will monitor temperature changes in the sample due to the exothermic reaction.

3.2. EXPERIMENTAL INVESTIGATION

This section outlines the materials selected for use in this study which are based on the recommendations made in Section 2.8. The adopted experimental techniques and procedures used to examine the cure behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites are summarised before the results are presented in Section 3.3.

3.2.1. MATERIALS

- Matrix Systems

In accordance with the conclusions of Chapter 2, two different vinyl ester matrix systems were utilised in this study of cure behaviour:

- Standard grade vinyl ester - Hetron 922 PAW

  Hetron 922 is a direct derivative of the original Epocryl vinyl ester resin introduced by the Shell Chemical Company in 1965, and along with Dow Chemical's Derakane 411 vinyl ester is considered one of the industry's standard products. Formulation rights for 922 are now owned by the Ashland Specialty Chemical Company and the product is manufactured in Australia under license by Huntsman Chemical Company (Australia). It is a basic methacrylated DGEBA epoxy resin solution containing 45% styrene monomer by weight. Hetron 922 PAW is a ready-to-use version of 922 which is supplied with promoters, accelerators and a thixotrope already blended. The resin sample used for this experimentation was not synthesised using Ashland's new F-Cat technology.

- Reduced styrene grade - Hetron 914

  Hetron 914 is a low styrene vinyl ester resin which is normally used as a basis for other formulated vinyl ester resins. It was selected for this investigation due to its very low styrene content (20% as opposed to 45% in Hetron 922 PAW) which allows for the investigation of styrene content influences through end user addition of extra styrene to the solution. The oligomer backbone of Hetron 914 also possesses a lower molecular weight compared to Hetron 922, allowing for investigation of molecular weight influences on cure behaviour. The resin is manufactured locally by Huntsman Chemical Company (Australia) under licence from Ashland Specialty Chemical Company. It is supplied unpromoted and without a thixotrope. For the purposes of the current study it was accelerated by the author with a cobalt octoate (cobalt(II)-ethylhexanoate) solution containing 6% cobalt (NL-51P, Akzo Nobel). Accelerator levels varied with different experiments as described in the relevant experiment details.

- Reactive monomer

Styrene monomer was used in conjunction with the Hetron 922 PAW to investigate the influence of styrene addition levels on cure characteristics. The styrene was supplied by Huntsman Chemical Company Australia Pty Ltd.

- Peroxide Initiators

Four different organic peroxide initiators were used for this study. These are listed in Table 3.1. The two MEKP grades were selected as being representative of the curing systems widely used within industry for this type of material. MEKP-SR was recommended by Huntsman Chemical Company for curing Hetron 922 and is referenced on the product data sheet [1].

Table 3.1 Organic peroxide initiators used in cure study.

Product Name	Description	Active Oxygen Content (%)	Manufacturer
Butanox M-60	General purpose MEKP, 36% solution in phlegmatiser.	9.8 – 10	Akzo Nobel
MEKP-SR	Slow reactivity MEKP	n/a	Laporte Organics
CHP 90	Cumyl hydroperoxide, 90% solution	n/a	Huntsman Chemical Company (Aust)
Trigonox 239	Cumyl hydroperoxide, 45% solution in solvent mixture, with promoter	4.6	Akzo Nobel

The two cumyl hydroperoxide (CHP) grades were chosen as ambient temperature cure options which would not induce fizzing in the resin. MEKP solutions contain a percentage of hydrogen peroxide (H_2O_2) which react with the cobalt accelerator to produce oxygen. This forms bubbles within the resin solution (fizzing) which can remain within the cured matrix as voids. The hydrogen peroxide in MEKP solutions is a by product of their production and cannot be entirely eliminated. CHP does not contain H_2O_2 and hence do not produce fizzing. A drawback of CHP systems is that they are typically much slower reacting than MEKP systems. Trigonox 239 contains a promoter to increase the reactivity of the system.

- Cenospheres

Cenospheres are available in a number of grades classed by particle size with the more finely graded particles typically having a higher cost. The cenosphere filler used in this study was E-spheres supplied by Envirospheres Pty Ltd. Based on the recommendation made in Chapter 2, only the more cost-effective general purpose E-spheres SLG grade which has a graded particle distribution (20 – 300μm) was used in the study.

Table 3.2 lists the materials used in this study. All materials utilised in subsequent investigations as part of this PhD project were made from this selection.

Table 3.2 Selected materials used in the investigations of this PhD study.

Product Number	Product Name	Description
1	Hetron 922 PAW	Standard grade vinyl ester resin
2	Hetron 914	Low styrene content vinyl ester resin
3	Accelerator NL-51P	Cobalt octoate medium-reactivity accelerator
4	Butanox M-60	General purpose medium-reactivity MEKP
5	MEKP-SR	Slow reactivity MEKP
6	CHP 90	Cumyl hydroperoxide, 90% solution
7	Trigonox 239	Cumyl hydroperoxide, 45% solution in solvent mixture, with promoter
8	E-Spheres SLG	20 - 300μm cenosphere filler
9	Styrene	Styrene monomer

3.2.2. EXPERIMENTAL TECHNIQUES

A number of techniques are available to examine the cure characteristics of thermosetting polymers. These techniques fall into two basic classes which either monitor changes in the chemical structure of a sample or which monitor energy changes in the sample.

Monitoring of molecular changes in vinyl esters typically relies on detection and monitoring of the number of unsaturation sites in both the VE oligomer and the reactive monomer. As the cure reaction progresses the number of these sites within the sample decreases as they are consumed in crosslink formations.

Spectroscopy analysis techniques investigate material structure on a molecular level. Fourier transform infrared spectroscopy (FTIR) monitors the functional groups of a material. Cure can be analysed by comparing the spectra of materials and monitoring changes in the signal peaks corresponding to the functional groups. Nuclear magnetic resonance spectroscopy (NMR) examines the actual molecular structure of a material. A material is characterised by a spectrum and the molecular structure inferred from the relevant signals of the spectrum.

The other means of characterising cure behaviour is through the monitoring of heat flows in a sample. The vinyl ester cure reaction is exothermic and thus its progress can be followed by measuring the generation of this heat. The two most widely used techniques for this type of measurement are differential thermal analysis (DTA) and differential scanning calorimetry (DSC). DSC is normally preferred due to its ability to quantify heat flows.

3.2.2.1. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique which evaluates the heat capacity characteristics of a material under specific thermal conditions. In DSC a test specimen and a reference specimen are simultaneously subjected to a controlled temperature programme within a high precision furnace (Figure 3.2). The temperatures of both the test and reference specimens are measured by thermocouples located underneath the base of each specimen holder. Differences in the temperature of the reference and sample are used to determine endothermic and exothermic thermal events in the sample material.

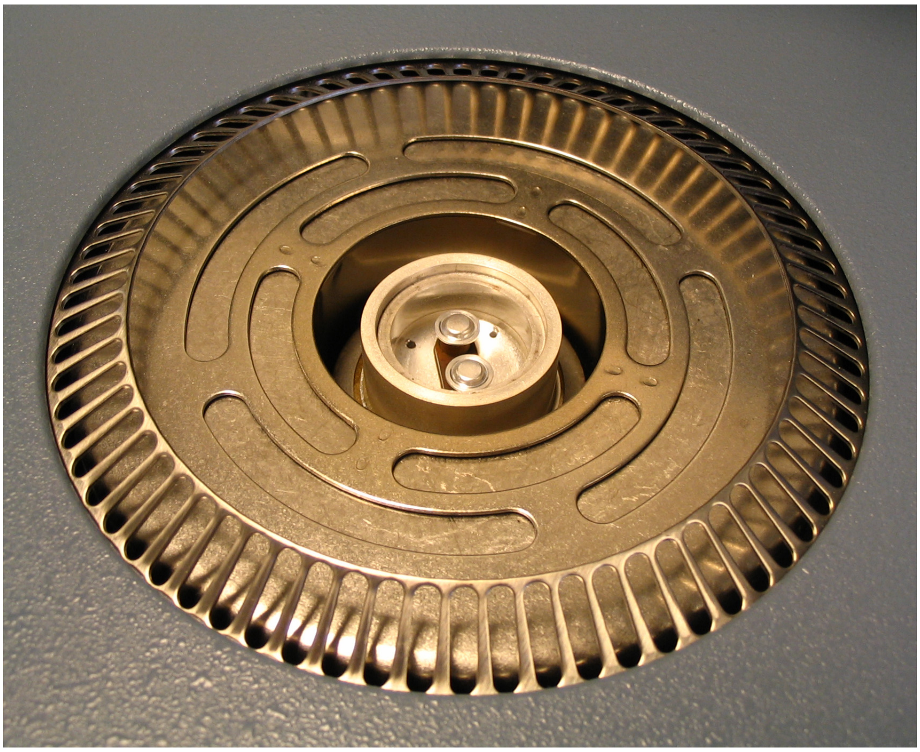


Figure 3.2 Test and reference specimens located on the thermocouple bases within the DSC furnace (lid removed).

Generally two types of test methods are utilised: temperature-scanning measurement where the temperature is ramped according to a specified cycle or isothermal measurement where the temperature is maintained at a specified value. All experiments in this current study were performed as temperature-scanning measurements to provide for detection of phase transition temperatures in addition to basic cure kinetics.

Through the specified temperature cycle, the changes in heat flow of a sample that occur due to the exothermic crosslinking reaction are measured. This enables the progression of the cure reaction to be analysed and phase transitions of a cured network determined.

- *Experimental Conditions*

All DSC measurements in this current study were performed using a TA Instruments Q100 DSC with refrigerated cooler (-90°C to 550°C temperature range) calibrated with an indium standard. Specimens were run in hermetically sealed aluminium pans.

Specimens were prepared by initiating a larger resin batch (100g) with the designated peroxide curative at ambient temperature (20°C). A small portion of the mixed resin (10mg) was then removed from the larger batch and sealed in the hermetic sample pan under air. Larger resin quantities were originally initiated to ensure the initiator and resin blend of the DSC specimen was homogenous.

DSC runs were then conducted on each specimen using a heat / cool / heat cycle running from -20°C to 250°C with a heating and cooling ramp rate of 10°C/min.

- *Evaluation Parameters*

The heat flow versus temperature data was recorded for each heating or cooling run. The DSC results of the first run on each sample were baseline corrected at a heat flow of 0 W/g at 25°C. The results of the second heating run were used to examine the transition behaviour. The transition curves on the plots were offset to allow a clearer interpretation of the transition behaviour. The following indicators from the DSC results were used to analyse the cure behaviour of the samples using the Universal Analysis software provided with the instrument. First and second run DSC curves with analysis indicators are shown in Figure 3.3 and Figure 3.4 respectively. The DSC results of Hetron 922 PAW initiated using 2.0% Butanox M-60 are used.

The onset temperature of the cure reaction provides an indication of the speed of formation of the network. A lower onset temperature indicates a more rapid network formation. The extrapolated onset temperature was used as it relates to the onset of the main cure reaction. The extrapolated onset temperature is defined as the intersection between the tangent to the maximum slope of the peak and the extrapolated baseline (Figure 3.3).

The heat of reaction is a measure of the release of heat due to the polymerisation cure reaction. The heat of reaction was determined by integrating the DSC curve over the temperature range of 25°C to 175°C (Figure 3.3).

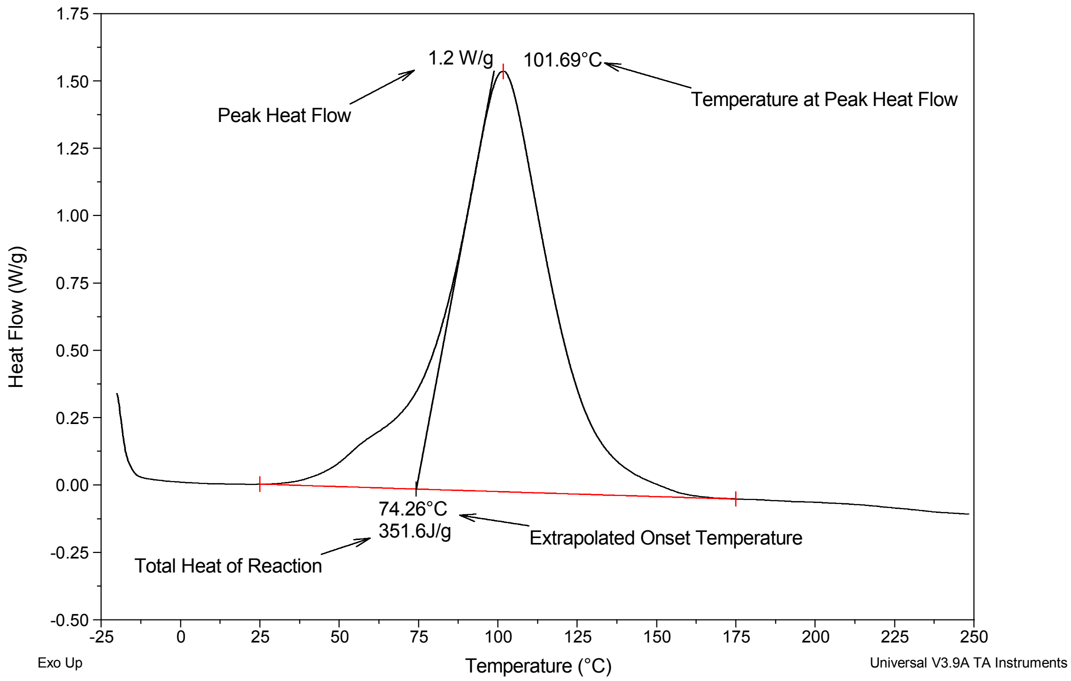


Figure 3.3 Interpreting first run DSC heat flow versus temperature curves to analyse cure behaviour.

The peak heat flow is indicative of the rates of cure of specimens with a higher peak heat flow associated with a faster rate of cure. The temperature corresponding to the peak heat flow is also indicative of the speed of the cure reaction (Figure 3.3).

The glass transition temperature is an important property of a polymer network that indicates its transition from a rigid glassy state to a flexible rubbery state. Although often described by a single temperature, the glass transition actually occurs over a temperature range (Figure 3.4) which can introduce some ambiguity with regard to the selection of the glass transition temperature. The glass transition temperature and transition behaviour is examined further in Chapter 6. For this investigation, the onset temperature and the point of inflection of the transition were interpreted from the second run DSC curves as the glass transition temperature. The onset temperature is indicative of the start of the transition and defined as the intersection between the tangent to the curve at the selected lower limit and the tangent through the point of inflection of the transition (Figure 3.4). The point of inflection describes the midpoint of the glass transition.

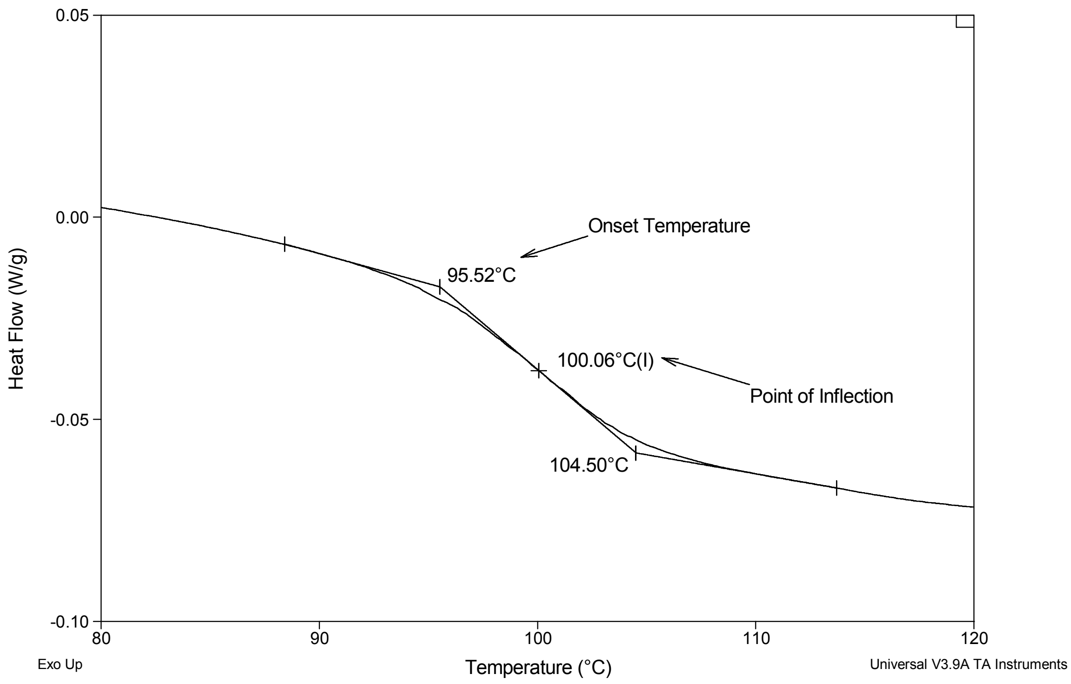


Figure 3.4 Interpreting second run DSC heat flow versus temperature curves to analyse the transition behaviour.

3.2.2.2. Cure Assessment of Cenosphere Composites

With such small sample sizes used for the DSC specimens, the accuracy of analysing filled samples using this technique was questioned with regard to the relatively small specimens being an accurate representation of the cenosphere composite material under investigation. Therefore a relatively simple method was devised to monitor the cure behaviour of vinyl ester / cenosphere composite systems.

Thermocouples were used to monitor the changes in temperature of neat resin and filled samples due to the exotherm of the cure reaction. By comparing the data of the two samples the relative influences due to the addition of the filler may be extricated. Resin samples (100g) were initiated with the designated peroxide curative at ambient temperature and a thermocouple secured in the sample. To isolate the influence of the filler in the cenosphere composite samples, the 100g of resin was maintained and the volume of filler added as determined by the adopted filler volume fraction. For the filled samples, the filler was combined with the resin prior to the addition of the initiator.

The changes in temperature of each specimen due to exotherm were recorded over time. The temperature was recorded at one minute intervals using T-type thermocouples and a Datataker 50 acquisition system.

The initial stages and onset of the cure were examined by determining a latency period that corresponded to an increase in temperature of 5°C. The magnitude of the peak temperature and the time to this temperature were established to study the main cure reaction.

3.3. RESULTS AND DISCUSSION

This section presents the experimental results of this investigation of cure behaviour. The cure behaviour of unfilled vinyl ester resins is considered first followed by the cure behaviour of filled vinyl ester resins. Where appropriate the discussion also draws on previous research material for the purpose of comparison.

3.3.1. CURE BEHAVIOUR OF UNFILLED VINYL ESTER RESINS

3.3.1.1. Influence of Initiator Concentration

The initial part of this investigation sought to evaluate the influence of increasing peroxide levels on the cure of the nominated vinyl ester systems. The aim of this work was to evaluate whether there were upper and lower bounds on the rate of initiator addition to the matrix system and if so what these bounds were. To achieve this aim, DSC testing was conducted on the Hetron 922 PAW system using Butanox M-60 as the initiator. Initiator concentration levels were varied from 0% to 5% to study the influence of the addition rate. Each specimen was subject to two heating ramps to assess the thermal kinetics of both a curing and a cured sample. Key data for each sample is summarised in Table 3.3. Full heat flow versus temperature plots for the first and second DSC heating runs are given in Appendix A.

General observation of the obtained data shows that at initiator addition levels above 1.0% all samples produced similarly shaped heat flow curves, although the curve for 1.0% initiator lagged behind the others in terms of both onset temperature and peak heat flow. At 0.5% initiator, the material still displayed an exothermic peak albeit at a noticeably lower level, however the heat flow plot also displays a plateau both before and after the peak. At addition levels of 0 and 0.25% initiator DSC curves did not show a normal exothermic reaction but instead displayed endothermic heat flows which would indicate a reaction other than peroxide initiated crosslinking.

Table 3.3 Key thermal data from DSC analysis of Hetron 922 PAW vinyl ester with varying initiator levels.

Resin	Hetron 922 PAW		**Initiator:**	Butanox M-60	
Initiator Addition Level (%)	**First Heating Run Cure Behaviour**			**Second Heating Run Glass Transition**	
	Reaction Onset Temp. (°C)	**Total Heat of Reaction (J/g)**	**Peak Heat Flow (W/g)**	**Temp at Peak Heat Flow (°C)**	**Onset (°C)**	**Point of Inflection (°C)**
0.0	145	-165	-0.61	160	82	84
0.25	144	-86	-0.27	165	92	97
0.5	102	291	1.09	120	95	101
1.0	79	316	1.34	104	89	94
1.5	75	364	1.52	101	94	99
2.0	74	352	1.53	102	96	100
2.5	73	360	1.58	102	91	95
3.0	74	377	1.63	102	87	92
4.0	75	369	1.57	103	84	89
5.0	71	378	1.52	104	82	86

The variation of the reaction onset temperature with initiator concentration is shown in Figure 3.5. It can be seen that at addition levels of 1.0% and above the temperature appears stable at approximately 75°C, independent of the initiator concentration.

For the 0 and 0.25% initiator levels, the onset temperature for the endothermic reaction was considerably higher at just over 140°C, supporting the theory that the reaction was enabled by the elevated temperatures and not peroxide decomposition. With the sample using 0.5% initiator addition, the plateau on the high temperature side of the heat flow plot also began at ≈140°C. Given the discontinuity in material behaviour in this range it would seem reasonable to conclude that the reaction seen with the 0 and 0.25% addition samples also occurs in the 0.5% sample, suggesting that the 0.5% addition rate is insufficient to effect full cure by standard means.

An examination of the variation in total heat of reaction (Figure 3.6), peak heat flow (Figure 3.7) and the peak heat flow temperature against increasing initiator addition rates further supports these findings. At addition rates of 1.5% and above, the heats of reaction and peak heat flows were relatively consistent at approximately 365 J/g and 1.56 W/g, indicating a stable cure behaviour that is independent of the initiator addition rate.

Similarly, the temperatures at which the peak heat flow occurred were all between 101°C and 104°C. While the peak heat flow temperatures do increase with the increasing addition rate, the magnitude of this increase is under 4% and it is difficult to ascertain whether this change is indicative of alterations in the cure mechanics without further testing.

Nevertheless, this data would appear to indicate that a stable reaction which is independent of the initiator addition rate can be achieved at addition levels above 1.5%.

The alternative reaction occurring in the 0% and 0.25% initiator addition samples is clearly demonstrated by the heat flow characteristics of the DSC samples. The total heat of reaction for each sample is negative indicating a net endothermic event taking place. Peak heat flows are similarly negative. The temperature at which the peak flow occurs is also distinctly different, occurring at around 160°C. While it is not possible to ascertain the nature of this reaction with DSC, it is clearly different than the reactions occurring at higher addition rates.

While the sample with the 0.5% addition rate highlights the occurrence of an exothermic reaction, the shoulder on either side of the peak indicates a significance difference in the cure cycle from that seen with addition levels over 1.5%. The exact reason for the shoulders is not known but it is thought that the initial shoulder may indicate the generation of an insufficient number of free-radicals at ambient temperature. After initial gelation, the molecular mobility is retarded and the reaction cannot progress without the increase in mobility granted by additional heat energy into the system. Verification of this theory would require the use of alternative techniques such as FTIR, however the data is sufficient to conclude that the addition of 0.5% initiator is insufficient to support a normal reaction.

The 1.0% initiator addition level appears to be around the minimum acceptable addition level to support normal curing of the matrix through peroxide decomposition. While the heat flow curve has the same characteristic shape as higher addition levels, the total heat of reaction and peak heat flow are both noticeably lower indicating differences in the reaction which is occurring. The lower heat of reaction may indicate that the radical distribution created by the peroxide decomposition is insufficient to progress cure to an optimal level before network formation restricts further molecular movement. Again this would need to be investigated by alternative techniques.

Observation of the glass transition temperatures obtained with the various initiator addition levels (Figure 3.8) also tends to support the proposition of a lower initiator addition level of between 1.0% and 1.5%. It can be seen that the T_g obtained with 1.0% initiator is noticeably lower than for 1.5 or 2.0%.This would support the suggestion that the molecular movement restrictions created by the evolving polymer network limit the ability of the reaction to progress further. While the same restrictions would occur with the higher addition levels, the increased distribution density of available free radicals would reduce the need for molecular mobility and would thus allow the reaction to progress further than with a lower distribution.

The drop off in T_g seen at the higher addition levels is thought to be due to the increasing amount of non-reactive material introduced into the system at higher initiator addition rates. The dimethyl phthalate used as a carrier/damper medium in the Butanox M-60 would remain within the cured network and act as a plasticiser.

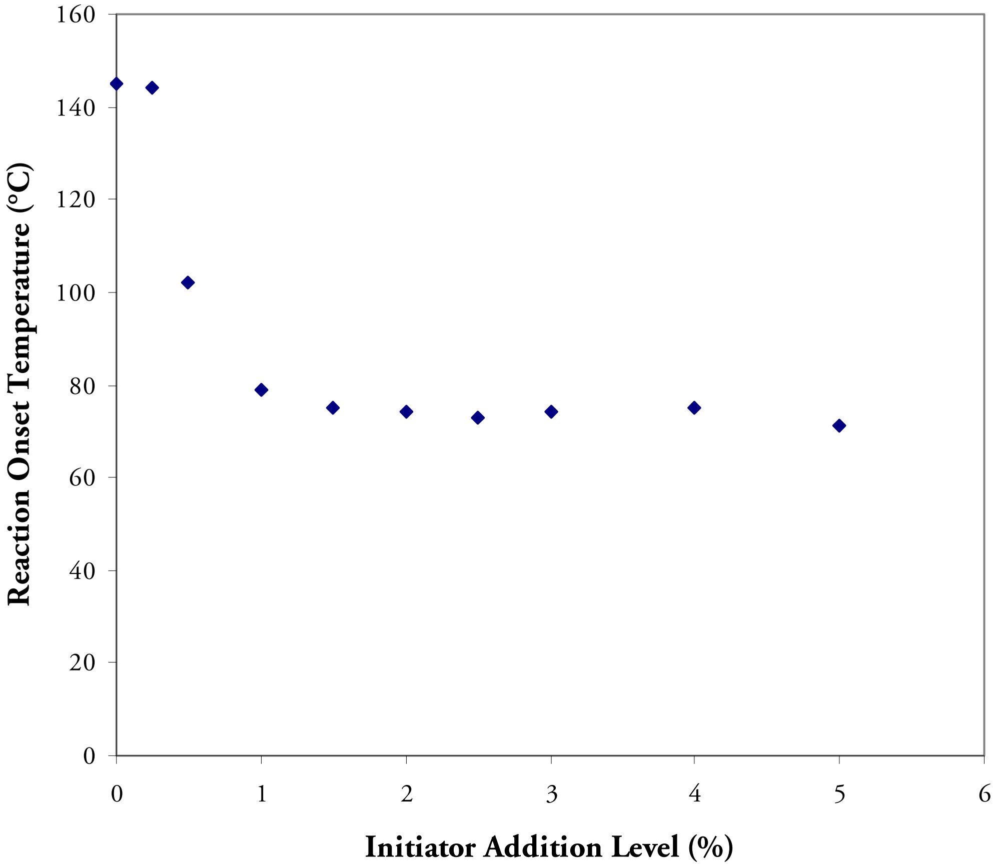


Figure 3.5 **Relationship of the reaction onset temperature of Hetron 922 PAW vinyl ester with varying initiator concentration.**

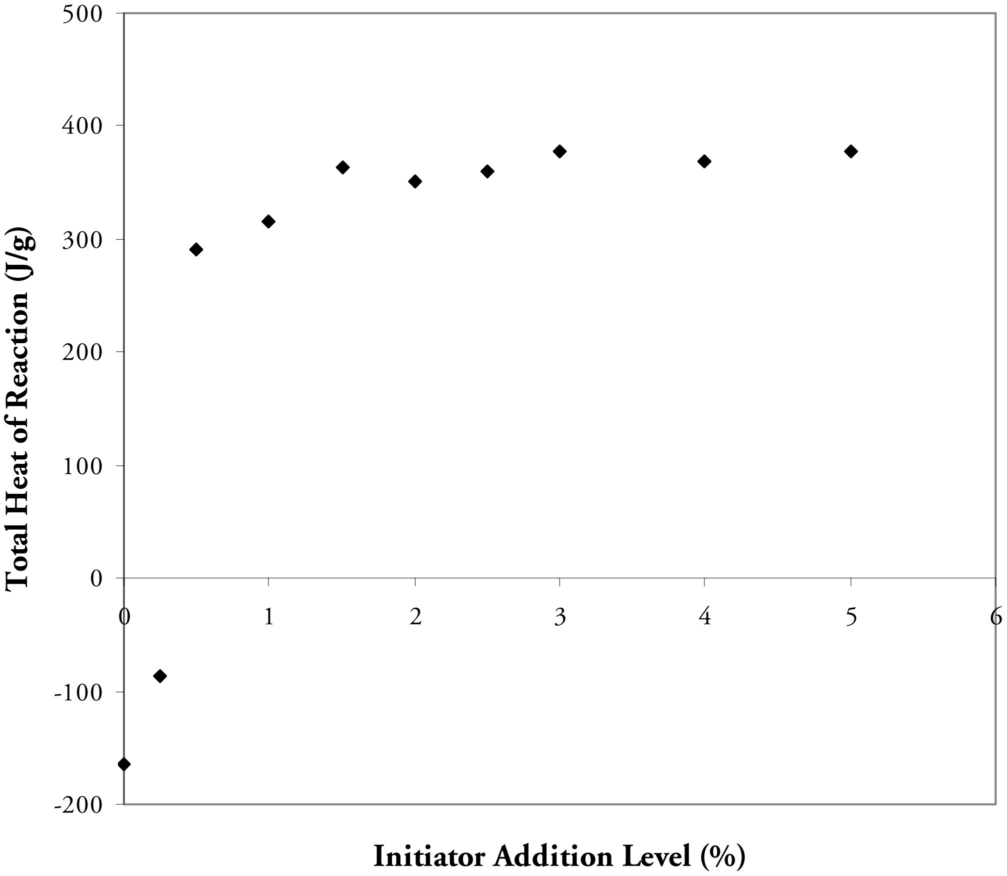


Figure 3.6 **Relationship of the total heat of reaction of Hetron 922 PAW vinyl ester with varying initiator concentration.**

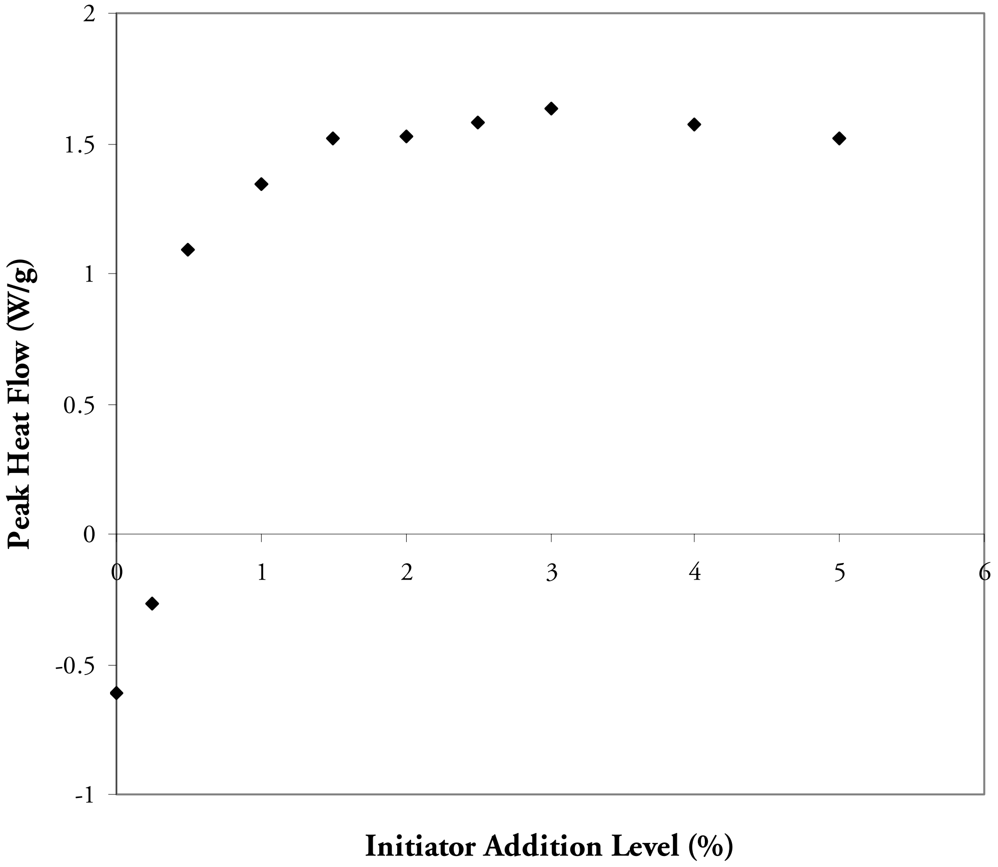


Figure 3.7 **Relationship of the peak heat flow of Hetron 922 PAW vinyl ester with varying initiator concentration.**

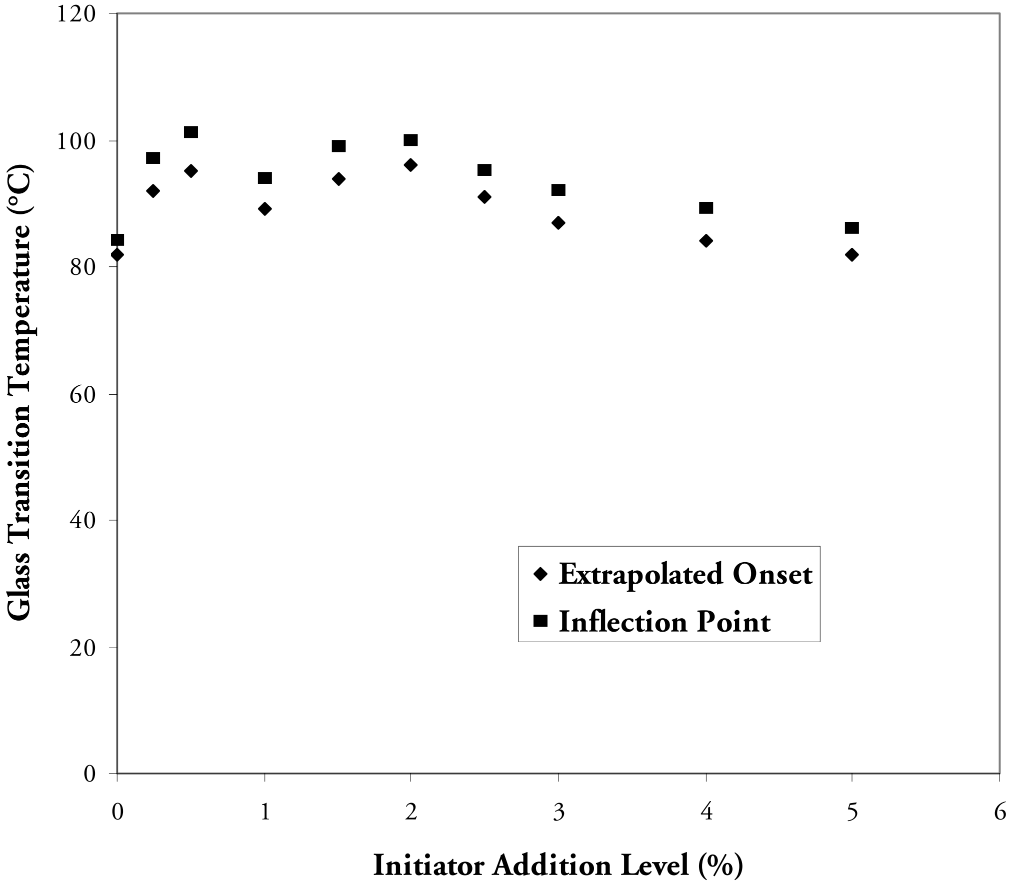


Figure 3.8 Relationship of the glass transition temperature of Hetron 922 PAW vinyl ester with varying initiator concentration.

Using the earlier discussion, it could then be concluded that while higher initiator levels do not retard the cure reaction there is ultimately not a lot to be gained through their use. The heat flow curves for addition rates above 1.5% are very similar except for their initial shoulder (Figure 3.9). Cook *et al.* [2] attributed the presence of the initial shoulder to small traces of H_2O_2 that react more readily with the cobalt to form radicals than the MEKP potentially causing early initiation of the resin. As the initiator concentration was increased the size of the shoulder increased indicating more of the reaction occurs at this early stage. This suggests that higher initiator concentrations may be utilised to increase the initial rate of cure and gelation of the resin to suit specific processing requirements. However initiator addition levels in the range of those studied do not appear to change the ultimate characteristics of the matrix cure.

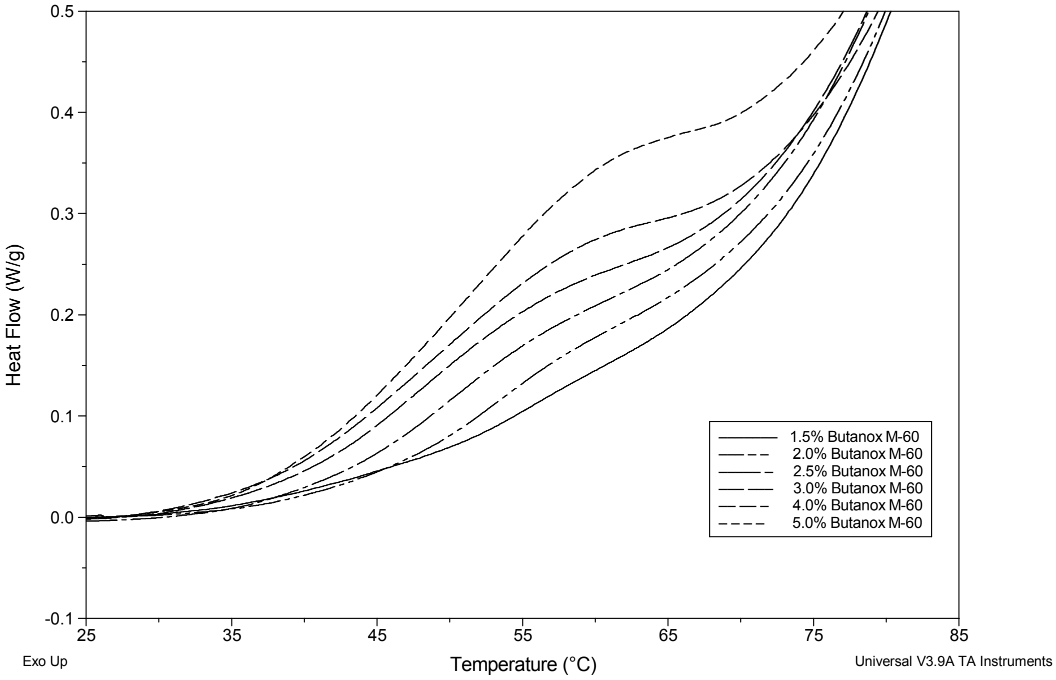


Figure 3.9 Initial section of DSC curves of Hetron 922 PAW vinyl ester with varying initiator concentration.

Overall, maintaining a minimum initiator level of 1.5% appears to produce stable cure behaviour with generally consistent cure characteristics. No significant changes in cure behaviour were achieved as the concentration was increased, indicating that if the distribution density of generated radicals is sufficient, the cure behaviour is largely independent of the initiator concentration. Higher initiator concentrations may be used to accelerate initial cure of the matrix, however this does begin to have a detrimental effect on the T_g above about 2.5% in the tested material. It is thought that similar effects would be observed for other vinyl esters due to the increase in non-reactive material within the system which will remain as a contaminant in the final cured matrix.

3.3.1.2. Influence of Peroxide Initiator Type

Having examined the variation in cure behaviour caused by alteration of the initiator addition level, testing was then conducted to investigate how the cure characteristics of the matrix system changed when alternative peroxides were used. For the purposes of this current study, DSC testing was conducted on the Hetron 922 PAW system using the four different peroxide initiators listed in Table 3.1. All samples used an initiator addition level of 2%, which is within the range identified, to isolate the influences of the different peroxides. Each specimen was subjected to two heating ramps to assess the thermal kinetics of both a curing and a cured sample. Full heat flow versus temperature plots for the first and second DSC heating runs are given in Appendix A. Key data from each sample is summarised in Table 3.4. The heat of reaction for the CHP initiated samples was determined over the range of 25°C to 225°C to encompass the plateau exhibited after the main exotherm peak.

Table 3.4 Key thermal data from DSC analysis of Hetron 922 PAW vinyl ester with different peroxide initiator types.

Resin	Hetron 922 PAW		**Initiator Addition Rate:**	2%		
	First Heating Run Cure Behaviour				**Second Heating Run Glass Transition**	
Initiator	**Reaction Onset Temp. (°C)**	**Total Heat of Reaction (J/g)**	**Peak Heat Flow (W/g)**	**Temp at Peak Heat Flow (°C)**	**Onset (°C)**	**Point of Inflection (°C)**
Butanox M-60	74	352	1.53	102	96	100
MEKP-SR	71	336	1.52	98	110	115
Trigonox 239	95	385	2.03	114	100	104
CHP 90	101	365	1.42	119	99	104

Both the MEKP based initiators produced similar shaped heat flow curves as did both of the samples cured with CHP based initiators. However the curves between the two different peroxide types were quite different with the CHP initiators exhibiting a plateau after the main exotherm peak.

The plateau on the high temperature side of these samples began at ≈140°C, approximately the same temperature of the plateau exhibited by a sample in the previous section. The presence of this plateau suggests part of the cure may be due to the elevated temperature. In the previous section, the plateau was not evident at higher initiator concentrations suggesting a 2% concentration of CHP based initiator solutions may be insufficient to effect cure entirely through peroxide decomposition. This indicates a different optimum concentration range for these initiator types may be required.

The lower reaction onset temperatures and temperatures at peak heat flow of the MEKP based initiator solutions highlights their comparably higher reactivity when compared to the CHP based initiators.

The Trigonox 239 sample exhibited a considerably higher peak heat flow attributed to an increased reactivity due to the promoter in the initiator solution. Overall the promoter appears to have only influenced the heat flow and potentially the total heat of reaction of the cure for this sample. The total heat of reaction of the samples initiated with CHP initiators appears higher than the MEKP initiators.

The differences between the extrapolated onset and point of inflection values for the glass transition temperature were consistent between each sample. The higher glass transition temperature of the MEKP-SR cured sample may be due to the lower comparable content of DMP phlegmatiser in the MEKP-SR initiator solution [3] compared to Butanox M-60 [4]. An unknown at this time is the relative influence of alternative phlegmatiser types or solvents contained in initiator solutions on the T_g, with some types potentially having more of an effect on the network properties than others.

In the previous section, the general stabilisation of first scan DSC results above an initiator concentration of 1.5% suggested that for peroxide cure, the behaviour is independent of the initiator concentration. The variability in the first scan DSC results between each of the initiator solutions and not just the base peroxide suggests that cure behaviour is very dependent on the composition of initiator solution utilised to effect cure.

3.3.1.3. Influence of Accelerator Level

The initial two portions of this study examined initiator influences on the curing of a vinyl ester system. Having examined such influences in relative isolation, it is desirable to extend the findings by assessing the consistency of the outcomes when changes are made to the vinyl ester oligomer itself. To investigate potential changes in behaviour, Hetron 914 was selected as it provided a lower molecular weight oligomer compared with Hetron 922.

While the Hetron 922 PAW was supplied as a pre-promoted system, Hetron 914 was not and it was therefore necessary to accelerate it for curing with the four peroxide initiators identified earlier. As discussed earlier, the acceleration of the resin solution is another variable which may significantly alter the cure characteristics. Testing was therefore undertaken in an effort to quantify such effects. DSC testing was conducted on the Hetron 914 system using the Butanox M-60 initiator at a set addition rate of 2%. Resin samples were prepared using the NL-51P cobalt accelerator with addition rates ranging from 0% to 0.4%. Each specimen was subject to two heating ramps to assess the thermal kinetics of both a curing and a cured sample. Full heat flow versus temperature plots for the first and second DSC heating runs are given in Appendix A. Key data from each sample is summarised in Table 3.5.

Table 3.5 Key thermal data from DSC analysis of Hetron 914 vinyl ester with varying levels of cobalt accelerator.

Resin	Hetron 914		**Initiator**	Butanox M-60 @ 2%		
Promoter Addition Level (%)	**First Heating Run Cure Behaviour**				**Second Heating Run Glass Transition**	
	Reaction Onset Temp. (°C)	**Total Heat of Reaction (J/g)**	**Peak Heat Flow (W/g)**	**Temp at Peak Heat Flow (°C)**	**Onset (°C)**	**Point of Inflection (°C)**
0	99	295	2.41	115	142	151
0.1	71	302	3.21	82	129	138
0.2	67	298	3.27	77	124	136
0.3	67	294	3.03	76	122	133
0.4	65	297	2.99	75	129	139

All samples accelerated with cobalt exhibited similar shaped heat flow curves. The curve for the un-accelerated sample was marginally broader with a lagged onset and lower peak heat flow.

The reaction onset temperatures of specimens with cobalt accelerator appear stable with only a very slight reduction as the accelerator level was increased (Figure 3.10). The onset temperature of the un-accelerated sample is considerably higher. The role of the accelerator is to promote the decomposition of the peroxide initiator at ambient temperatures. With no accelerator present in the system, the decomposition of the initiator appears due to the elevated temperature. These results indicate the need for the presence of an accelerator within the system to facilitate an effective peroxide cure, particularly for curing in ambient conditions.

The total heats of reaction appear stable at ≈300J/g and independent of the accelerator level (Figure 3.11). Results from previous sections have indicated that for cure through peroxide decomposition, the heat of reaction is independent of the initiator concentration but dependent on the initiator solution. With these results and the initiator influences a constant, it appears that the total heat of reaction is dependent on the characteristics of the resin being cured and not the level of accelerator within the resin.

The cobalt level appears to have a varied effect of the peak heat flow behaviour of the resin (Figure 3.12). The peak heat flow of the sample with no cobalt was considerably lower but is attributed to potentially different cure reaction mechanisms. The highest peak heat flow coincided with a cobalt level of 0.2% with further increases in cobalt lowering the heat flow, apparently impeding the rate of the reaction. The temperature at the peak heat flow showed a similar trend to that observed for the reaction onset temperatures, lowering as the cobalt level was increased.

Cook *et al.* [2] and Abadie *et al.* [5] observed peaks occurring at higher temperatures as cobalt concentrations were increased and suggested that the cobalt salt actually retards the reaction at higher concentrations. The retardation of the reaction at higher cobalt levels may be due to excessive cobalt within the system. However Abadie *et al.* [5] observed the retardation of reaction at 0.7% and 1% levels of NL51P and Cook *et al.* [2] at 0.8% and 3.2% levels of a similar cobalt solution (6% weight of cobalt in white oil). This suggests the accelerator levels used in this study may not be of sufficient magnitude to clearly show the behaviour.

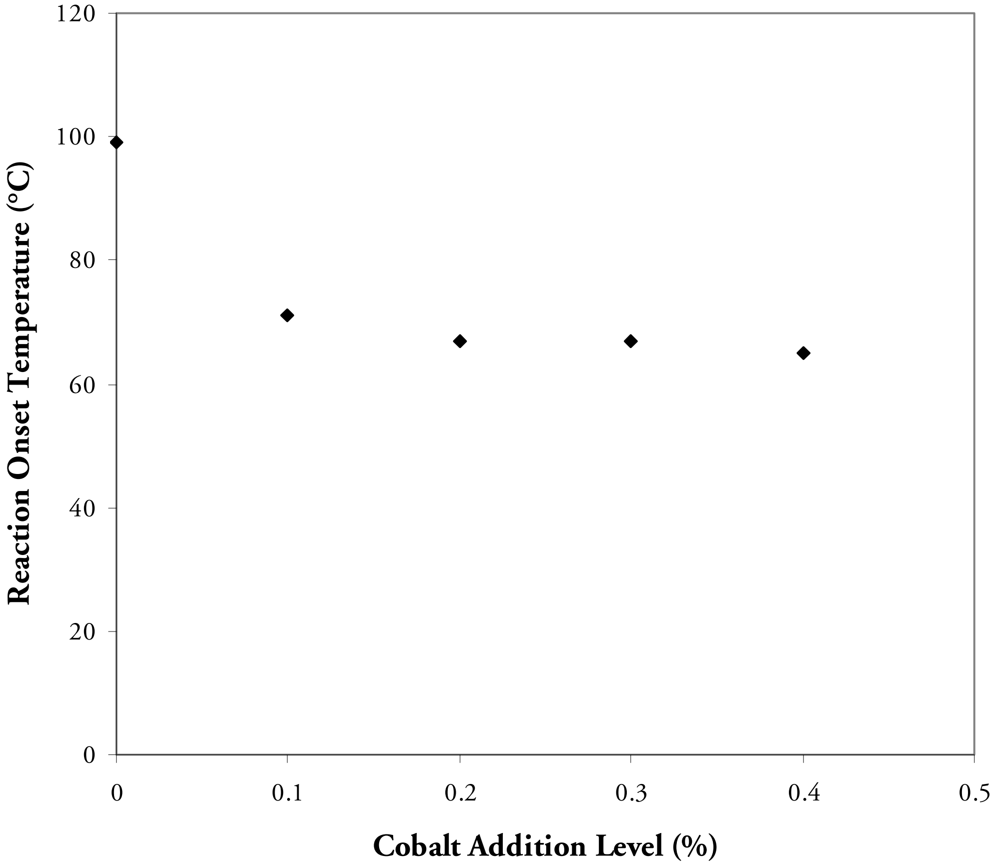


Figure 3.10 **Relationship of the reaction onset temperature of Hetron 914 vinyl ester with varying cobalt accelerator level.**

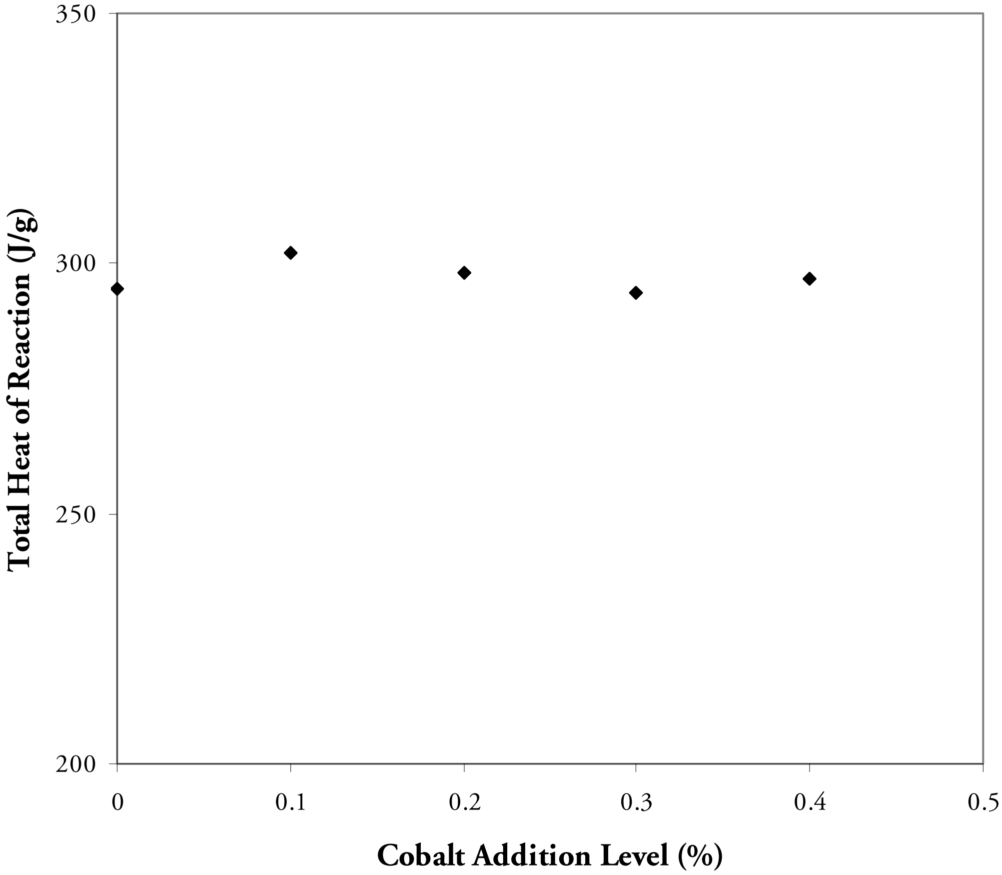


Figure 3.11 **Relationship of the total heat of reaction of Hetron 914 vinyl ester with varying cobalt accelerator level.**

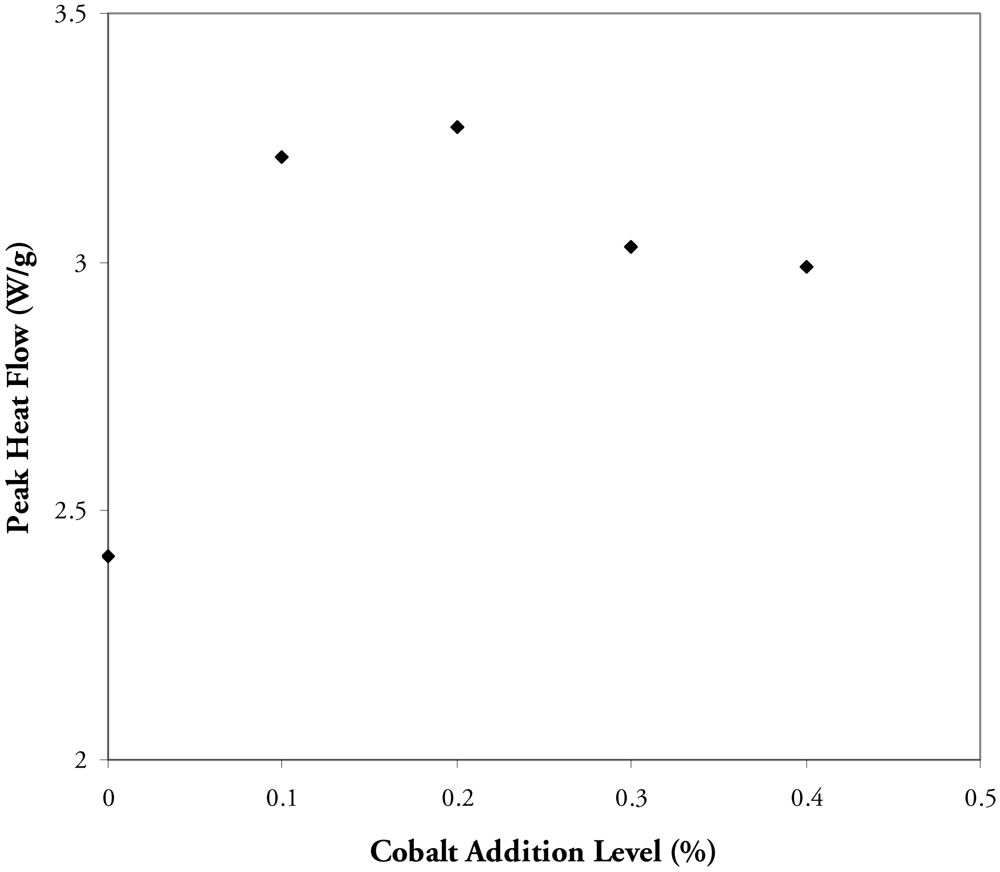


Figure 3.12 Relationship of the peak heat flow of Hetron 914 vinyl ester with varying cobalt accelerator level.

Both the extrapolated onset and point of inflection methods of interpretation of the glass transition temperature show a consistent difference between the values at each of the cobalt levels (Figure 3.13). The glass transition temperatures lowered as the cobalt content was increased however the T_g of the 0.4% cobalt level sample was marginally higher. The reason for this is unknown at this time.

The accelerator is actually cobalt in a solution so a higher level of addition leads to a higher content of diluent within the system. At higher initiator concentrations it was observed that a higher content of this non-reactive material degraded the properties of the network. Therefore it is reasonable to conclude that a similar behaviour may occur with regard to increasing the accelerator addition level. This is supported by the considerably higher T_g values observed for the un-accelerated sample with no cobalt in the system.

Overall the results indicate the presence of an accelerator is necessary for peroxide decomposition to cure vinyl ester resins at ambient temperatures. Over the range of levels examined in this study, the predominant influence of the cobalt addition level appeared to be the rate of the cure reaction with a 0.2% cobalt level producing the highest peak heat flow. The results suggested that higher concentrations of cobalt accelerator solution may actually retard the reaction and lower the network properties however further investigations are required to examine these behaviours.

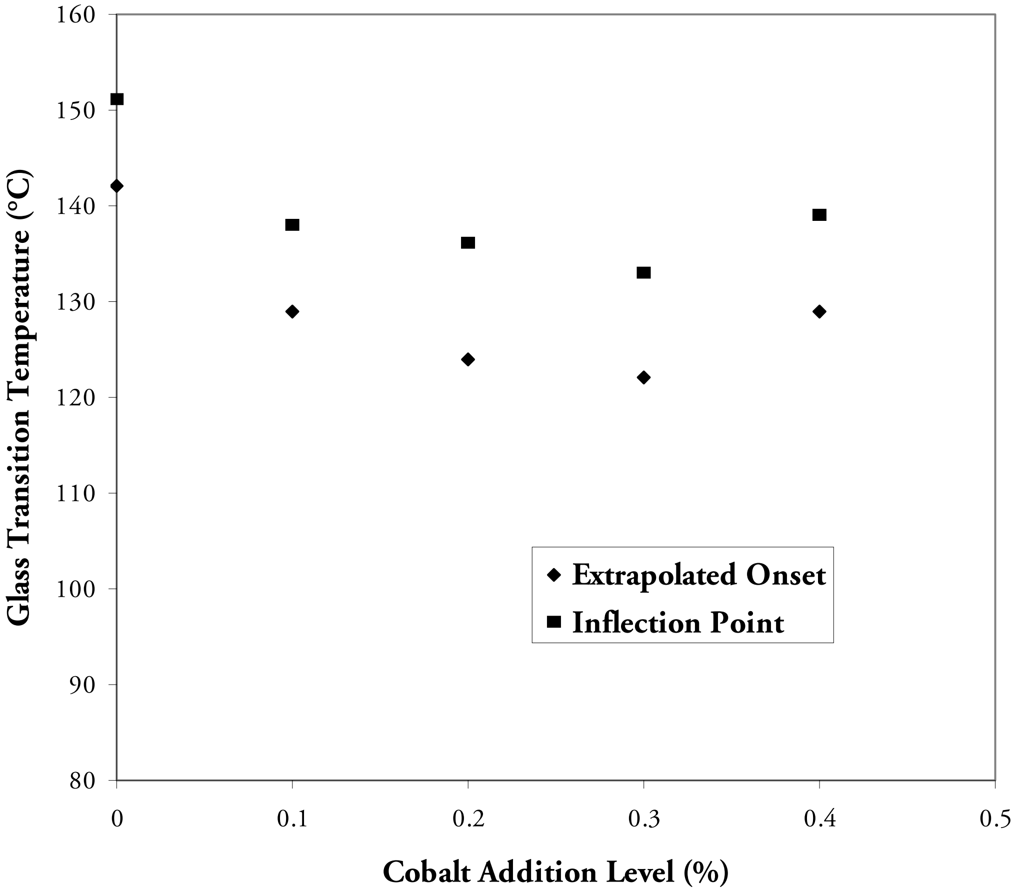


Figure 3.13 Relationship of the glass transition temperature of Hetron 914 vinyl ester with varying cobalt accelerator level.

3.3.1.4. Influence of the Oligomer Molecular Weight

Applying an accelerator regime of 0.2% cobalt octoate for the Hetron 914 from the previous testing, an investigation was then undertaken to examine cure differences resulting from a change in the oligomer. Hetron 922 PAW and Hetron 914 were used for this work with a primary focus on the molecular weight differences between the two oligomers. DSC data was obtained for both Hetron 922 PAW and Hetron 914 using each of the four peroxide initiators listed earlier in Table 3.1. An initiator addition level of 2% was maintained for all tests. Each sample was subjected to a heat/cool/heat test cycle to obtain data for both the resin cure process and the final cured product. Key data for the Hetron 922 PAW system was presented earlier in Table 3.4. Full heat flow versus temperature plots for the first and second DSC heating runs are given in Appendix A. Key data points for Hetron 914 are given in Table 3.6.

Table 3.6 Key thermal data from DSC analysis of Hetron 914 vinyl ester with different peroxide initiator types.

Resin	Hetron 914		**Initiator Addition Rate:**	2%		
	First Heating Run Cure Behaviour				**Second Heating Run Glass Transition**	
Initiator	**Reaction Onset Temp. (°C)**	**Total Heat of Reaction (J/g)**	**Peak Heat Flow (W/g)**	**Temp at Peak Heat Flow (°C)**	**Onset (°C)**	**Point of Inflection (°C)**
Butanox M-60	67	298	3.27	77	124	136
MEKP-SR	69	303	3.20	79	133	140
Trigonox 239	94	287	4.21	101	144	150
CHP 90	99	291	4.68	107	137	146

The different resin types produced different shaped heat flow curves. The curves of the Hetron 914 samples were acute with a relatively narrow base compared to the broader based curves of Hetron 922 PAW samples.

The plateau observed on the high temperature side of the CHP initiated Hetron 922 PAW samples was not evident when curing Hetron 914. This suggests that the Hetron 914 with the 0.2% cobalt may be a more reactive resin system compared to Hetron 922 PAW with an initiator concentration of 2% sufficient to effect cure.

Independent of initiator type, the reaction onset temperatures were lower for the lower molecular weight Hetron 914 suggesting a comparably higher reactivity of this resin formulation compared to Hetron 922 PAW (Figure 3.14).

The apparent increased reactivity of the Hetron 914 formulation is possibly attributable to its lower oligomer molecular weight compared to Hetron 922 PAW. Resins with lower molecular weight have higher numbers of unsaturation points per unit mass than resins of higher molecular weight. This higher unsaturation point "density" facilitates faster curing in lower molecular weight resins since the radicals do not have to travel as far for the crosslinking of molecules to occur. Thus the cure onset time and temperature is shortened in these resins.

The relationship of the effect of different initiator types on the reaction onset temperatures for each resin appears relatively consistent indicating the peroxide type has a predominant influence on the reaction onset temperature.

The total heat of reaction for Hetron 914 appears relatively stable at ≈300J/g when compared to Hetron 922 PAW (Figure 3.15). From previous sections, the total heat of reaction appears dependent on the characteristics of the resin and initiator solution. The higher molecular weight and styrene concentration of Hetron 922 PAW led to a higher heat of reaction. The lower molecular weight and styrene concentration of Hetron 914 led to a lower heat of reaction. Similar relationships were observed by Scott *et al.* [6]. This is potentially due to the crosslinking of the oligomer and styrene producing less heat compared to the crosslinking of adjacent styrene molecules forming polystyrene that may be associated with higher styrene concentrations. Again the relative influences of the molecular weight and styrene concentration need to be isolated through further investigation.

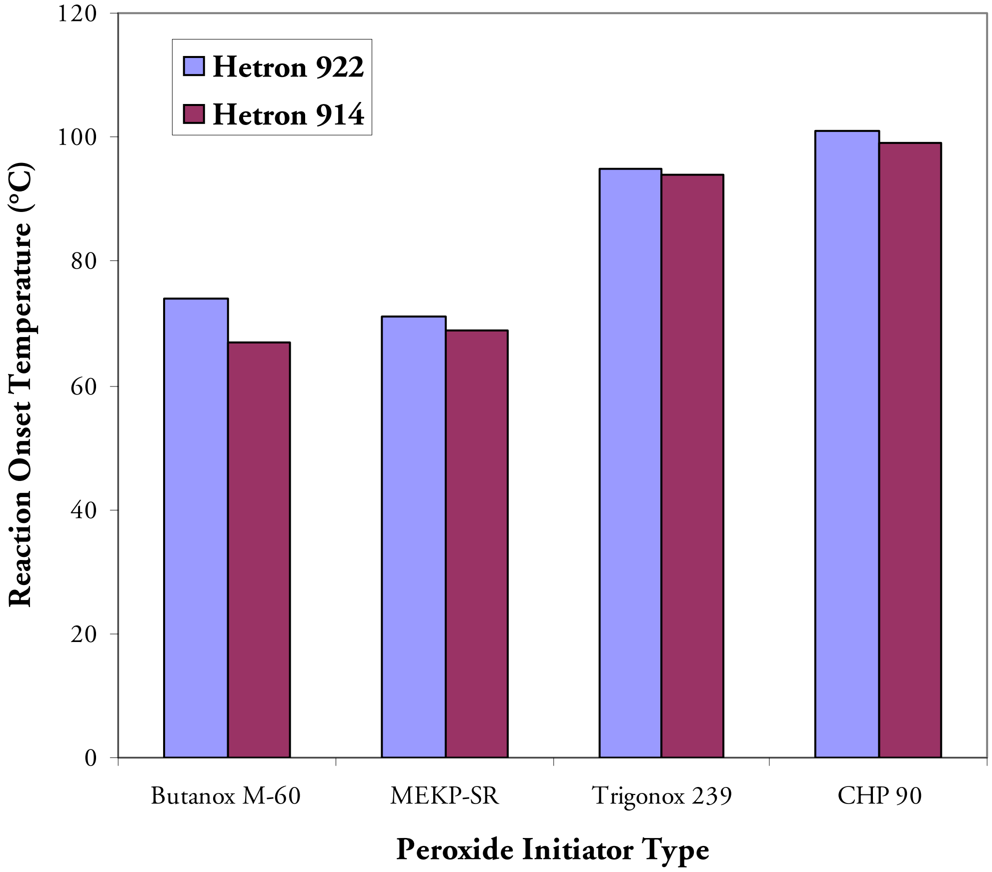


Figure 3.14 **Relationship of the reaction onset temperature of vinyl ester resins of different molecular weight cured with alternative peroxide initiators.**

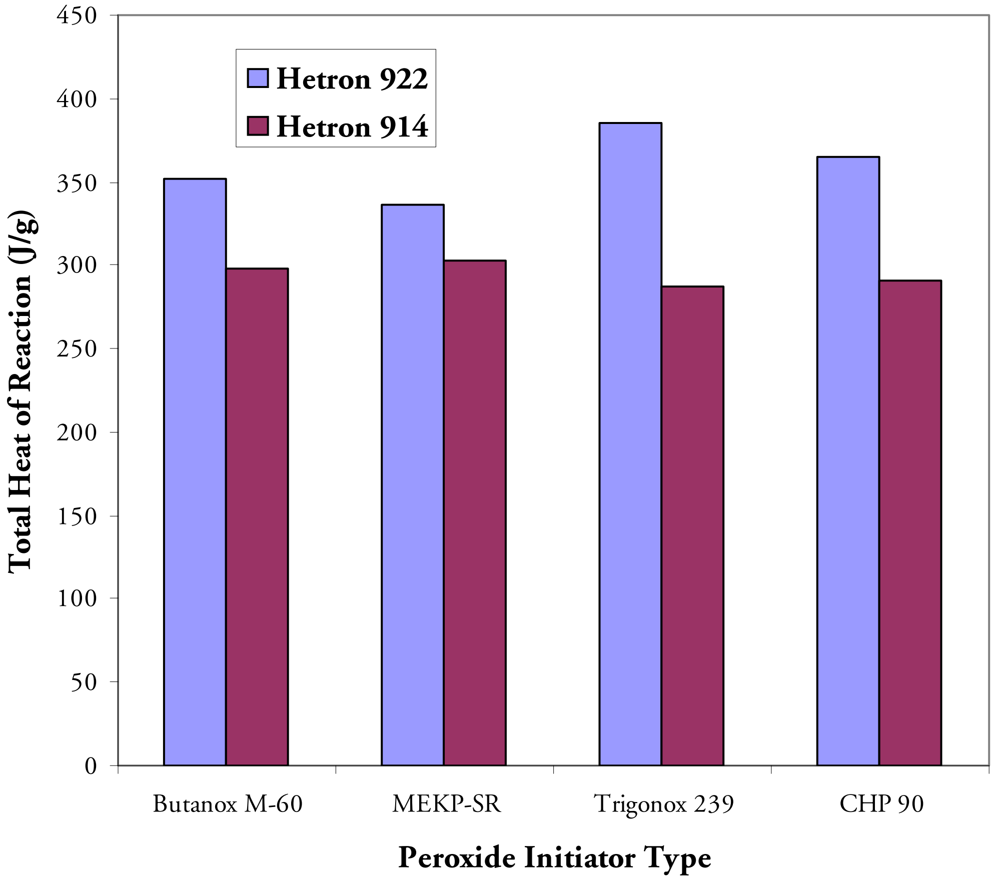


Figure 3.15 Relationship of the total heat of reaction of vinyl ester resins of different molecular weight cured with alternative peroxide initiators.

For each initiator type, the peak heat flows of Hetron 914 are more than double those of Hetron 922 PAW (Figure 3.16). The considerably higher peak heat flows are attributed to the lower molecular weight of the Hetron 914 oligomer. The shorter chain lengths increase the number of unsaturation sites within a given volume. The breaking of the double-bonds which are at a higher concentration and closer proximity, leads to a more rapid reaction and rapid generation of heat with an associated higher peak heat flow.

The relationship of the glass transition temperature with initiator type is shown in Figure 3.17. The crosslink density of a network is a primary influence on the glass transition temperature and can be increased by using oligomers of lower molecular weight [7,8,9,10]. For each peroxide type, the glass transition temperature of Hetron 914 was higher compared to Hetron 922 PAW. This is attributed to the lower molecular weight of the Hetron 914 oligomer producing a network of higher crosslink density.

Styrene concentration also influences the crosslink density of networks with higher concentrations leading to lower crosslink densities [8,9]. Therefore the 20% styrene content of the Hetron 914 compared to 45% of Hetron 922 PAW would contribute to the higher crosslink density and resulting higher glass transition temperature. Again further testing would be required to isolate the relative influences of the differences in molecular weight and styrene concentration.

Overall the predominant influence of the molecular weight appears to be on the network properties with a lower molecular weight and styrene concentration resulting in a higher glass transition temperature. For the resins used in this study, the results suggest that less energy is required to cure resins of lower molecular weight with the associated heat flow considerably higher.

The use of different initiator types indicates that for a resin and accelerator system of appropriate reactivity, the main difference between the types is the delayed cure of the CHP based solutions when compared to MEKP based initiators. The onset temperature and temperature at peak heat flow appear dominated by the selected initiator type.

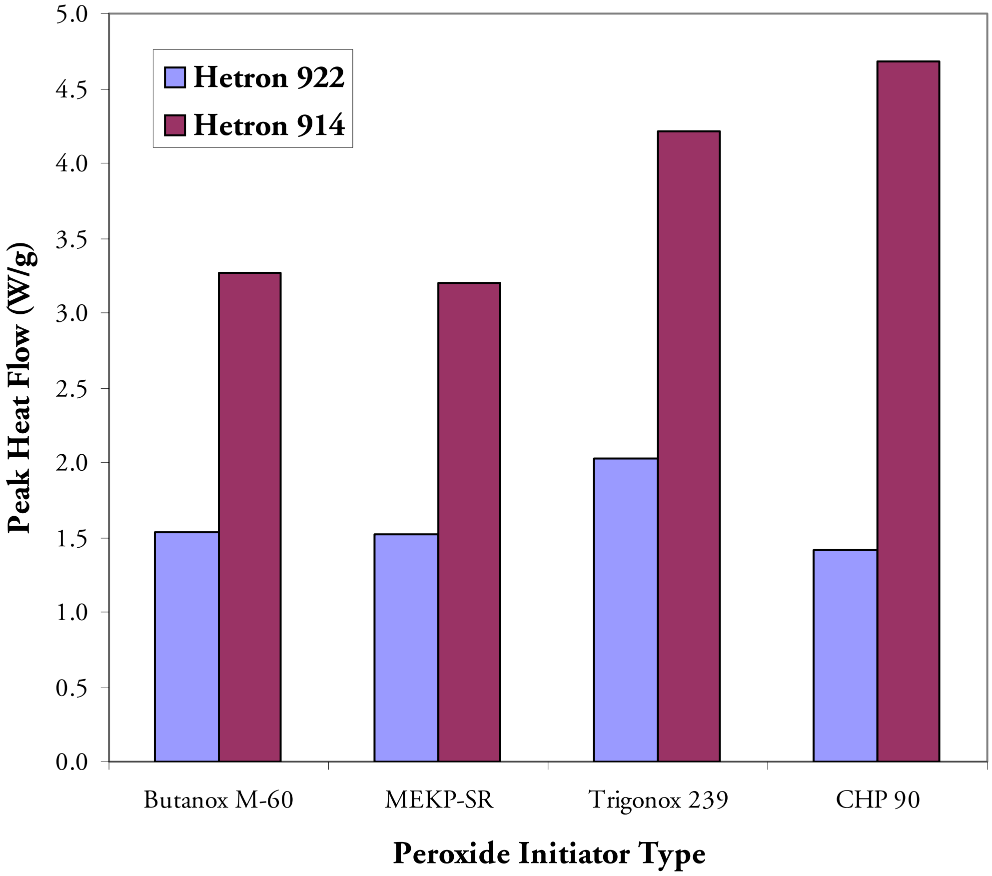


Figure 3.16 Relationship of the peak heat flow of vinyl ester resins of different molecular weight cured with alternative peroxide initiators.

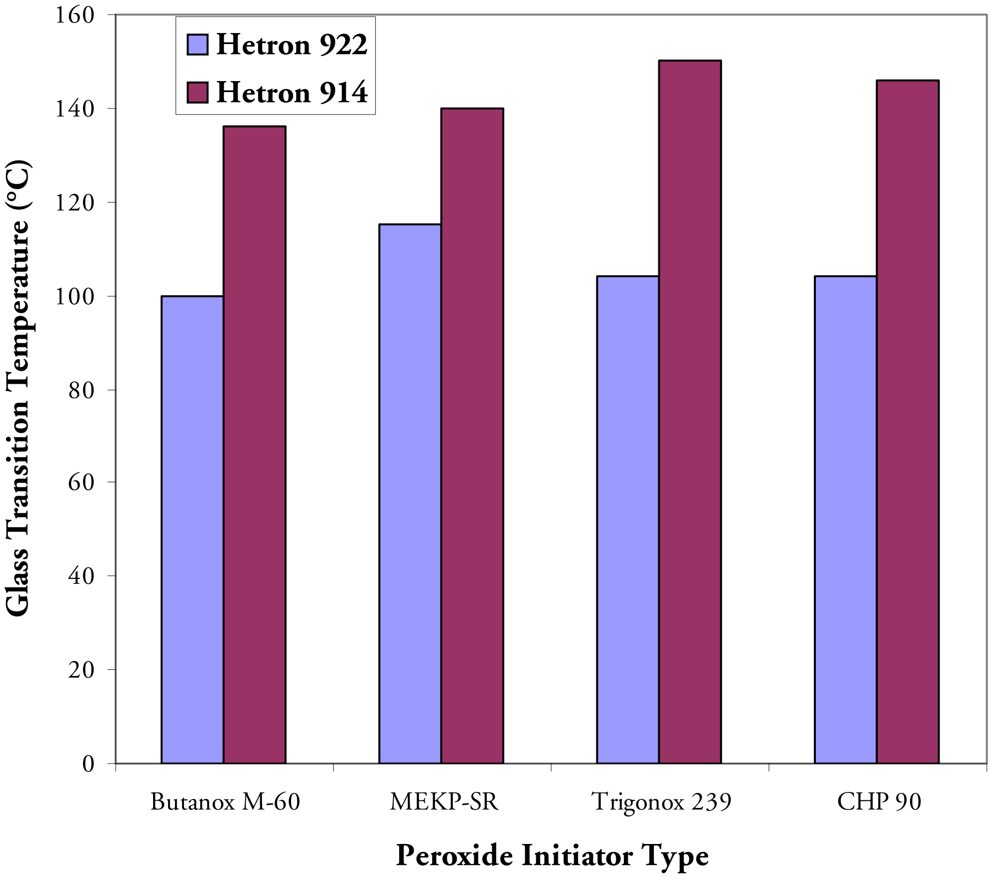


Figure 3.17 **Relationship of the glass transition temperature of vinyl ester resins of different molecular weight cured with alternative peroxide initiators.**

3.3.1.5. Influence of Styrene Concentration

The influence of styrene concentration on the cure behaviour was investigated using the standard grade Hetron 922 PAW. Samples were prepared by adding extra styrene monomer to the resin which is supplied with a styrene content of 45%. Styrene additions ranged up to 15% of the initial resin weight with the styrene concentration of the samples ranging from 45% to 60%. All samples were cured using the Butanox M-60 initiator at an addition level of 2%. Each DSC test included two heating runs to examine both curing and cured behaviour of the matrix. Full heat flow versus temperature plots for the first and second DSC heating runs are given in Appendix A. Key data for each sample is summarised in Table 3.7.

Table 3.7 Key thermal data from DSC analysis of Hetron 922 PAW vinyl ester with varying styrene levels.

Resin	Hetron 922 PAW		**Initiator**	Butanox M-60 @ 2%		
Styrene Addition Level (%)	**First Heating Run Cure Behaviour**				**Second Heating Run Glass Transition**	
	Reaction Onset Temp. (°C)	**Total Heat of Reaction (J/g)**	**Peak Heat Flow (W/g)**	**Temp at Peak Heat Flow (°C)**	**Onset (°C)**	**Point of Inflection (°C)**
0	74	352	1.53	102	96	100
2	75	374	1.54	101	90	95
5	75	379	1.49	103	90	95
10	76	376	1.48	103	94	98
15	77	398	1.47	106	88	93

Each level of the styrene addition produced a similarly shaped heat flow curve. The type of initiator solution used to effect cure has been shown in previous sections to be a dominant influence on both the onset temperature and the temperature at peak heat flow. Over the range of addition levels investigated, the incorporation of additional styrene into the system showed minimal influence on both these temperatures.

The properties of both the resin and initiator solution have been shown to significantly influence the total heat of reaction. The total heat of reaction of the samples appears to increase as the styrene concentration was increased (Figure 3.18) which is consistent with results reported by Scott *et al.* [6].

The increased concentration of styrene unsaturation points may promote the crosslinking of styrene molecules forming polystyrene. The associated higher total heat of reaction may suggest more heat is generated from this reaction compared to the crosslinking of the oligomer and styrene, thus increasing the heat of reaction. This behaviour was suggested earlier with regard to the lower styrene content of Hetron 914 influencing the cure reaction.

The influence of the increased styrene concentration on the peak heat flow appears minimal.

Both the extrapolated onset and point of inflection methods of interpretation of the glass transition temperature show a consistent difference between the two values for each sample (Figure 3.19). Generally the glass transition temperature appears to lower as the styrene concentration is increased. However the T_g of the sample with 10% styrene addition does not match this trend.

An increased styrene concentration appears to lower the glass transition temperature which is consistent with the results of Li *et al.* [8] and Shan *et al.* [9] who reported that the addition of styrene to lower the T_g of systems with lower molecular weight oligomers but to have only minor effects on the T_g of high molecular weight systems.

Overall the predominant influence of the additional styrene appears to be on the density of unsaturation sites available for crosslinking during cure and the crosslink density of the final cured network. For the range of levels investigated, the increasing styrene concentration appeared to have only minimal influence on the cure behaviour.

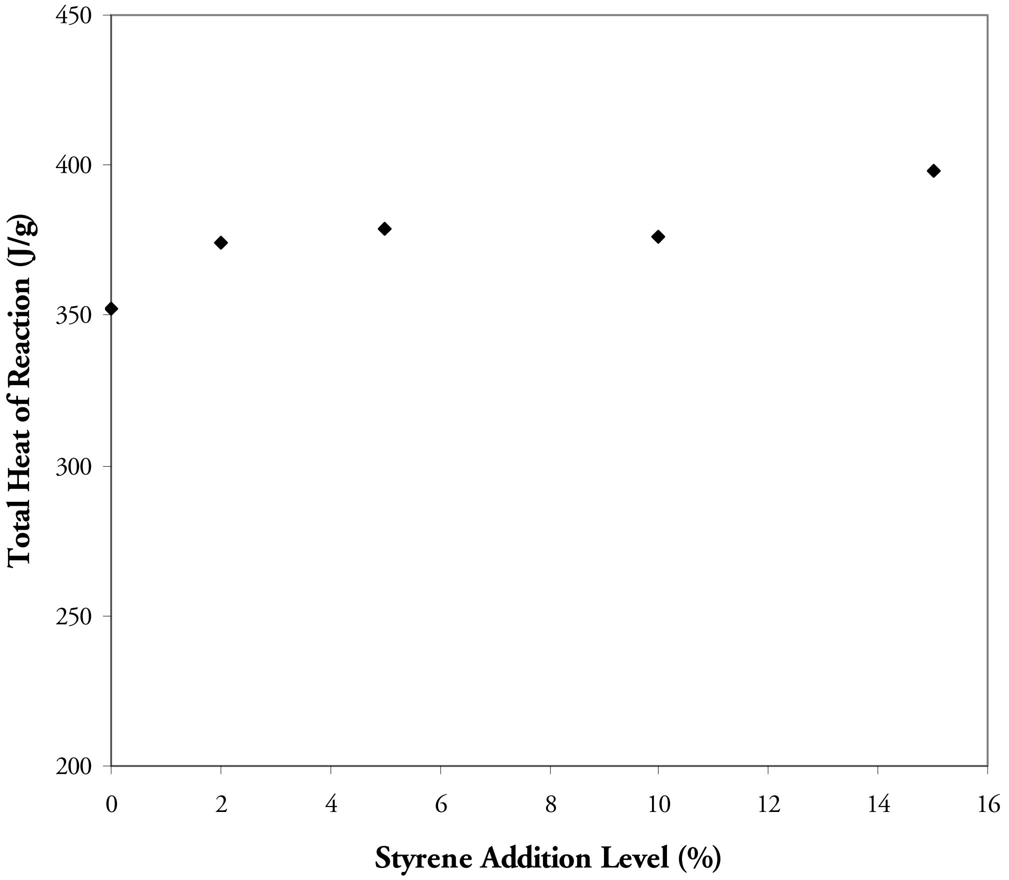


Figure 3.18 Relationship of the total heat of reaction of Hetron 922 PAW vinyl ester with additional styrene.

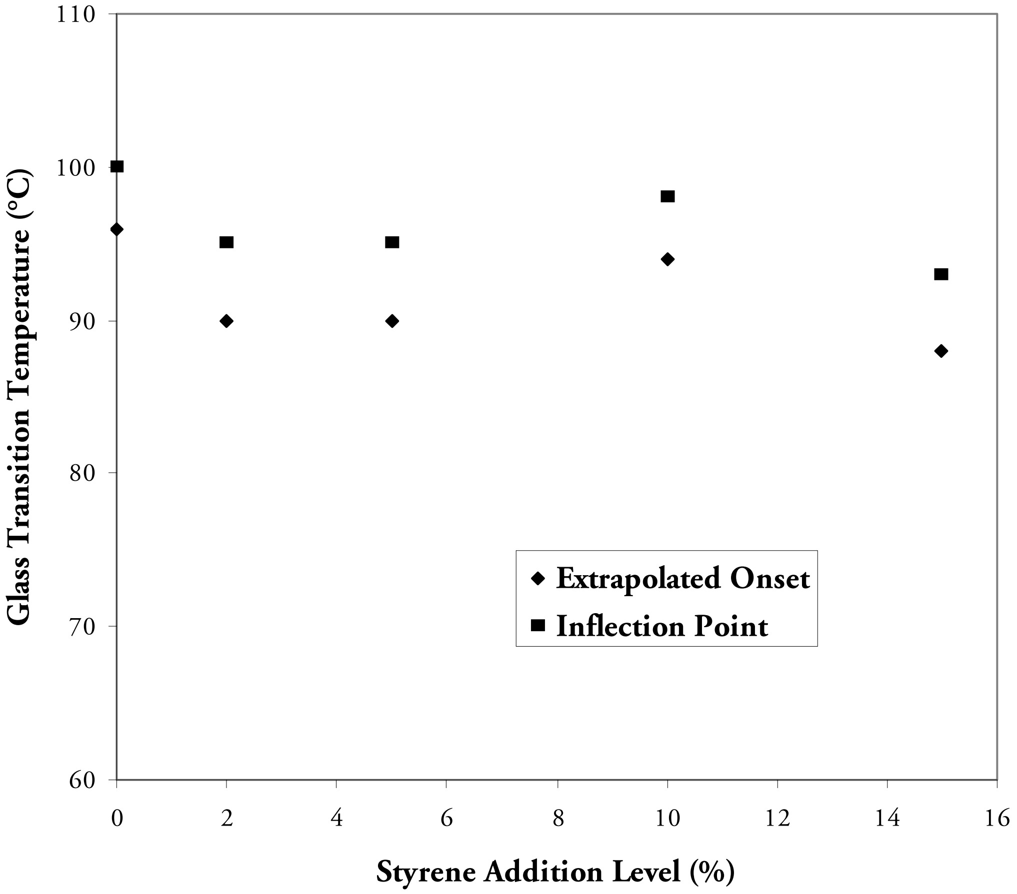


Figure 3.19 **Relationship of the glass transition temperature of Hetron 922 PAW vinyl ester with additional styrene.**

3.3.2. CURE BEHAVIOUR OF FILLED VINYL ESTER RESINS

The previous section has outlined findings regarding the behaviour of unfilled vinyl ester matrix systems. In the context of this current study of vinyl ester / cenosphere composites it is necessary to establish how the identified trends are altered by the addition of the cenosphere fillers to the curing matrix. Due to the addition of filler to the matrix, continued cure investigation using DSC was not regarded as an optimal approach. This is because of the very small sample size used in DSC and the consequential risk of non-representative sampling of the filled resins. Therefore the cure behaviour of the vinyl ester / cenosphere composites was characterised using the temperature monitoring procedure outlined in Section 3.2.2.2.

For this foundational study, a filler volume fraction of 40% was selected to investigate the cure behaviour of vinyl ester / cenosphere composites. The temperature monitoring experiments were completed on both neat resin and filled samples so the relative influences due to the addition of filler may be extricated. The assessment of cure behaviour in the vinyl ester / cenosphere composites was constrained to the following effects:

- Influence of peroxide initiator type.
- Influence of accelerator level.
- Influence of oligomer type.

Once an initial understanding of the cure behaviour is developed, it would be useful to investigate the influence of gradually increasing filler volume fractions for each of the effects above.

3.3.2.1. Influence of Peroxide Initiator Type

Following on from the neat resin investigations, temperature monitoring was conducted for the cenosphere composites with different initiator types. Testing was conducted using Hetron 922 PAW resin with each of the four initiators outlined previously in Table 3.1. An initiator addition rate of 2% was used for all samples. Testing was conducted with both neat resin and 60% vinyl ester / 40% cenosphere composite blends (by volume). A temperature versus time plot for the neat resin and composite samples are shown in Appendix A. Key data of each sample is summarised in Table 3.8.

Table 3.8 Key thermal data from thermocouple monitoring of Hetron 922 PAW vinyl ester neat resin and with 40% filler using different peroxide initiator types.

Resin	Hetron 922 PAW	**Initiator Addition Level**	2%	**Filler Type**	E-Spheres SLG	
	Unfilled Resin			**Resin with 40% Filler**		
Initiator	**Latency Period (h:min)**	**Peak Temp. (°C)**	**Time to Peak Temp (h:min)**	**Latency Period (h:min)**	**Peak Temp. (°C)**	**Time to Peak Temp (h:min)**
Butanox M-60	0:11	162	0:30	0:11	148	0:34
MEKP-SR	0:11	167	0:30	0:17	152	0:35
Trigonox 239	1:47	133	4:24	2:40	118	5:16
CHP 90	1:05	85	6:17	1:11	63	7:26

Generally the shape of the cure relationship for both neat resin and filled samples were similar for each initiator type. However a small plateau was observed before the main peak of the CHP 90 initiated samples. The relationship of the latency period with initiator type for neat resin and filled systems is shown in Figure 3.20. The shorter periods for the MEKP initiators compared to CHP solutions shows the higher reactivity of the MEKPs with a similar relationship observed using DSC.

The addition of the filler generally increased the latency period but appeared to have a significantly lower influence on the MEKP initiators compared to the CHP solutions which may be due to their higher reactivity. The increased latency period is attributed to the filler component absorbing exotherm heat which consequently delays the initial stages of the reaction. The higher reactivity of the MEKP means that sufficient heat is still being developed to limit the influence of the heat absorption. It may also be influenced by the filler reducing the proximity of crosslink sites within a volume causing the radicals to travel further which may delay the onset of the reaction. The more rapid generation of radicals of the MEKP initiators may lower the effects of this influence.

Results from the DSC analysis suggest the type of initiator solution was the predominant influence on the reaction onset temperatures are supported by the behaviours observed in this investigation.

The comparably higher peak temperatures observed for MEKP initiated samples was attributed to the higher reactivity of these initiator types (Figure 3.21). The addition of the filler lowered the peak temperature for each initiator type with the reduction in temperature quite consistent at ≈16°C. The lowering of the peaks is attributed to the filler absorbing a portion of the heat generated by the exothermic reaction.

The addition of the filler led to increases in the time to the peak temperature for each of the samples. Again the addition of filler to MEKP initiated samples showed less of an influence on the time which is attributed to their higher reactivity.

Overall the addition of filler appeared to lower the intensity of the cure reactions initiated by each initiator type, delaying the reaction times and lowering temperatures. The use of MEKP based initiator solutions appeared to show more resilience to the effects of the filler, particularly with regard to reaction times.

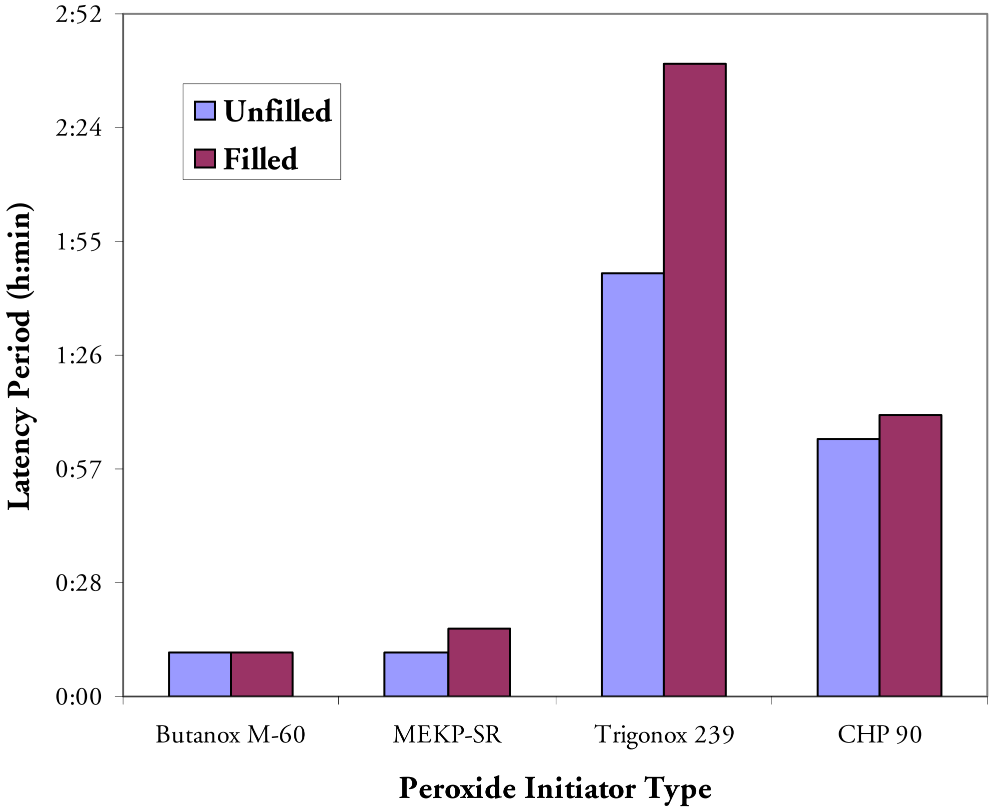


Figure 3.20 Relationship of the latency period of Hetron 922 PAW vinyl ester neat resin and filled systems cured with alternative peroxide initiators.

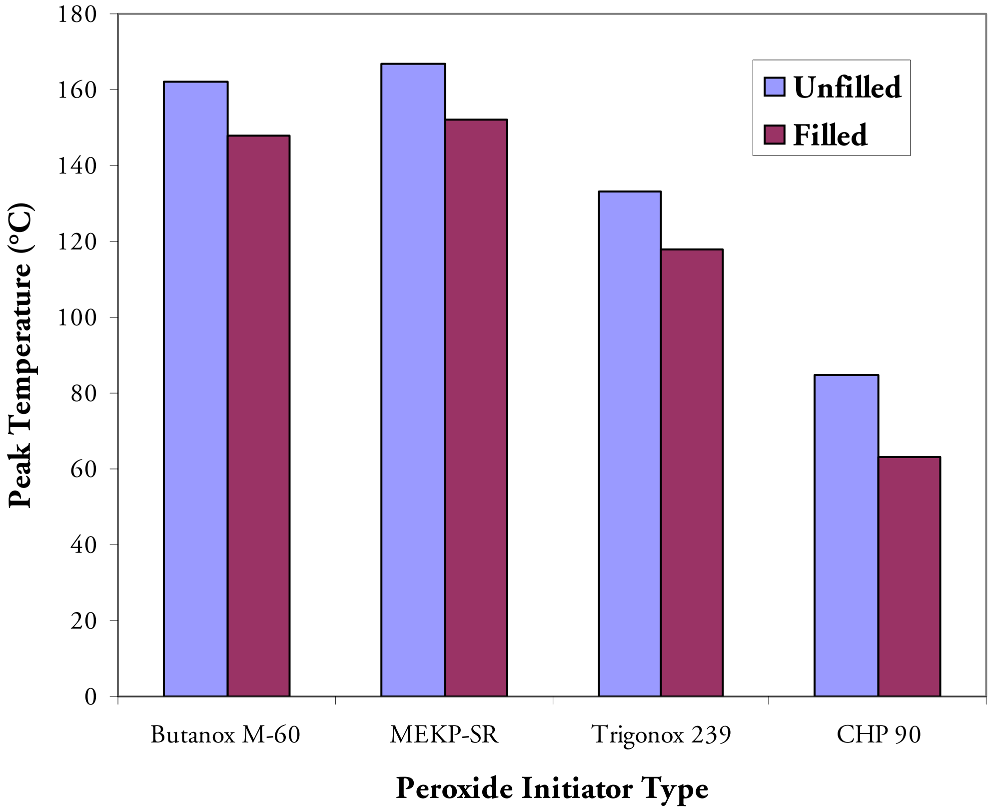


Figure 3.21 **Relationship of the peak temperature of Hetron 922 PAW vinyl ester neat resin and filled systems cured with alternative peroxide initiators.**

3.3.2.2. Influence of Accelerator Level

As with the earlier DSC characterisation, temperature monitoring was conducted on composite samples to assess the influence of resin acceleration on cure characteristics. This work was conducted using Hetron 914 vinyl ester with the Butanox M-60 initiator. An initiator addition level of 2% was used for all samples. The resin was promoted using the NL-51P cobalt accelerator at addition levels of 0.1, 0.2, 0.3 and 0.4%. Testing was conducted with both neat resin and 60% vinyl ester / 40% cenosphere composite blends. Temperature versus time plots for the neat resin and composite samples are shown in Appendix A. Key data of each sample is summarised in Table 3.9.

Table 3.9 Key thermal data from thermocouple monitoring of Hetron 914 vinyl ester neat resin and with 40% filler using different levels of cobalt accelerator.

Resin	Hetron 914	**Initiator**	Butanox M-60 @ 2%	**Filler**	E-Spheres SLG	
Promoter Addition Level (%)	**Unfilled Resin**			**Resin with 40% Filler**		
	Latency Period (h:min)	**Peak Temp. (°C)**	**Time to Peak Temp (h:min)**	**Latency Period (h:min)**	**Peak Temp. (°C)**	**Time to Peak Temp (h:min)**
0.1	0:14	162	0:22	0:22	138	0:32
0.2	0:12	173	0:19	0:09	149	0:15
0.3	0:06	178	0:12	0:06	149	0:12
0.4	0:05	175	0:11	0:06	147	0:12

The cure relationships of both neat resin and composite samples were very similar for each level of cobalt accelerator. As the level of cobalt was increased, the latency periods and times to peak temperature lowered, indicating an increased reactivity of the system. At low cobalt levels, the addition of filler increased these times and which could be attributed to the filler reducing the proximity of crosslink sites thus delaying the onset of the reaction. At higher cobalt levels the decomposition of the initiator is more rapid leading to a greater density of radicals present potentially reducing the effect of the lower mobility.

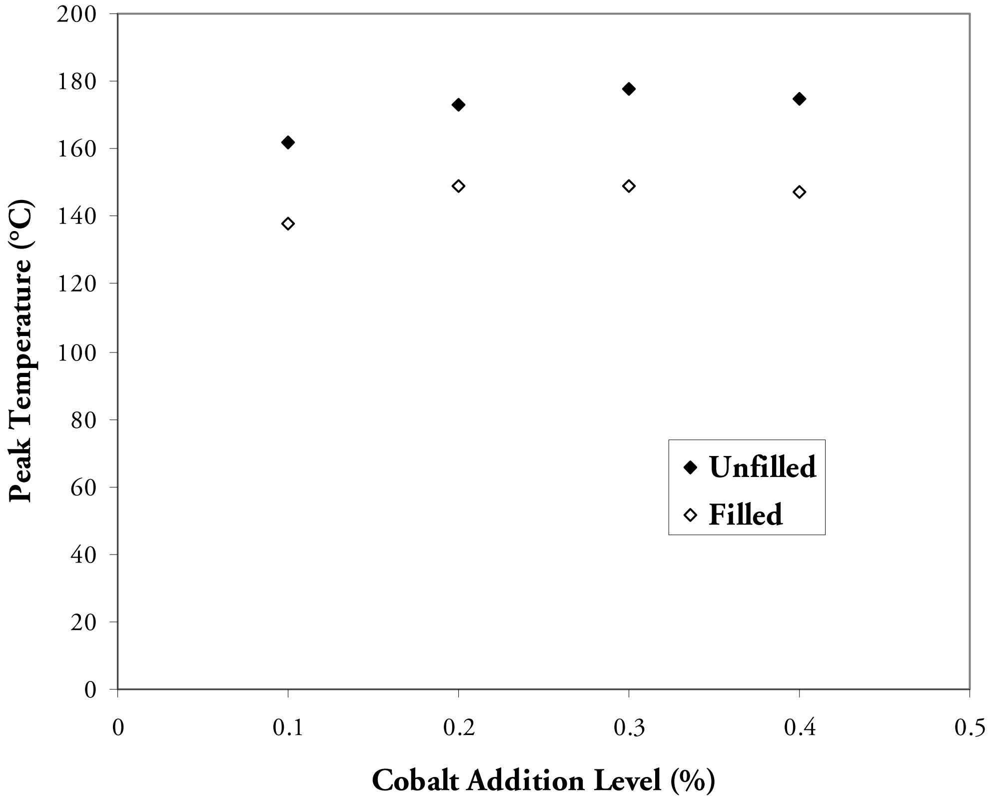


Figure 3.22 Relationship of the peak temperature of Hetron 914 vinyl ester neat resin and filled systems cured with varying cobalt accelerator levels.

At a concentration of 0.2% and above, the peak temperatures appear consistent for both neat resin and filled systems with the subsequent addition of filler lowering the peak temperature of all samples by similar amount (Figure 3.22).

Overall the results suggest minimum cobalt accelerator of 0.2% to produce a stable cure behaviour of neat resin and filled samples. Using a high cobalt level, the filled systems appeared to maintain similar cure characteristics as the neat resin matrices.

3.3.2.3. Influence of the Oligomer Molecular Weight

Temperature monitoring was also conducted to assess changes in cure characteristics in the cenosphere composites as a result of changes to the vinyl ester oligomer. Tests were conducted using Hetron 922 PAW and Hetron 914, the Hetron 914 having been promoted with 0.2% cobalt. Tests were conducted using each of the four peroxides listed in Table 3.1 with an initiator addition rate of 2% used for all tests. Both neat resin and 60% vinyl ester / 40% cenosphere composite blends were investigated.

Key data for the Hetron 922 PAW samples were presented previously in Table 3.8 with the plots shown in Appendix A. The time versus temperature plots for Hetron 914 neat resin and composite samples are shown Appendix A. Key data points are summarised in Table 3.10.

The shape of the cure curves for both neat resin and filled samples were similar for each initiator type. The addition of filler increased the latency periods and times to peak temperature for each of the samples however the differences in times between the neat resin and filled samples cured with the MEKP initiators are negligible.

The DSC analysis results suggested the initiator was the dominant influence with regard to the onset and peaks of cure behaviour. These trends are also apparent in the thermocouple monitoring with similar reaction times exhibited by the Hetron 922 PAW and Hetron 914 samples.

Table 3.10 Key thermal data from thermocouple monitoring of Hetron 914 vinyl ester neat resin and with 40% filler using different peroxide initiator types.

Resin	Hetron 914	Initiator Addition Level	2%	Filler Type	E-Spheres SLG

Initiator	Unfilled Resin			Resin with 40% Filler		
	Latency Period (h:min)	Peak Temp. (°C)	Time to Peak Temp (h:min)	Latency Period (h:min)	Peak Temp. (°C)	Time to Peak Temp (h:min)
Butanox M-60	0:08	173	0:15	0:09	149	0:15
MEKP-SR	0:11	176	0:19	0:13	147	0:20
Trigonox 239	4:30	122	5:16	5:06	66	5:39
CHP 90	7:15	120	8:14	8:15	63	8:57

The relationship of the peak temperature with initiator type of the Hetron 914 neat resin and filled system is shown in Figure 3.23. The Hetron 914 samples exhibited higher peak temperatures compared to the Hetron 922 PAW. The addition of filler lowered the peak temperature of each of the initiated Hetron 922 PAW samples by a similar magnitude of ≈16°C. The drop in peak temperature for Hetron 914 was not consistent at ≈25°C for the MEKP based initiators and ≈55°C for the CHP type initiators. This may be due to a combined effect of the apparent longer reaction times and relatively higher peak temperatures of the Hetron 914 resin.

Overall the lower molecular weight Hetron 914 samples possessed higher peak temperatures and similar reaction times to the Hetron 922 PAW. The influences of the filler were generally consistent but were more pronounced on the CHP initiated samples.

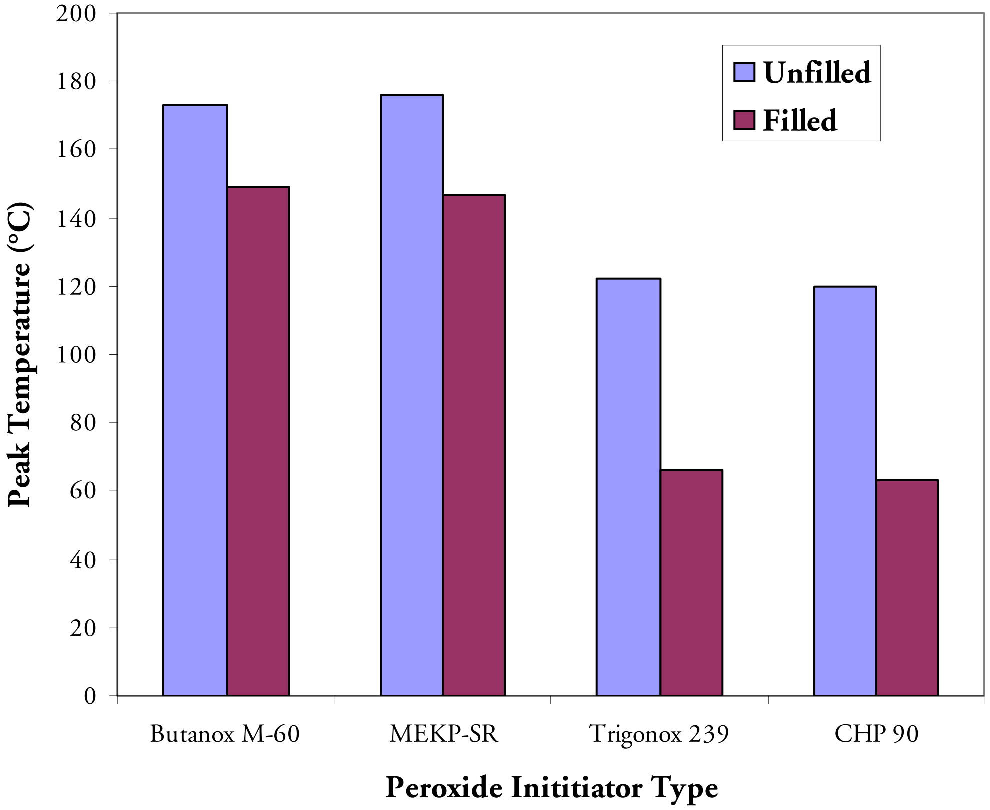


Figure 3.23 **Relationship of the peak temperature of Hetron 914 vinyl ester neat resin and filled systems cured with alternative peroxide initiators.**

3.4. SUMMARY AND CONCLUSIONS

This Chapter has investigated the cure behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites examining the relationships between constituent materials and the cure kinetics. The findings of this investigation are summarised as follows:

- Operating limits for the initiator concentration were established with a lower limit of 1.5% to produce stable cure behaviour and an upper limit of 2.5% to maintain good network properties with the T_g observed to degrade above this level. The MEKP based initiator solution Butanox M-60 was used for this investigation.
- The utilisation of different peroxide initiator types and initiator solutions were shown to result in different cure characteristics. MEKP based initiators appear to have a higher reactivity compared to CHP based initiators. The results indicate the type used significantly influences the start of the cure reaction with CHP initiators resulting in a delayed onset. MEKP initiators also appear to provide an initial rapid gel of the resin.
- The requirement of an accelerator to effect cure at ambient temperatures was established. The results indicate that the cobalt accelerator level is a predominant influence on the rate of cure with a peak rate corresponding to 0.2% cobalt. Higher concentrations appear to retard the reaction and degrade the network properties.
- The styrene concentration and oligomer molecular weight of the resin were found to predominantly influence the network properties and the reaction energy. Lower styrene levels and a lower oligomer weight improved the network properties, increasing the T_g. The addition of styrene to a higher molecular weight oligomer appeared to have only a minimal effect on the cure behaviour.
- The addition of filler generally appeared to lower the intensity of the cure reaction, extending reaction times and lowering peak temperatures. The use of MEKP based initiators appeared less sensitive to the influences of filler with peak temperatures lowering but reaction times remaining similar to those of the neat resin matrix.

This investigation has highlighted the considerable flexibility available to cure vinyl ester matrix systems and composites. Cure systems may be tailored to meet specific working conditions and processing requirements, a feature which is taken advantage of in the following Chapters.

3.5. REFERENCES

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CHAPTER 4.

THE PROCESSING CHARACTERISTICS OF VINYL ESTER / CENOSPHERE COMPOSITES

4.1. INTRODUCTION

An understanding of the cure mechanisms of vinyl ester resin and cenosphere composite systems was developed in the previous Chapter, along with an understanding of the influences of the constituent options on the cure behaviour. While still in their uncured state, the constituent materials must be combined, then handled and placed utilising any number of manufacturing techniques to ultimately produce a cured product that meets specified dimensions. The physical properties of composite systems that facilitate their transformation from a formless substance into a rigid and structured composite can be classified as processing characteristics.

This Chapter presents a review of processing characteristics of composite systems and relevant influences on these characteristics. Following the review, an experimental investigation aimed at developing an understanding of the relationships between constituent materials and key processing characteristics of vinyl ester / cenosphere composite systems is presented.

4.1.1. REVIEW OF PROCESSING CHARACTERISTICS

Previous research by the author [1] included the fabrication of a particulate composite prototype deck unit. Approximately 180 litres in volume, the unit was cast in a single continuous operation using a vinyl ester / cenosphere composite. Before the unit was cast, a suitable viscosity of the formulation had to be established to allow the vinyl ester / cenosphere composite to flow appropriately and minimise air voids.

As the unit cured, it shortened and developed a large bow over its length with distortions appearing along its sides (see Figure 4.1). These problems were attributed to internal forces developed due to large volumetric shrinkage contractions. The shrinkage was attributed to the high exotherm temperatures and the considerable volume of material within the unit. Li *et al.* [2] explained that "the combination of rapid reactions, large volume contractions, and highly cross-linked products (low mobility) may result in residual mechanical stresses which are not yet fully understood" [3,4].

Figure 4.1 Distortions that appeared along the sides of the decking unit that were attributed to shrinkage forces.

This relatively simple practical exercise demonstrated the importance of:

- viscosity, and
- shrinkage;

on the processing of vinyl ester / cenosphere composites. Shrinkage is not an entirely negative attribute having processing advantages by promoting the easy removal of manufactured parts. However the shrinkage behaviour and its influences must be quantified to prevent or minimise the effect of potential problems resulting from shrinkage.

The rationales used to select a resin / cenosphere formulation are often conflicting. High filler volume fractions are sought to improve the cost-effectiveness of the composite but these high filler levels increase the viscosity (lowering the flow characteristics). Styrene can be added to reduce the viscosity to maintain flow characteristics but subsequently can increase the shrinkage and affect other properties. Understanding the complexities of these relationships is an important consideration.

This section outlines characteristics that may influence the processing of vinyl ester / cenosphere composite materials, focussing on viscosity and shrinkage. Both the viscosity and shrinkage behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites are influenced by many parameters including the:

- styrene concentration,
- oligomer molecular weight,
- temperature, and:
- additives,
- filler characteristics.

Additives are often incorporated into a resin formulation enabling enhanced properties to meet desired requirements of product quality, ease of manufacture and processing and mechanical and physical performance [5]. Common additives that can influence these characteristics are also discussed.

- *Viscosity*

The measure of a fluid's resistance to flow is viscosity. The shear stress in a solid material is proportional to shear strain whereas the shear stress in a viscous fluid is proportional to the time rate of strain. When the shear stress is directly proportional to the rate of strain, fluids are called Newtonian fluids. Where the shear stress is not directly proportional to the rate of strain, fluids are called non-Newtonian fluids. The unit of viscosity is the Pascal.second (Pa.s) however viscosity is often expressed in Poise (P) with $1\text{Pa.s} = 10^5\text{P}$.

Quantifying viscosity is important because it has a significant influence on the processing of fibre composite and particulate composite products. A lower viscosity resin formulation leads to improved handling and processing characteristics. Particulate composite systems require a base resin of low viscosity or additional methods to maintain a workable formulation at cost-effective higher filler volume fractions. A higher styrene content VE resin will have a lower viscosity, permitting the addition of filler at higher volume fractions. For VE resins that are dissolved in a reactive diluent, additional quantities of styrene can be added to lower the viscosity, increasing the allowable filler volume fraction and maintaining the viscosity at a workable level. Although a cost-effective method, increasing the styrene concentration can significantly influence other resin properties (eg: glass transition temperature) as discussed in Chapter 2.

Li [6] and Burts [7] reported that for a constant styrene concentration at ambient temperatures, VE resins with a higher molecular weight oligomer possess a higher viscosity. Thus VE resins with a lower molecular weight oligomer possess a lower viscosity. Therefore selecting a resin formulation with a lower molecular weight oligomer may permit higher filler volume fractions without requiring additional styrene.

The viscosity of a VE resin can also be lowered by heating the resin above ambient temperature. When using this method to lower viscosity, the filler should also be heated so as not to absorb heat from the resin when the materials are combined. As a consequence, the desired cure system may require modification to take into consideration the elevated temperatures. For example, a heat activated BPO initiator may be appropriate. However heating constituents to lower the viscosity requires heating equipment and potentially other adjustments to processing procedures.

There are a range of additives commercially available (eg: by BYK Chemie) which are designed to improve the wetting and dispersing speed of fillers and lower the viscosity enabling higher loadings of filler [8]. Many of these additives have been developed for use with polyester resins, moulding compounds and putties and can accommodate a number of common filler types. However some additives are limited to use with certain resins and can increase the gel time of UP resins promoted with cobalt accelerators.

Thixotropy is the property of a material which enables it to stiffen or thicken on a relatively short time on standing but upon agitation or manipulation to change to a low viscosity fluid [9]. These fluids have a high static shear strength and low dynamic shear strength. When fabricating fibre composites, a resin may have a tendency to drain from a laminate reducing the quality of the overall product. Additives known as thixotropes can be used to modify the thixotropy of a resin which limits this tendency to drain.

When fabricating particulate composites, the matrix resin phase and filler phase can separate before the gelation of the resin locks the filler in place. This is particularly noticeable when low density fillers are used. A heterogeneous material can result with resin rich and resin poor surfaces leading to uneven mechanical properties within the cross-section. The use of thixotropes in the resin can reduce the tendency to separate. At low levels of addition (2%), thixotropes maintain a low resin viscosity at high shear rates and increase the resin viscosity at low shear rates [10]. Therefore, processing operations such as mixing and casting are not adversely affected by its presence. Many commercial grades of resin are supplied with thixotropes present in the formulation.

The selection of a rapid cure system will also assist in preventing the separation of the resin and filler components. By rapidly hardening the resin matrix, the filler remains suspended throughout the network and maintains the homogeneity of the composite. However the cure system must still allow sufficient time for processing activities to be completed.

The inclusion of filler in a vinyl ester matrix system will increase the viscosity. For a given volume, a higher volume fraction of filler will lead to an increase in viscosity. The viscosity will also be influenced by the characteristics of the nominated filler including the type of filler, particle size, particle size distribution and particle surface treatment [11].

- *Shrinkage*

The shrinkage of a vinyl ester resin occurs as a consequence of two effects:

- the polymerisation cure reaction, and
- cooling after exotherm or post-cure.

In free radically cured networks, cure shrinkage results from the conversion of double-bonds to single-bonds [7]. Shrinkage can lead to problems such cracking, warping, porosity and poor dimensional accuracy in a completed part.

Li [6] and co-authors [2] and Burts [7] reported that using a lower molecular weight oligomer and increasing the styrene content leads to increased volumetric shrinkage upon cure. This was attributed to the shorter chains of the lower molecular weight oligomer shrinking more when cured. By increasing the styrene content, the shrinkage increased due to a reduction in density in going from monomeric styrene to polystyrene during cure [7].

Burts [7] also examined the influence of cure conditions, investigating the effects of cure temperatures, post-cure and the degree of conversion of double-bonds to single-bonds on the shrinkage. Cure shrinkage is influenced by vinyl group conversion with the more groups that are converted, the more shrinkage will occur [7]. Lower shrinkage was observed when samples were cured at ambient temperatures followed by an elevated post-cure rather than a single complete cure at elevated temperatures. The higher shrinkage was attributed to the greater mobility of molecular chains at the elevated temperatures and a greater degree of conversion [7]. The degree of conversion was low after the ambient cure stage and increased after post-cure but not to the degree of the single elevated temperature cured sample.

Low-profile additives (LPAs), generally a type of thermoplastic, have been shown to compensate or eliminate the polymerisation shrinkage of UP resins. However, LPAs have been shown to be less effective with VE resins particularly when curing at low temperatures [12]. Often called low-shrinkage additives (LSAs) when used with VE resins, Cao and Lee [12] found volumetric shrinkage decreases with increasing LSA concentrations.

The inclusion of cenospheres with a VE resin will lower shrinkage by two means. First, by replacing resin with filler, the resin volume is lowered leading to reduced polymerisation shrinkage and reduced cooling shrinkage due to lower exotherm temperatures. Second, the spherical shape of the cenospheres effectively resists shrinkage forces pushing the particles together [13].

4.1.2. MATERIAL COMBINATIONS FOR INVESTIGATION

Standard grade Hetron 922 PAW was selected as the base resin for both viscosity and shrinkage investigations, and combined with quantities of E-Spheres SLG cenosphere filler and styrene monomer to examine the respective influences of filler volume fraction and styrene concentration on the viscosity and shrinkage behaviour.

Hetron 922 is significantly higher in molecular weight when compared to Hetron 914 and also has a greater styrene concentration of 45% compared to 20% [14]. The Hetron 914 was used to primarily examine the influence of molecular weight differences on the shrinkage behaviour.

All samples were initiated at a 2.5% concentration of Butanox M-60. The cure investigations of Chapter 3 found this initiator type and concentration provided a relatively rapid cure. The Hetron 914 was accelerated with 0.2% cobalt octoate due to results from Chapter 3 indicating this accelerator level combined with an MEKP based initiator provided a relatively rapid cure. A single initiator type was selected for this investigation as the influence of the cure system on the shrinkage behaviour is beyond the scope of this research.

Although no specific examination of thixotropy was conducted, the pre-promoted Hetron 922 PAW formulation contains a thixotrope. An indication of its influence, if any, may be obtained by comparing results of the non-thixotroped Hetron 914 with the Hetron 922 PAW. However due to the selection of a fast cure system its influence may not be obvious due to the rapid formation of the network preventing the segregation of the resin and filler.

Only the influence of the E-Spheres SLG on the viscosity was considered with the effects of particle size, particle size distribution and particle surface treatment on the viscosity behaviour is beyond the scope of this research. With regard to the viscosity behaviour, the effect of particle size distribution is nominal at filler volume fractions of less than 20%, however at high volume fractions the viscosity is significantly reduced by increasing the modality of particle size [11]. Using a broad particle size distribution as opposed to a single particle size, the filler content can be increased without increasing the viscosity of the system [11]. This suggests that the graded particle distribution of E-

Spheres SLG may permit higher filler volume fractions than other grades with a narrower distribution of particle sizes.

4.1.3. CHARACTERISATION PARAMETERS

The previous review has highlighted a number of processing characteristics and a range of influential parameters that affect these characteristics.

In the practical applications of interest to this investigation, the viscosity must remain at a castable level such that the material possesses good flow characteristics, filling moulds quickly, enveloping and flowing around and between reinforcement while minimising the entrapment of air. As the filler volume fraction is increased, the viscosity will also increase but can be lowered through the addition of a styrene monomer to maintain the flow characteristics. However, the degree at which the filler volume fraction and styrene concentration influences the viscosity is not fully understood. Therefore the influence of:

- styrene concentration, and
- filler volume fraction,

on the viscosity and shrinkage of vinyl ester / cenosphere composites will be the main focus of this investigation.

The shrinkage behaviour is dependent on a number of additional factors however this shrinkage investigation will be constrained to the following additional parameters:

- Oligomer molecular weight.
- Volume of material.

Shrinkage before and after final cure was investigated because quantifying the initial shrinkage after ambient cure and total shrinkage after post-cure can facilitate the adoption of appropriate processing techniques and procedures to ensure the quality of end products.

4.2. EXPERIMENTAL INVESTIGATION

This section summarises the materials selected for the investigation of processing characteristics. Experimental techniques and procedures to examine the influence of the parameters presented in Section 4.1.3 on the viscosity and shrinkage behaviour are summarised before the results are presented in Section 4.3.

4.2.1. MATERIALS

The experimental investigation utilised a number of different materials that were detailed in Section 3.2.1 and listed in Table 3.2. Their selection was based on recommendations made in Section 2.8. The selected materials for use in this part of the study are shown in Table 4.1.

Table 4.1 Materials used for the investigation of the viscosity and shrinkage behaviour.

Product Number	Product Name	Description
1	Hetron 922 PAW	Standard grade vinyl ester resin
2	Hetron 914	Low styrene content vinyl ester resin
3	Accelerator NL-51P	Cobalt octoate medium-reactivity accelerator
4	Butanox M-60	General purpose medium-reactivity MEKP
8	E-Spheres SLG	20 - 300μm cenosphere filler
9	Styrene	Styrene monomer

4.2.2. EXPERIMENTAL TECHNIQUES

There are a number of techniques available to characterise the viscosity and shrinkage behaviour of polymers. This section outlines a range of techniques and describes the adopted methods for characterising the viscosity and shrinkage behaviour. The rationale for adopting the techniques used in this investigation is then presented.

- *Viscosity*

Typically viscosity can be measured using three types of devices: capillary, orifice, and rotational.

The use of capillary devices to measure the viscosity is limited to substances of low viscosity (eg: paint). Capillary devices rely on measuring the time for a known quantity of fluid to flow from a higher reservoir to a lower reservoir through a capillary tube. Viscosity is then calculated from this measurement of time. The use of this method is limited (due to the fragility of the instrument) to very low shear rates and the technique is not easily adapted to field use [15].

Orifice flow devices (viscosity cups) generally consist of a series of specific cups with an orifice in their base. The viscosity is determined by measuring the time to the first break in the stream of fluid from the orifice which is converted to a viscosity using tables specific to each cup. Due to gravity being a contributing factor in this type of test, the viscosity is the Stoke viscosity which is defined as the Poise viscosity divided by the material density. Viscosity cups are widely used due to their low cost, suitability to field use, ease of cleaning and the method is quite accurate [15].

Rotational instruments are widely used and can measure over a wide range of viscosities at different shear rates. In these methods, a spindle is immersed in the fluid material and driven at a constant rotational frequency with the recorded torque resistance of the spindle used to determine viscosity. The spindle type and rotational frequency can be altered to accommodate measurements over a range of viscosities. Rotational viscometers are generally complex instruments, being costly, and may require practice to achieve good results. Evaluation of the flow properties of mixtures where the solid content is relatively high is best accomplished using rotational type devices with a variable shear rate [15].

- *Shrinkage*

Shrinkage can be determined by measuring the volumetric contractions that occur during cure, and is typically expressed as a percentage of the original dimensions.

The volumetric shrinkage can be calculated using a density method which was used by Li [6] to determine the cure shrinkage of VE networks. The shrinkage is calculated by comparing the density of cured and uncured samples with the density determined by measuring the weight of samples in air and in water. Automatic density analysers are also available such as the AccuPyc 1330 Pycnometer [16]. This device uses a gas displacement technique to provide high-speed volume and density measurements by measuring the amount of displaced gas from a sample chamber into a second chamber.

Burts [7] used a dilatometer to measure the cure shrinkage of VE networks. In this method, a degassed resin sample was sealed in a pouch, placed in the dilatometer chamber and encapsulated in oil. The pouch was pressurised in the closed system with volumetric changes during cure measured using an LVDT attached to a piston that recorded the response of the oil and sample as it cured. An advantage of this method is that the volumetric changes are recorded throughout the entire cure reaction.

Although shrinkage occurs volumetrically, an indication of the shrinkage can be obtained using linear shrinkage methods. In these methods, samples are cast in moulds of specified dimensions and the shrinkage determined by measuring the change in dimensions of the sample compared to its original moulded length. This method is relatively quick and simple and, from a processing perspective, provides shrinkage data that is directly relevant to a manufacturing and production environment.

4.2.2.1. Viscosity Measurement Using the Brookfield Test Method

A rotational device was selected to measure the viscosity using the Brookfield Test method in accordance with the International Standard ISO 2555:1989 [17]. This method provides for the measurement of apparent viscosity of resins in the liquid state, as emulsions or dispersions (generally non-Newtonian) using a rotational viscometer. It is conventionally known as apparent viscosity because the velocity gradient on the spindle for these viscometer types varies and does not provide a true viscosity at a known velocity gradient as is the case for non-Newtonian fluids.

A type "A" Brookfield Viscometer was used for this investigation. The viscometer was calibrated using liquid 500 with a viscosity of 4830cP at 25°C. Spindle number 4 and a rotational frequency of 20rpm was selected using Table 2 in ISO 2555 [17], providing for measurements up to a maximum viscosity of 10000cP (10 Pa.s). All materials were conditioned at 25°C in the temperature-controlled laboratory for 24 hours prior to testing.

For each filler volume fraction, the required quantities of resin and filler were combined in cylindrical glass beakers and blended, ensuring the filler was wet-out. As required, styrene quantities were then incorporated. The beaker was positioned centrally under the viscometer and the activated spindle immersed to the mark on its shaft, ensuring the spindle end remained more than 10mm from the bottom of the beaker in accordance with the standard. Measurements were recorded after the reading stabilised or after one minute had elapsed. This period of fixed rotation was set to take into account the thixotropic nature of the Hetron 922 PAW formulation. The spindle was removed and cleaned with a solvent after each test.

The samples were not initiated due to the nature of this experimental technique thus the influence of initiator concentration on the viscosity of a composite formulation is not included in these results.

4.2.2.2. Shrinkage Measurement Using a Linear Method

A linear method was selected to assess the shrinkage in accordance with the ASTM standard D6289 – 98 [18]. This test method provides for the measurement of shrinkage of thermosetting plastics from their moulds both initially and after post-cure. A multiple cavity steel mould, shown in Figure 4.2, was fabricated with cavities to the dimensions specified for bars of:

Length = 127mm,

Width = 12.7mm, and

Depth = 12.7mm.

The pre-calculated masses of resin and filler for each volume fraction were combined by hand and blended to ensure all of the filler was wet out and distributed evenly throughout the mix. The initiator was added and thoroughly mixed. Three specimens were cast for filler volume fraction and allowed to cure at room temperature. The specimens were measured along the major axis within 16 to 72 hours of casting to determine initial shrinkage. After post-cure at 110°C for a period of 48 hours, the samples were measured again to determine post-cure shrinkage. The total shrinkage was calculated from this value after comparison with the initial mould dimensions. Measurements were made to the nearest 0.01mm using vernier callipers.

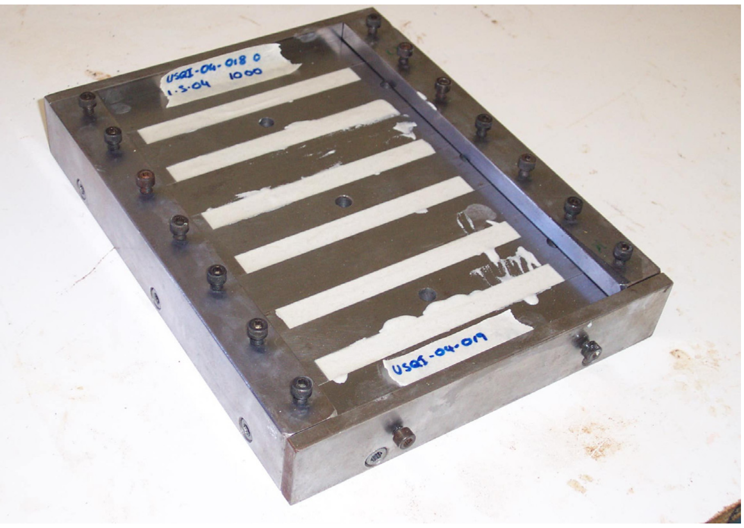

Figure 4.2 Multiple cavity mould fabricated in accordance with ASTM D 6289 – 98 for the determination of linear shrinkage.

4.2.2.3. Shrinkage Measurement Using a Block Method

To examine volume effects associated with shrinkage, a relatively simple method was developed by measuring the shrinkage of blocks of higher volume compared to the linear shrinkage bars. Samples were cast in a steel mould, shown in Figure 4.3, fabricated to the dimensions of:

Length = 225mm,

Width = 100mm, and

Depth = 50mm.

The individual specimens were subjected to an equivalent cycle of measurement and post-cure as specified for the linear shrinkage method. Measurements were made to the nearest 0.5mm using vernier callipers.

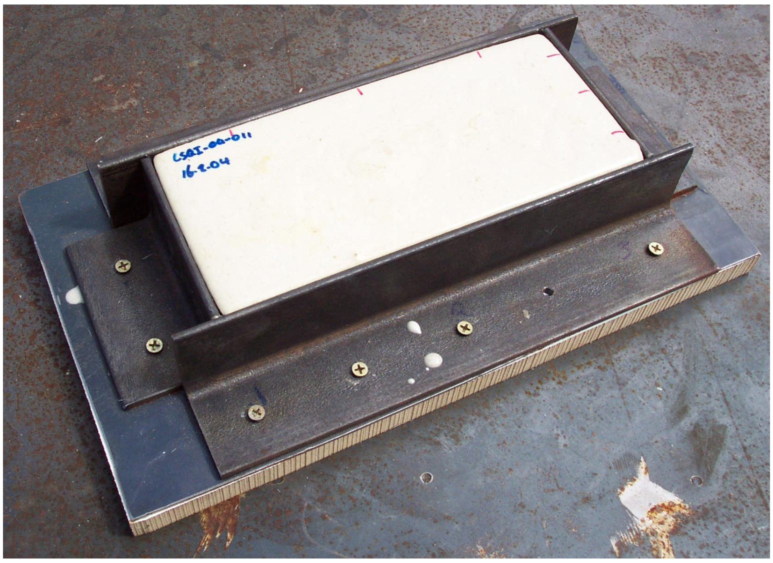

Figure 4.3 Block shrinkage mould used to examine the influences of material volume on shrinkage.

4.3. RESULTS AND DISCUSSION

This section presents the experimental results of the investigation of the viscosity and shrinkage behaviour of vinyl ester / cenosphere composites using the techniques described in Section 4.2. Where appropriate the discussion also draws on previous research material discussed in Section 4.1.1 for the purpose of comparison.

4.3.1. CHARACTERISATION OF VISCOSITY BEHAVIOUR

4.3.1.1. Influence of Filler Volume Fraction

An investigation was undertaken to examine the influence of filler volume fraction on the viscosity of vinyl ester / cenosphere composite systems. Experiments were performed using Hetron 922 PAW with alternative filler volume fractions ranging from 0 to 50% in 10% increments. The 50% filler volume fraction represents the practical limit for processing identified during previous related research by the author [1,19]. Specimens with a 55% filler volume fraction were used in the following shrinkage investigation but proved very difficult to cast.

ISO 2555:1989 [17] recommends that the choice of spindle and rotational frequency be such that no measurement is outside the range of 20% to 95% of full-scale, and for the best accuracy, to keep to the range of 45% to 95% of full-scale. However because viscosities of non-Newtonian materials are being compared, the standard states it is necessary to use the same spindle/rotational frequency combination for all the measurements, even if the accuracy of some measurements is markedly decreased.

The sample with 50% filler was tested first as this combination would possess the highest viscosity. However a measurement could not be obtained as the viscosity of the material exceeded the upper limit of the selected 4/20 spindle/rotational frequency combination. A 6/50 combination was trialled and the viscosity was successfully measured. However the use of this spindle/rotational frequency combination to measure the viscosity of all material combinations introduced some uncertainty with respect to the precision of results.

Due to the broad range of material combinations being assessed, viscosity measurements for the samples with low filler contents using the 6/50 were at the lower end of the recommended precision scale. Therefore to improve the overall accuracy of results and aid in the establishment of trends, the 4/20 combination was used where possible but when its capacity exceeded, the 6/50 combination utilised. For comparison, some readings were also recorded using the 4/50 combination. The results are summarised in Table 4.2 and shown graphically in Figure 4.4.

Table 4.2 Viscosity of Hetron 922 PAW vinyl ester / cenosphere composite systems with increasing filler volume fraction.

Resin	Hetron 922 PAW			**Filler**	E-Spheres SLG	
Viscometer / Spindle / Rotational frequency	**Viscosity (cP)**					
	Filler Volume Fraction (%)					
	0	**10**	**20**	**30**	**40**	**50**
A / 4 / 20	380	530	800	1660	4180	
A / 4 / 50	384	532	808	1760		
A / 6 / 50					3060	12800

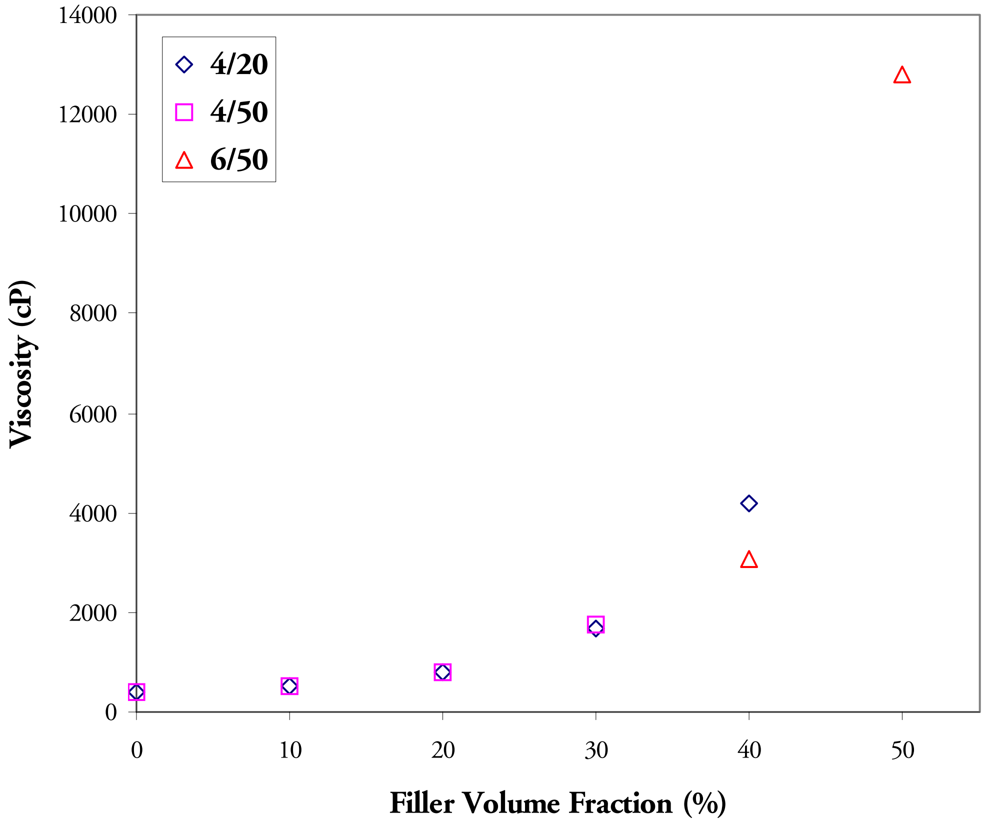

Figure 4.4 **Influence of filler volume fraction on the viscosity of Hetron 922 PAW vinyl ester / cenosphere composite systems.**

As expected, an increase in the filler volume fraction led to an increase in the viscosity. The measured neat resin viscosity of 380cP is similar to the manufacturer reported value of 450cP [20] for Hetron 922. The difference may be attributed to the manufacturer's test using a Brookfield 2/30 combination at 25°C. The addition of 50% filler increased the viscosity of neat resin more than thirty times.

There are only minor differences between viscosity values measured using the 4/20 and 4/50 combinations. At the lower filler levels the readings were easier to obtain due to the measurements stabilising quickly. The readings from the 6/50 combination, used to measure the viscosity at the higher filler levels of 40 to 50%, were harder to obtain due to the samples containing high concentrations of air bubbles.

Figure 4.4 shows the resultant non-linear relationship between viscosity and filler volume fraction. The graphical presentation highlights the sensitivity of the relationship between viscosity and filler volume fraction at higher filler levels. At the higher filler levels (greater than 40%), significantly greater increases in viscosity were experienced for the 10% incremental increases in filler content. This is attributed to increasing interactions between the particles themselves.

As the filler volume fraction increases the interaction between filler particles will increase and have a greater influence on the viscosity of the formulation. The concentration at which this particle-to-particle interaction begins depends on the geometry and surface activity of the particles [11]. For non-agglomerated randomly dispersed spherical particles, Shenoy [11] identified a volume fraction of 40% as corresponding to the point when a complete network formation occurs due to particle-to-particle contact. Reported data shows a sharp rise in viscosity at the volume fraction beyond which particle-to-particle contact occurs. The observed large increase in viscosity at a filler volume fraction above 40% is consistent with this elucidation of particle interaction.

From these viscosity experiments, the viscosity at a 50% filler volume fraction appears in the order of 12000cP at 25°C. The 50% filler volume fraction was identified as the practical limit for processing in previous research [1,19]. This viscosity investigation did not consider the influence of initiator concentration and further investigations are required to quantify its influence on the viscosity.

4.3.1.2. Influence of Styrene Concentration

An investigation was undertaken to examine the influence of styrene concentration on the viscosity behaviour of vinyl ester / cenosphere composite systems. Experiments were performed again using Hetron 922 PAW with alternative filler volume fractions (0 to 50% in 10% increments) and styrene at addition levels of 5%, 10% and 15% by volume. However for 5% and 15% additional styrene, the viscosity was determined only for neat resin samples and those with 40% and 50% filler. The styrene was incrementally combined into the samples with the viscosity determined for each combination. The experimental results are summarised in Table 4.3.

Table 4.3 Viscosity of Hetron 922 PAW vinyl ester / cenosphere composite systems with increasing styrene concentration.

Resin	Hetron 922 PAW			**Filler**		E-Spheres SLG	
Styrene Addition (%)	**Viscometer / Spindle / Rotational Frequency**	**Viscosity (cP)**					
		Filler Volume Fraction (%)					
		0	**10**	**20**	**30**	**40**	**50**
0	A / 4 / 20	380	530	800	1660	4180	
	A / 6 / 50					3060	12800
5	A / 4 / 20	250				2530	
	A / 6 / 50					2040	5100
10	A / 4 / 20	190	290	400	760	2020	6520
	A / 6 / 50					1560	4060
15	A / 4 / 20	140				1130	4710
	A / 6 / 50					1240	3000

The inclusion of additional quantities of styrene monomer lowered the viscosity of neat resin and filled samples. Reductions in viscosity of approximately 50% were realised after an additional 10% of styrene monomer was incorporated into each composite system. At a filler volume fraction of 50%, the viscosity was reduced by almost 70% through the addition of only 10% styrene monomer.

Figure 4.5 shows the relationship of viscosity and filler volume fraction for standard vinyl ester / cenosphere composite systems and similar systems with an additional 10% styrene monomer. The non-linear relationship between viscosity and filler volume fraction is maintained even with the additional styrene. The addition of styrene produces a more pronounced reduction in viscosity at the higher filler volume fractions.

Figure 4.6 illustrates how the viscosity decreases as the addition level of styrene monomer is increased. The relationship appears almost linear for neat resin however the incorporation of filler appears to introduce a non-linearity into the relationship. Li [6] reported that the viscosity of vinyl ester resins decreases with increases in styrene concentration. This study encompassed VE resins with a greater range of styrene contents from 20% to 60% and ultimately suggested a logarithmic equation to describe the relationship between viscosity and styrene content. Results of this investigation suggest a linear relationship exists between the styrene concentration and viscosity of neat resin systems. However the observed linear relationship may also be related to the considerably narrower range of styrene concentrations of 45% to 60% used in this investigation.

As the styrene monomer content was increased, the viscosity measurements for the higher filler volume fractions (40 - 50%) were easier to obtain. There was a visible decrease in the concentration of air bubbles and the lower viscosity led to a rapid stabilisation of the measurements.

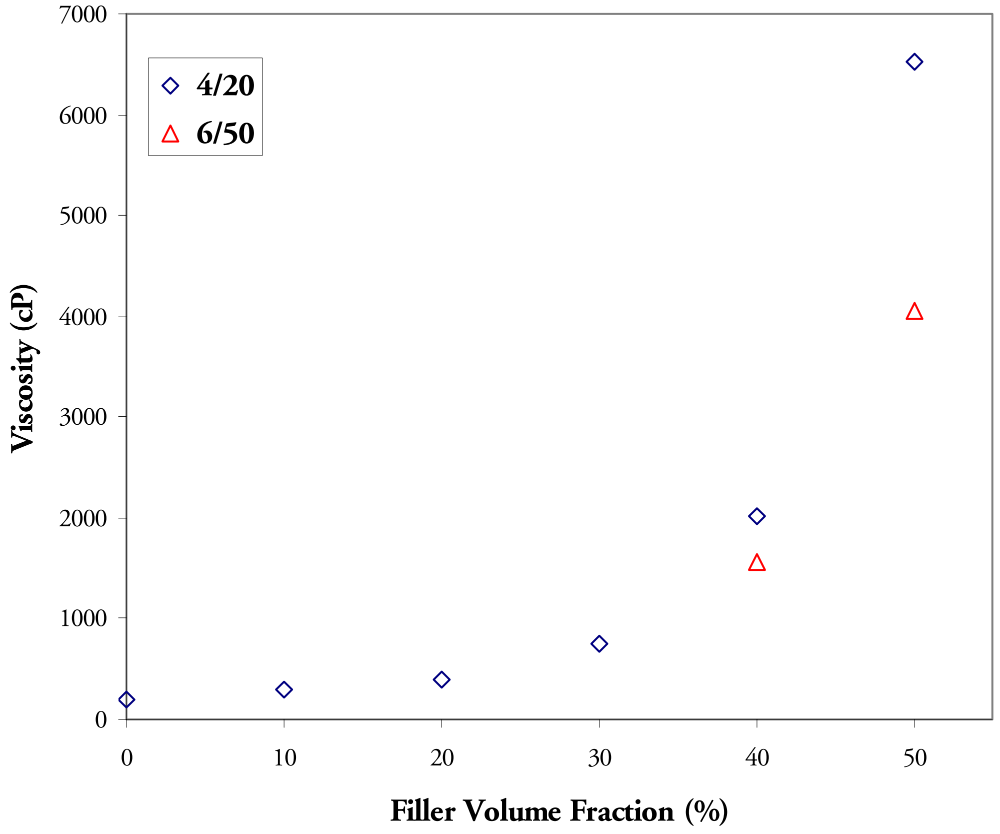

Figure 4.5 **Influence of 10% additional styrene on the viscosity of Hetron 922 PAW vinyl ester / cenosphere composite systems.**

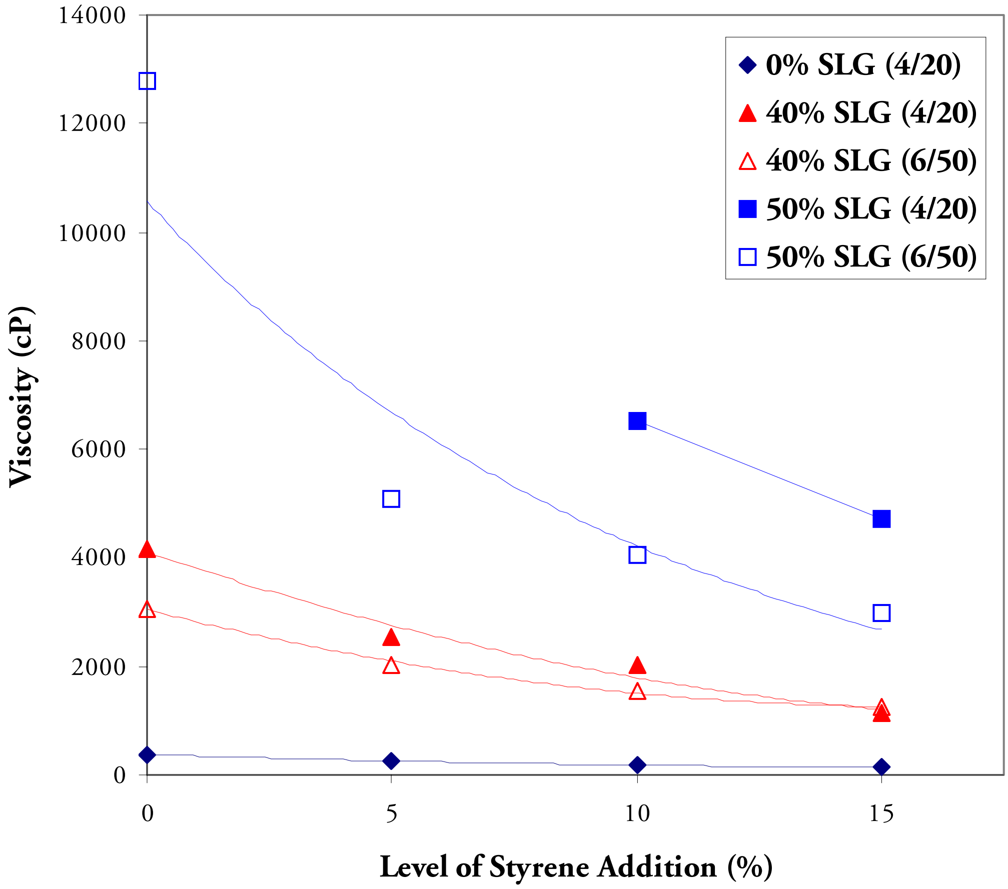

Figure 4.6 **Influence of styrene addition level on the viscosity of Hetron 922 PAW vinyl ester / cenosphere composite systems.**

4.3.2. CHARACTERISATION OF SHRINKAGE BEHAVIOUR

4.3.2.1. Influence of Filler Volume Fraction

An investigation was undertaken to examine the influence of filler volume fraction on the shrinkage behaviour of vinyl ester / cenosphere composite systems. Shrinkage experiments were conducted according to ASTM D6289 [18] using Hetron 922 PAW with filler volume fractions from 0 to 50% in 10% increments. Samples with filler contents of 35%, 45% and 55% were also included to provide more detailed information at the higher volume fractions. The 55% volume fraction specimens were very viscous and proved difficult to cast with some specimens discarded due to the presence of large air voids.

Table 4.4 shows the initial shrinkage after ambient cure and total shrinkage after post-cure of Hetron 922 PAW / cenosphere composite systems. These values are the average of the measured shrinkages of each specimen. The results are presented graphically in Figure 4.7.

Table 4.4 Linear shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems with increasing filler volume fraction.

Resin	Hetron 922 PAW		**Initiator**	Butanox M-60		**Filler**	E-Spheres SLG		
Shrinkage	**Linear Shrinkage (%)**								
	Filler Volume Fraction (%)								
	0	**10**	**20**	**30**	**35**	**40**	**45**	**50**	**55**
Initial	0.53	0.68	0.48	0.48	0.82	0.81	0.71	0.74	0.55
Total	1.31	1.21	1.01	0.88	0.99	0.93	0.85	0.80	0.65

The total shrinkage consistently exceeded the initial shrinkage due to the elevated temperature post-cure progressing the cure and increasing the degree of conversion of the networks and it ensures all samples ultimately experience a comparable thermal cycle and subsequent thermal shrinkage.

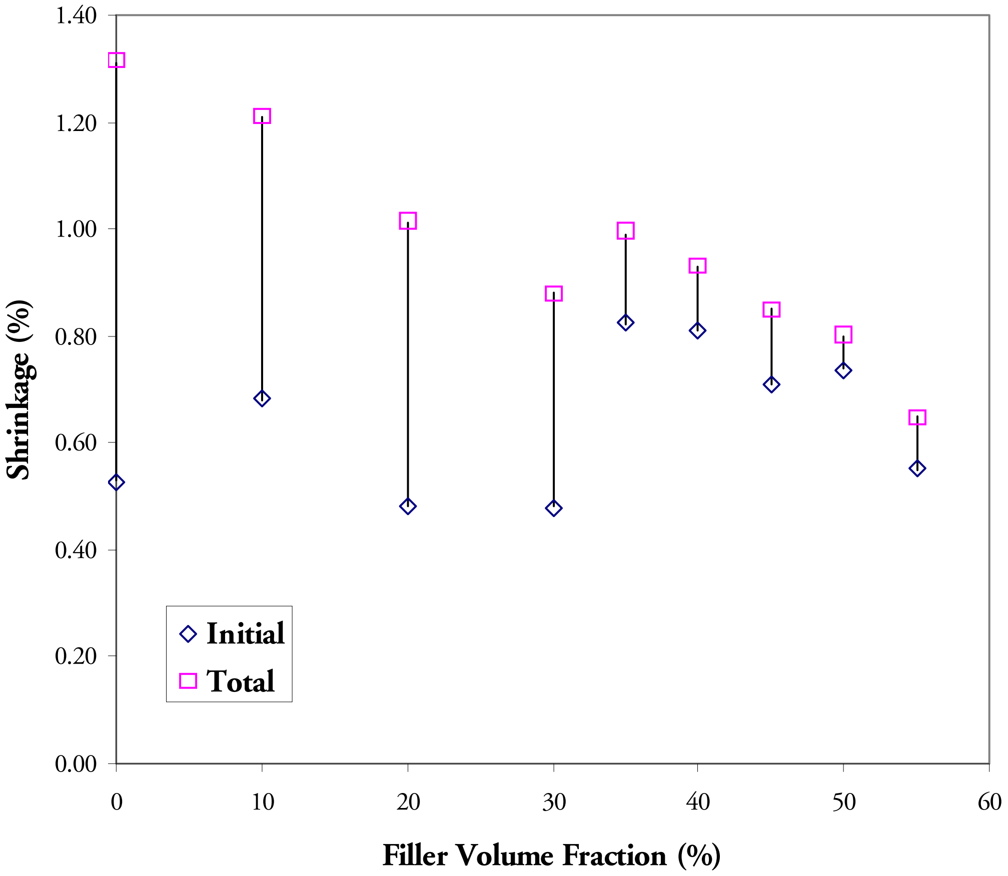

Figure 4.7 Variation of the initial and total shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems with increasing filler volume fraction.

An increasing filler volume fraction had varying effects on the initial cure shrinkage behaviour of Hetron 922 PAW. It was expected that as the filler volume fraction was increased, the initial shrinkage would decrease due to a combination of two influences of the lowering resin content:

- reduced polymerisation shrinkage, and
- reduced thermal shrinkage due to lower exotherm temperatures.

Cure investigations presented in Chapter 3 showed the addition of filler lowered the peak temperature of curing composite systems. Contrary to expectation, the initial shrinkage behaviour exhibited considerable variability. This is particularly evident for samples with filler volume fractions less than 35%, at which a step in both the initial and total behaviour was observed. Overall the total shrinkage behaviour generally followed the expected trend of decreasing with increasing filler volume fraction.

Due to the observed variability and step in the results, the shrinkage experiments for samples with filler volume fractions of 0, 10, 20, 30 and 40% were repeated. The results of these experiments were similar to those of the original tests, supporting the observed behaviours.

The vitrification of the resin matrix is believed to contribute to the variation in the initial shrinkage behaviour of Hetron 922 PAW vinyl ester / cenosphere composite systems with low filler contents.

Vitrification relates to the resin transforming from a liquid rubbery state to a rigid glassy state during cure. Vitrification occurs when the T_g of the system reaches the cure temperature and the reaction stops due to a lack of mobility [7]. Martin *et al.* [21] stated that near vitrification, the cure kinetics are affected by the local viscosity of the resin which is influenced by the extent of the reaction and the temperature. The cessation of the reaction is not necessarily an indication that the cure is complete but may have quenched due to vitrification of the resin matrix. It follows that if the temperature is increased above the T_g the chains regain the mobility to continue the reaction.

The results show that, in general, after post-cure the total shrinkage behaviour follows the expected trend of decreasing with increasing filler volume fraction. This was attributed to the elevated temperatures increasing the mobility of the chains, progressing the cure and increasing the degree of conversion of the network. The degree of conversion of the network directly influences the cure shrinkage [7]. Therefore the shrinkage values also provide an indication of the degree of conversion of the network.

If it is assumed that all specimens reach an equivalent degree of conversion due to the post-cure temperature being above the T_g of Hetron 922 PAW (≈95°C from Chapter 3), the initial shrinkage and the links between the initial and total shrinkage values (Figure 4.7) provide an indication of the initial degree of conversion of the network. The higher initial shrinkage values and relatively shorter links suggest a higher degree of conversion is achieved initially in the more highly filled specimens compared to those with a low filler and high resin content. The relatively lower degree of conversion of the specimens with high resin content is attributed to vitrification of the resin matrix. These specimens with high resin content were believed to have hardened more rapidly locking the network in place but possessing an associated low degree of conversion. Further investigations are required to verify this behaviour with FTIR spectroscopy a potentially suitable technique for this investigation.

There was quite a significant step in the initial and total shrinkage behaviour corresponding to a 35% filler volume fraction. This filler volume fraction may represent a transition from resin dominated behaviour to filler dominated behaviour. It was also at a similar level of filler concentration that the viscosity behaviour became dominated by particle-to-particle interaction (see Section 4.3.1).

The total shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems was reduced from 1.31% for neat resin to 0.80% through the addition of 50% filler. This equates to an approximate 40% reduction in shrinkage.

4.3.2.2. Influence of the Oligomer Molecular Weight

An investigation was undertaken to examine the influence of a change in the oligomer molecular weight on the shrinkage behaviour. Additional shrinkage experiments were conducted according to ASTM D6289 [18] using Hetron 914 with filler contents equivalent to those used in the previous investigation of Hetron 922 PAW composite systems.

Shrinkage results for the Hetron 922 PAW composite systems were presented earlier in Figure 4.7 with key data provided in Table 4.4. The shrinkage behaviour of Hetron 914 is shown in Figure 4.8 with the key data presented in Table 4.5. The values are the average of the measured shrinkages of each specimen.

Table 4.5 Linear shrinkage of Hetron 914 vinyl ester / cenosphere composite systems with increasing filler volume fraction.

Resin	Hetron 914		**Initiator**	Butanox M-60		**Filler**	E-Spheres SLG		
Shrinkage	**Linear Shrinkage (%)**								
	Filler Volume Fraction (%)								
	0	**10**	**20**	**30**	**35**	**40**	**45**	**50**	**55**
Initial	0.89	0.31	0.22	0.27	0.30	0.49	0.16	0.43	0.19
Total	1.13	0.66	0.51	0.45	0.39	0.58	0.32	0.53	0.31

The initial cure shrinkage behaviour of Hetron 914 with increasing filler content was varying, but appeared marginally more consistent than that observed for the Hetron 922 PAW. The variability may be the result of the vitrification behaviour described previously.

Generally after post-cure, the total shrinkage of the Hetron 914 samples followed the expected behaviour of decreasing with increasing filler volume fraction. Considerably higher initial and total shrinkage values were observed at volume fractions of 40% and 50%. The shrinkage experiments for samples with filler volume fractions of 30, 35, 40 and 45% were repeated with the results of these experiments similar to those of the original tests. A step in the shrinkage behaviour was observed at similar filler volume fractions for Hetron 922 PAW indicating that a potentially complex behaviour exists at these higher volume fractions. Further investigation of this behaviour is warranted but is beyond the scope of this research.

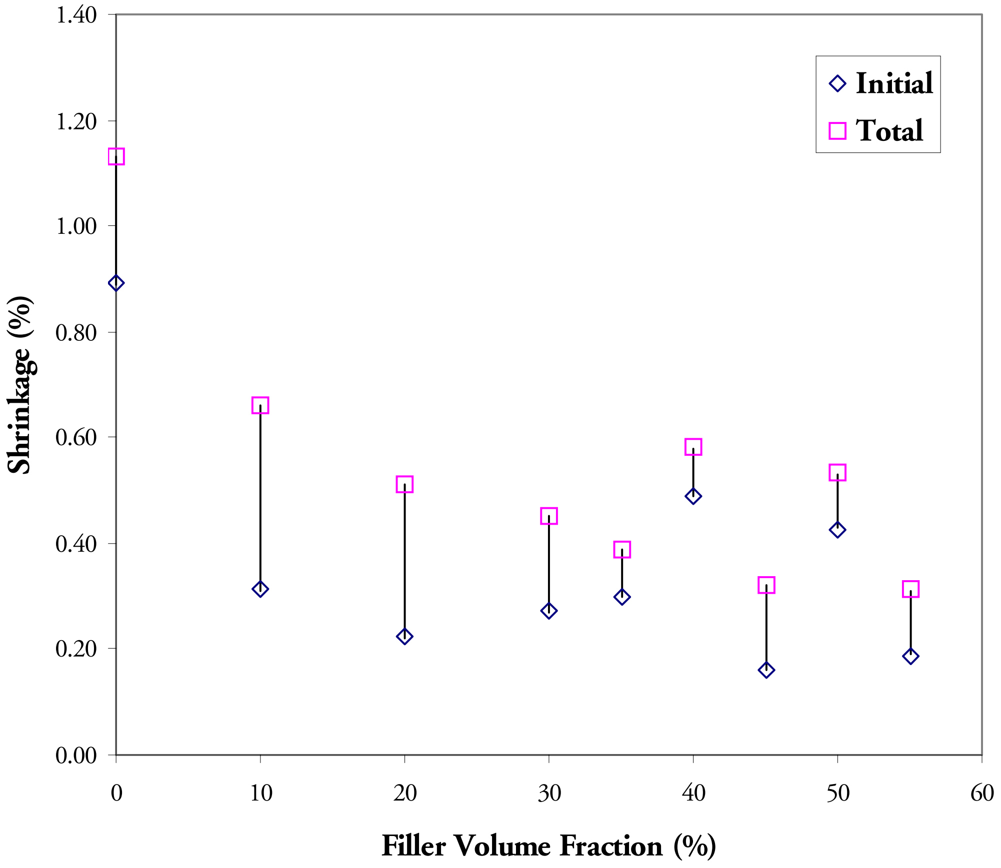

Figure 4.8 **Variation of initial and total shrinkage of Hetron 914 vinyl ester / cenosphere composite systems with increasing filler volume fraction.**

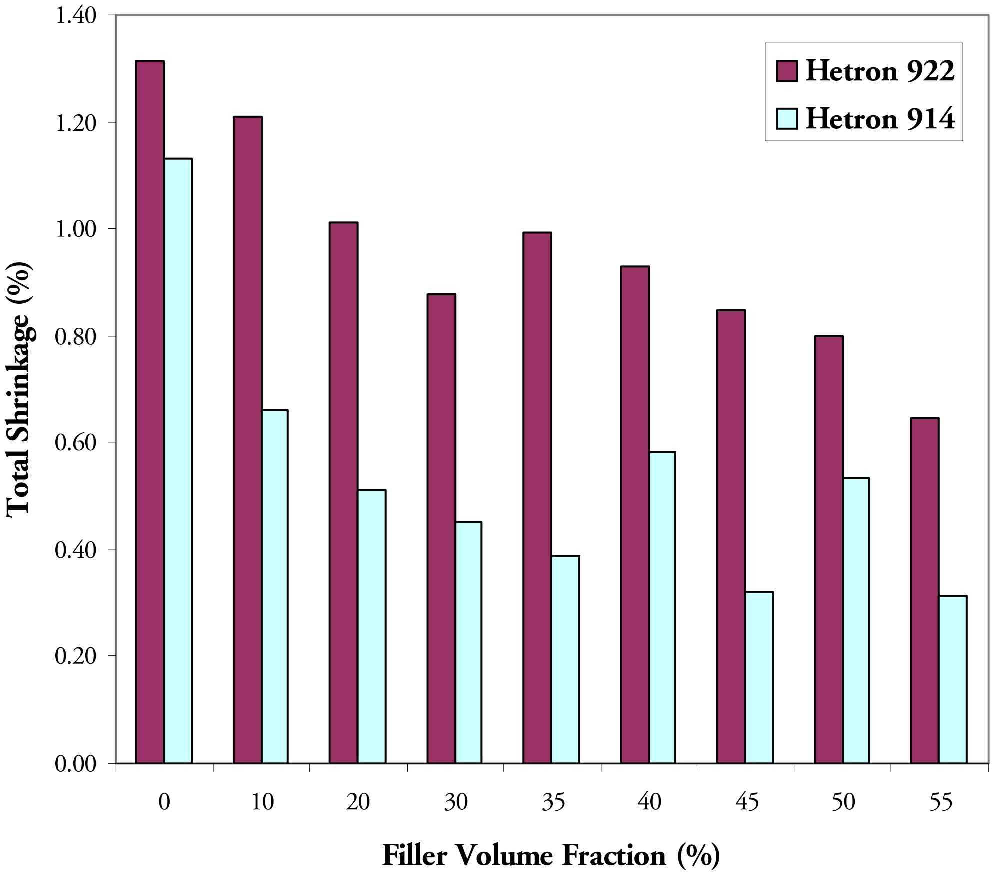

Figure 4.9 **Comparison of the total shrinkage of Hetron 922 PAW and Hetron 914 vinyl ester / cenosphere composite systems with increasing filler volume fraction.**

The test method used for this shrinkage investigation specified a post-cure temperature of 110°C [18]. As part of the cure studies presented in Chapter 3, the T_g of Hetron 914 was determined as ≈136°C which is higher than the post-cure temperature used in this study. This indicates that the Hetron 914 samples may possess a comparably lower degree of conversion after post-cure compared to the Hetron 922 PAW samples with a T_g of ≈95°C.

The total shrinkage of Hetron 914 vinyl ester / cenosphere composite systems was reduced from 1.13% for neat resin to 0.53% through the addition of 50% filler. This equates to an approximate 50% reduction in shrinkage.

The total shrinkage behaviour of Hetron 922 PAW and Hetron 914 shown in Figure 4.9 highlights the comparably lower shrinkage of Hetron 914 at each filler volume fraction.

On average the total shrinkage of Hetron 914 composite systems was 44% lower than that of Hetron 922 PAW composite systems. Reported results by Burts [7] and Li [6] and co-authors [2] indicated that a lower molecular weight and higher styrene content led to increased shrinkage. Even though possessing a comparably lower molecular weight, the Hetron 914 samples exhibited a lower shrinkage. This is attributed to the lower styrene content which suggests that the styrene concentration may have a more significant influence on shrinkage behaviour than the molecular weight of the oligomer. Further investigations are required to isolate the relative influences of oligomer molecular weight and styrene concentration on the shrinkage behaviour.

4.3.2.3. Influence of Styrene Concentration

An investigation was undertaken to examine the influence of styrene concentration on the shrinkage behaviour of vinyl ester / cenosphere composite systems. Experiments were performed using Hetron 922 PAW neat resin and 60% vinyl ester / 40% cenosphere composite formulations, similar to the combinations used for the cure investigation of composites presented in Chapter 3. Styrene was incorporated into these systems at addition levels of 5%, 10% and 15% by volume. The experimental results are summarised in Table 4.6 and presented graphically in Figure 4.10. The values are the average of the measured shrinkages of each specimen.

Table 4.6 Linear shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems with increasing styrene concentration.

Resin	Hetron 922 PAW	**Initiator**	Butanox M-60	**Filler**	E-Spheres SLG

Shrinkage	**Filler Volume Fraction (%)**	**Linear Shrinkage (%)**			
		Styrene Addition (%)			
		0	**5**	**10**	**15**
Initial	0	0.53	0.24	0.38	0.41
Total	0	1.31	1.31	1.30	1.32
Initial	40	0.81	0.63	0.77	0.76
Total	40	0.93	0.93	0.97	1.03

Reported results indicate that increasing the styrene concentration of neat vinyl ester resins increases the shrinkage [6,2,7]. The results of this study show that the addition of styrene actually lowered the initial shrinkage of neat resin and filled samples. In the previous investigations, considerable variation in the initial shrinkage behaviour was observed. It is reasonable to assume that the discussed influences of vitrification may be extended to this shrinkage study.

The total shrinkage behaviour of the filled samples increased as the styrene concentration was increased. However the total shrinkage of neat resin samples showed no significant changes with increasing styrene concentration. This could indicate that an upper limit to the shrinkage behaviour of neat resin may exist, above which further increases in styrene concentration have no significant effect on the shrinkage behaviour. Further investigations over a wider range of styrene addition levels are required to further examine this relationship.

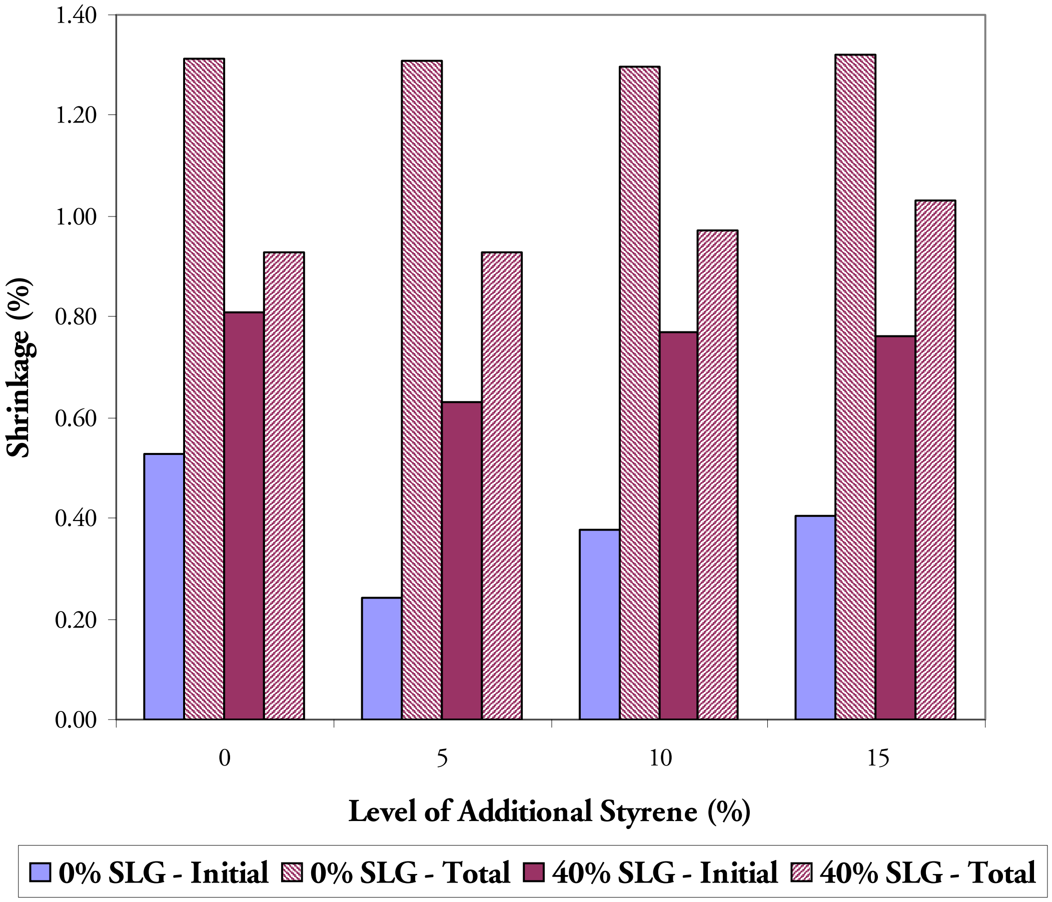

Figure 4.10 Influence of styrene concentration on the linear shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems.

4.3.2.4. Influence of Material Volume

An investigation was undertaken to examine the influence of material volume on the shrinkage behaviour of vinyl ester / cenosphere composite systems. Shrinkage experiments were performed in accordance with the block method, outlined in Section 4.2.2.3, using Hetron 922 PAW with filler volume fractions of 0%, 20% and 40%. The shrinkage values from the block samples were compared to those of linear bars cast from equivalent composite formulations to determine the volume effects. The results are summarised in Table 4.7 and presented graphically in Figure 4.11.

Table 4.7 Linear shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems of increased material volume.

Resin Hetron 922 PAW **Initiator** Butanox M-60 **Filler** E-Spheres SLG

Shrinkage	**Test Type**	**Linear Shrinkage (%)**		
		Filler Volume Fraction (%)		
		0	**20**	**40**
Initial	Linear Bar	0.53	0.48	0.81
Total	Linear Bar	1.31	1.01	0.93
Initial	Block	1.77	1.33	1.33
Total	Block	2.65	1.77	1.33

Both the initial and total shrinkage of the blocks were higher than the bars indicating that increased material volume leads to increased shrinkage. The greater volume of material may lead to higher exotherm temperatures which are sustained for longer thus maintaining the mobility of the chains leading to a greater degree of conversion of the network (and associated shrinkage) compared to lower volume samples. Further investigation is required to quantify the effects of material volume on the shrinkage behaviour.

In addition, a reason for selecting a linear method to examine the shrinkage behaviour was that the data is relevant to production. This study suggests that shrinkage values obtained using the linear method may not be directly applicable to a practical manufacturing situation and may only be indicative of the shrinkage behaviour.

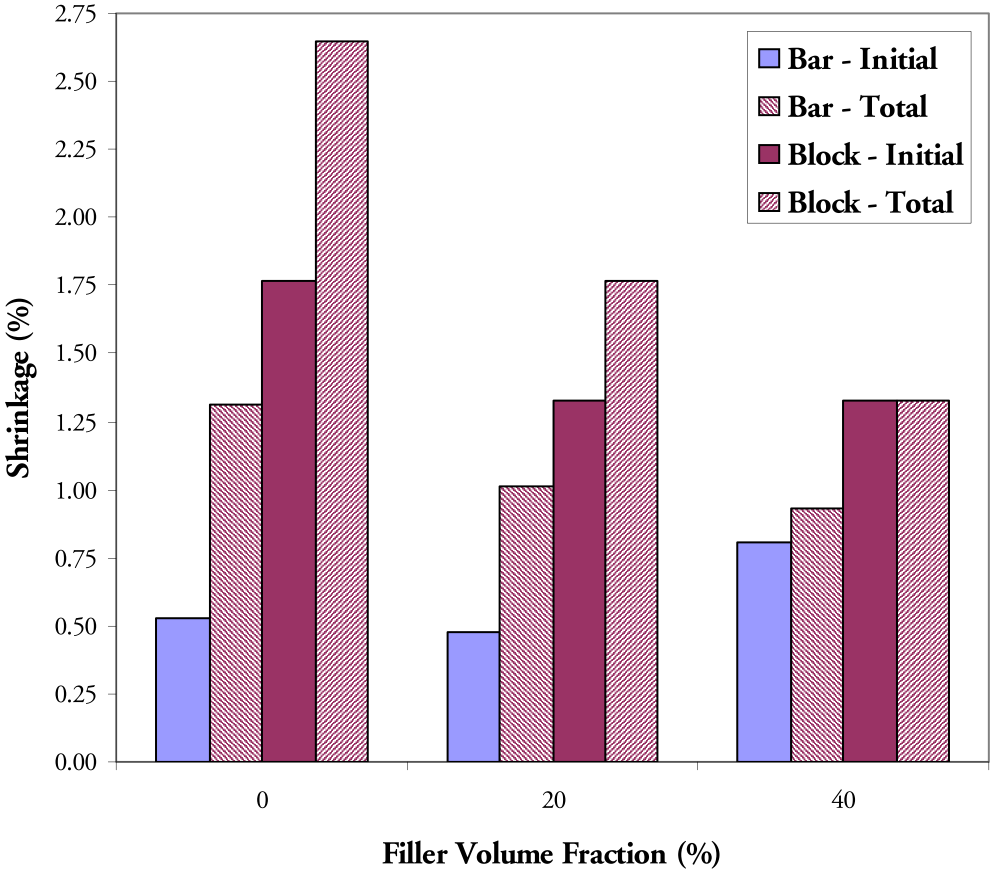

Figure 4.11 Influence of material volume on the initial and total shrinkage of Hetron 922 PAW vinyl ester / cenosphere composite systems.

4.4. SUMMARY AND CONCLUSIONS

This Chapter has presented a review and results of an investigation of the processing characteristics of vinyl ester / cenosphere composites, examining the relationships between constituent materials and the viscosity and shrinkage behaviour. The findings of this investigation are summarised as follows:

- The viscosity of vinyl ester / cenosphere composites in their uncured state was found to increase non-linearly with increasing filler volume fraction. At high filler levels the viscosity behaviour appeared dominated by particle interaction, characterised by significant increases in viscosity for only small increases in filler volume fraction.
- The established techniques for measuring viscosity were not able to provide consistent precision for the significant variations in the order of magnitude of the different viscosities associated with the large parameter variations.
- The viscosity at a 50% filler volume fraction (practical processing limit) appears in the order of 12000cP at 25°C.
- The experiments highlighted the sensitivity of the viscosity behaviour to styrene concentration with only small additions of styrene producing large decreases in viscosity, particularly at higher filler volume fractions.
- The shrinkage behaviour of vinyl ester / cenosphere composites was found to be relatively complex, particularly the initial shrinkage behaviour. The variation of initial shrinkage values was attributed to different degrees of conversion achieved in samples at each filler volume fraction.
- The total shrinkage behaviour generally followed the expected trend of decreasing with increasing filler volume fraction. This was attributed to the post-cure progressing the degree of conversion such that each sample was cured to a similar extent and the post-cure exposing each sample to an equivalent thermal cycle.
- The shrinkage is lower when curing occurs at ambient temperatures followed by an elevated temperature post-cure compared to a single complete cure at elevated temperatures.

- The styrene concentration appeared to have a more dominant influence on the shrinkage behaviour than the oligomer molecular weight of the VE resin. Generally increases in styrene concentration led to increases in the total shrinkage which was more apparent in filled systems.
- Increases in material volume also led to increases in shrinkage indicating that results obtained using the linear shrinkage tests may not be directly applicable to a production environment where three-dimensional volumetric shrinkage effects may be significant.
- The observed shrinkage behaviour of these composite systems suggests that for their application to structural elements, the required shape and final dimensions must be carefully considered during both the element design and mould design phases.

4.5. REFERENCES

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CHAPTER 5.

THE MECHANICAL PROPERTIES OF VINYL ESTER / CENOSPHERE COMPOSITES

5.1. INTRODUCTION

The previous Chapters have investigated the processes involved in the creation of a vinyl ester / cenosphere composite. The mechanisms of cure that transform the blended constituents into a rigid network and the parameters that influence the cure were examined. The processing characteristics were analysed, investigating the viscosity behaviour which affects the handling and placing of the materials and the shrinkage behaviour which influences the tolerances and quality of the final products.

For vinyl ester / cenosphere composite systems to be utilised in structural applications it is necessary to understand the mechanical behaviour of the cured networks and the relative influence of the constituents on the mechanical properties. For primary structural applications, the mechanical performance of the material combinations must be quantified to facilitate the accurate design and analysis of structural elements.

This Chapter reviews research relating to the mechanical performance of resin / cenosphere composite systems and establishes characterisation parameters for the evaluation of mechanical properties of vinyl ester / cenosphere composite systems. An experimental investigation assessing the strength and stiffness characteristics of these composite systems is then presented.

5.1.1. BACKGROUND

Preliminary applications of resin / cenosphere composite materials have utilised sandwich construction techniques in which the particulate composite core is combined with high strength fibre composite laminates [1,2,3,4,5]. For this technique, the laminates typically provide the bending strength and longitudinal stiffness while the core supports the shear forces and provides local performance. Investigations examining the mechanical behaviour of particulate composite systems were previously outlined in Chapter 2.

Foundational studies by Ayers [6] examined the properties of particulate composites and included vinyl ester / cenosphere systems however the study was limited to stiffness characteristics in flexure and compression. Investigations of stiffness behaviour were also been reported by Ayers and Van Erp [7,8,9]. A subsequent study by Ayers and Van Erp [10] examined constituent influences on the properties of vinyl ester / cenosphere composites but focussed on the flexural strength and stiffness behaviour.

Research by Cardoso *et al.* [11] examined the properties of polyester / cenosphere composites. These investigations primarily focussed on the influences of particle size and surface treatment of cenospheres on mechanical properties with material combinations of this study limited to a 25% volume fraction of filler.

Chalivendra *et al.* [12] investigated the influence of cenospheres over a wider range of volume fractions (0 to 40%) on the tensile and compressive behaviour of composites however these systems used a polyurethane resin matrix.

These investigations are limited in their evaluation of strength and stiffness characteristics of vinyl ester / cenosphere composite systems in tension and compression.

5.1.2. CHARACTERISATION PARAMETERS

An experimental program was developed to characterise the basic mechanical properties of vinyl ester / cenosphere composite systems by assessing their behaviour in:

- Tension,

- Compression, and
- Flexure.

Flexural performance was included in this investigation as a benchmark against previous research which used flexural properties to examine material behaviour [6,7,8,9,10,13]. Standard test procedures, which will be outlined in Section 5.2.2, were used to determine the following material properties:

- Strain at failure
- Modulus
- Stress at failure
- Poisson's ratio

The strength characteristics of the composite systems were examined using the strain at failure values with failure stress values calculated at these strains. The stiffness characteristics were examined using the modulus properties. The Poisson's ratio was also determined to examine the relationship of the transverse and axial strain.

The current investigation examines the influence of filler volume fraction on the strength and stiffness characteristics by varying the content from 0 to 50% in 10% increments. A filler volume fraction of 45% was also included to provide more detailed data at the higher filler levels. The investigations presented in earlier Chapters included the influence of initiator type, oligomer molecular weight and styrene on the behaviour however these influences are not considered in this study of mechanical properties and may be the subject of future research.

To aid in the development of an understanding of the relationships between the mechanical behaviours and the filler volume fraction of the composite systems, polynomial interpolation was used to identify behavioural relationships. Where appropriate, linear trends are preferred due to the foundational nature of the investigation and the limited variation of parameters examined. For each of the polynomials, the coefficient of determination or R-squared value was determined as a measure of the variability of the established relationships. The R-squared value is an indicator between 0 and 1 which shows how close the estimated values for the polynomial correspond to the data [14].

5.2. EXPERIMENTAL INVESTIGATION

This section summarises the materials selected for use in this study and the experimental techniques and procedures used to characterise the mechanical behaviour. The results are presented in Section 5.3.

5.2.1. MATERIALS

The materials used for the characterisation program were detailed in Section 3.2.1 and Table 3.2. The selected materials for this part of the study are listed in Table 5.1.

Table 5.1 Constituent materials selected for the characterisation of mechanical properties of vinyl ester / cenosphere composite systems.

Product Number	Product Name	Description
1	Hetron 922 PAW	Standard grade vinyl ester resin
4	Butanox M-60	General purpose medium-reactivity MEKP
8	E-Spheres SLG	20 - 300μm cenosphere filler

All samples were initiated with Butanox M-60 at a 2.5% concentration. The cure study presented in Chapter 3 showed this initiator level of Butanox M-60 produced a relatively rapid cure. As outlined in Section 4.1.1, a rapid cure limits the opportunity for segregation of the resin and filler particles ensuring the production of a homogeneous composite. The cure investigation also showed the cure times of samples initiated using MEKP based solutions were quite consistent even after the addition of filler.

5.2.2. EXPERIMENTAL TECHNIQUES

The tension, compression and flexure specimens for each filler volume fraction were cast from a single batch of material. The types of test specimens used in the study are shown in Figure 5.1. The pre-calculated constituent resin and filler quantities were combined by hand and blended ensuring the filler was wet out and distributed evenly throughout the mix. The initiator was added and thoroughly blended. Generally six specimens were produced for each volume fraction. All castings were allowed to cure at ambient temperatures, removed from the moulds and post-cured using a general (industry recommended) post-cure schedule of 80°C for a period of 8 hours. All testing was conducted using a universal testing machine.

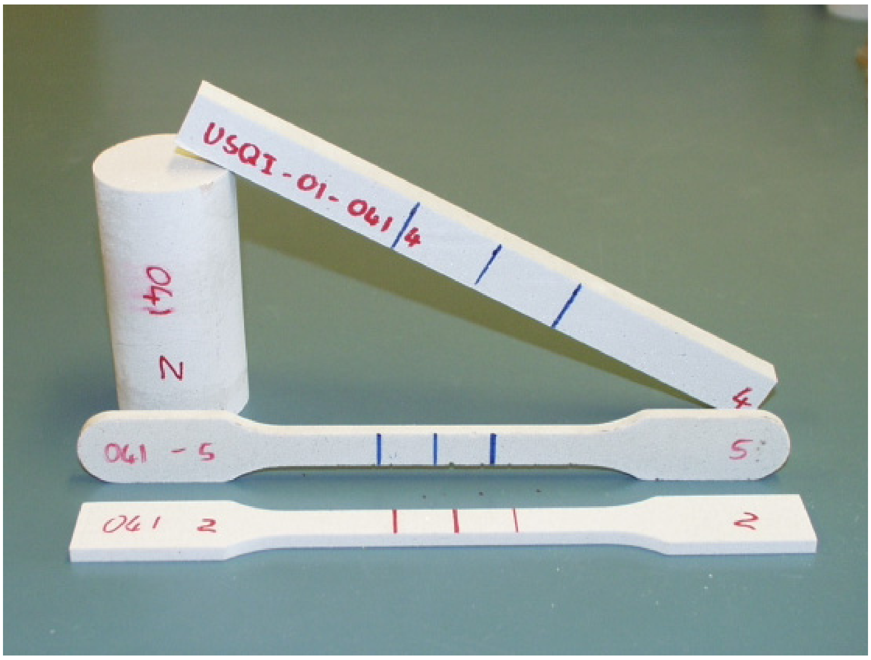


Figure 5.1 A compression cylinder, flexure bar (inclined) and two types of tension specimens.

5.2.2.1. *Characterisation of Tensile Properties*

Tension specimens were produced using two methods to ascertain whether the method of fabrication influences the results. All specimens were fabricated to the dimensions specified in ISO 527-2:1993 [15] of:

Length = 160mm,

Width = 10mm, and

Thickness = 4mm.

In the first method, the specimens were cast in a six cavity steel mould which is shown in Figure 5.2. Each of the identical "dog-bone" shaped cavities was sized to produce specimens of the specified dimensions. In the second method, the specimens were cut from a single flat 250mm x 210mm x 6mm cast panel and machined to size.

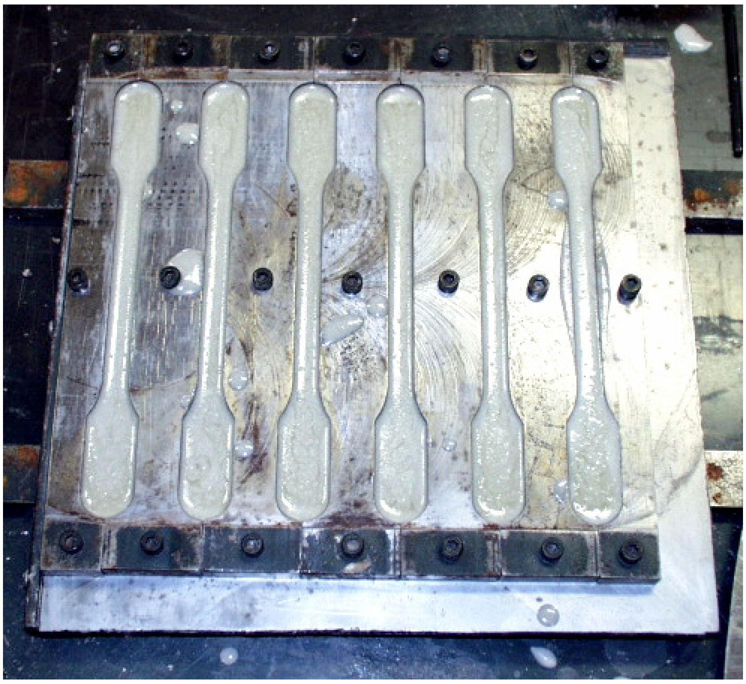
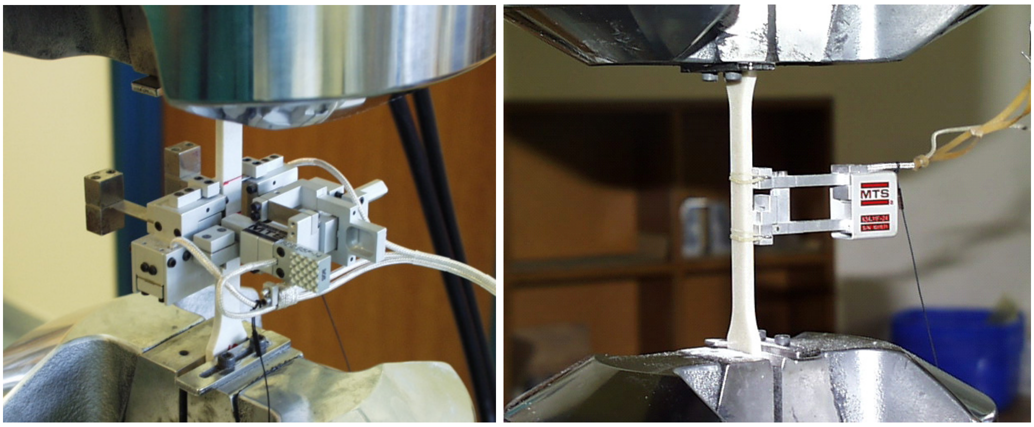


Figure 5.2 Tensile test specimens cast in a multiple cavity "dog-bone" shaped mould.

The tensile properties were assessed using a direct tension test in accordance with ISO 527-1:1993 [16]. The specimens were first tested using a dual extensometer to calculate Poisson's ratio. The specimens were loaded to an axial strain of approximately 0.15% and the Poisson ratio was calculated from this initial linear portion of the axial strain / transverse strain relationship.

The specimens were then tested to failure with the recorded applied load used to determine the stress in the specimen at failure. The elongation was measured using a single extensometer to determine the strain on the surface of the specimen at failure. The modulus of elasticity was determined over a strain range of 0.05-0.25% as specified by ISO 527-1 [16]. Typical tensile test configurations are shown in Figure 5.3.



a) b)

Figure 5.3 Typical tensile test configuration using: (a) dual extensometer to determine Poisson's ratio and, (b) single extensometer to determine stress, strain and modulus of elasticity values.

5.2.2.2. Characterisation of Compressive Properties

Compression specimens were cast in individual cylindrical moulds. The specimens were approximately 36mm in diameter and had a height of 72mm in accordance with the 2:1 aspect ratio specified in ASTM D 695 [17]. The applied load and cross-head displacement were continuously monitored and used to determine the stress and strain in the specimen. The compression modulus was determined from a tangent drawn through the initial linear portion of the stress / strain relationships to compensate for the initial alignment and seating adjustment of the specimen.

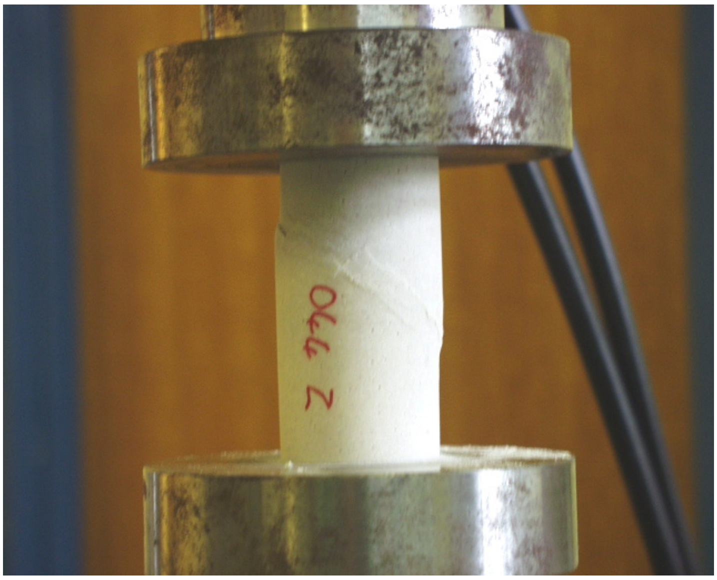


Figure 5.4 A typical compression specimen under load (note the shear failure plane).

5.2.2.3. Characterisation of Flexural Properties

The flexural properties were assessed using a three-point bending flexure test in accordance with ISO 178:1993 [18] (see Figure 5.5). Blocks were cast in individual 190mm x 150mm x 16mm vertical steel moulds and the individual flexure specimens cut from these castings to the dimensions of approximately:

Length = 190mm,

Width = 16mm, and

Thickness = 9mm.

These specimen dimensions exceed the values preferred by the standard but were adopted for ease of manufacture. The supported span was determined for each sample using the 16:1 span-depth ratio specified by ISO 178 [18]. The applied load and central deflection were continuously monitored and used to determine the stress and strain on the outer surface of the specimen. The flexural modulus was determined over a strain range of 0.05-0.25% as specified by ISO 178 [18].

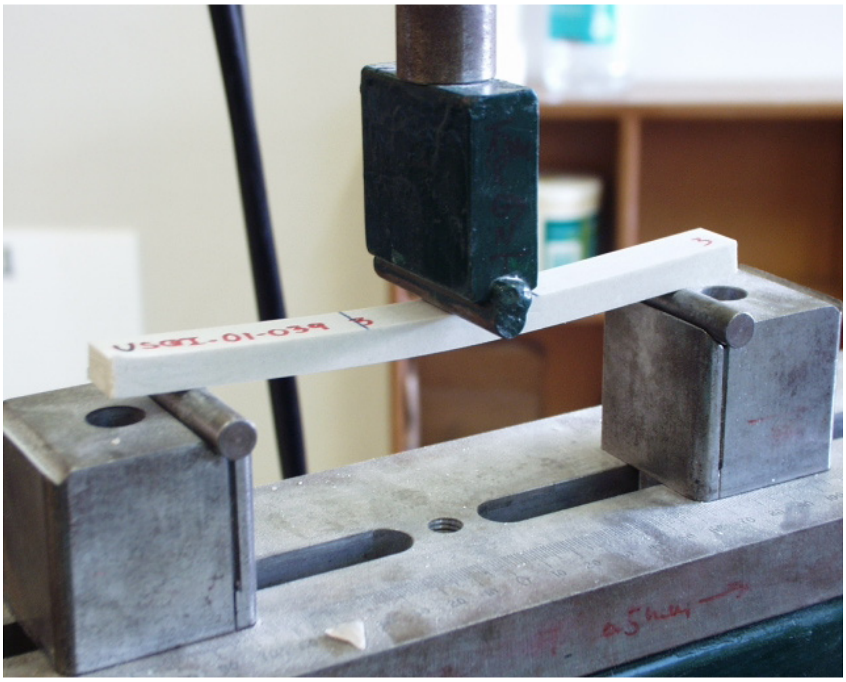


Figure 5.5 Typical test configuration for the determination of flexural properties.

5.2.3. SAMPLE DETAILS

Sample details for the characterisation of mechanical properties of vinyl ester / cenosphere composites are shown in Table 5.2. The "T" suffix identifies tension specimens machined from a cast flat panel, the "DB" suffix identifies tension specimens cast using the dog-bone shaped mould, the "C" suffix identifies compression specimens and the "F" suffix identifies flexure specimens.

The experimental data and results are available in the Appendices: details of the characterisation of tensile properties are presented in Appendix B, details of the characterisation of compressive properties are presented in Appendix C and details of the characterisation of flexural properties are presented in Appendix D.

Table 5.2 Sample details for the experimental characterisation of mechanical properties of vinyl ester / cenosphere composites.

Resin	Hetron 922 PAW	**Filler**	E-Spheres SLG
Sample ID		**Filler Volume Fraction (%)**	
USQI-01-038-T, DB, C, F		0	
USQI-01-042-T, DB, C, F		10	
USQI-01-043-T, DB, C, F		20	
USQI-01-044-T, DB, C, F		30	
USQI-01-039-T, DB, C, F		40	
USQI-01-040-T, DB, C, F		45	
USQI-01-041-T, DB, C, F		50	

5.3. RESULTS AND DISCUSSION

This section presents the results of the experimental investigation of the mechanical behaviour of vinyl ester / cenosphere composites. As mentioned earlier, the filler volume fraction was varied from 0 to 50% in 10% increments and included a 45% filler level. The viscosity investigations presented in Chapter 4 have shown that within this range, the viscosity of the composite systems remains suitable from a practical ambient temperature processing perspective.

5.3.1. INFLUENCE OF SPECIMEN FABRICATION

The variation of tensile strain and the Modulus of Elasticity with filler volume fraction are shown respectively in Figure 5.6 and Figure 5.7 for both the moulded and machined specimens. For each data point, the maximum, minimum and mean values are displayed. To aid in the interpretation of the Figures, the mean values were connected by straight lines. The coefficients of variation (COV) of the results are presented in Table 5.3.

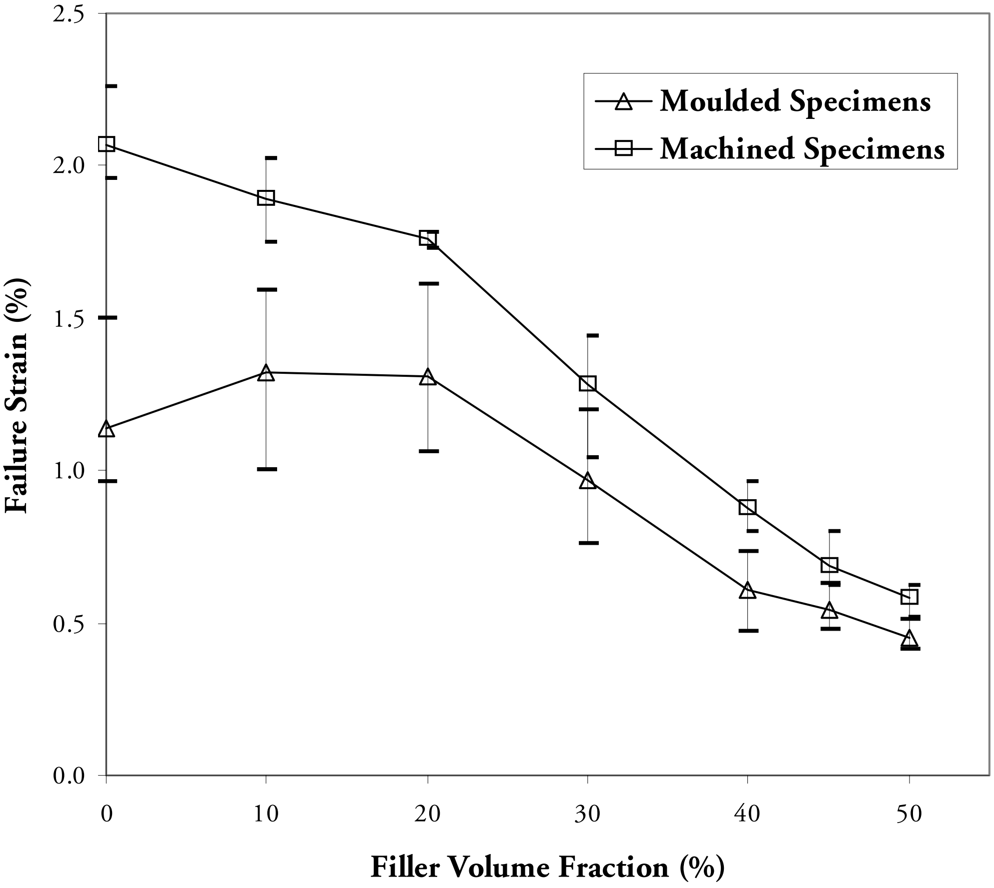


Figure 5.6 **The tensile strain at failure of Hetron 922 PAW vinyl ester / cenosphere composite systems obtained from specimens prepared using alternative fabrication methods.**

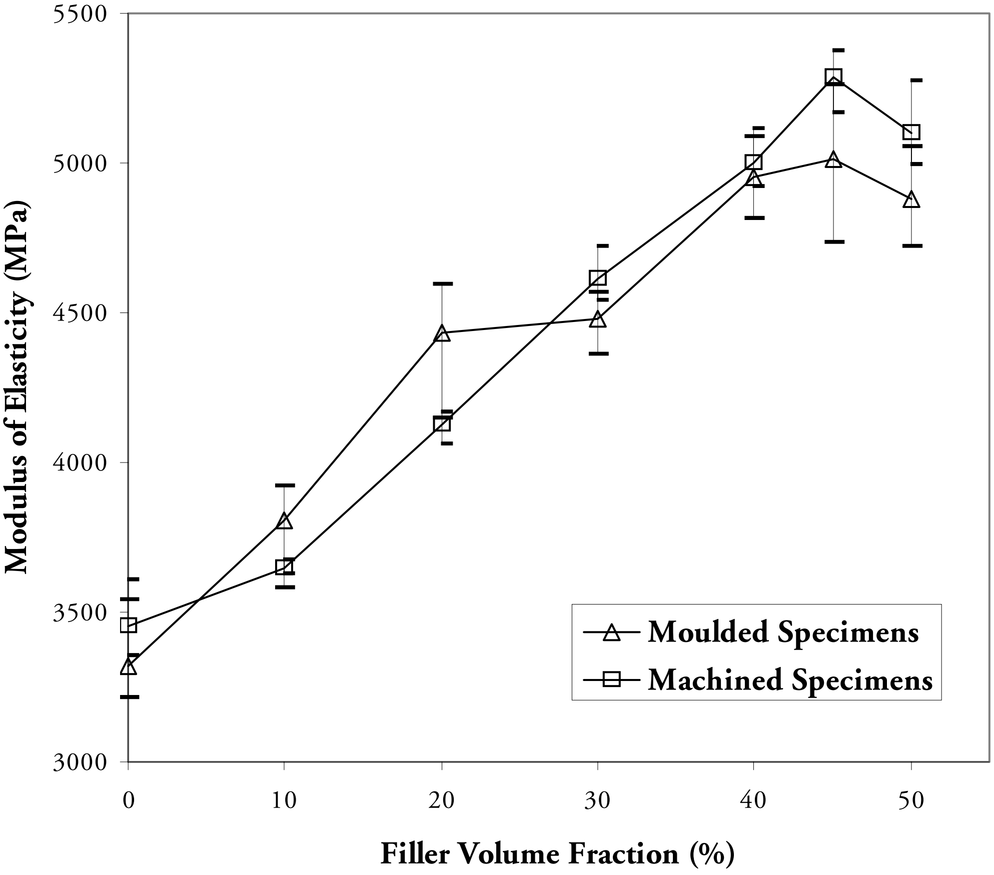


Figure 5.7 The Modulus of Elasticity of Hetron 922 PAW vinyl ester / cenosphere composite systems obtained from specimens prepared using alternative fabrication methods.

Table 5.3 Coefficients of variation for tensile test results of specimens fabricated using alternative methods.

Filler Volume Fraction (%)	Moulded Specimens Coefficient of Variation (%)		Machined Specimens Coefficient of Variation (%)	
	Strain	Modulus	Strain	Modulus
0	19.7	4.0	6.3	3.1
10	18.5	3.3	6.0	0.6
20	18.0	3.9	1.2	1.0
30	15.9	1.8	12.3	1.4
40	17.7	2.1	6.5	1.4
45	9.3	4.4	11.1	1.6
50	8.3	2.6	8.2	2.1

The COV values of the strain and modulus properties determined from the moulded specimens is much higher, particularly for the strain properties for low filler levels. The comparable COV values for strain properties at filler levels greater than 40% suggests that the high filler content may alleviate the apparent detrimental influences of the moulding method on the specimen behaviour.

The greater variation in results of the moulded specimens is also apparent in Figure 5.6 and Figure 5.7. The range of the results obtained from the moulded specimens is greater than those of the machined specimens, indicating a greater variation in the test results obtained from moulded specimens. The results obtained from the moulded specimens were also generally lower, particularly the failure strain properties.

The variation and comparably lower properties of the moulded specimens is attributed to a number of influences.

- Visual inspection of specimens confirmed that air voids were often present in the failure zone. This entrapped air in the moulded specimens appeared due to the casting process with the surface tension of the material with the sides of the mould restricting the escape of the air. Air voids effectively reduce the cross-sectional area of the specimen, potentially leading to a premature failure.

- The shape of the moulded dog-bone specimens with the larger ends restricts the specimens from shrinking during cure, leading to the development of internal stresses that may initiate the premature failure of the specimens. Investigations in Chapter 4 showed that the shrinkage of a vinyl ester resin is reduced through the addition of filler. The difference in strain values (Figure 5.6) between the samples fabricated using each method lowered as the filler content was increased, almost appearing to converge. This suggests that as the filler content was increased and the shrinkage reduced, the internal stresses were also reduced and subsequently had less influence on the failure strain behaviour.

The imperfections present in the tensile specimens fabricated using the moulded method appears to have a significant influence on the test results. This suggests that these specimens do not provide an accurate representation of material behaviour. Specimens fabricated using the machining method provided good, consistent results. Consequently the results from this method will be used in the following sections.

5.3.2. STRENGTH CHARACTERISTICS

The relationships of the strain at failure in tension, compression and flexure with increasing filler volume fraction are shown in Figure 5.8. The results for each individual test specimen are plotted to show the variation of the results.

For each filler volume fraction, the tension and flexure specimens fractured in a brittle manner with the failure coinciding with the peak of the stress / strain relationships. The failure mechanism of the flexure specimens is further discussed later. The peak values were accepted as the strain (and stress) at failure for the tension and flexure behaviour.

Different modes of failure were observed for the compression specimens as the filler volume fraction was increased. For specimens with filler volume fractions from 0 to 40%, loads continued to be supported after the peak of the stress / strain relationship was reached, exhibiting a relatively ductile behaviour (Figure 5.9). For the neat resin specimens, approximately 75% of the peak stress was still supported at a 15% strain level. For the specimens with filler levels of 20%, 30% and 40%, failure occurred after the peak of the stress / strain relationship but with no significant plateau. Failure occurred through a shear plane at 45° to the direction of loading (Figure 5.4). Research by Cardoso *et al.* [11] reported that the inclusion of 25% cenospheres lowered the compressive strength of polyester matrices. It was also reported that the compression specimens failed in shear along a plane at 45° to the loading direction.

For the specimens with filler volume fractions greater than 40%, fracture occurred almost immediately after the peak of the stress / strain relationship (Figure 5.9). In these specimens the failure occurred due to a combination of shear and crushing.

Although a ductile failure behaviour may have significant advantages in some specific applications, for this investigation once the peak of the stress / strain relationship was attained the specimens were deemed to have failed from an engineering perspective. The peak values were accepted as the strain and stress at failure properties for the compression behaviour.

First order polynomials or linear trendlines were fitted to the data. The R-squared value of 0.95 for the compression and tension results generally indicates good correlation between the trendline and data exists. The 0.89 value for the flexural data is lower but attributed to the large scatter of results from the neat resin specimens. Due to the high comparable loads supported by the specimens with lower filler contents, the performance may be more susceptible to the presence of air than the more highly filled specimens that fail at considerably lower loads.

Increases in filler volume fraction led to decreases in the strain at failure values. The reduction in strain capacity was attributed to the reduced resin content of the formulations.

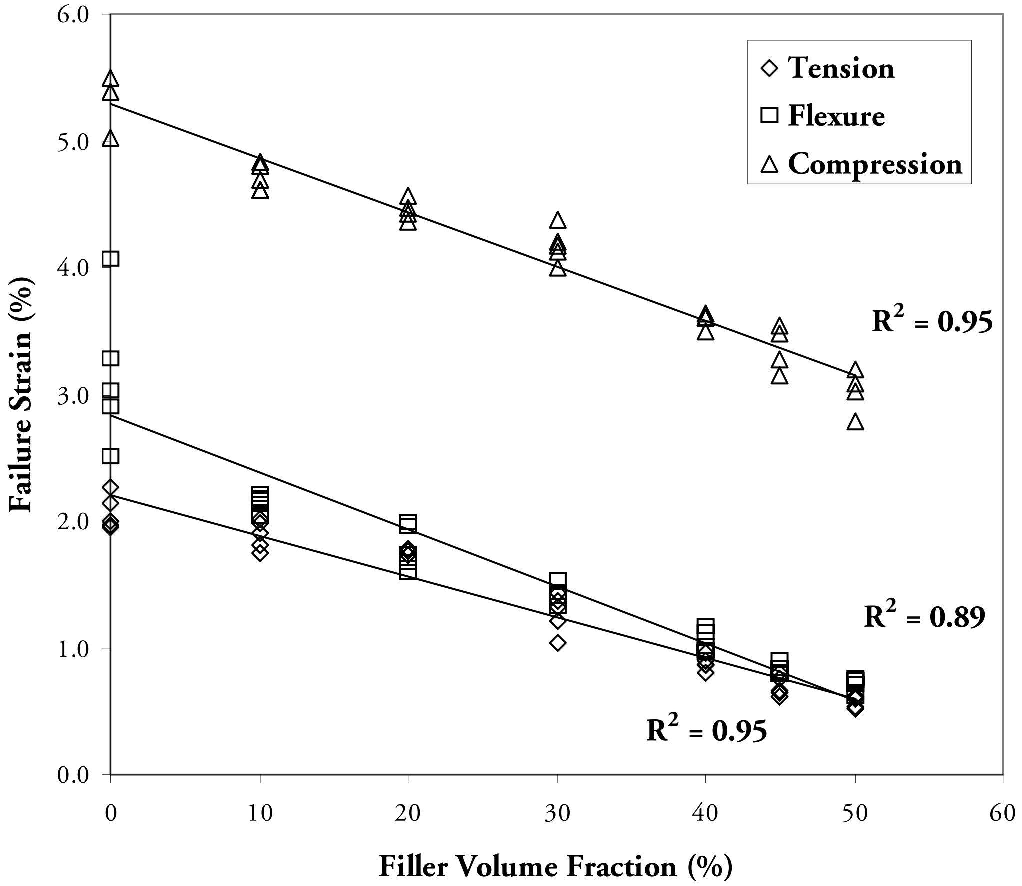


Figure 5.8 Relationship of strain at failure with filler volume fraction of Hetron 922 PAW vinyl ester / cenosphere composites in tension, compression and flexure.

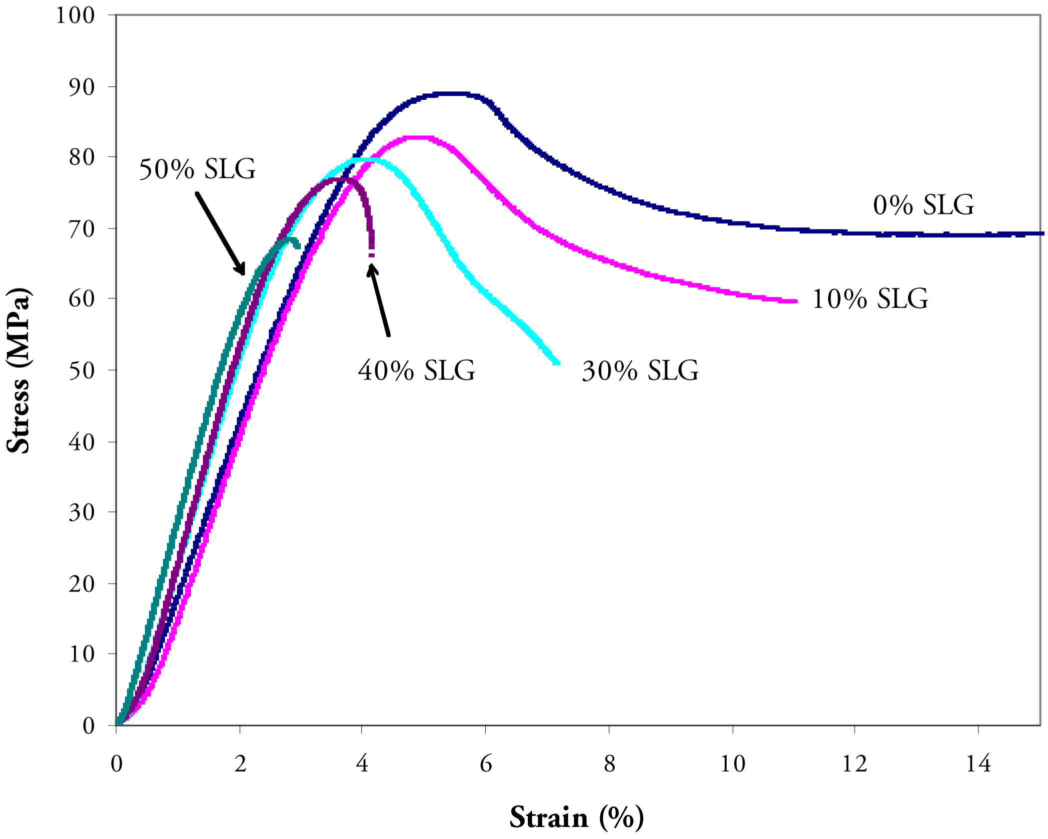


Figure 5.9 **Typical stress versus strain relationships of Hetron 922 PAW vinyl ester / cenosphere composites with varying filler volume fractions in compression.**

The compressive strain at failure values are considerably higher compared to the failure strain values of the systems in tension and flexure. The closeness of the tension and flexure results suggests that the flexure behaviour of the composite systems may be highly influenced by the tensile properties. This is particularly evident at high filler volume fractions where the results appear to converge.

A study by Ayers and Van Erp [10] using alternative VE resin matrix systems reported a convergence of flexure strain properties at higher filler levels and concluded that at high filler levels (greater than 30%), the capacity of the composite is filler dominated.

The stress values were calculated as a secondary descriptor of the strength characteristics of the vinyl ester / cenosphere composite systems. The relationship of the stress values with increasing filler volume fraction are shown in Figure 5.10.

First order polynomials or linear trendlines were fitted to the data. The R-squared value of approximately 0.97 for the tension results shows good correlation between the trendline and the data. The compression and flexure data R-squared values of 0.88 and 0.90 respectively are lower but are attributed to the scatter in results, particularly for the neat resin flexure data. The scatter in results of the neat resin flexure samples is largely attributed to air trapped in the specimens.

An increase in the filler volume fraction lowered the stress at failure values and was attributed to the reduced resin content of the composites. A similar trend was observed with the failure strain properties.

The compressive failure stress is considerably higher compared to the stress in tension. This is similar to the relationship between the strain at failure behaviour in compression and tension. The flexure stress behaviour appears quite different to the strain behaviour. For neat resin, the flexure stress values were similar to the compression values and lowered as the filler content was increased, approaching the tensile stress values. This relationship suggests that at low filler volume fractions, the flexure behaviour is highly influenced by the compression properties and as the filler content is increased the behaviour becomes more influenced by the tension properties of the composite system.

These results suggest that considerable flexibility is available to the tailor the properties of the composite to meet desired performances by varying the content of filler.

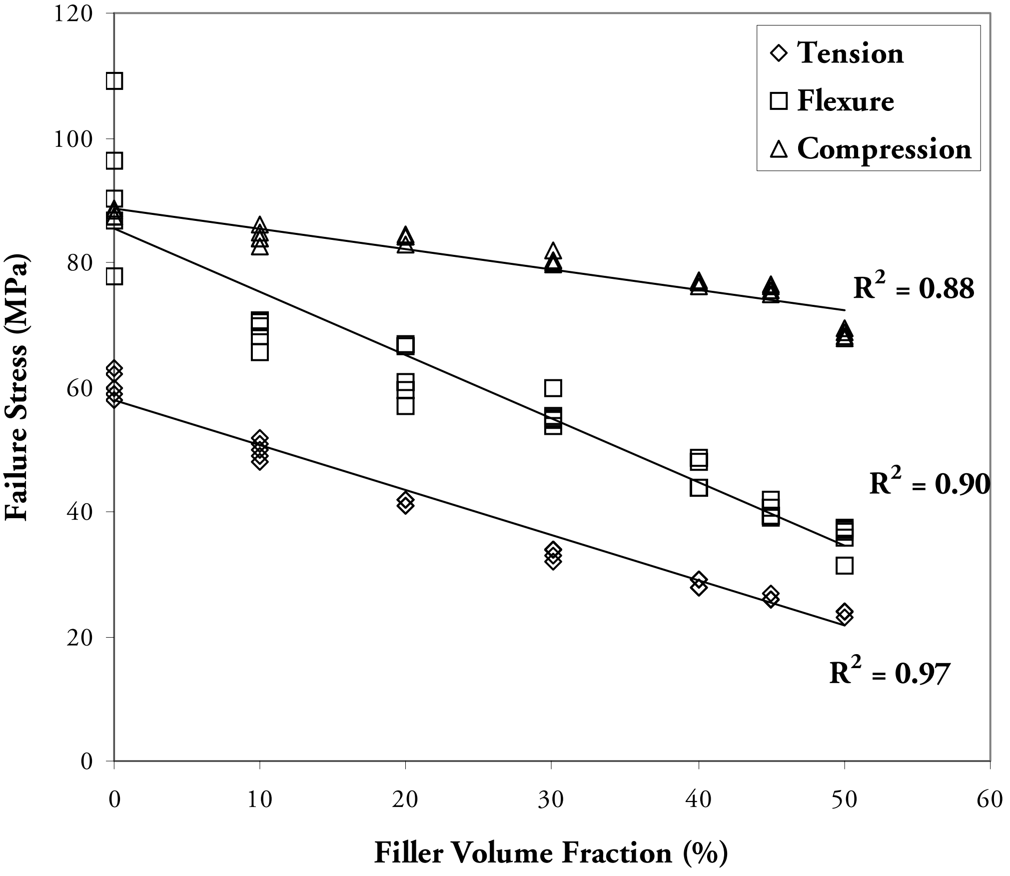


Figure 5.10 Relationship of stress at failure with filler volume fraction of Hetron 922 PAW vinyl ester / cenosphere composites in tension, compression and flexure.

The failure observed in the flexure specimens may support the suggested influences. Loading in three-point bending leads to both compression and tension forces within the specimen. Although all specimens failed in a brittle manner, the actual fracture behaviour changed as the filler content was increased.

The neat resin specimens failed in a brittle manner with a segment of the material from the compression face that straddled the main cleavage line breaking away, shown in Figure 5.11. As the filler volume fraction was increased, the release of energy at failure appeared of lower magnitude with the segment breaking from the compression face reducing in size (Figure 5.12). At filler volume fractions of 30% and higher, no segment broke away from the compression face and the specimen failed through a single cleavage line (Figure 5.13). Further investigations are required to examine the failure mechanisms of vinyl ester / cenosphere composite systems.

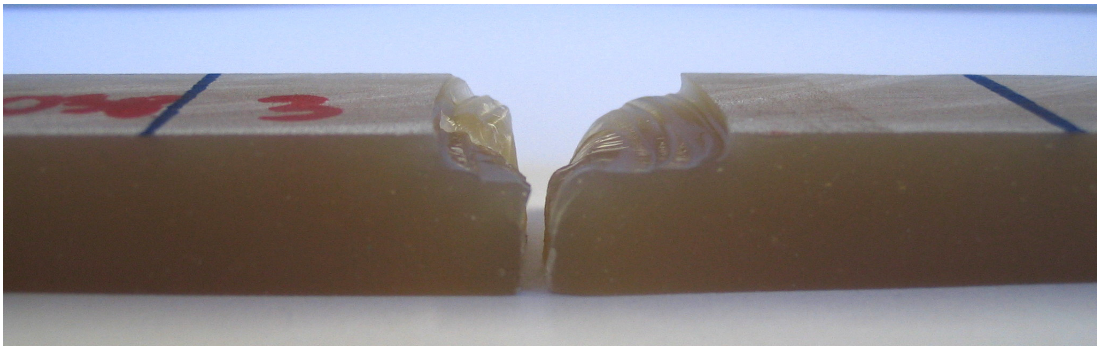


Figure 5.11 A neat resin flexure specimen showing the break away segment from the compression face over the main cleavage line.

Figure 5.12 A flexure specimen with a 10% filler content showing the reduced size of the break away segment from the compression face.

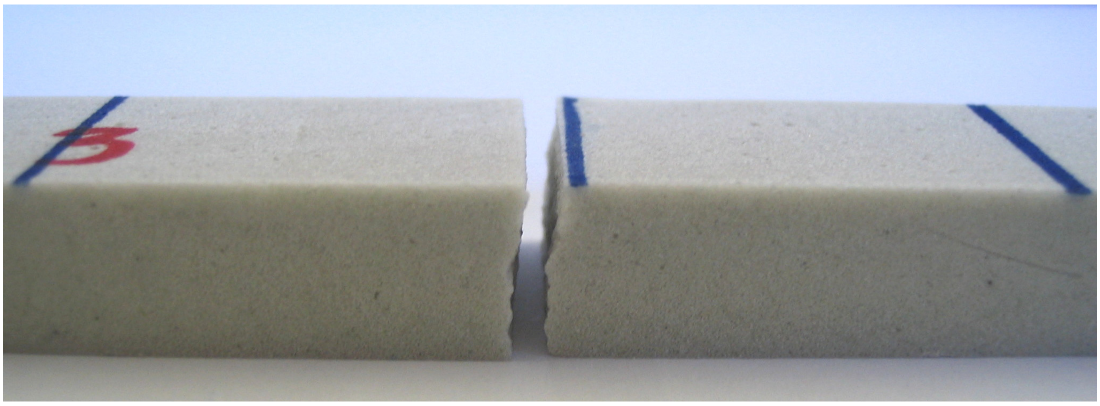


Figure 5.13 A flexure specimen with a 40% filler content showing the single cleavage line of failure.

5.3.3. STIFFNESS CHARACTERISTICS

The modulus properties were used to examine the stiffness characteristics of vinyl ester / cenosphere composite systems. The relationships of the modulus in tension, compression and flexure with increasing filler volume fraction are shown in Figure 5.14. The results of each individual test specimen are plotted to show the variation of the results.

First order polynomials or linear trendlines were fitted to the data. The R-squared values for the tensile behaviour of 0.96 and flexural behaviour of 0.97 show a good correlation between the trendlines and the data. The 0.80 value for the compression data is lower however smaller sample sizes were used leading to any outlying values significantly influencing the R-squared value. The presence of air in the neat resin samples does not appear to have as significant an influence on the stiffness behaviour as it does on strength.

An increase in the filler volume fraction increased the modulus values and improved the stiffness of the composites. This is due to the reinforcing effect of the more rigid filler particles increasing the stiffness of the composite as their volume in the matrix increases. The filler particles restrict the deformation of the matrix thus stiffening the composite.

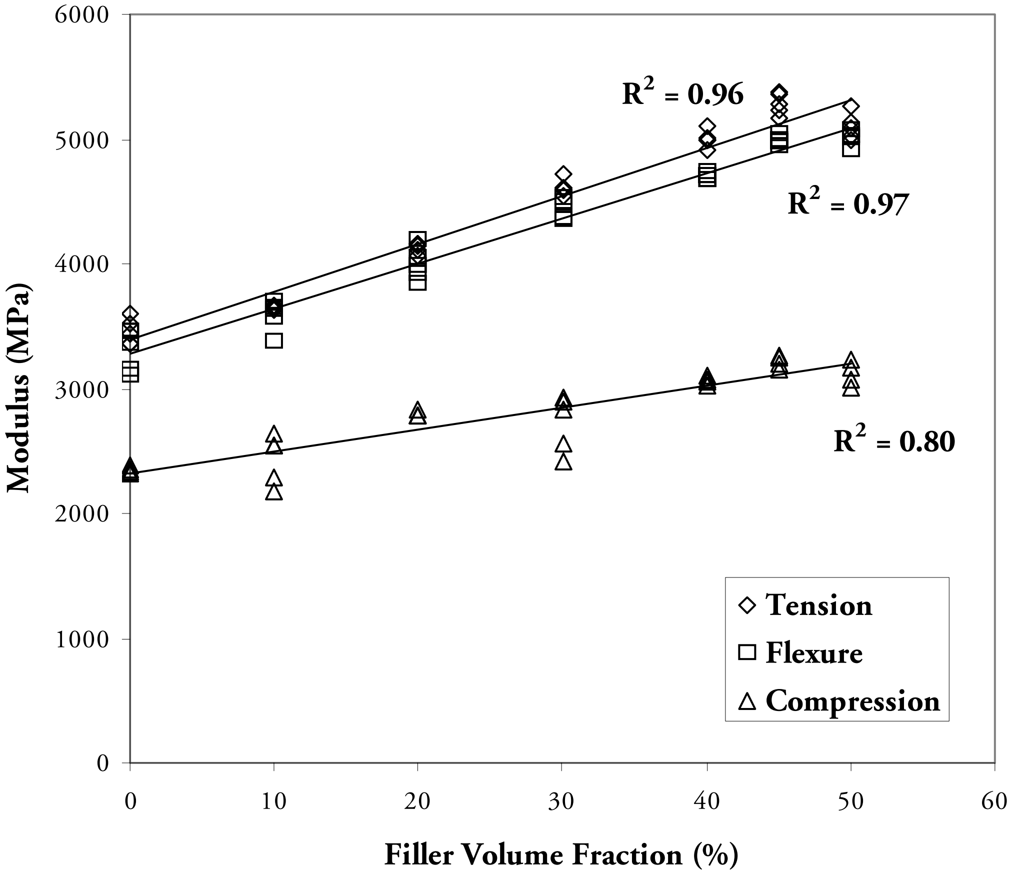


Figure 5.14 Relationship of modulus with filler volume fraction of Hetron 922 PAW vinyl ester / cenosphere composites in tension, compression and flexure.

Upon closer observation of Figure 5.14, an increase in the filler volume fraction from 45% to 50% appears to slightly lower the stiffness particularly in tension and flexure. This suggests that a filler content of 45% may be an optimum volume fraction with increases above this level actually lowering the stiffness properties.

The modulus relationships in flexure and tension with increasing filler volume fraction are quite similar suggesting the flexure stiffness behaviour is highly influenced by the tension properties. This indicates that the flexure modulus values, which are easier to acquire through a much simpler specimen fabrication and test process, may be conservatively used in place of tensile modulus properties for design and analysis.

The compression modulus values are considerably lower than the tension values indicating the comparably low stiffness of the composites when used in compression. However this may be due to influences of the testing process such as the testing platens not being exactly horizontal or the load may not have been applied axially through the machine. With the strain being determined from the cross-head displacement, these influences may have affected the accuracy of the results.

5.3.4. POISSON'S RATIO

Poisson's ratio was calculated using lateral and axial strain measurements recorded by the dual extensometer. The relationship of Poisson's ratio with increasing filler volume fraction is shown in Figure 5.15.

A first order polynomial (linear trendline) was fitted to the data. The R-squared value of 0.82 shows a lower correlation between the trendline and the data exists compared to other data. A high degree of scatter exists at most of the data points which contributes to the lower correlation.

Poisson's ratio decreased as the filler content was increased. This was attributed to the observed decreases in lateral strain values lowering the ratio with the axial strain values. The failure strain properties examined in relation to the strength characteristics were also observed to decrease with the addition of filler.

Cardoso *et al.* [11] reported reductions in Poisson's ratio after the inclusion of 25% cenosphere particles in polyester matrices.

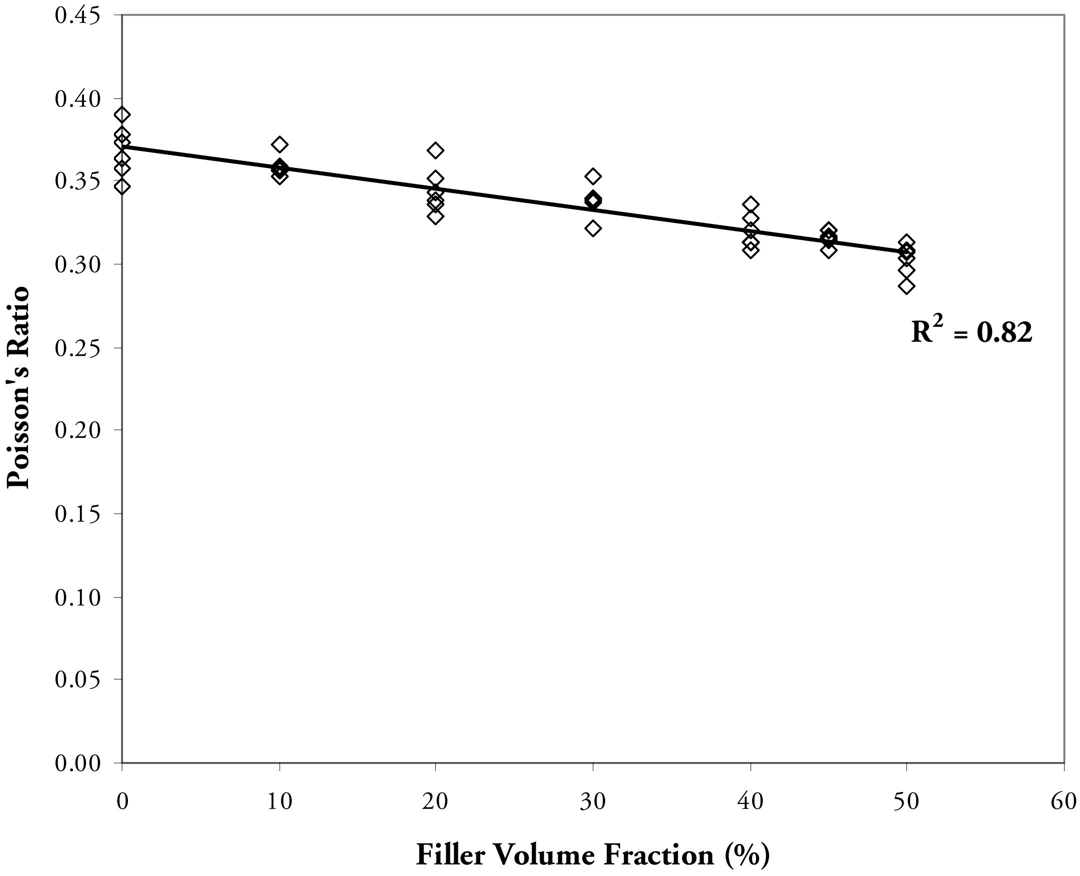


Figure 5.15 Relationship of Poisson's ratio with filler volume fraction of Hetron 922 PAW vinyl ester / cenosphere composites.

5.4. SUMMARY AND CONCLUSIONS

This Chapter has presented the experimental characterisation of the mechanical properties of selected vinyl ester / cenosphere composite systems in tension, compression and flexure. The strength characteristics were examined using the failure strain and the failure stress with the stiffness characteristics examined using the modulus values. Poisson's ratios were also determined.

Through the completion of this investigation, the following observations were made:

- The addition of filler to a vinyl ester resin matrix was found to lower the properties of strain and stress at failure and increase the modulus. Overall, for vinyl ester / cenosphere composite systems as the filler volume fraction was increased the strength characteristics were reduced and stiffness characteristics improved in tension, compression and flexure.

- A filler volume fraction of 45% appeared to produce optimum stiffness characteristics particularly in tension and flexure.

- The strain capacity of composites in compression was considerably higher than in tension with the flexure strain behaviour appearing highly influenced by the tension properties.

- The failure stress of the composites was consistently higher in compression than tension. The flexure strength at low filler levels appeared highly influenced by the compression properties of the composite and at high filler levels highly influenced by the tension properties.

- The composites are stiffer in tension than compression with the flexure stiffness behaviour appearing highly influenced by the tension properties.

- Poisson's ratio was found to decrease with increasing filler volume fraction.

Alternative methods of tensile specimen preparation were trialled as part of the investigation. The fabrication of specimens using a machining method led to improved consistency and a lower variation of the tension results.

To aid in the development of an understanding of the mechanical behaviour of the composite systems, polynomials were used to examine the data and identify behavioural relationships. The polynomials are indicative of the material behaviour. The equations to the polynomials for each material property are presented in Table 5.4. For these equations the filler volume fraction, v_f is expressed as a percentage.

Table 5.4 Relationship of the mechanical properties of vinyl ester / cenosphere composites with filler volume fraction.

Resin	Hetron 922 PAW	**Filler**	E-Spheres SLG
Behaviour	**Material Property**		**Equation**
Tension	Failure Strain (%)		$\varepsilon = -0.032\ v_f + 2.20$
	Failure Stress (MPa)		$\sigma = -0.72\ v_f + 57.78$
	Modulus of Elasticity (MPa)		$E = 38.38\ v_f + 3394$
	Poisson's Ratio		$\nu = -0.0013\ v_f + 0.37$
Compression	Failure Strain (%)		$\varepsilon = -0.043\ v_f + 5.29$
	Failure Stress (MPa)		$\sigma = -0.33\ v_f + 88.77$
	Modulus (MPa)		$E = 17.41\ v_f + 2324$
Flexure	Failure Strain (%)		$\varepsilon = -0.045\ v_f + 2.84$
	Failure Stress (MPa)		$\sigma = -1.02\ v_f + 85.54$
	Modulus (MPa)		$E = 36.07\ v_f + 3287$

Note: v_f = filler volume fraction (%)

These equations describe mean value relationships between the filler volume fraction and mechanical properties for the selected constituent materials. This investigation has been constrained to characterising the behaviour of vinyl ester / cenosphere composite systems using a single resin and a single filler type as material constituents. The parameter varied for this investigation was the filler volume fraction.

While these investigations have focussed on a single resin / filler combination the results suggest that modification of key engineering parameters with the addition of fillers tend to follow linear relationships (change of filler volume fraction). More accurate establishment of such relationships is quite important for materials design purposes.

5.5. REFERENCES

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CHAPTER 6.

THE TRANSITION BEHAVIOUR OF VINYL ESTER / CENOSPHERE COMPOSITES UNDER ELEVATED TEMPERATURES

6.1. INTRODUCTION

Thus far, this dissertation has examined the curing behaviour, processing characteristics and the mechanical properties of vinyl ester matrix systems and vinyl ester / cenosphere composites. Now it is important to understand how the properties of these materials are maintained during service. The effects of temperature are an important consideration in the design of civil structures [1]. Of particular interest to this current project is the retention of material properties under elevated temperature conditions.

As discussed earlier in Chapter 2, vinyl ester resins are amorphous polymers consisting of networks of randomly arranged polymer chains. They do not possess the ordered molecular orientation of crystalline polymers. Unlike crystalline polymers, amorphous polymers do not melt. When exposed to heat, crystalline polymers increase in temperature until they reach the melting temperature at which point they change completely from solid to liquid state. At the melting temperature, increases in heat do not result in a temperature increase until all material is converted from solid to liquid state.

Amorphous polymers do not melt but exhibit a softening transition where they pass from a glassy to a rubbery state. The temperature at which this transition occurs is known as the glass transition temperature or T_g. When cooled below the T_g the polymer is hard and rigid but heated above the T_g it becomes soft and flexible. Unlike a crystalline material melt transition, the glass transition does not involve the breaking of intermolecular bonds. It does however involve a change in molecular mobility thereby creating a change in material heat capacity. This change in heat capacity can be monitored using the DSC techniques previously discussed in Chapter 3. Observation of DSC plots indicates that the glass transition occurs over a temperature range rather than at a single distinct temperature.

On a mechanical level the glass transition is characterised by a loss of material stiffness which is exhibited by both the elastic modulus and shear modulus. Reported experimental data indicates that the loss of elastic modulus across the glass transition can be in the order of 95% [2,3]. Such degradation in properties may have serious ramifications on the overall performance of a structure. Understanding the behaviour of this transition is imperative in assessing the suitability of a polymer to a given application.

This Chapter presents an experimental investigation of the behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites under elevated temperatures. The aim of this work is to develop an improved understanding of glass transitions in these materials and related effects on mechanical properties. The study uses dynamic mechanical analysis to investigate the influence of several key constituent and curing parameters on resulting mechanical behaviour of the neat resins and composites.

6.1.1. GLASS TRANSITIONS IN VINYL ESTER RESINS

As discussed previously in Chapter 2, the crosslink density of a network is the primary influence on the glass transition temperature of a vinyl ester resin. The crosslink density can be increased through the use of oligomers of lower molecular weight [4,5,6,7] or different backbone chemistry (eg: novolac) [2,8].

An increase of the reactive monomer (styrene) has been shown to reduce the crosslink density and consequently lower the T_g of systems with lower molecular weight oligomers, though the effect on high molecular weight systems is only minor[5,6].

Cook *et al.* [3] reported that the T_g strongly depends on the degree of cure of a vinyl ester resin, with a greater degree of cure (conversion) leading to a higher T_g. As the degree of conversion is characterised by the amount of crosslink formation, it follows that higher degree of conversion will translate to an increased crosslink density. One of the functions of an elevated temperature post-cure is to progress the cure such that a high crosslink density is obtained and hence a high T_g.

Investigations by Ziaee and Palmese [9] examined the influence of curing cycles on the mechanical properties of vinyl ester resins. It was reported that post curing of materials performed below the “full-cure” T_g resulted in glass transition temperatures below the ultimate full-cure T_g. However post-curing performed above the ultimate T_g temperature resulted in transition temperatures approaching the ultimate T_g, regardless of the initial isothermal cure temperature used.

Due to the relationship between the glass transition temperature and the degree of conversion of the network, comparing of the T_g achieved after an ambient cure and after an elevated temperature post-cure will provide an indication of the initial degree of cure achieved in a network. Comparing these T_g values will provide details regarding the development of properties of the network.

6.1.2. CHARACTERISATION OF GLASS TRANSITIONS

Glass transitions can be characterised in a number of ways. As discussed earlier in Chapter 3, differential scanning calorimetry is one common method of determining a glass transition temperature. With this technique the glass transition is determined by a change in material heat capacity. As the material passes from a rigid to a rubbery state there is a change in molecular mobility which displays itself in a corresponding change in heat capacity. As can be seen from the DSC results of Chapter 3, the change in heat capacity occurs over a temperature range rather than at a single temperature, thus creating some debate over what actually constitutes the glass transition temperature (extrapolated onset temperature, inflection point temperature). Irrespective of the value used, DSC determination of T_g is somewhat limited in its direct engineering application as it does not actually quantify mechanical changes in the material.

An alternative to DSC is thermomechanical analysis (TMA). In TMA the T_g of a material is generally assessed in terms of material softening and the penetration of a probe into the test sample. The T_g can also be determined as the temperature at which the sample exhibits a significant change in thermal expansion or from the derivative TMA curve. These methods provide a measure of the glass transition temperature but not the associated changes in engineering properties (E or G).

Dynamic mechanical analysis (DMA) offers several advantages over DSC or TMA for the engineer seeking to evaluate glass transitions of polymers and composites. In DMA a sample is mechanically deformed at alternative rates and the response of the sample is measured as a function of temperature or time [10]. Samples can be tested in either tension, compression or bending modes. DMA measures the applied load and corresponding displacement of the sample allowing for direct determination of mechanical properties. As polymer materials are non-Newtonian, viscoelastic materials the time response of the material to applied loads is also important. DMA can assess these behaviours measuring both the input signal of the instrument and the time response of the specimen. Time lag between input and response can be assessed as a function of temperature.

Dynamic mechanical analysis (DMA) has been reported to offer advantages in the measurement of glass transition temperatures in highly crosslinked networks where there are only small measurable changes in heat flow in the transition region and DSC is not as sensitive as DMA in detecting these changes [4,7].

These alternative methods use different responses of the materials to characterise glass transitions which can lead to variability in the results. Furthermore these techniques are directed towards measuring a singular value of the glass transition temperature to represent the temperature performance of the networks. An advantage of DMA from a structural engineering perspective is that it allows for direct monitoring of mechanical property variations as a function of temperature. This provides the engineer with information relating to the actual changes in mechanical performance due to an elevating temperature.

6.1.3. INTERPRETATION OF DMA DATA

A number of materials, including polymers, flow when subjected to stress or strain at elevated temperatures. This flow is accompanied by the dissipation of energy due to an internal loss mechanism [11]. Such materials are known as viscoelastic materials, exhibiting both elastic and viscous properties.

Under dynamic loading linear viscoelastic properties can be described by a modulus (*E*) which is a function of the frequency of loading (ω) with a linear relationship existing between stress and strain [11]. For periodic loading, the modulus consists of real (*E'*) and imaginary (*E"*) components, and the stress and strain will generally be out of phase due to the effects of delayed elasticity and viscous flow in the material. The phase angle of strain behind stress is δ and related to the moduli *E'* and *E"* by the relationship:

$$\tan\delta = \frac{E''}{E'} \qquad \textbf{(6.1)}$$

The *E'* component which is in phase with the strain, is often referred to as the **storage modulus** and is associated with the energy stored in the specimen due to the applied strain. The *E"* component which is out of phase with the strain, is often referred to as the **loss modulus** and is associated with the dissipation of energy. **Tan** δ is conventionally employed as a measure of internal friction.

DMA provides three alternative values that are often interpreted as the glass transition temperature [10], namely:

- onset (extrapolated) of loss of storage modulus which occurs at the lowest temperature and relates to mechanical changes in the material;
- loss modulus peak which occurs at a middle temperature and is more closely related to the molecular changes attributed to the glass transition in plastics; and
- tan δ peak which occurs at the highest temperature and is a good measure of the midpoint between the glassy and rubbery states.

The temperature at the peak of the tan δ curve appears to be the most widely applied measure of glass transition temperature [2,4,5,6,12] in polymer research. The value of this particular T_g interpretation is questionable from a civil engineering perspective, as will be discussed.

Figure 6.1 shows a typical DMA plot for a vinyl ester polymer (Hetron 922 PAW Butanox M-60 @ 1.0%). The storage modulus, loss modulus and tan δ are all shown plotted against temperature. The glass transition temperatures for each of the three interpretations above are shown. An additional value at the inflection point of the storage modulus is also shown. A list of these values is shown in Table 6.1. From these figures it can be seen that each interpretation yields a significantly different T_g and it can thus be concluded that it is of paramount importance that T_g values determined by DMA should be accompanied by a qualifying statement giving the particular method of determination used.

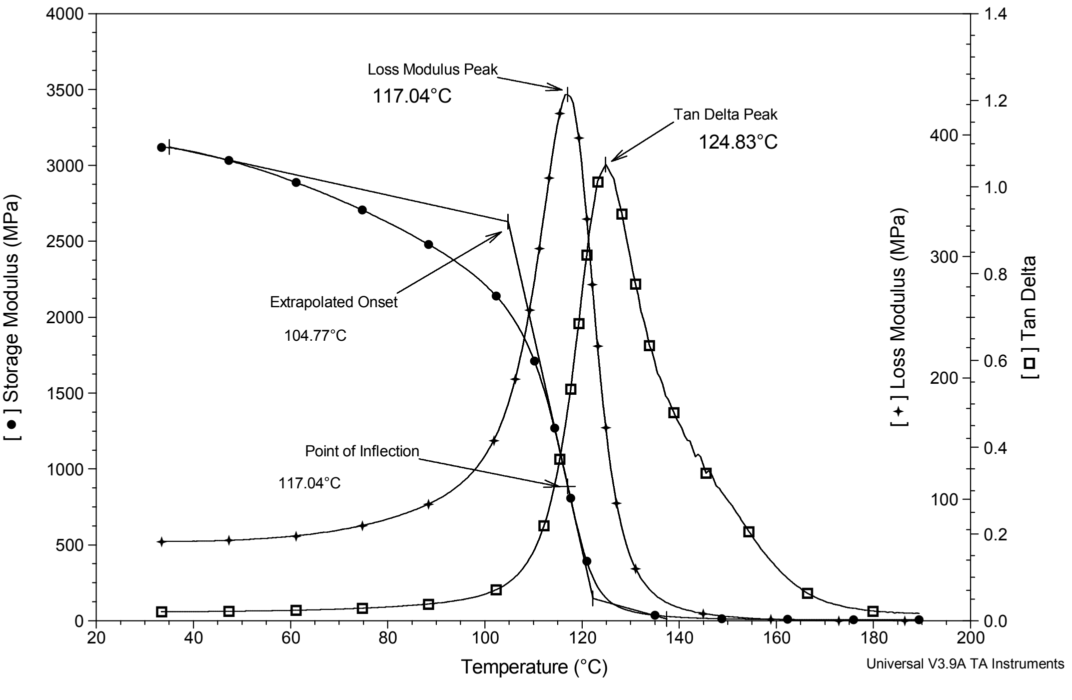

Figure 6.1 DMA results of a vinyl ester matrix showing alternative interpretations of the glass transition temperature.

As noted previously, from an engineering perspective the key issue with a material going through its glass transition is its corresponding loss of mechanical capacity, specifically the loss in Modulus of Elasticity. Table 6.1 also shows the storage modulus of the material at the T_g given by each interpretation and the relative magnitude of modulus loss between ambient temperature and each T_g. From these figures it can be observed that by the time a material reaches the T_g given by any of the interpretations, there has already been a significant drop in material stiffness. Thus the provision of an ambient temperature Modulus of Elasticity and T_g for a material would appear to be an inadequate representation of material behaviour for civil engineering applications.

Table 6.1 Variation of glass transition temperature using alternative interpretations with the associated loss in storage modulus.

Resin	Hetron 922 PAW	**Initiator**		Butanox M-60 @ 1.0%	
	Extrapolated Onset (Storage Modulus)	**Point of Inflection (Storage Modulus)**	**Peak of Loss Modulus**	**Peak of Tan δ**	**DSC Point of Inflection**
Glass Transition Temperature (°C)	105	117	117	125	94
Storage Modulus at T_g (MPa)	2039	885	885	151	2369
Reduction in Storage Modulus from Ambient Temp. (3116MPa) to T_g	35%	72%	72%	95%	24%

What is more important from an engineering perspective is the loss of mechanical performance over typical civil engineering services ranges. Figure 6.2 shows a more detailed plot of the storage modulus loss of the same material over the 35°C to 120°C temperature range. The rate of modulus drop as a function of temperature is also shown. As can be observed from this plot, the material displays a relatively uniform rate of storage modulus loss up to around 90°C. Above this temperature there is a rapid increase in the rate of modulus loss through the glass transition of the material. This behaviour is typical of most thermoset polymers.

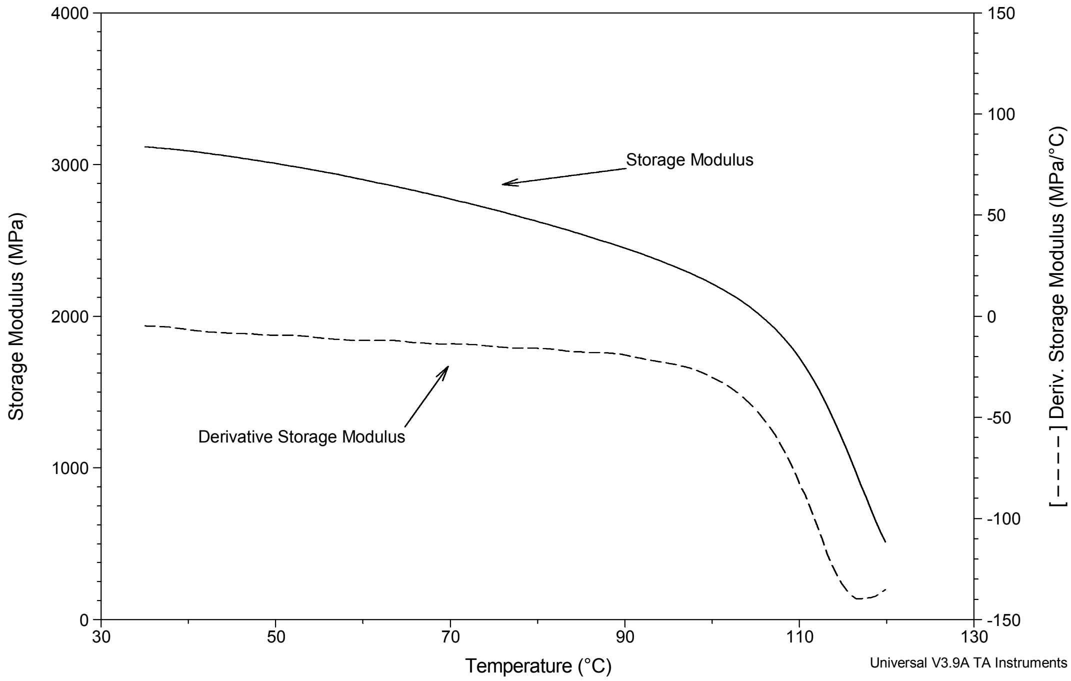

Figure 6.2 Storage modulus loss of a vinyl ester matrix between 35°C and 120°C.

As it would normally be desirable to maintain a material at a temperature below its glass transition for structural applications, understanding of the pre-transition modulus drop would appear relatively important from an engineering perspective. It would also appear equally important to understand the way in which modulus losses are accelerated as the material enters the glass transition. Given that the glass transition occurs over a relatively narrow temperature band and that the net modulus loss can be over 90%, the behavioural changes of the material through this temperature range are of great significance.

For this study, the primary aim of performing dynamical mechanical analysis is to develop a better understanding of how the vinyl ester matrices and their corresponding cenosphere composites behave under conditions of elevated temperature. Therefore, while T_g values will be calculated on the grounds of their current widespread usage, the analysis will focus on the rate of modulus loss in the pre-transition region and the rate of loss through the glass transition itself. The pre-transition changes are considered of major importance as the temperature range of this region lies within that which could be expected in typical civil engineering structures. The influence of constituent and curing changes on behaviour in this temperature range may thus play a critical role in the development of successful structures.

6.2. EXPERIMENTAL INVESTIGATION

This section outlines the materials selected for use in this study and the experimental techniques and procedures used to examine the transition behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites.

6.2.1. MATERIALS

The experimental investigation utilised a number of different materials that were detailed in Section 3.2.1 and listed in Table 3.2. The selected materials for use in this study are shown in Table 6.2.

Table 6.2 Materials used for the investigation of transition behaviour.

Product Number	Product Name	Description
1	Hetron 922 PAW	Standard grade vinyl ester resin
2	Hetron 914	Low styrene content vinyl ester resin
3	Accelerator NL-51P	Cobalt octoate medium-reactivity accelerator
4	Butanox M-60	General purpose medium-reactivity MEKP
5	MEKP-SR	Slow reactivity MEKP
6	CHP 90	Cumyl hydroperoxide, 90% solution
7	Trigonox 239	Cumyl hydroperoxide, 45% solution in solvent mixture, with promoter
8	E-Spheres SLG	20 - 300μm cenosphere filler
9	Styrene	Styrene monomer

6.2.2. EXPERIMENTAL TECHNIQUES

6.2.2.1. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis of the material combinations was performed on a TA Instruments Q800 DMA in dual cantilever mode (see Figure 6.3). Samples were prepared in ambient conditions and not exposed to an elevated temperature post-cure and were machined to dimensions of:

Length = 60mm,

Width = 10mm, and

Thickness = 4mm.

Each sample was subjected to an oscillating displacement of ±10μm at a frequency of 1Hz. The dynamic analysis was performed from 25°C to 200°C with a heating ramp of 10°C/min. The cell and specimen were allowed to cool between each run. Two runs were performed on each specimen to assess behaviour before and after an elevated temperature post-cure. Data was analysed using the Universal Analysis software provided with the instrument. Generally only single specimens were tested for each material combination.

The glass transition temperature of each sample was calculated by three different methods as follows:

- The inflection point of the storage modulus.
- The peak of the loss modulus.
- The peak of the tan δ.

As discussed earlier, the T_g characterises the material transition by a single temperature which is not directly linked to a specific mechanical behaviour. From an engineering perspective the key issue is not the value of the T_g but the way in which the mechanical characteristics of the material change as it approaches and goes through the glass transition. To gain better insight into these changes, this current study also investigated changes in the storage modulus both prior to and through the glass transition region.

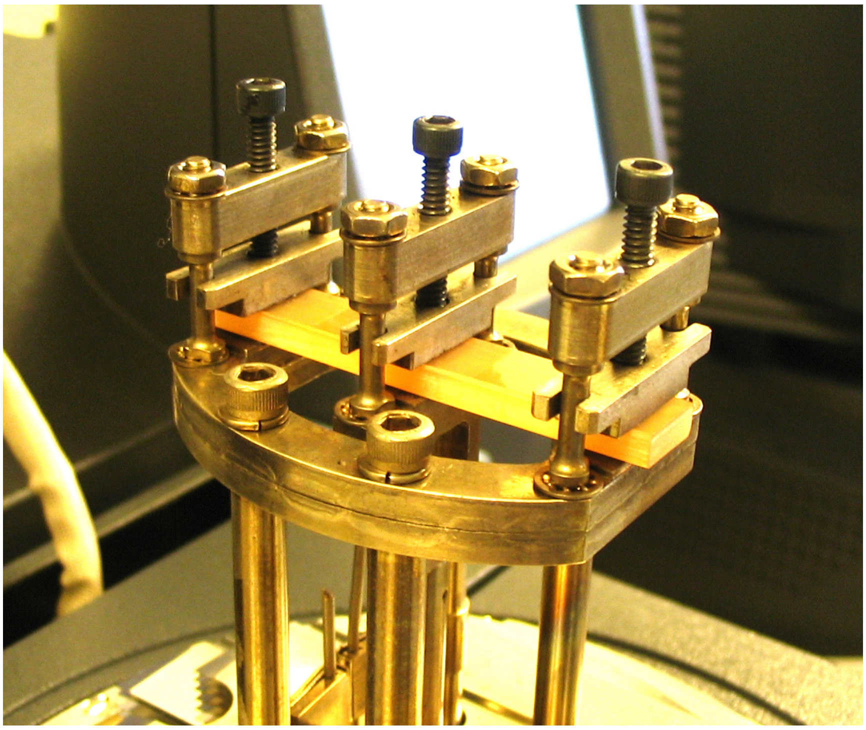

Figure 6.3 Test specimen positioned in the DMA dual cantilever clamp arrangement.

The changes in mechanical performance through the glass transition were examined using two parameters:

- The loss of storage modulus between 40°C and the inflection point T_g
- The rate of loss for the storage modulus at the inflection point T_g

The lower temperature of 40°C may be considered high however the behaviour at this temperature appeared quite stable and was selected to exclude some inconsistencies present in the initial lower temperature stages of some DMA scans.

A temperature range over 40°C to 80°C was adopted to examine the mechanical behaviour prior to the transition. These limits are reasonably indicative of the elevated temperature environments which may be seen in civil engineering structures with the investigation of modulus changes over this range providing an indication of behavioural changes which may be exhibited in such structures [1]. The factors considered in this current study were the rate of modulus loss over the designated temperature range and the corresponding absolute losses between the lower and upper temperatures.

All specimens were prepared from the same batches of resin and the transition behaviour determined from individual specimens to examine influences of the selected parameters. The behavioural relationships were established using these results. Additional investigations may address the variability of these established relationships both within and between batches to further consolidate the understanding of this behaviour.

6.3. RESULTS AND DISCUSSION

This section presents the results of the experimental investigation of the transition behaviour of vinyl ester / cenosphere composites at elevated temperatures. The use of the glass transition temperature as an indicator of temperature performance is examined and followed by the transition behaviour of unfilled and filled vinyl ester resins. The temperature performance of ambient cured systems is also considered. Where appropriate, other research material is referred to during the discussion for the purpose of comparison.

6.3.1. USING THE GLASS TRANSITION TEMPERATURE TO GAUGE ELEVATED TEMPERATURE PERFORMANCE

The selected interpretation of the T_g to describe the elevated temperature performance of composites may have significant consequences. This section examines the associated mechanical behaviour of materials at alternative glass transition temperatures. Results from investigations of the influences of initiator concentration on the behaviour of vinyl ester matrix systems are used.

The glass transition temperature of Hetron 922 PAW cured with varying initiator concentrations determined using both DSC and DMA techniques is shown in Table 6.3. The DSC values (extrapolated onset, point of inflection) were determined as part of the cure behaviour investigations presented in Chapter 3. The DMA values (point of inflection, loss modulus peak, tan δ peak) were determined from a second scan of specimens after exposure to an elevated temperature post-cure. The complete storage modulus transition curves and the loss modulus and tan δ relationships for the second scans are presented in Appendix E.

Table 6.3 Alternative interpretations of the glass transition temperature.

Initiator Addition Level (%)	Glass Transition Temperature (°C)				
	DSC		DMA		
	Extrapolated Onset	Point of Inflection	Point of Inflection Storage Modulus	Peak Loss Modulus	Peak Tan δ
1.0	89	94	117	117	125
1.5	94	99	115	115	123
2.0	96	100	111	111	119
2.5	91	95	109	109	117
3.0	87	92	102	103	113
4.0	84	90	99	99	107
5.0	82	86	92	92	101

Each interpretation of the glass transition temperature produces a markedly different value leading to a wide variation of results. This variation in T_g values using the alternative interpretations was highlighted in Section 6.1.3.

The loss of mechanical properties, represented by the change in storage modulus, associated with heating to the glass transition temperature is shown in Table 6.4. The loss of storage modulus was calculated between 40°C and the applicable glass transition temperature.

Table 6.4 Corresponding loss of storage modulus at the glass transition temperature.

Initiator Addition Level (%)	% Loss of Storage Modulus (E')				
	DSC		DMA		
	Extrapolated Onset	Point of Inflection	Point of Inflection Storage Modulus	Peak Loss Modulus	Peak Tan δ
1.0	20	23	71	71	95
1.5	24	27	70	70	95
2.0	27	32	67	67	95
2.5	30	34	67	70	93
3.0	28	36	70	71	96
4.0	34	41	62	62	89
5.0	34	43	64	65	90

The DSC onset temperature T_g values were the lowest with the associated loss in storage modulus relatively low. The loss in storage modulus associated with the DMA T_g values was much higher, particularly for the tan δ peak values with losses in the order of 90%.

The relatively high losses in storage modulus associated with heating to the T_g supports the suggestion that the glass transition temperature may not be the most appropriate indicator of elevated temperature performance from an engineering perspective. Monitoring of the actual changes in mechanical behaviour of the material when exposed to elevated temperatures, which is used in the following sections appears a more suitable measure of the temperature performance.

In addition it is desirable to minimise the viscoelastic behaviour of the materials thus curtailing influences of creep and relaxation. This suggests a focus on the elastic characteristics of the materials and monitoring the elastic (storage) modulus properties.

The following investigations focus on the mechanical behaviour of the materials when exposed to elevated temperatures by analysing the storage modulus properties. Both the pre-transition and glass transition behaviour are analysed by examining the loss in storage modulus and the rate of the loss of storage modulus. The interpretation of the glass transition temperature for this investigation is the point of inflection of the storage modulus.

6.3.2. TRANSITION BEHAVIOUR OF UNFILLED VINYL ESTERS

This section examines the transition behaviour of unfilled vinyl ester matrix systems. The selected parameters for investigation were also used to examine the cure behaviour of vinyl ester matrix systems presented in Chapter 3. The assessment of transition behaviour of vinyl ester matrix systems includes the effects of:

- The concentration of initiator.
- The type of peroxide initiator.
- The promotion regime.
- The molecular weight of the oligomer.
- The reactive monomer concentration.

6.3.2.1. Influence of Initiator Concentration

Cure investigations discussed earlier in Chapter 3 have shown that the cure behaviour of vinyl ester resins can be modified by altering the initiator addition level. Test data indicated a lower limit for initiator addition of around 1.5%. Above this level the cure behaviour appears relatively consistent. However the use of addition rates above 2.5% resulted in decreases to the glass transition temperature.

This investigation sought to understand the impact of these variations in cure behaviour, specifically the influence of initiator concentration on the transition behaviour of vinyl ester resins.

Specimens of Hetron 922 PAW cured with increasing initiator levels of Butanox M-60 from 1.0% to 5.0% were prepared. While the earlier cure characterisation work also investigated addition rates of 0, 0.25 and 0.5%, these were discounted for the current study due to their alternative cure behaviour exhibited in Chapter 3. Key transition data from post-cured samples of each addition rate are summarised in Table 6.5. The complete storage modulus transition curves for the post-cured samples are presented in Appendix E. Transition curves for the post-curing cycle are also given in Appendix E.

Table 6.5 Key transition data of Hetron 922 PAW vinyl ester with varying initiator levels.

Resin	Hetron 922 PAW				**Initiator**	Butanox M-60		
Initiator Addition Level (%)	**Pre-Transition Behaviour**				**Glass Transition Behaviour**			
	E' 40°C (MPa)	**E' 80°C (MPa)**	**E' Loss (%)**	**Rate of E' Loss (MPa/°C)**	**T_g (°C)**	**E' T_g (MPa)**	**E' Loss (%)**	**Peak Rate of Loss (MPa/°C)**
1.0	3090	2624	15	11.6	117	885	71	140
1.5	3050	2586	15	11.7	115	926	70	151
2.0	3050	2577	16	11.9	111	1017	67	151
2.5	2835	2398	15	10.9	109	932	67	129
3.0	3203	2481	23	17.9	102	959	70	128
4.0	2594	2135	18	11.3	99	975	62	117
5.0	2992	2184	27	18.8	92	1082	64	122

As can be observed from the data in Table 6.5, the pre-transition behaviour appears stable up to an initiator addition rate of around 2.5%, with consistent initial storage modulus values at 40°C and a relatively uniform loss in storage modulus of 15 to 16% when the sample is heated to 80°C. This similarity is further highlighted in the average rate of loss over the 40 to 80°C temperature range.

Above a 2.5% initiator concentration, storage modulus losses were significantly greater than the 15% seen at the lower initiator addition rates (Figure 6.4). While the data does display some significant scatter, the overall trend is still clear enough to question the use of higher addition rates.

Increases in the initiator concentration also led to significant decreases in the glass transition temperature as determined from the inflection point of the storage modulus curve (Figure 6.5). This drop is evident across the range of addition levels studied and progresses in a relatively linear relationship with increasing initiator addition rates.

A similar trend was observed during the cure investigations (Chapter 3) and is attributed to an increasing content of non-reactive material (eg: phlegmatiser) within the cured network. This material decreases the crosslink density of the network, thereby degrading the elevated temperature properties.

In an apparent contradiction to earlier results, the loss in storage modulus associated with reaching the glass transition temperature actually decreased with increasing initiator concentration (Table 6.5). The magnitude of the storage modulus at the T_g also increased with increasing initiator levels. However, while this may appear to indicate a more desirable transition behaviour, such a conclusion would be erroneous. The reduced modulus loss is only due to the lower temperature range of the glass transition associated with higher initiator concentrations. Consideration of the storage modulus at a given service temperature (eg: 100°C) shows that the loss of modulus at that temperature still increases with increasing initiator content.

Thus it can be reasonably concluded that the addition of higher initiator levels to a resin system will have a detrimental effect on mechanical performance in terms of both pre-transition behaviour, as well as the temperature range over which the glass transition occurs.

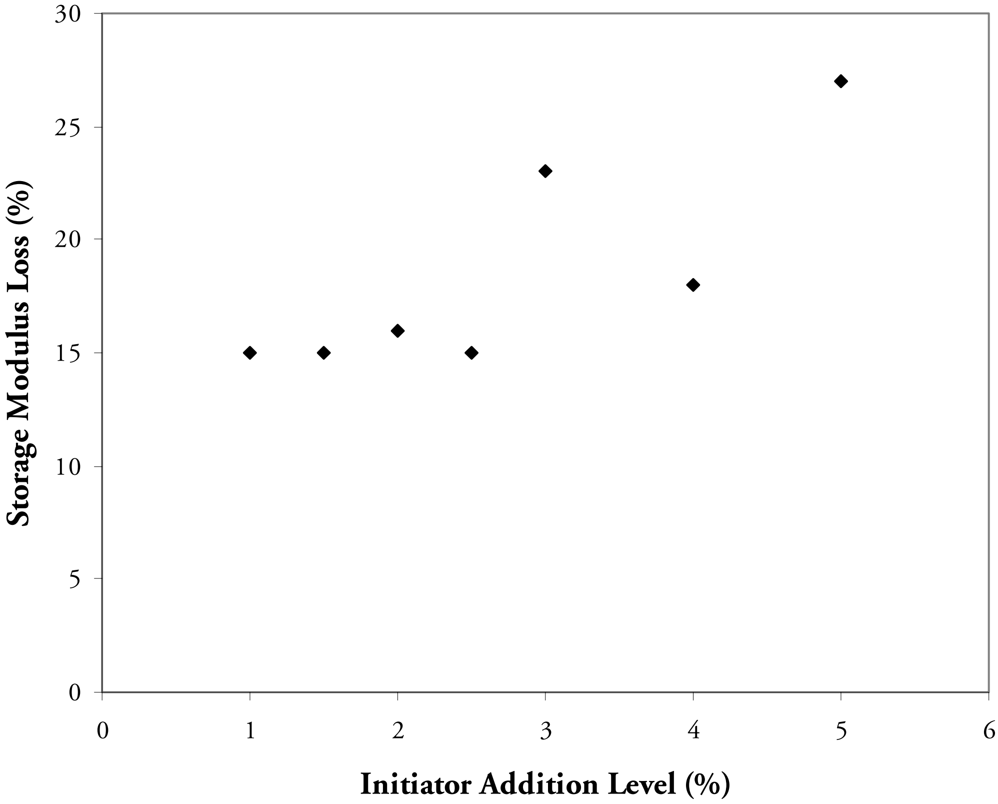

Figure 6.4 **Relationship of the pre-transition loss of storage modulus between 40°C and 80°C of Hetron 922 PAW vinyl ester with varying initiator concentration.**

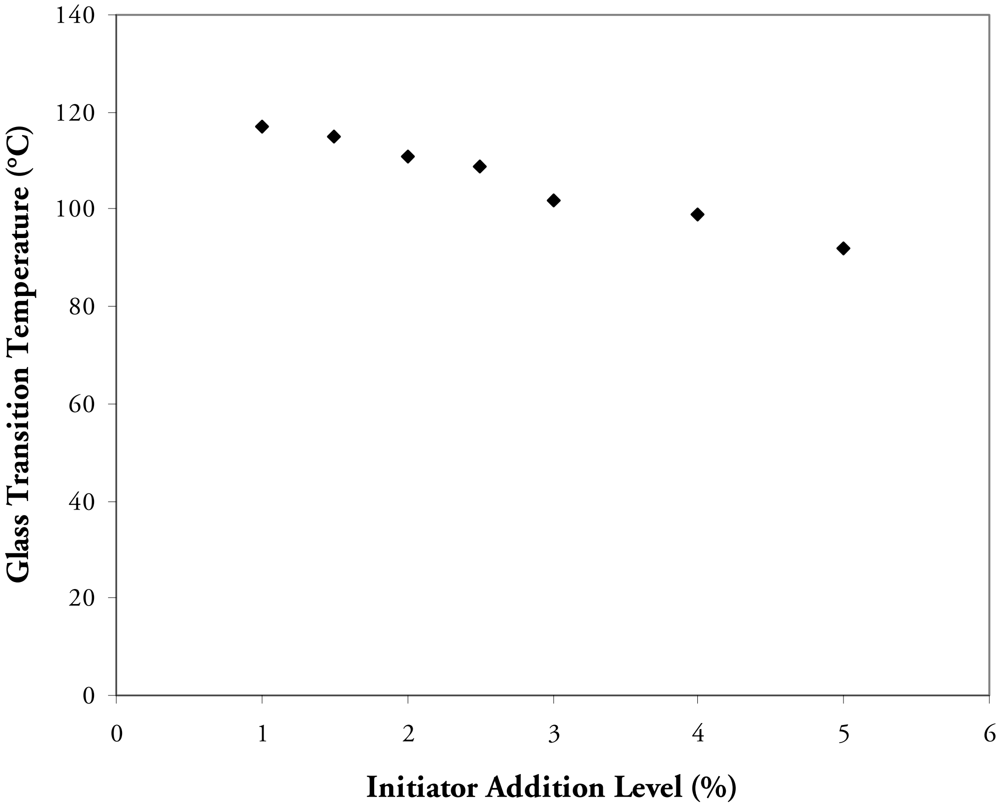

Figure 6.5 **Relationship of the glass transition temperature of Hetron 922 PAW with varying initiator concentration.**

6.3.2.2. Influence of Peroxide Initiator Type

Cure investigations discussed in Chapter 3 have shown that different initiator types and solutions produce different cure behaviours. The results indicated that MEKP based initiator solutions (Butanox M-60, MEKP-SR) produced a more rapid cure compared to CHP initiators (Trigonox 239, CHP 90) with a relatively consistent cure behaviour.

This investigation was undertaken to examine the influence of the cure achieved using different peroxide initiator types on the transition behaviour of vinyl ester resins.

Specimens of Hetron 922 PAW cured with alternative initiator types at a 2% concentration were prepared. Key transition data from post-cured samples of each initiator are summarised in Table 6.6. The complete storage modulus transition curves for the post-cured samples and for the post-curing cycle are presented in Appendix E.

Table 6.6 Key transition data of Hetron 922 PAW vinyl ester with varying initiator types.

Resin	Hetron 922 PAW			**Initiator Addition Level**	2%			
	Pre-Transition Behaviour				**Glass Transition Behaviour**			
Initiator	**E' 40°C (MPa)**	**E' 80°C (MPa)**	**E' Loss (%)**	**Rate of E' Loss (MPa/°C)**	**T_g (°C)**	**E' T_g (MPa)**	**E' Loss (%)**	**Peak Rate of E' Loss (MPa/°C)**
Butanox M-60	3050	2577	16	11.9	111	1017	67	151
MEKP-SR	3108	2579	17	13.3	109	1034	67	139
Trigonox 239	2858	2379	17	11.6	111	966	66	129
CHP 90	2752	2343	15	10.2	113	968	65	131

As observed from the data in Table 6.6, the different initiator types produced different pre-transition behaviours. The pre-transition behaviour of the samples initiated with MEKP solutions were similar with consistent storage modulus values at 40°C and 80°C.

The CHP initiated samples also exhibited similar storage modulus values for each of the solutions but were lower when compared to the MEKP specimens.

All samples had similar glass transition temperatures and comparable losses in modulus when heated to the T_g. However the storage modulus at the T_g was higher for the MEKP initiated samples and is attributed to the comparably higher modulus values at 40°C.

For Trigonox 239, the DMA was completed on three specimens to achieve consistent results and a stable transition behaviour. The initially inconsistent results were attributed to the uneven and generally poor surface quality of these specimens. The final specimen from which the consistent results were obtained was sanded smooth prior to testing. Although ultimately exhibiting a comparable transition behaviour, the apparent inconsistency in the results of the Hetron 922 PAW samples cured with Trigonox 239 may preclude its use.

Overall the use of the MEKP initiators produced a slightly superior mechanical performance over the temperature range of the pre-transition and glass transition.

6.3.2.3. Influence of Accelerator Level

Cure investigations discussed in Chapter 3 established that the presence of an accelerator was required to produce stable cure behaviour with a minimum 0.1% cobalt level used in these investigations. It was also surmised that an upper limit to the level of accelerator may exist, above which the cure reaction appeared retarded and the glass transition temperatures lowered by the higher concentrations of cobalt.

This investigation was undertaken to examine the influence of the cure achieved using alternative accelerator levels on the transition behaviour of vinyl ester resins. Specimens of Hetron 914 accelerated with cobalt at 0.1, 0.2, 0.3 and 0.4% and initiated with 2% Butanox M-60 were prepared. Key transition data from post-cured samples of each accelerator level are summarised in Table 6.7. The complete storage modulus transition curves for the post-cured samples and post-curing cycles are presented in Appendix E.

A second transition was observed in the storage modulus curves of the post-curing cycle for each of the samples. This second transition was attributed to the heat from the thermal cycle progressing the cure of each of the samples after being only partially cured at ambient. The molecular mobility of the network is increased as the temperature is raised which allows the cure to continue, increasing the degree of conversion and crosslink density and thus improving the modulus of the network as it approaches full-cure. Once the temperature is raised above the T_g, the storage modulus again lowers as the material passes through the transition. A similar behaviour was observed by Cook *et al.* [3].

Table 6.7 Key transition data of Hetron 914 vinyl ester with varying accelerator levels.

Resin	Hetron 914			**Initiator**		Butanox M-60 @ 2%		
Accelerator Addition Level (%)	**Pre-Transition Behaviour**				**Glass Transition Behaviour**			
	E’ 40°C (MPa)	**E’ 80°C (MPa)**	**E’ Loss (%)**	**Rate of E’ Loss (MPa/°C)**	**T_g (°C)**	**E’ T_g (MPa)**	**E’ Loss (%)**	**Peak Rate of E’ Loss (MPa/°C)**
0.1	3032	2679	12	9.0	146	840	72	58
0.2	3131	2672	15	11.6	143	853	73	58
0.3	3173	2688	15	12.1	140	869	73	61
0.4	3511	3028	14	12.0	141	951	73	66

As observed form the data in Table 6.7, the pre-transition behaviour appears to stabilise above a level of 0.2% cobalt illustrated by the uniform loss in storage modulus of ≈15% when heated to 80°C and similar rates of loss of storage modulus over the 40 to 80°C temperature range (Figure 6.6). The storage modulus values of the 0.4% sample were comparably higher however the temperature performance through the transition was similar.

Increases in the cobalt levels led to decreases in the glass transition temperature (Figure 6.7). A similar trend was observed in DSC investigations and was attributed to non-reactive material in the cobalt solution degrading the network properties.

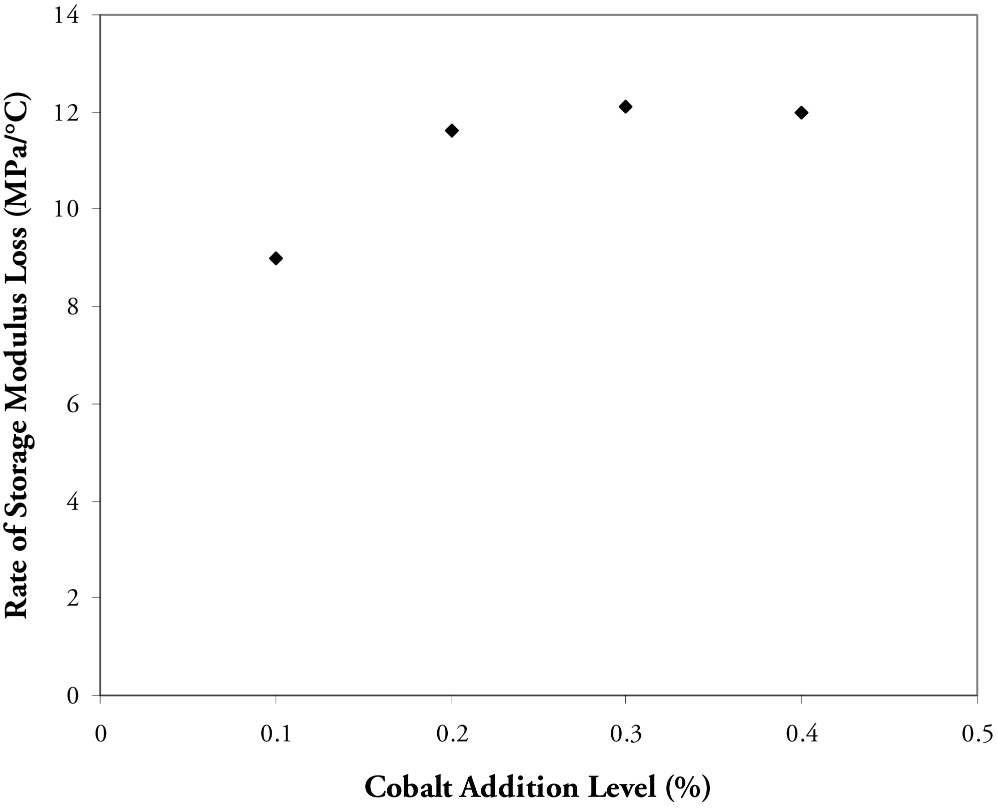

Figure 6.6 Relationship of the pre-transition rate of loss of storage modulus between 40°C and 80°C of Hetron 914 vinyl ester with varying cobalt accelerator level.

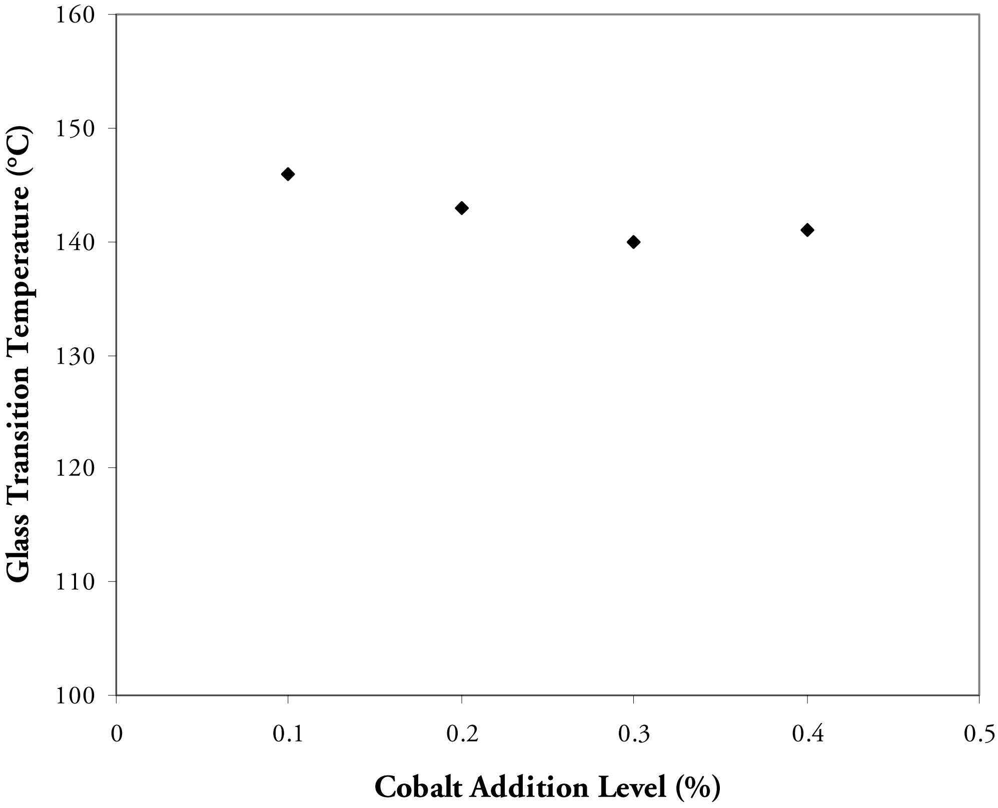

Figure 6.7 Relationship of the glass transition temperature of Hetron 914 vinyl ester with varying cobalt accelerator level.

The temperature performance through the glass transition was stable for each cobalt level with similar losses in storage modulus to the glass transition temperature (Table 6.7). The peak rate of loss of storage modulus through the glass transition increased as the level of cobalt was increased however the highest rate corresponding to the 0.4% cobalt may only be relative to the higher initial storage modulus of this sample.

Overall for the range of cobalt levels examined, the results suggest a cobalt level of 0.2% to produce a stable pre-transition behaviour with increases above this level lowering the T_g and increasing the peak rate of loss through the glass transition. Further investigations over a wider range of addition levels are required to further examine the behaviour.

6.3.2.4. Influence of the Oligomer Molecular Weight

The influence of molecular weight on the cure behaviour was examined previously in Chapter 3 using both Hetron 922 PAW and Hetron 914. Test data indicated the predominant influence of oligomer molecular weight was on the network properties with a lower molecular weight resulting in higher glass transition temperatures.

This investigation was undertaken to examine the influence of the molecular weight of the oligomer on the transition behaviour of vinyl ester resins.

Key data for Hetron 922 PAW specimens cured with each of the four initiator types was presented earlier in Table 6.6. An accelerator level of 0.2% cobalt for the Hetron 914 was used based on recommendations made in Chapter 3. An initiator addition level of 2% was maintained for each of the four initiator types. Key transition data from post-cured samples of each initiator type are summarised in Table 6.8. The complete storage modulus transition curves for the post-cured samples are presented in Appendix E. Transition curves for the post-curing cycle are also given in Appendix E.

Table 6.8 Key transition data of Hetron 914 vinyl ester with alternative initiator types.

Resin	Hetron 914 (0.2% Cobalt)			**Initiator Addition Level**			2%	
	Pre-Transition Behaviour				**Glass Transition Behaviour**			
Initiator	**E' 40°C (MPa)**	**E' 80°C (MPa)**	**E' Loss (%)**	**Rate of E' Loss (MPa/°C)**	**T_g (°C)**	**E' T_g (MPa)**	**E' Loss (%)**	**Peak Rate of E' Loss (MPa/°C)**
Butanox M-60	3131	2672	15	11.6	143	853	73	58
MEKP-SR	3175	2724	14	11.2	147	826	74	60
Trigonox 239	3374	2916	14	11.5	149	920	73	70
CHP 90	3059	2699	12	9.2	151	852	72	67

Other than for CHP 90, the pre-transition behaviour of each sample appeared stable with consistent storage modulus values at 40°C and comparable losses in modulus of ≈15% and rates of loss of storage modulus associated with heating the samples to 80°C. The pre-transition behaviour of the CHP 90 sample was marginally improved. Notably the specimen quality of the Trigonox 239 initiated Hetron 914 samples was markedly improved when compared to Hetron 922 PAW.

The glass transition temperature for the Hetron 914 samples of ≈145°C is considerably higher than those for the Hetron 922 PAW samples of ≈110°C (Figure 6.8). The pre-transition behaviour of both resins is generally quite similar even though the T_g values are different. The higher glass transition temperatures is attributed to the significantly lower molecular weight of the Hetron 914 vinyl ester [13] compared to Hetron 922 PAW, producing a network with a higher crosslink density. The low mobility of the increased crosslink density network results in higher glass transition temperatures with similar results reported by Li [4] and Burts [7]. The lower styrene content of the Hetron 914 would also contribute to the higher crosslink density of the cured network with further investigations required to isolate the relative influences.

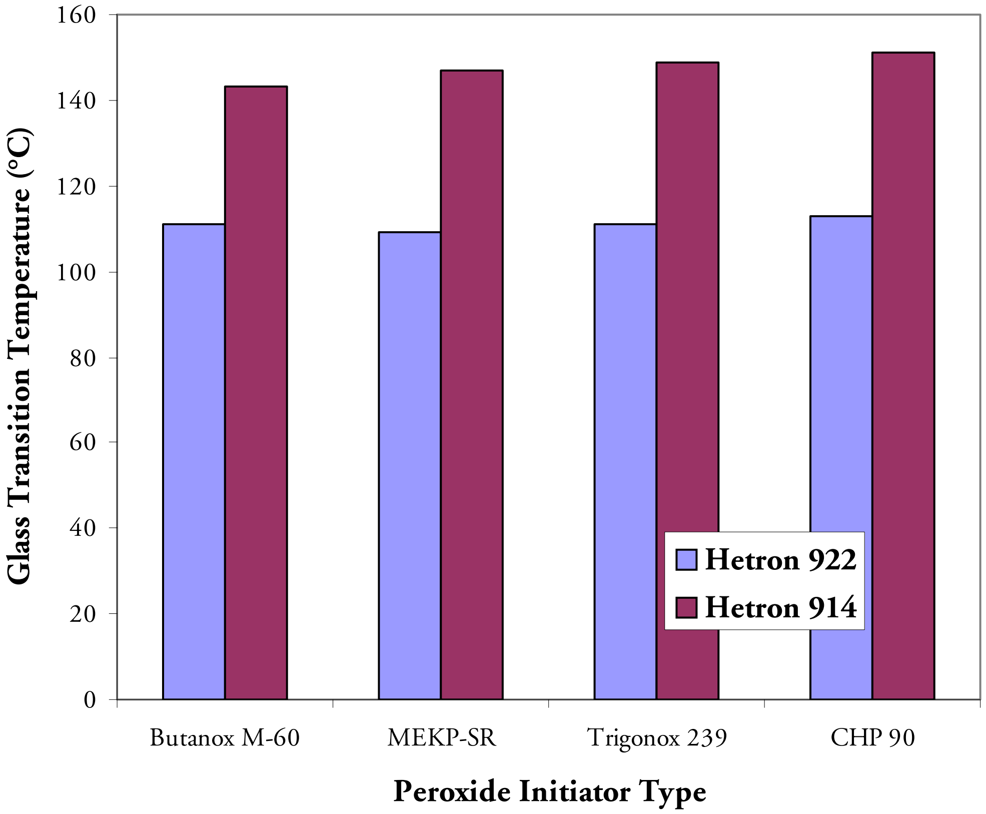

Figure 6.8 **Relationship of the glass transition temperature of different molecular weight vinyl ester resins cured with alternative peroxide initiators.**

The behaviour through the transition of the Hetron 914 samples was quite stable with consistent storage modulus values after heating to the glass transition temperature and comparable rates of storage modulus loss through the transition (Table 6.8).

The loss in modulus to the T_g was marginally higher for the Hetron 914 specimens at ≈73% compared to ≈67% for Hetron 922 PAW. The peak rate of loss of modulus through the glass transition for Hetron 914 was significantly lower at ≈65MPa/°C compared to ≈140MPa/°C for Hetron 922 PAW. The lower molecular weight Hetron 914 maintains its properties and remains functional to considerably higher temperatures due to its higher T_g with the associated rate of loss of mechanical properties through the transition considerably lower (Figure 6.9).

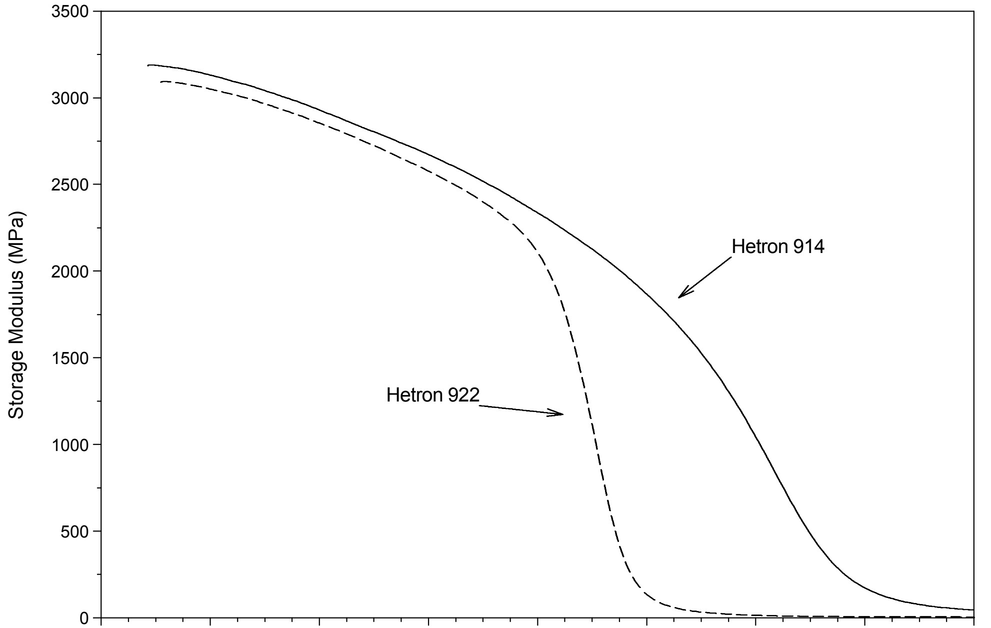

Figure 6.9 Storage modulus transition curves for vinyl ester resins of different molecular weight.

The lower molecular weight oligomer (and lower styrene content) led to higher glass transition temperatures with broader transition behaviours. Although these networks had a lower peak rate of loss through the glass transition, the higher glass transition temperature meant that the mechanical properties were maintained to significantly higher temperatures.

6.3.2.5. Influence of Styrene Concentration

The styrene concentration was observed to have only minimal influence on the cure behaviour but did effect the properties of the cured network in cure investigations discussed in Chapter 3. This investigation was undertaken to examine the influence of the styrene levels on the transition behaviour of vinyl ester resins.

Specimens of Hetron 922 PAW were prepared by adding extra styrene monomer to the resin at levels up to 15% by weight. All samples were cured using Butanox M-60 at an addition level of 2%. Key transition data from post-cured samples for each styrene concentration are summarised in Table 6.9. The complete storage modulus transition curves for the post-cured samples and the post-curing cycle are presented in Appendix E.

Table 6.9 Key transition data of Hetron 922 PAW vinyl ester with varying styrene addition levels.

Resin	Hetron 922 PAW				**Initiator**	Butanox M-60 @ 2%		
Styrene Addition Level (%)	**Pre-Transition Behaviour**				**Glass Transition Behaviour**			
	E’ 40°C (MPa)	**E’ 80°C (MPa)**	**E’ Loss (%)**	**Rate of E’ Loss (MPa/°C)**	**T_g (°C)**	**E’ T_g (MPa)**	**E’ Loss (%)**	**Peak Rate of Loss of Modulus (MPa/°C)**
0	3050	2577	16	11.9	111	1017	67	151
2	3067	2567	16	12.5	109	1046	66	140
5	3092	2536	18	13.7	111	927	70	131
10	2970	2366	20	14.9	107	913	69	128
15	2993	2416	19	14.2	108	925	69	132

As can be observed from the data in Table 6.9, increasing the level of styrene within the system appeared to degrade the pre-transition behaviour by lowering the storage modulus at 40°C and increasing the loss in storage modulus and associated rate of loss in storage modulus (Figure 6.10) when heating the specimens to 80°C.

No significant changes in the glass transition temperature were observed as the styrene concentration was increased. It was expected that as the styrene concentration was increased the T_g would decrease due to a lowering crosslink density [4,7]. The investigation on molecular weight influences highlighted the significant influence of crosslink density on material properties. Auad *et al.* [12] found increases in styrene content lowered the T_g however the applied concentrations ranged from 3.4 to 80%. For this investigation the range of concentrations was significantly narrower from 45 to 60%. By broadening the range of investigated levels, the influences of styrene concentration may become more apparent.

However Li *et al.* [5] found the glass transition temperature decreased with increasing styrene concentration for vinyl ester resins with low molecular weight oligomers, however no significant influence on the T_g of high molecular weight oligomers. Scott *et al.* [2] also found no consistent decrease in T_g with increasing styrene concentration reporting a more significant contribution of the resin backbone on the T_g.

The loss in storage modulus to the glass transition temperature was quite consistent as the styrene concentration was increased (Table 6.9). However observing the magnitude of the storage modulus, the storage modulus value at the T_g generally decreased as the styrene concentration was increased. Although no significant changes in the T_g or modulus loss were observed, the peak rate of loss through the transition also decreased as the styrene concentration was increased.

The results indicate that the temperature performance is lowered as the styrene concentration is increased. These results also highlight how by considering the T_g in isolation, changes in material behaviour may be overlooked. Only by examining the actual mechanical performance through the transition can changes in material behaviour due to the elevated temperatures be detected.

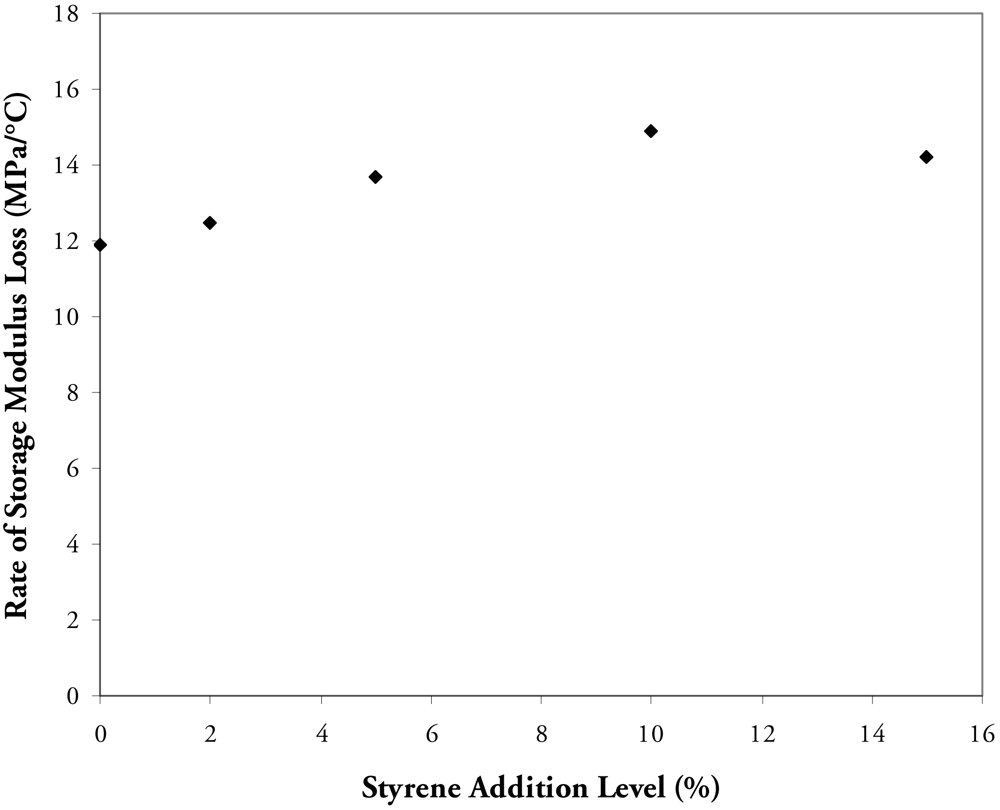

Figure 6.10 Relationship of the rate of storage modulus loss between 40°C and 80°C of Hetron 922 PAW vinyl ester with additional styrene.

6.3.3. TEMPERATURE PERFORMANCE AFTER AN AMBIENT TEMPERATURE CURE

This section examines the requirement of an elevated temperature post-cure to fully develop the properties of the vinyl ester matrix systems. Samples used for this analysis are those used to investigate the influence of the initiator concentration on the transition behaviour. The alternative interpretations of the glass transition temperature for the first post-curing cycle and second scans of a post-cured sample for each of the investigated parameters are tabulated in Appendix E.

The glass transition temperatures of Hetron 922 PAW samples from the post-curing cycle and of a post-cured sample are shown in Table 6.10. Irrespective of the interpretation of the glass transition temperature, the T_g values are higher after exposure to an elevated temperature post-cure. The elevated temperature increases the mobility of the molecular chains which progresses the cure and increases the degree of conversion of the network which subsequently increases the glass transition temperature [3]. The differences in transition behaviour between samples cured at ambient temperature and after an elevated temperature post-cure is shown in Figure 6.11.

Table 6.10 Ambient and post-cure glass transition temperatures of Hetron 922 PAW vinyl ester with varying initiator concentration.

Initiator Addition Level (%)	Glass Transition Temperature (°C)					
	Point of Inflection		Peak Loss Modulus		Peak Tan δ	
	First Run	Second Run	First Run	Second Run	First Run	Second Run
1.0	71	117	75	117	115	125
1.5	73	115	77	115	111	123
2.0	74	111	77	111	106	119
2.5	74	109	79	109	100	117
3.0	80	102	82	103	96	113
4.0	74	99	74	99	89	107
5.0	76	92	78	92	90	101

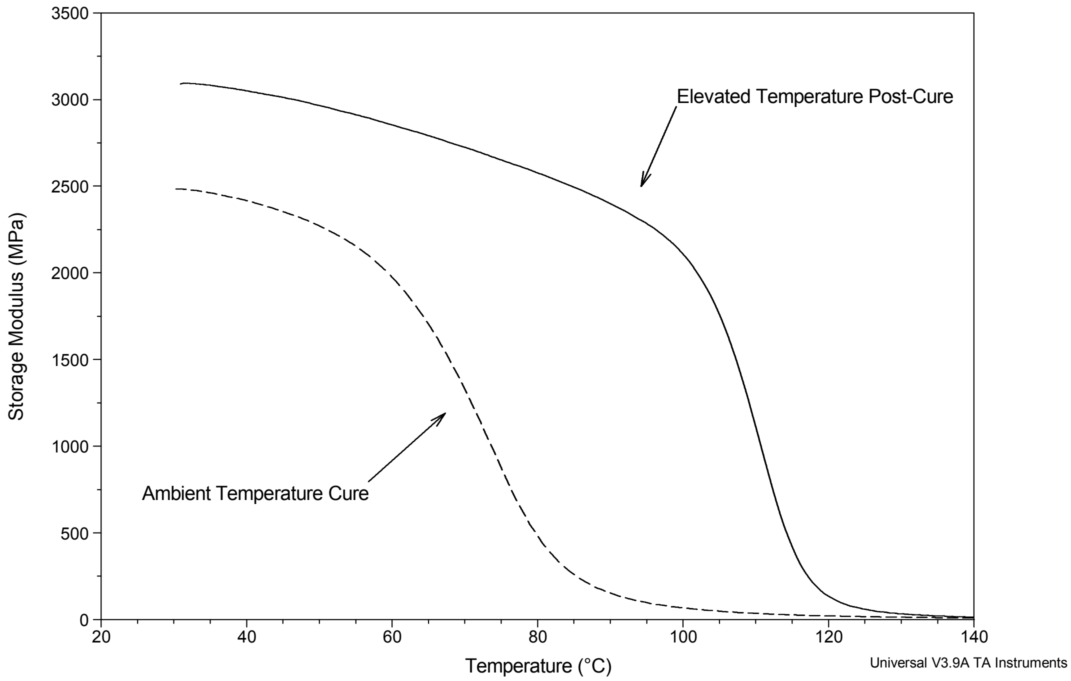

Figure 6.11 Transition behaviour of ambient temperature cured and elevated temperature post-cured Hetron 922 PAW vinyl ester cured with 2.0% Butanox M-60.

The changes in storage modulus transition behaviour due to the post-cure are clearly evident. Table 6.11 presents key transition data that describe the mechanical performance to compare the transition behaviour after ambient temperature cure and after an elevated temperature post-cure.

The initial storage modulus values of the ambient temperature cured samples were increased after post-cure. The rate of loss of storage modulus in the pre-transition of the ambient cured specimens was significantly higher with the upper bound of the range actually exceeding the glass transition temperature of most specimens. The peak rate of loss of storage modulus through the transition was generally higher for each specimen after post-cure.

The results illustrate the relatively poor temperature performance of the ambient cured specimens and emphasise the requirement of an elevated temperature post-cure to achieve good network properties and superior elevated temperature performance.

Table 6.11 Key transition data of ambient and post-cured Hetron 922 PAW vinyl ester with varying initiator levels.

Resin	Hetron 922 PAW			**Initiator**	Butanox M-60	
Initiator Addition Level (%)	**Ambient Temperature Cure**			**Elevated Temperature Post-Cure**		
	E’ 40°C (MPa)	**Rate of E’ Loss 40°C –80°C (MPa/°C)**	**Peak Rate of E’ Loss (MPa/°C)**	**E’ 40°C (MPa)**	**Rate of E’ Loss 40°C –80°C (MPa/°C)**	**Peak Rate of E’ Loss (MPa/°C)**
1.0	2145	47.5	74	3090	11.6	140
1.5	2378	47.0	83	3050	11.7	151
2.0	2416	47.4	92	3050	11.9	151
2.5	1831	35.7	60	2835	10.9	129
3.0	2644	42.1	90	3203	17.9	128
4.0	2285	50.8	93	2594	11.3	117
5.0	2565	47.5	119	2992	18.8	122

These results also indicate that the general industry standard 80°C post-cure temperature, which was utilised to post-cure the test specimens fabricated for the investigation presented in Chapter 5, may result in inferior network and subsequent material properties and poor elevated temperature performance.

6.3.4. TRANSITION BEHAVIOUR OF FILLED VINYL ESTERS

The findings regarding the transition behaviour of unfilled vinyl ester matrix systems were outlined in Section 6.3.2. This investigation draws on these findings to examine the transition behaviour of vinyl ester / cenosphere composites. The influence of the molecular weight of the oligomer on the transition behaviour of vinyl ester resins was shown to be significant. The influence of the filler addition level is obviously an important parameter when considering the behaviour of composite systems. The assessment of transition behaviour of vinyl ester / cenosphere composites includes the effects of:

- The filler addition level.
- The molecular weight of the oligomer.

6.3.4.1. Influence of Filler Volume Fraction

This investigation was undertaken to examine the influence of the filler volume fraction on the transition behaviour and temperature performance of vinyl ester / cenosphere composite systems.

Samples of Hetron 922 PAW were prepared with increasing filler volume fractions from 0 to 50%. All samples were cured using Butanox M-60 at an addition level of 2%. Key transition data from the post-cured samples for each filler volume fraction are summarised in Table 6.12. The complete storage modulus transition curves for the post-cured samples and the post-curing cycle are presented in Appendix E.

Table 6.12 Key transition data of Hetron 922 PAW vinyl ester with varying filler volume fraction.

Resin	Hetron 922 PAW	**Initiator**	Butanox M-60 @ 2%

Filler Addition Level (%)	**Pre-Transition Behaviour**				**Glass Transition Behaviour**			
	E’ 40°C (MPa)	**E’ 80°C (MPa)**	**E’ Loss (%)**	**Rate of E’ Loss (MPa/°C)**	**T_g (°C)**	**E’ T_g (MPa)**	**E’ Loss (%)**	**Peak Rate of E’ Loss (MPa/°C)**
0	2768	2382	14	9.7	110	960	65	131
10	3272	2710	17	14.1	109	1131	65	145
20	3237	2771	14	11.6	111	1144	65	156
30	3083	2541	18	13.3	109	989	68	124
40	3372	2932	13	10.9	110	1248	63	143
50	3347	2919	13	10.5	110	1320	61	133

As can be observed from the data in Table 6.12, no significant trends are evident in the pre-transition behaviour. The relationship of the storage modulus values at 40°, 80°C and the glass transition temperature is shown in Figure 6.12. The relationship at each temperature is consistent with quite similar losses in storage modulus experienced as the temperature was increased.

Increases in the addition of filler generally stiffened the composite systems (Figure 6.12). Improvements in stiffness characteristics of Hetron 922 vinyl ester / cenosphere composite systems with increasing filler content were reported in Chapter 5.

The inclusion of filler showed little effect on the glass transition temperature (Table 6.12). The peak rate of storage modulus loss through the transition appeared relatively consistent as the filler content was increased.

The relationship of the average flexural modulus properties of Hetron 922 PAW vinyl ester / cenosphere composites determined by the investigation presented in Chapter 5 and the storage modulus at 40°C for similar systems is shown in Figure 6.13. The storage modulus values are lower and as the filler volume fraction was increased the difference between the two properties increased.

This investigation has shown the loss of modulus for only small increases in temperature so it is reasonable for the storage modulus values at 40°C to be lower than flexural modulus properties which were typically determined at ambient temperatures (≈25°C). However the increasing difference between the modulus values as the filler volume fraction increases suggests the influence of other factors potentially a combination of dynamic and size effects whose influence becomes more prominent at higher filler volume fractions. Further investigations are required to quantify these relationships.

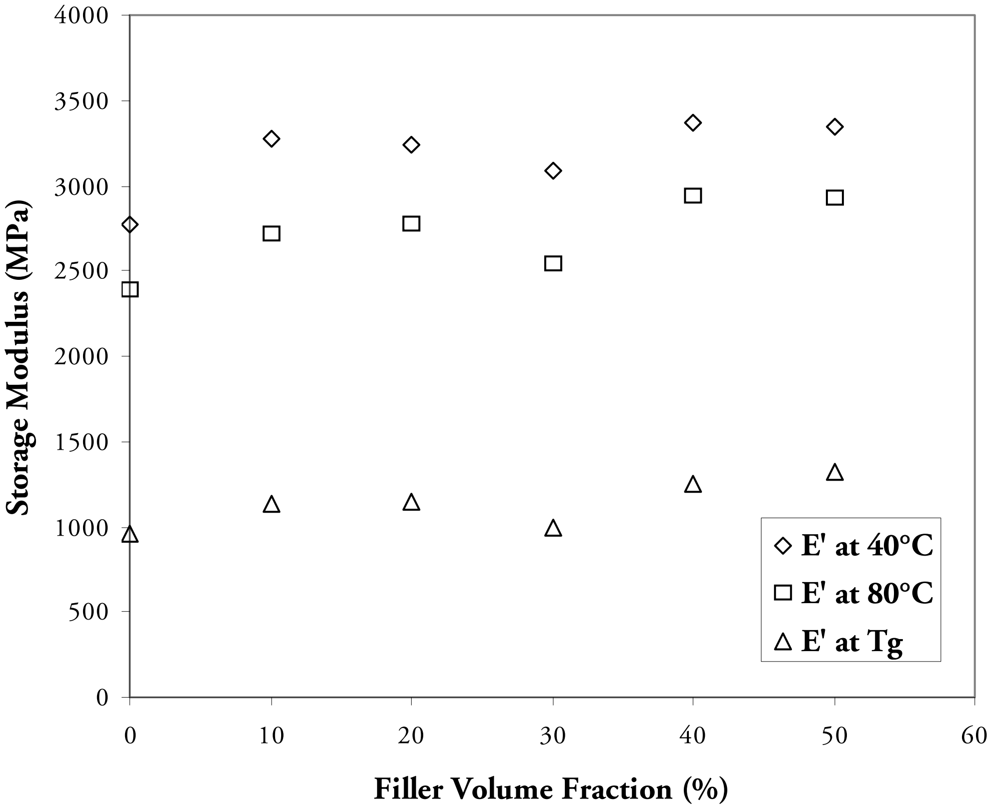

Figure 6.12 Relationship of the storage modulus of Hetron 922 PAW vinyl ester at 40°C, 80°C and the glass transition temperature with increasing filler volume fraction.

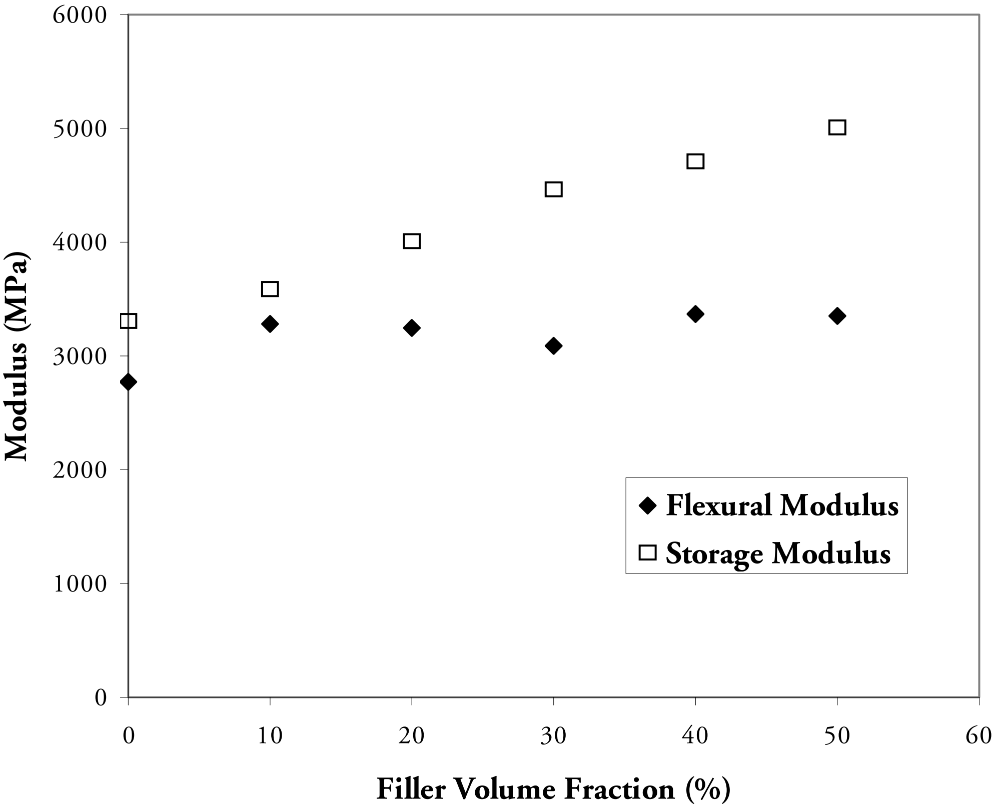

Figure 6.13 Relationship of the flexural and storage modulus (40°C) of Hetron 922 PAW vinyl ester with increasing filler volume fraction.

6.3.4.2. Influence of the Oligomer Molecular Weight

This investigation was undertaken to examine the influence of the oligomer molecular weight on the transition behaviour of vinyl ester / cenosphere composite systems. Both Hetron 922 PAW and Hetron 914 were used for this work with a focus on the influence of the different molecular weights.

Key transition data for Hetron 922 PAW specimens with varying filler volume fractions was presented previously in Table 6.12 with the storage modulus transition curves in Appendix E. Hetron 914 specimens were prepared with increasing filler volume fractions from 0 to 50%. The Hetron 914 was accelerated with 0.2% cobalt and all samples cured using Butanox M-60 at an addition level of 2%. Key transition data from post-cured samples for each filler volume fraction are summarised in Table 6.13. The complete storage modulus transition curves for the post cured samples are presented in Appendix E. Transition curves for the post-curing cycle are also given in Appendix E.

Table 6.13 Key transition data of Hetron 914 vinyl ester with varying filler volume fraction.

Resin	Hetron 914 (0.2% Cobalt)				**Initiator**	Butanox M-60 @ 2%		
Filler Addition Level (%)	**Pre-Transition Behaviour**				**Glass Transition Behaviour**			
	E’ 40°C (MPa)	**E’ 80°C (MPa)**	**E’ Loss (%)**	**Rate of E’ Loss (MPa/°C)**	**T_g (°C)**	**E’ T_g (MPa)**	**E’ Loss (%)**	**Peak Rate of E’ Loss (MPa/°C)**
0	3178	2621	18	13.9	140	849	73	58
10	3338	2872	14	11.6	141	959	71	64
20	3408	2932	14	11.9	141	989	71	66
30	3842	3377	12	11.6	141	1239	68	79
40	3471	3091	11	9.5	142	1174	66	70
50	4398	3939	10	11.4	140	1573	64	86

Although producing a more random effect on the pre-transition behaviour of Hetron 922 PAW, the addition of filler appeared to improve the behaviour of Hetron 914 generally reducing the loss and rate of loss of storage modulus between 40°C and 80°C (Figure 6.14). This may be due to the formation of a denser network from the higher crosslink density and filler restricting the mobility of the chains. The crosslink density of the Hetron 922 PAW matrix may be too low for the filler to have any significant effect.

The glass transition temperature of the Hetron 914 vinyl ester / cenosphere composites was consistently ≈140°C compared to ≈110°C for Hetron 922 PAW systems (Figure 6.15). This is attributed to an increased crosslink density due to the lower molecular weight and lower styrene content of the Hetron 914. The consistent results for both resins suggest that the glass transition temperature of the composite systems may be independent of the filler volume fraction. This would appear reasonable as the glass transition temperature is a property of the amorphous polymer resin matrix and the addition of the inert filler does not effect the molecular structure of the resin.

The addition of the filler also improved the glass transition behaviour by lowering the loss of modulus to the T_g (Table 6.13). This is in contrast to the behaviour observed for Hetron 922 PAW. This may suggest that the inclusion of filler with lower molecular weight oligomer vinyl ester resins improves the performance but for higher molecular weight oligomer vinyl ester resins the influence is negligible.

Of significance is the general increase in storage modulus of the composite systems as the filler volume fraction was increased. This trend also extends to the storage modulus at the glass transition temperature (Figure 6.16) with the behaviour observed for both resin types. Improvements in stiffness characteristics of Hetron 922 vinyl ester / cenosphere composite systems with increasing filler content were reported in Chapter 5.

Although the addition of filler showed negligible effects on the glass transition temperatures, the observed behaviour suggests that the transition behaviour of vinyl ester matrix systems is improved through the addition of filler and the temperature performance of composite systems is superior to the neat resin matrices.

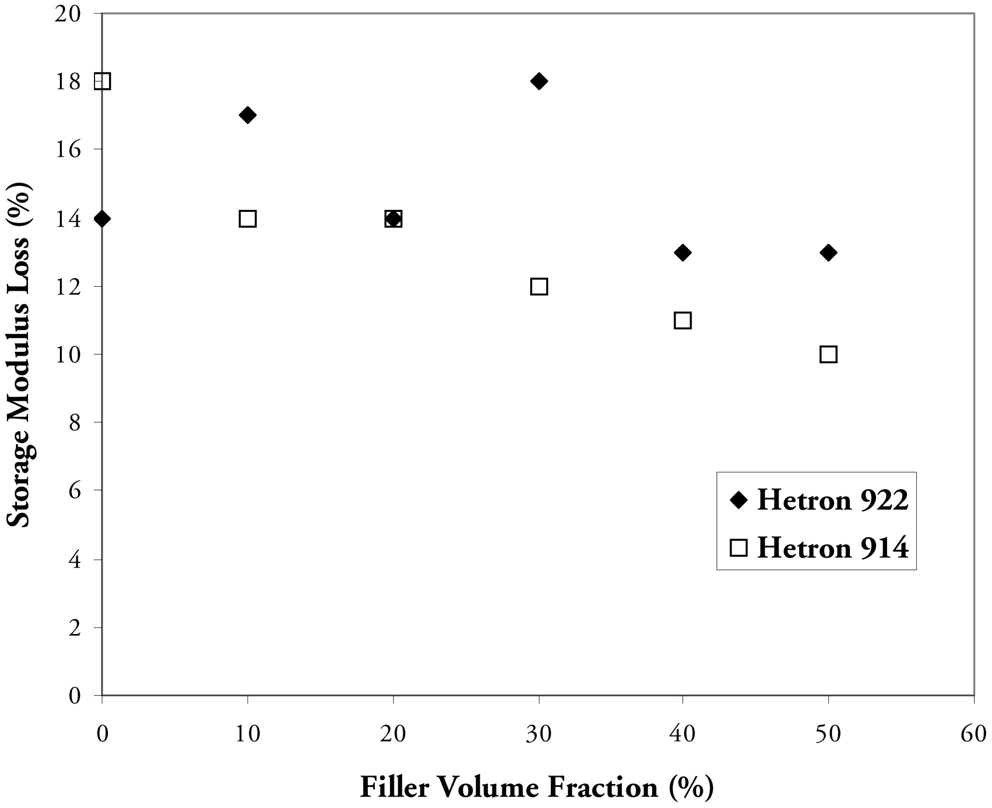

Figure 6.14 Relationship of the storage modulus loss between 40°C and 80°C of vinyl ester / cenosphere composites with increasing filler volume fraction.

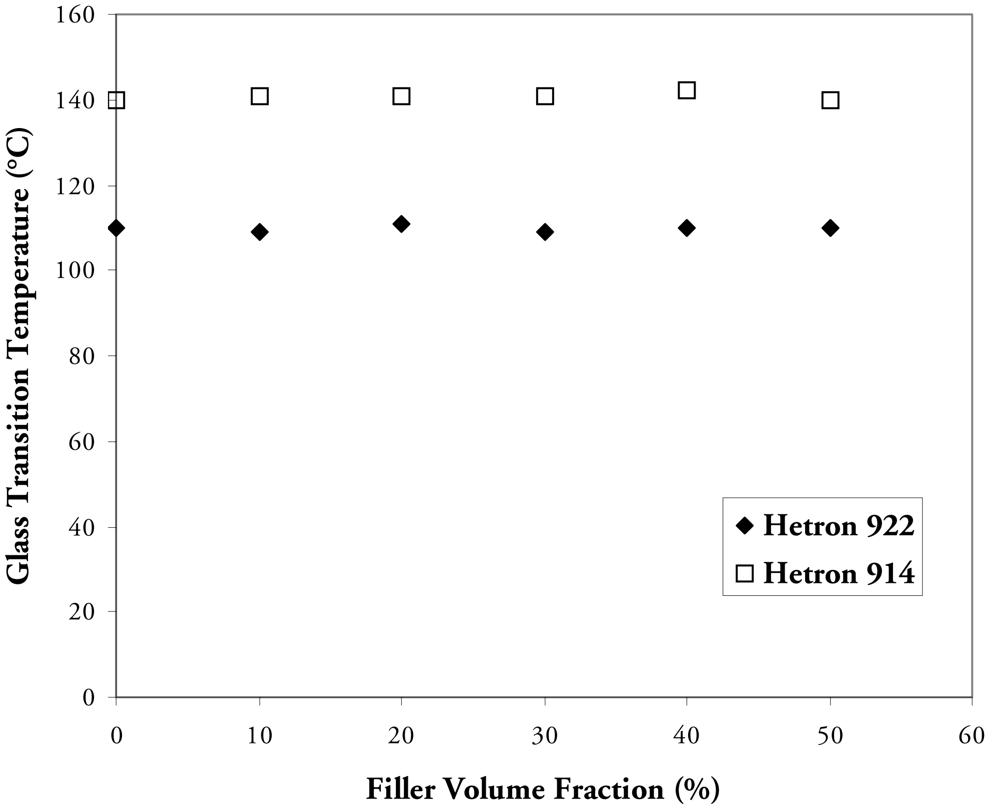

Figure 6.15 Relationship of the glass transition temperature of vinyl ester / cenosphere composites with increasing filler volume fraction.

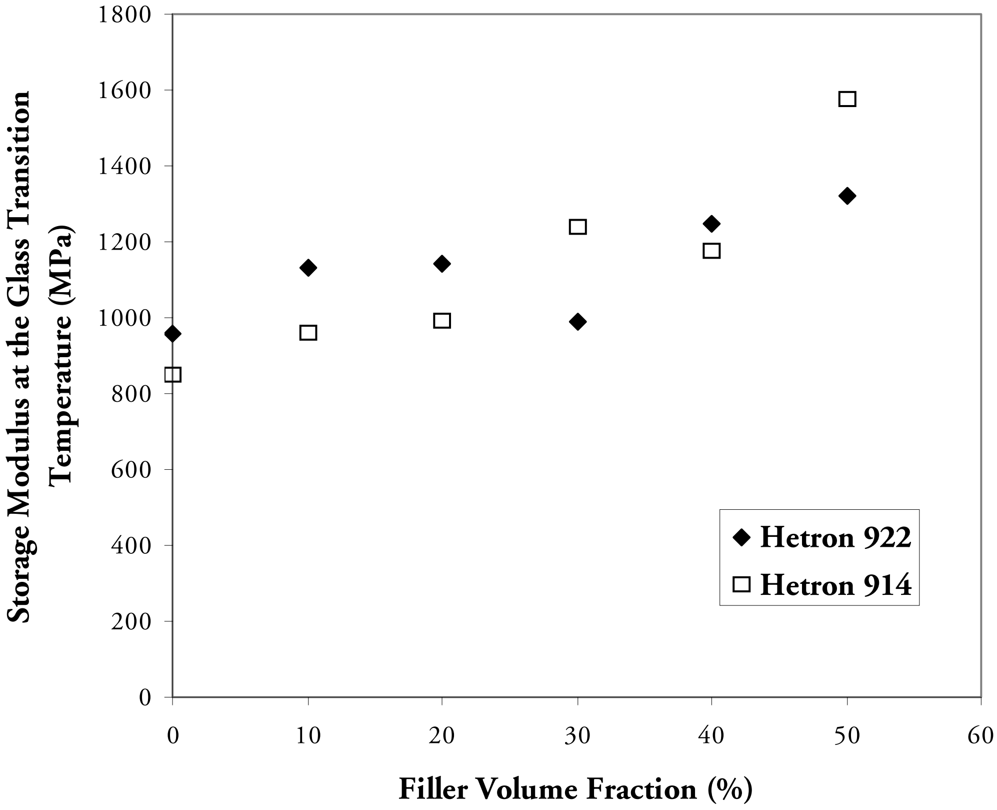

Figure 6.16 Relationship of the storage modulus at the glass transition temperature of vinyl ester / cenosphere composites with increasing filler volume fraction.

6.4. SUMMARY AND CONCLUSIONS

This Chapter has investigated constituent influences on the transition behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites under elevated temperatures. The development of properties in cured networks and the temperature performance were examined by analysing the glass transition temperatures and transition curves using dynamic mechanical analysis (DMA) techniques.

The glass transition temperature values often interpreted from DMA results (loss modulus peak, tan δ peak) were shown to be an inadequate representation of the elevated temperature performance. An alternative approach to gauging the temperature performance of systems using DMA was suggested. The approach encompassed monitoring the changes in mechanical performance that occur at elevated temperatures by examining the storage modulus transition behaviour and the associated glass transition temperature (point of inflection). The adopted approach is directed more towards meeting the requirements of engineering.

Using alternative interpretations of the glass transition temperature yields different T_g values which suggests that T_g values determined using DMA techniques should be accompanied by a qualifying statement providing the utilised interpretation.

The changes in mechanical behaviour in the pre-transition between 40°C and 80°C and through the glass transition were analysed. The results are summarised as follows:

- The influence of initiator concentration on the elevated temperature performance was examined with the losses in storage modulus in the pre-transition behaviour increasing significantly above an initiator concentration of 2.5%. Higher initiator levels also detrimentally affected the mechanical performance through the glass transition. The glass transition temperature decreased almost linearly as the initiator concentration was increased.
- Both the MEKP initiator solutions and both the CHP initiator solutions produced similar transition behaviours. Overall the MEKP initiated samples possessed higher storage modulus values and a superior transition behaviour. The use of the Trigonox 239 initiator solution produced samples with a poor surface quality which led to inconsistent results. Although stable transition values were finally determined, the

use of this initiator to cure Hetron 922 PAW based products should be carefully considered.

- A minimum cobalt accelerator level of 0.2% was shown to produce a stable pre-transition behaviour with increases above this concentration degrading the network properties, lowering the glass transition temperature.
- The crosslink density of networks was found to be a significant contributing factor on the glass transition temperature and transition behaviour. Increasing the crosslink density by using a resin with a lower molecular weight and lower styrene concentration typically improved elevated temperature performance. The pre-transition behaviour was similar however the glass transition occurred at significantly higher temperatures with the associated rate of loss of mechanical properties at these temperatures significantly lower.
- The results indicate that the temperature performance is lowered as the styrene concentration is increased. Although no significant changes in the glass transition temperature were observed with an increase in styrene content the results highlight how by considering the T_g in isolation, changes in material behaviour may be overlooked. Only by examining the actual mechanical performance through the transition can changes in material behaviour due to the elevated temperatures be detected.
- The necessity of an elevated temperature post-cure above the glass transition temperature to develop optimal network properties and subsequent superior elevated temperature performance was established.
- The temperature performance of vinyl ester / cenosphere composites was superior to the neat resin matrix systems. Although possessing similar glass transition temperatures, increases in the filler volume fraction generally led to higher storage modulus values at the T_g.
- The improvements in temperature performance were significantly higher for the more highly crosslinked networks when the lower molecular weight oligomer resin was used. Improvements in the pre-transition and glass transition behaviour were observed.

The established requirement of a post-cure temperature above the glass transition temperature also indicated that the general industry recommended 80°C post-cure temperature utilised to post-cure the test specimens (Hetron 922 PAW vinyl ester based composites, $T_g \approx 110°C$) fabricated for the investigation presented in Chapter 5, would not result in optimal network and subsequent material properties. The consequence of incomplete cure obtained by standard industry cure procedures should be seriously evaluated for each application.

The advantages of monitoring the changes in mechanical behaviour at elevated temperatures suggest that the heat distortion temperature or HDT (see Section 2.4.6) may be a more appropriate indicator of elevated temperature performance than the glass transition temperature.

From a design perspective, the use of a single glass transition temperature value has advantages. Therefore it may be suggested that both of these properties are still quite important with the T_g used to determine appropriate post-cure temperatures and the HDT as an indicator of elevated temperature performance.

6.5. REFERENCES

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CHAPTER 7.

CONCLUSIONS

7.1. OVERVIEW

Particulate reinforced composites are at a relatively early stage of development. With a range of constituent material options available to optimise performance, vinyl ester / cenosphere composites may offer considerable flexibility in design and application to civil engineering structures. An understanding of the fundamentals of behaviour should be developed by examining systems based on standard materials before specialised performances are considered.

To meet this requirement, the following criteria were identified and utilised to select constituent materials for this investigation:

- A standard grade vinyl ester resin that offers a good balance of mechanical and physical performance while remaining cost-effective.
- Alternative grade of vinyl ester resin with a basic oligomer type modification which may possess improved performances.
- An ambient temperature cure system that offers considerable flexibility to cure VE resins using standard equipment in a range of conditions.
- A class of cenospheres with a graded particle distribution and a range of particle sizes.

This foundational PhD study focussed on determining the existence (or lack) of relationships between parameters and fundamental behaviours rather than the precise nature of the relationships. Through completing over 500 individual tests and applying a variety of experimental techniques, this strategic investigation provides the platform to undertake more detailed investigations to further establish and verify these relationships.

7.2. KEY FINDINGS

This PhD study has examined the influence of a number of parameters on the behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites. The investigations have shown that complex interrelationships exist between the constituent materials and the behaviour of the system. The findings of this research are numerous and diverse. The investigated parameters and behaviours with the associated key findings are summarised in Table 7.1. References to the relevant Sections of this dissertation corresponding to the findings are provided.

The influence of the parameters on the performance of vinyl ester matrix systems and vinyl ester / cenosphere composites were examined under two broad performance categories:

1. **Processing Performance** including:
    - Cure Characteristics
    - Viscosity Behaviour
    - Shrinkage Behaviour

2. **Product Performance** including:
    - Mechanical Properties
    - Temperature Performance

The influence of the parameters in the shaded cells in Table 7.1 were considered primarily on the behaviour of vinyl ester matrix systems with the other parameters focussed towards addressing composite system behaviour in addition to the resin system.

The relationships between the parameters and behaviours in the cells of Table 7.1 marked with an “X” were not addressed as part of this investigation.

The relationships between the behaviours are significant demonstrating the necessity to collectively consider the relative influences of parameters on the behaviours (Table 7.1). From an engineering perspective, the systems must meet the requirements of the desired application. This implies the consideration of the end product performance then adapting the processing performance to meet these requirements.

Table 7.1 Key Findings from Investigations of the Influence of Selected Parameters on Fundamental Behaviour.

		Processing & Curing Temperatures	Initiator Concentration (MEKP)	Initiator Type (MEKP and CHP)	Accelerator Level (Cobalt)	Oligomer Molecular Weight	Styrene Concentration	Filler (E-Spheres SLG)	Remarks
Processing Performance	**Cure Characteristics**	▪ Elevated temperatures required to complete reaction	▪ 1.5% min. for stable behaviour ▪ above 2.5% reduction in T_g	MEKP – initial kick ▪ higher reactivity ▪ rapid cure CHP – delayed onset ▪ lower reactivity	▪ required for stable cure at ambient ▪ 0.2% rapid cure ▪ higher levels - retard reaction, reduce T_g	Lower MW - ▪ more rapid cure reaction ▪ considerably higher T_g	▪ minimal cure influences ▪ low effect on T_g due to high MW resin	▪ lowers reaction intensity ▪ reduces peak temperatures ▪ extends reaction times ▪ MEKP less sensitive to effects of filler	▪ Considerable flexibility available to effect cure. ▪ Important to achieve full cure.
	Section 3.4		Section 3.3.1.1	Section 3.3.1.2	Section 3.3.1.3	Section 3.3.1.4	Section 3.3.1.5	Section 3.3.2	
	Viscosity Behaviour	▪ Higher temperature, lower viscosity.	X	X	X	X	▪ reduces viscosity ▪ significant reduction at high filler levels	▪ increases viscosity ▪ significant increase at higher filler levels ▪ ≈12000cp @50% filler, practical max. viscosity	▪ Only higher MW resin investigated. ▪ Initiator concentration not assessed but consideration noted. ▪ Lower MW resin, lower viscosity.
	Section 4.4						Section 4.3.1.2	Section 4.3.1.1	
	Shrinkage Behaviour	▪ Shrinkage behaviour stabilises after post-cure at elevated temp.	X	X	X	Lower MW – ▪ Should lead to higher shrinkage but styrene greater influence.	▪ neat resin - no significant effect ▪ filled resin – slightly increased shrinkage	▪ initial shrinkage variable – attributed to vitrification ▪ total shrinkage reduced by 40% with 50% filler	▪ Measured shrinkage not fixed but indicative. ▪ Actual shrinkage related to volume of sample. (Section 4.3.2.4) ▪ Need examination of broader range of styrene levels.
	Section 4.4	Section 4.3.2				Section 4.3.2.2	Section 4.3.2.3	Section 4.3.2.1	
Product Performance	**Mechanical Properties**	▪ T_g ambiguous for mechanical properties. ▪ Requirement to understand relationships.	X	X	X	X	X	▪ reduced strength ▪ increased stiffness ▪ reduced Poisson's ratio ▪ degree of influence depends on loading (tension, compression)	▪ Linear behavioural relationships suggested. (Section 5.3.4) ▪ Superiority of machining method of tensile specimen preparation. (Section 5.3.1)
	Section 5.4	Section 6.3						Section 5.3.2, Section 5.3.3	
	Temperature Performance	▪ Dependent on thermal history.	▪ 2.5% max. for stable pre-transition ▪ above 2.5%, reduction in T_g	▪ no significant effect on transition behaviour ▪ variability in CHP results ▪ no significant effect on T_g	▪ 0.2% min. for stable pre-transition ▪ above 0.2%, reduction in T_g	Lower MW – ▪ considerably higher T_g ▪ broader glass transition	▪ degraded pre-transition ▪ no significant effect on T_g	Higher MW – ▪ no significant influence Lower MW – ▪ improved pre-transition ▪ improved temp. performance	▪ Considerable variation in T_g using different methods. (Section 6.3.1) ▪ Correlation between storage and flexural modulus. (Section 6.3.4.1) ▪ Standard post-cure schedules may not be sufficient.
	Section 6.4	Section 6.3.3	Section 6.3.2.1	Section 6.3.2.2	Section 6.3.2.3	Section 6.3.2.4	Section 6.3.2.5	Section 6.3.4	

7.3. PRIMARY CONCLUSIONS

A plethora of materials are available to form vinyl ester / cenosphere composites resulting in a range of performance outcomes to suit specific applications. The development of particulate reinforced composite systems functional as core materials for civil and structural engineering applications is relatively adolescent. This investigation has been constrained to a limited number of constituent materials primarily suitable for civil engineering applications as defined by previous research. Very little rigorous research has previously been conducted in this area.

Complex relationships exist between the constituent materials and the behaviour of the composite system. Four key parameters (see Table 7.1) influence the end product performance and processing characteristics, namely:

- Filler volume fraction
- Molecular weight of the vinyl ester oligomer
- Styrene concentration
- Processing and curing temperatures

Other important parameters (see Table 7.1) which primarily influence the processing performance of vinyl ester / cenosphere composites are:

- Initiator concentration
- Initiator type
- Accelerator level

These secondary parameters can be used to adjust finer aspects of processing performance once the key parameters have been defined.

Approximate relationships between filler volume fraction and the physical characteristics were established, in particular:

- Stiffness increases with filler content
- Strength decreases with filler content

- Viscosity increases non-linearly with filler content

Shrinkage behaviour is complex and varies with respect to the key performance parameters listed above. However the geometry of the specimen appears to have a significant effect on measured shrinkage values particularly as the sample volume increases. This suggests that the measured shrinkage values may only be an indicator of the overall shrinkage behaviour of a product.

Similarly cure behaviour appears quite complex. Both the processing and product parameters can be significantly influenced by the thermal history of a specific product. While a range of techniques can be used as indicators of performance (eg: DMA, DSC) further development of an understanding of the fundamental influences on this complex behaviour and their application to the curing of actual products is required.

This investigation of vinyl ester / cenosphere composites has shown particulate composite systems offer improved performances when compared to neat resin matrices in a range of areas. The characteristics of the matrix resin and the volume fraction of filler used significantly influence the performance outcomes as summarised in Table 7.1. The main advantages of particulate composite systems when compared to neat resins are:

- Lower cost
- Reduced cure reaction temperatures
- Reduced total shrinkage
- Increased stiffness characteristics
- Improved temperature performance

However this improved performance also has associated detrimental side effects including:

- Increased viscosity
- Reduced strength

A number of experimental techniques and procedures were utilised to complete this investigation examining the behaviour of vinyl ester matrix systems and vinyl ester / cenosphere composites.

As part of the experimental program to characterise the mechanical properties of vinyl ester / cenosphere composites, two methods of fabrication of tensile test specimens were trialled. The machining method of manufacture of specimens (developed as part of this investigation) produced results of improved consistency and lower variation.

Differential scanning calorimetry (DSC) was used as a relatively simple and quick method of examining the cure behaviour and development of network properties of vinyl ester matrix systems. Dynamic mechanical analysis (DMA) provided valuable information relating the actual changes in mechanical properties of materials when exposed to elevated temperatures. From an engineering perspective, this information appears to have considerably more value than the traditional measure of the glass transition temperature to gauge the elevated temperature performance.

For the effective use of these materials an understanding of the processing and mechanical performance is required. These techniques may be readily applied to assess material performance relating to the cure behaviour and mechanical properties of polymer matrices and particulate composite systems. The techniques are not only rapid but provide detailed information applicable to engineering requirements.

Meeting the requirements of civil engineering applications, requires simple and consistent experimental techniques that relate to physical properties of interest to structural and production engineers. A number of techniques currently used to quantify polymer behaviour are inconsistent with these requirements. Further development of these concepts to suit civil engineering applications may require adjustments to materials characterisation paradigms commonly available.

The outcomes of this investigation have significantly improved the understanding of the processing and end performances of vinyl ester / cenosphere composite materials. This improved understanding may facilitate the continued development and integration of these systems into FRP composite structural solutions for civil engineering applications.

7.4. RECOMMENDATIONS FOR FUTURE RESEARCH

This research has identified a number of relationships that relate constituent material parameters to fundamental behaviour of vinyl ester / cenosphere composite systems. More work is required to further develop and quantify these relationships.

During the course of this PhD research a number of other issues have become apparent that warrant further investigation. The main topics for further investigation are categorised into those that are:

1. Extensions of parametric investigations presented in this research.
2. Significant relationships identified but beyond the scope of the current investigation.
3. Production application investigations.

7.4.1. EXTENSIONS OF CURRENT RESEARCH

- An investigation to determine **optimum initiator concentrations** for other types of peroxide initiator and initiator solutions.

- An investigation of the influence of cure conditions on the **cure behaviour** of vinyl ester matrix systems and vinyl ester / cenosphere composites.

- A detailed investigation to isolate the relative influences of the oligomer molecular weight and styrene concentration on the **cure behaviour** of vinyl ester matrix systems and vinyl ester / cenosphere composites.

- An investigation of the influence of high levels of cobalt accelerator on the **cure behaviour** and **network properties** of vinyl ester matrix systems.

- An investigation to examine the influence of vitrification on the **shrinkage behaviour** of vinyl ester matrix systems and vinyl ester / cenosphere composites.

- A detailed investigation of the **shrinkage behaviour** of vinyl ester / cenosphere composites at high filler volume fractions including the examination of the potential influences of particle distribution within the composite.

- An investigation of the **failure mechanisms** of vinyl ester / cenosphere composites (eg: matrix failure, filler failure).

- A detailed investigation of the relationship between **flexure performance** and the **tensile** and **compressive properties** of the composite and its application to the design and analysis of structures.

- An investigation of oligomer molecular weight and styrene influences on the **mechanical properties** of vinyl ester / cenosphere composites.

7.4.2. ADDITIONAL FOUNDATIONAL INVESTIGATIONS

- An investigation of alternative filler types on the **viscosity behaviour** of vinyl ester / cenosphere composites including the influence of:

    - Filler particle size
    - Filler particle size distribution

- An investigation of the influence of particle / matrix adhesion on the **mechanical properties** of vinyl ester / cenosphere composites.

- An investigation of the **shear strength characteristics** of vinyl ester / cenosphere composites.

- An investigation of the **toughness characteristics** of vinyl ester / cenosphere composites including the influence of:

    - Filler type (particle size and particle size distribution)
    - Filler volume fraction
    - Resin type

- An investigation of the **creep behaviour** of vinyl ester / cenosphere composites including the influence of:

  - Filler type (particle size and particle size distribution)
  - Filler volume fraction
  - Resin type

- Continued development of the use of DMA techniques and alternative indicators to gauge the **elevated temperature performance** of polymer matrices and composite systems.

- The correlation of DMA results (transition behaviour and glass transition temperature) with the **heat distortion temperature** (HDT) of vinyl ester matrix systems and vinyl ester / cenosphere composites.

7.4.3. PRODUCTION INVESTIGATIONS

- An investigation of the influence of cure conditions and the cure system on the **shrinkage behaviour** of vinyl ester / cenosphere composites.

- An investigation of **post-cure procedures** for composite products to ensure the adequate distribution of heat to progress the cure and facilitate the development of optimal network properties.

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APPENDIX A.

DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND THERMOCOUPLE MONITORING RESULTS

This Appendix contains the DSC curves of the first and second heating runs and the thermocouple monitoring results from the investigation of cure behaviour presented in Chapter 3. The investigated parameters are listed below and the results are presented overleaf.

Cure Behaviour of Unfilled Vinyl Esters

- Influence of Initiator Concentration
- Influence of Peroxide Initiator Type
- Influence of Accelerator Level
- Influence of Oligomer Molecular Weight
- Influence of Styrene Addition Level

Cure Behaviour of Filled Vinyl Esters

- Influence of Peroxide Initiator Type
- Influence of Accelerator Level
- Influence of Oligomer Molecular Weight

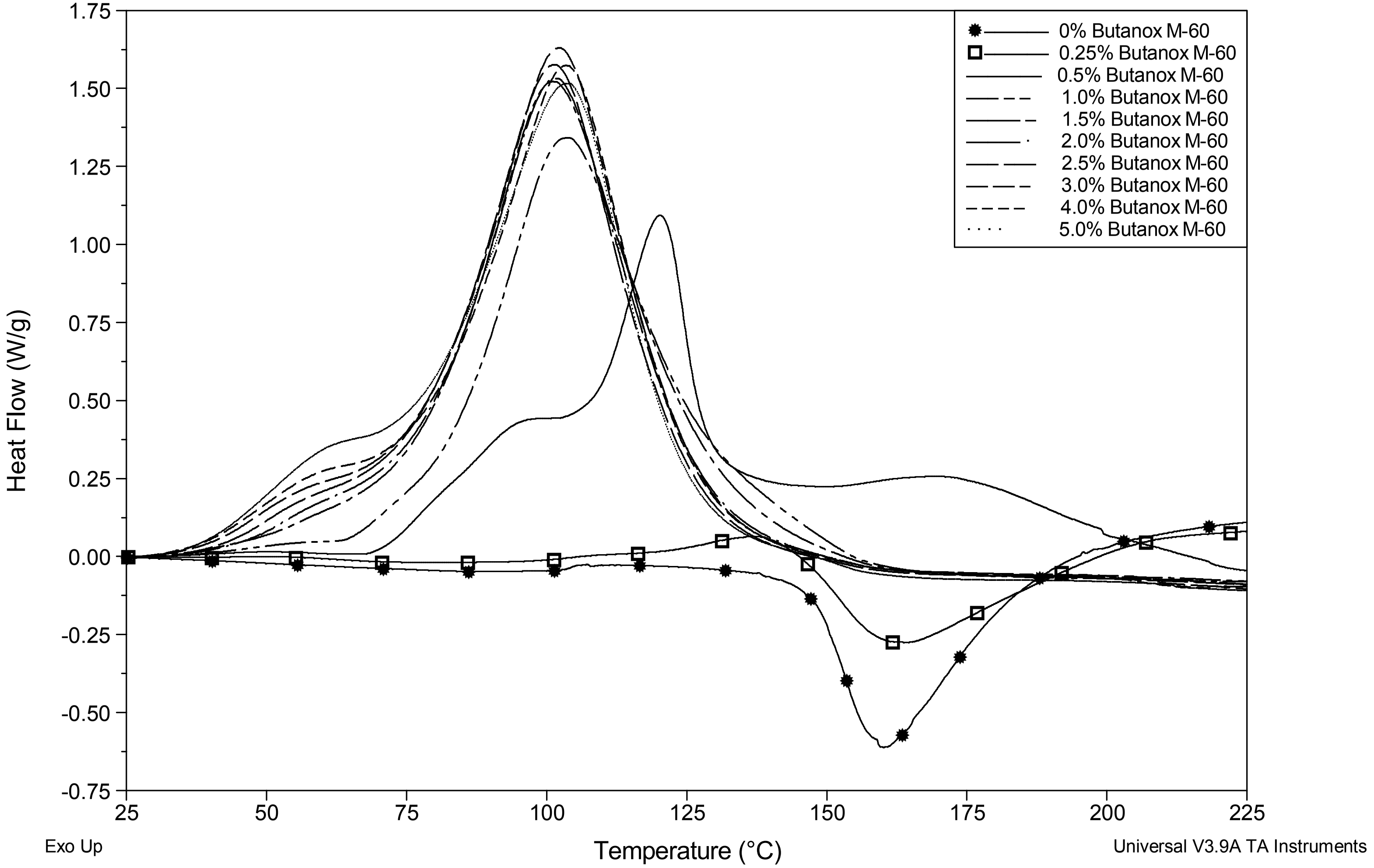

Figure A.1 First DSC heating run for Hetron 922 PAW vinyl ester with varying initiator levels (25°C to 225°C range).

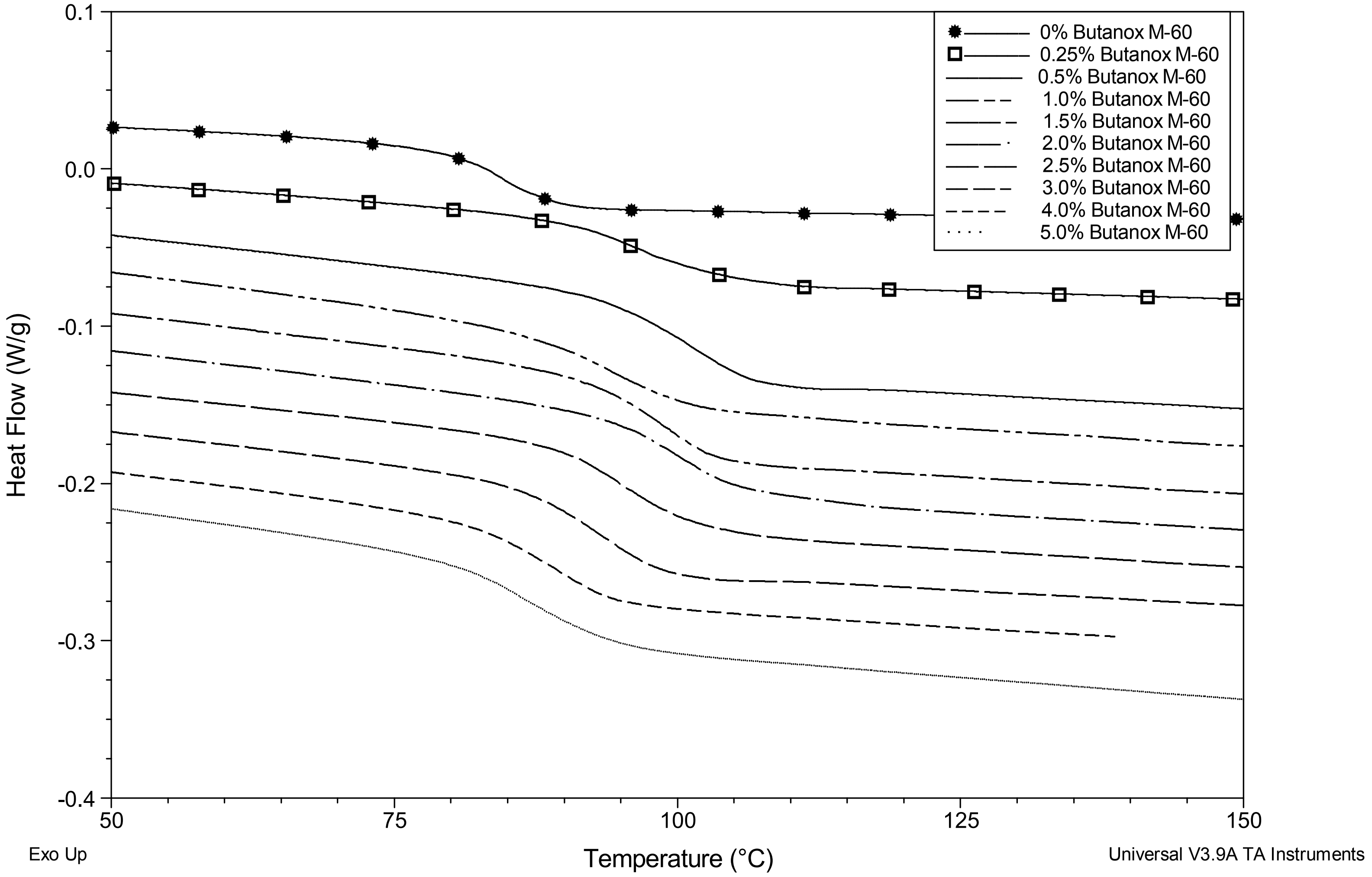

Figure A.2 Second DSC heating run for Hetron 922 PAW vinyl ester with varying initiator levels (50°C to 150°C range).

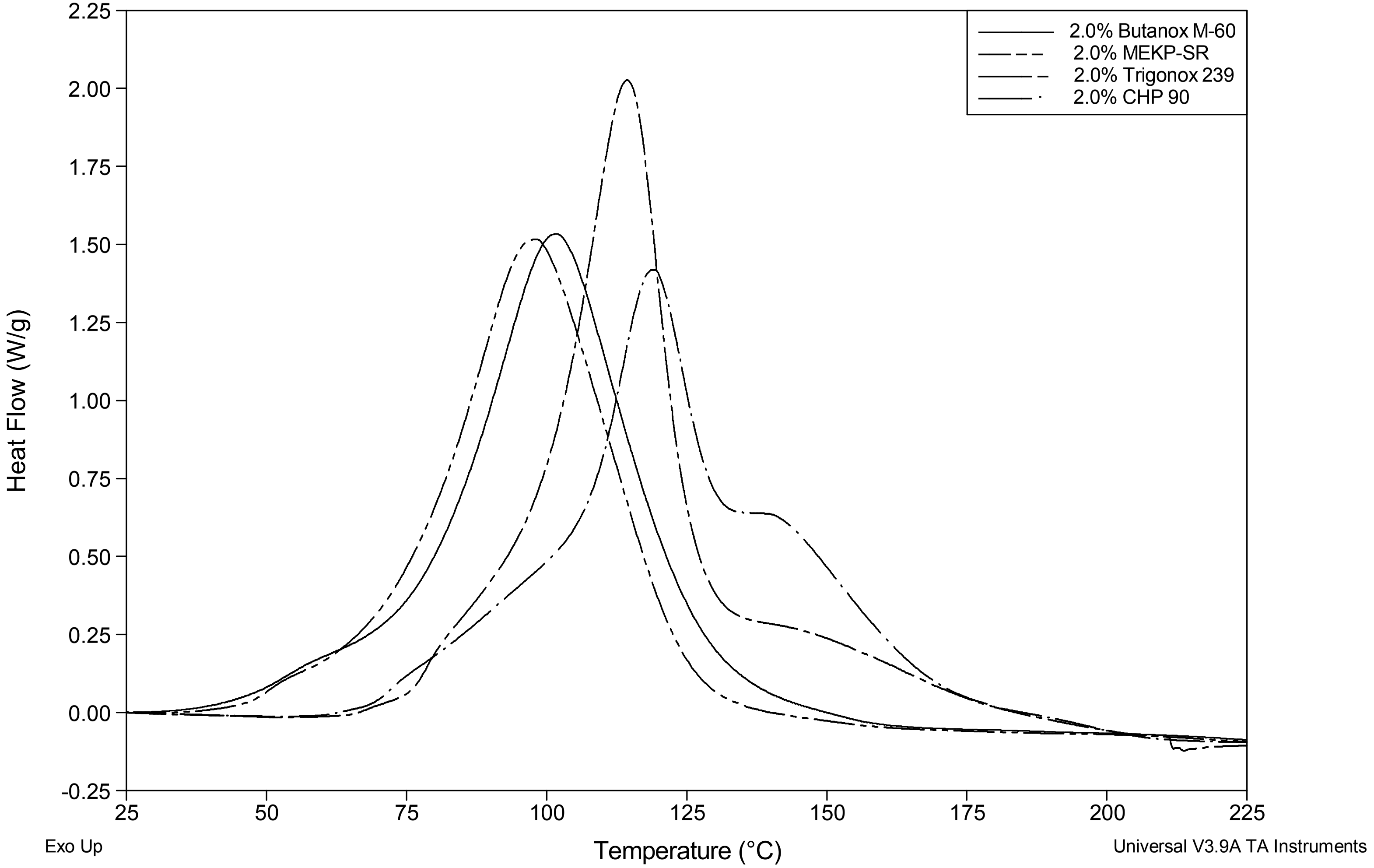

Figure A.3 **First DSC heating run for Hetron 922 PAW vinyl ester with alternative initiator types (25°C to 225°C range).**

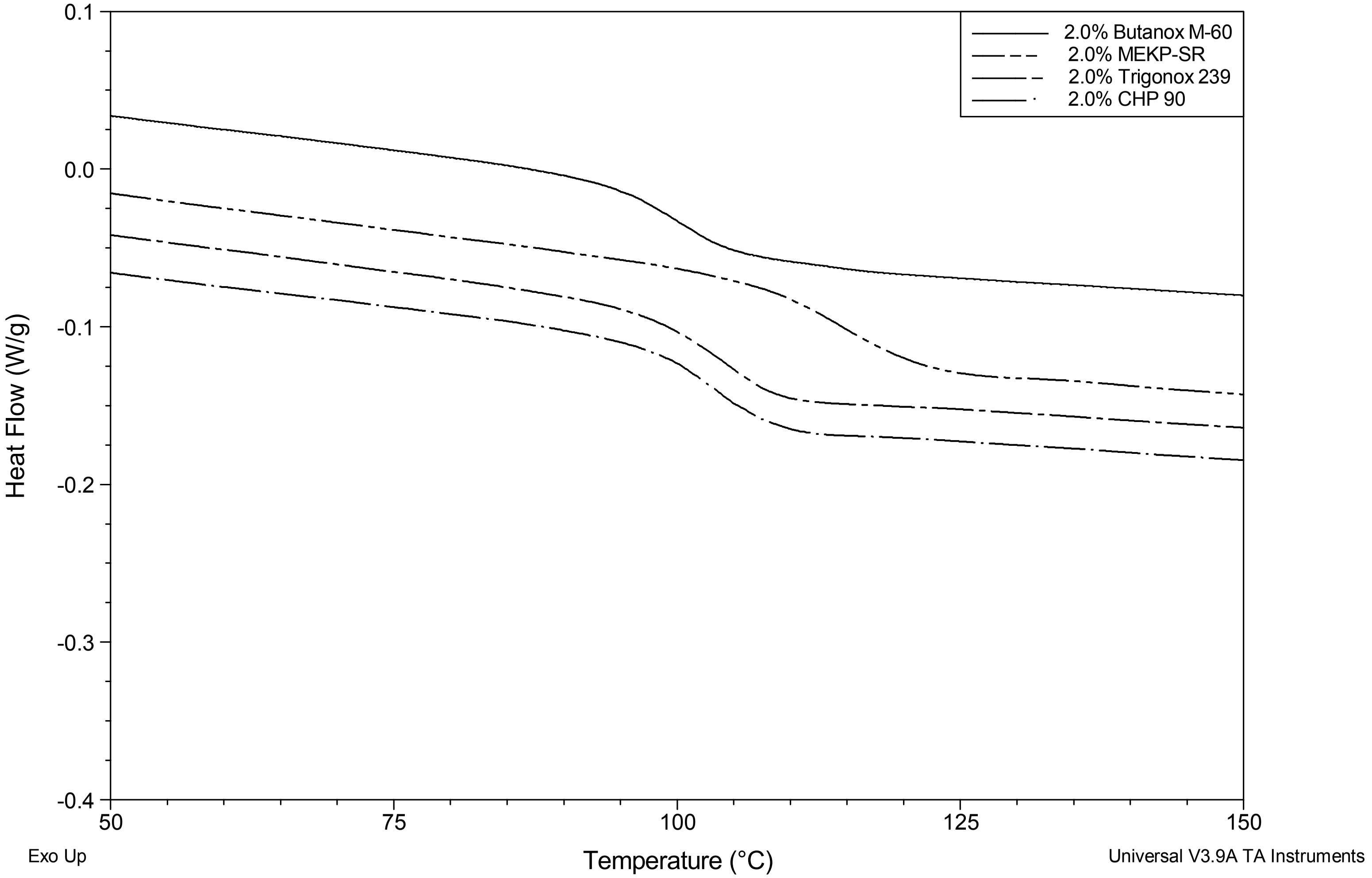

Figure A.4 Second DSC heating run for Hetron 922 PAW vinyl ester with alternative initiator types (50°C to 150°C range).

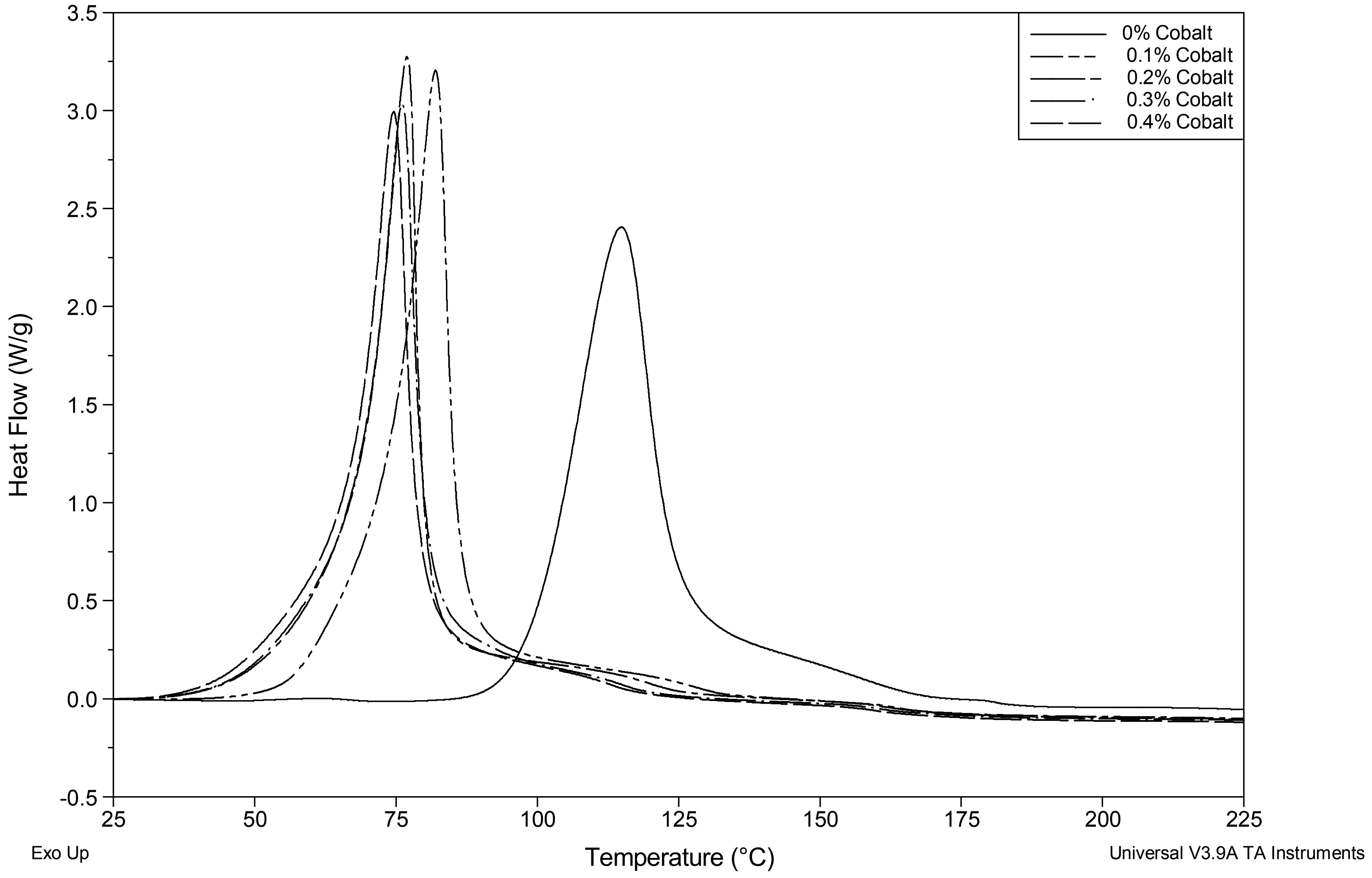

Figure A.5 First DSC heating run for Hetron 914 vinyl ester with varying accelerator levels (25°C to 225°C range).

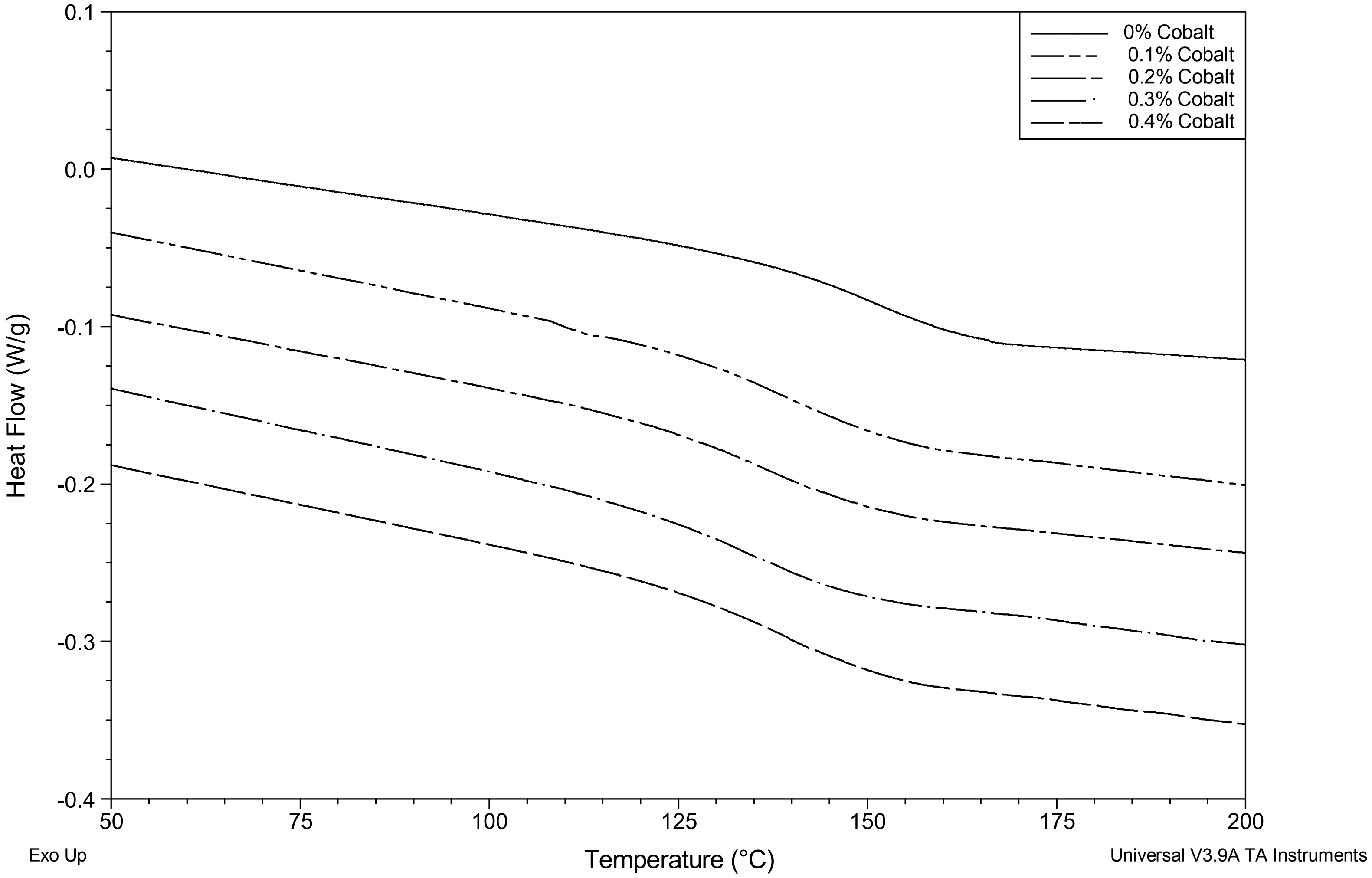

Figure A.6 Second DSC heating run for Hetron 914 vinyl ester with varying accelerator levels (50°C to 200°C range).

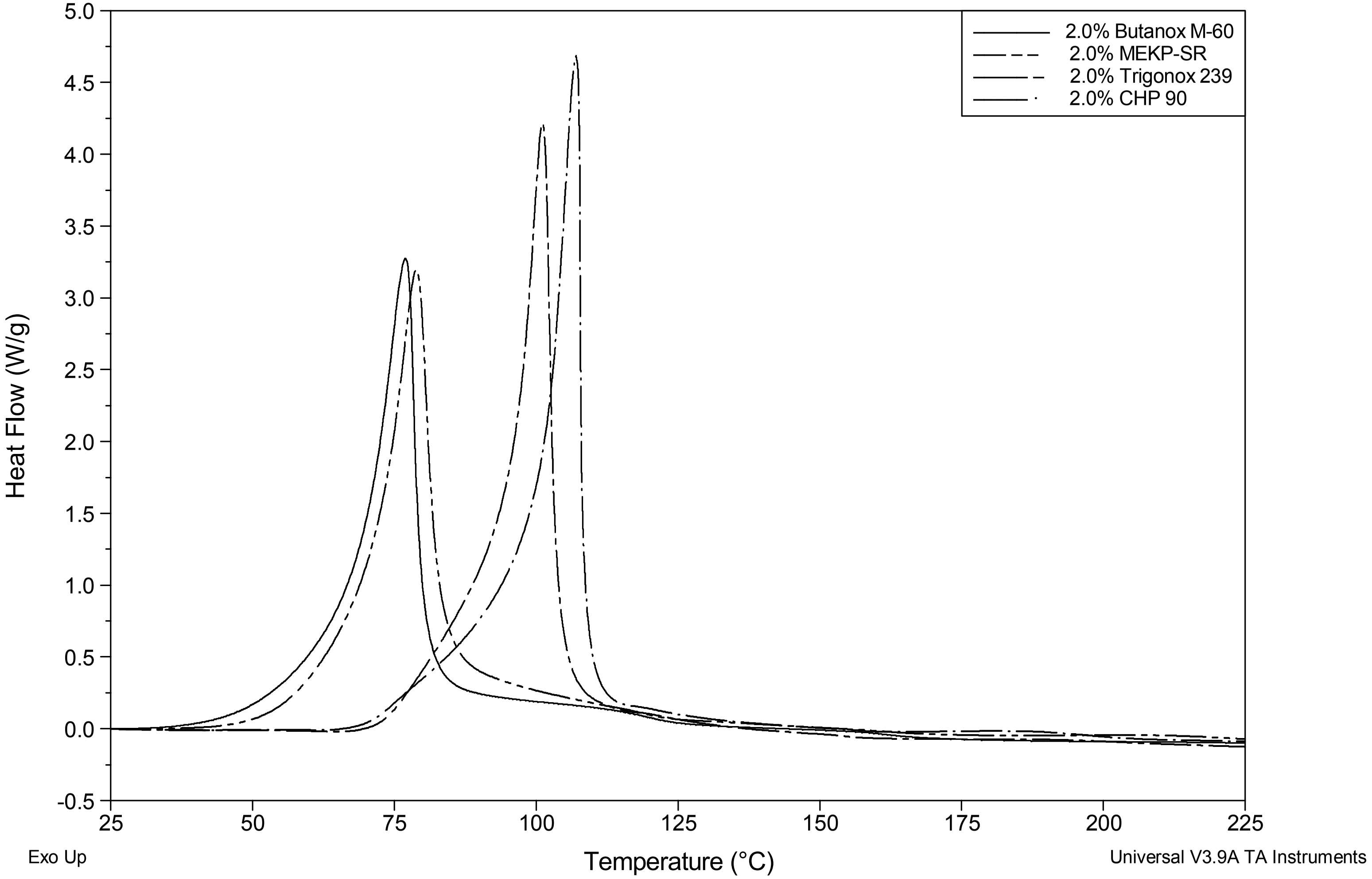

Figure A.7 First DSC heating run for Hetron 914 vinyl ester with alternative initiator types (25°C to 225°C range).

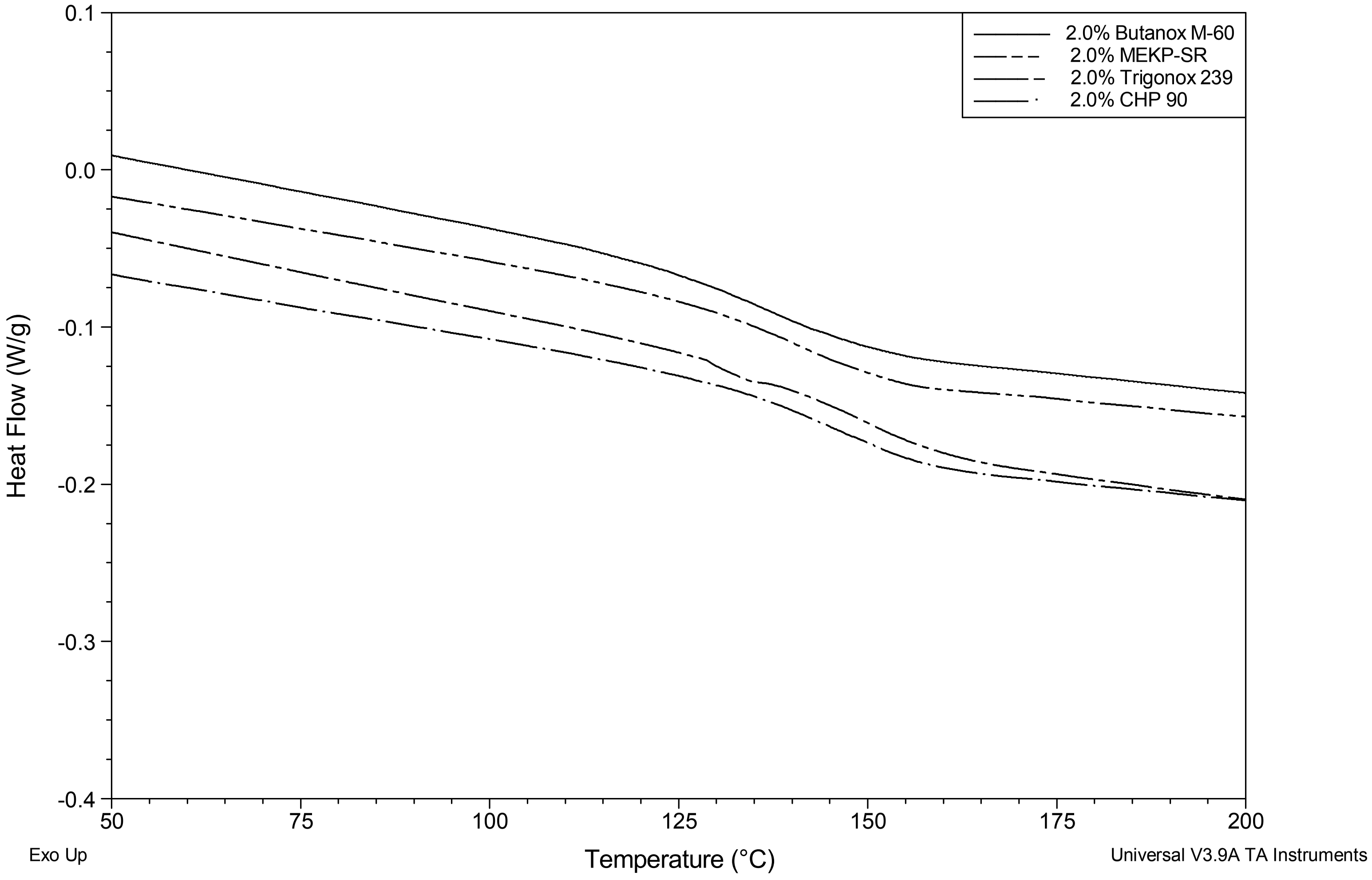

Figure A.8 **Second DSC heating run for Hetron 914 vinyl ester with alternative initiator types (50°C to 200°C range).**

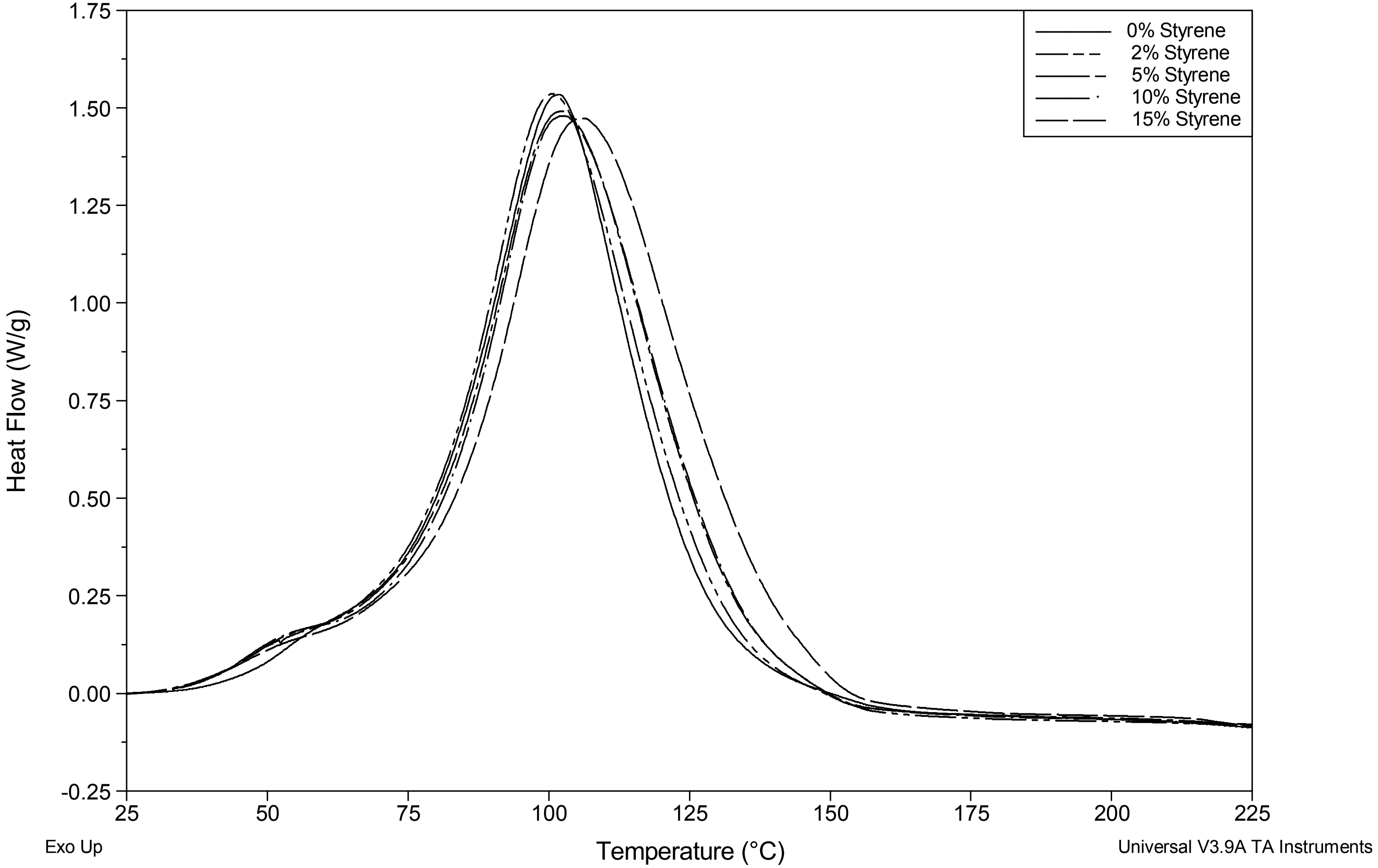

Figure A.9 First DSC heating run for Hetron 922 PAW vinyl ester with varying levels of additional styrene (25°C to 225°C range).

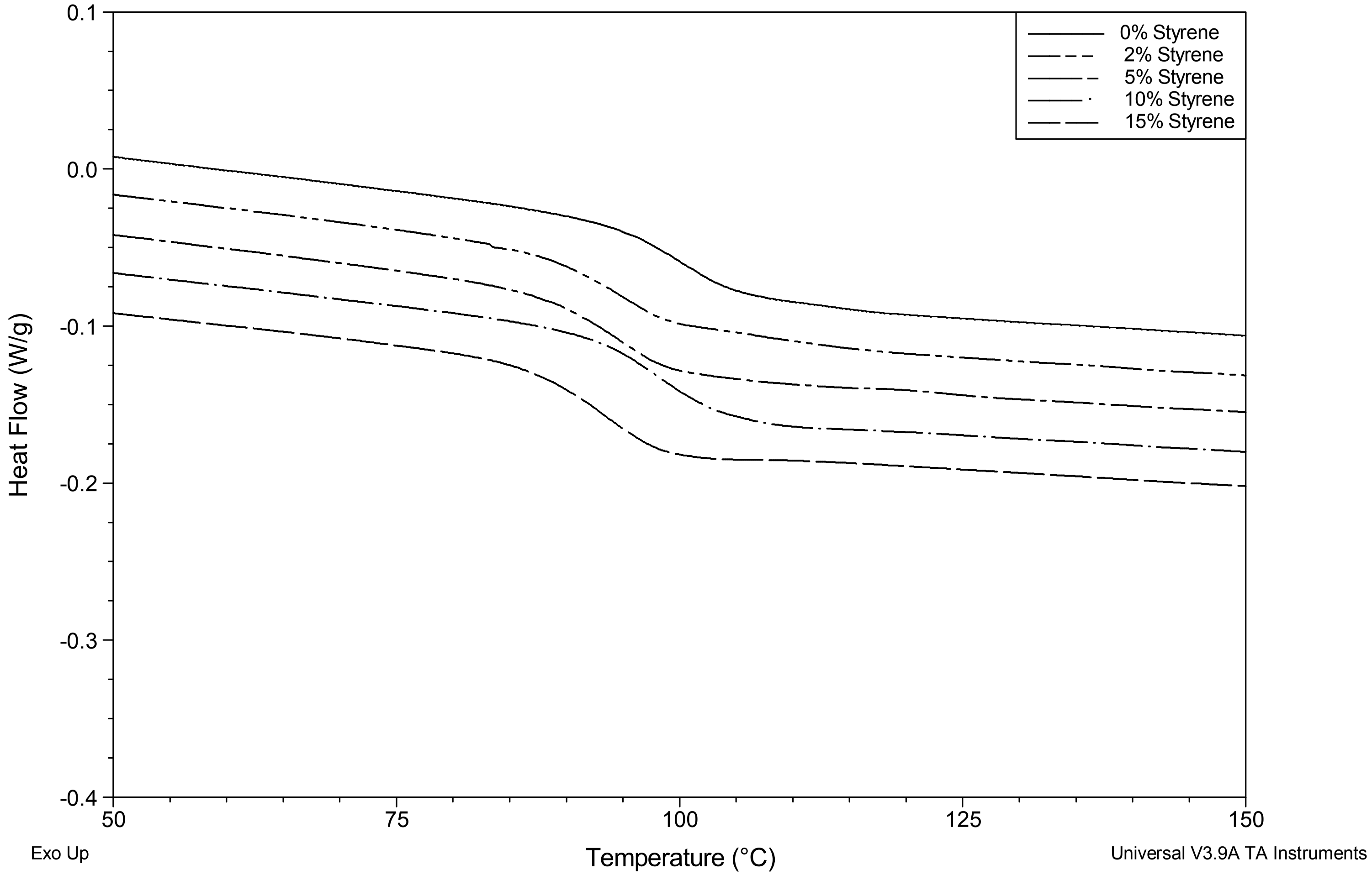

Figure A.10 **Second DSC heating run for Hetron 922 PAW vinyl ester with varying addition levels of styrene (50°C to 150°C range).**

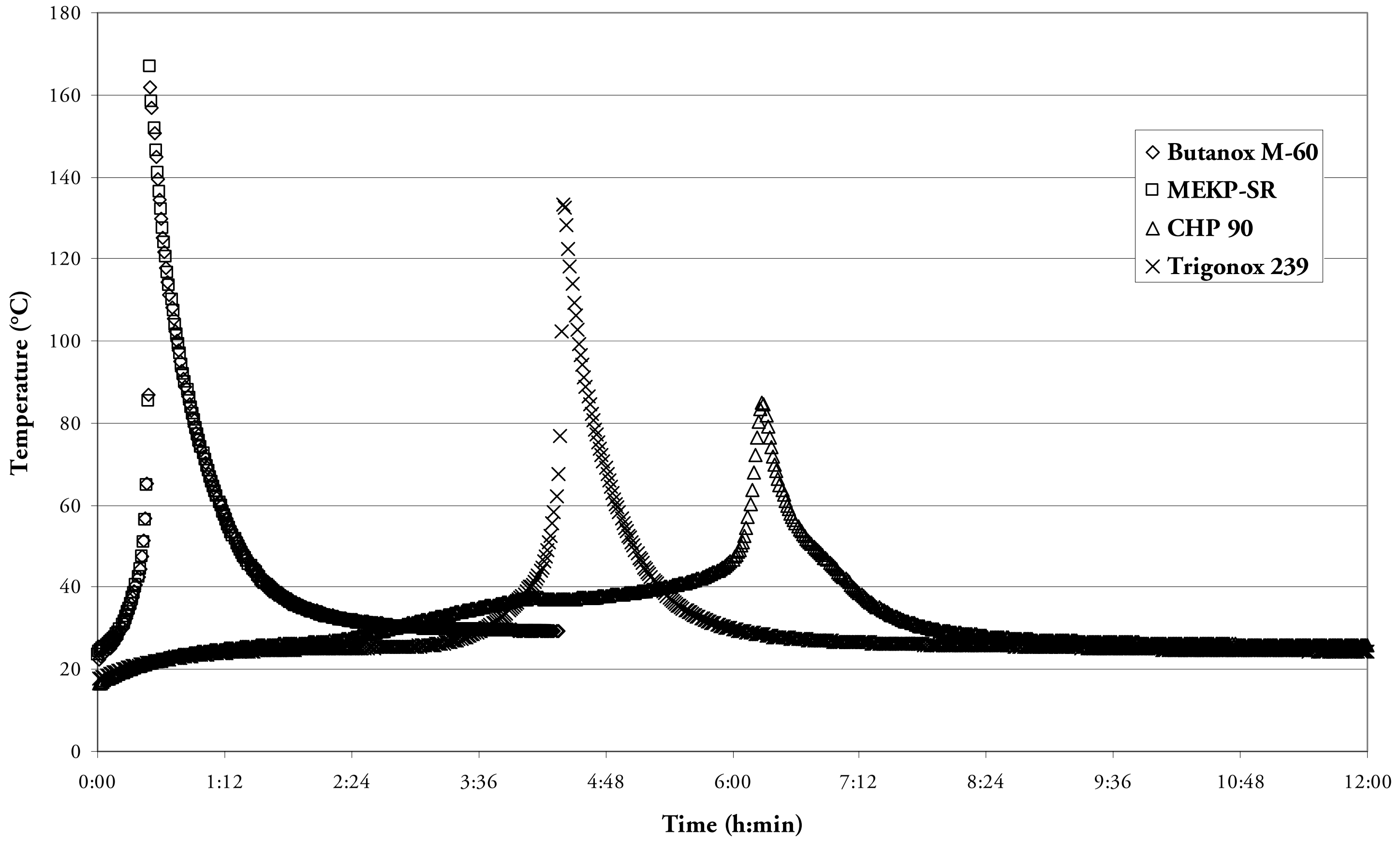

Figure A.11 Thermocouple scan of Hetron 922 PAW vinyl ester cured with alternative initiator types.

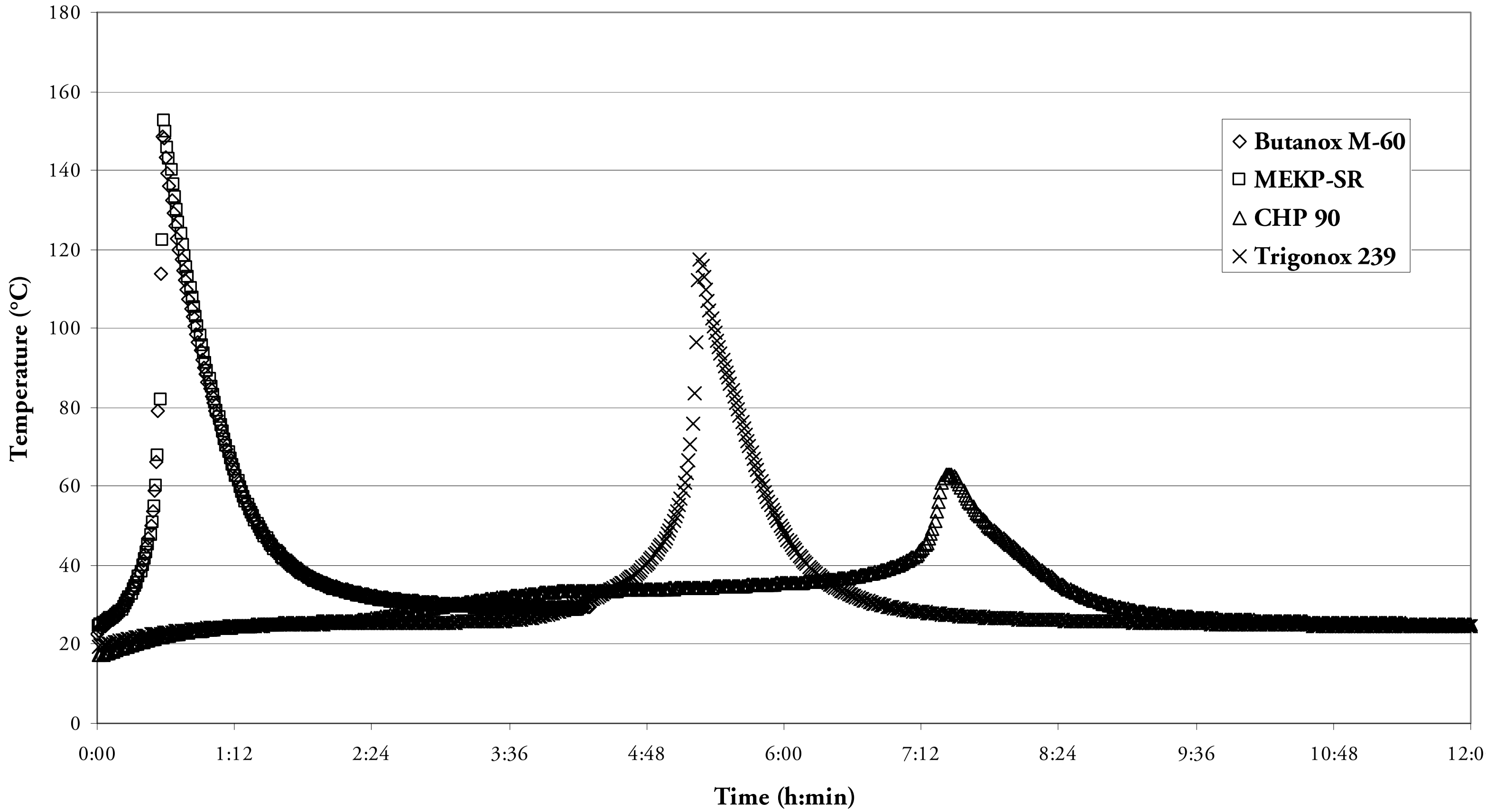

Figure A.12 Thermocouple scan of Hetron 922 PAW vinyl ester with 40% filler cured with alternative initiator types.

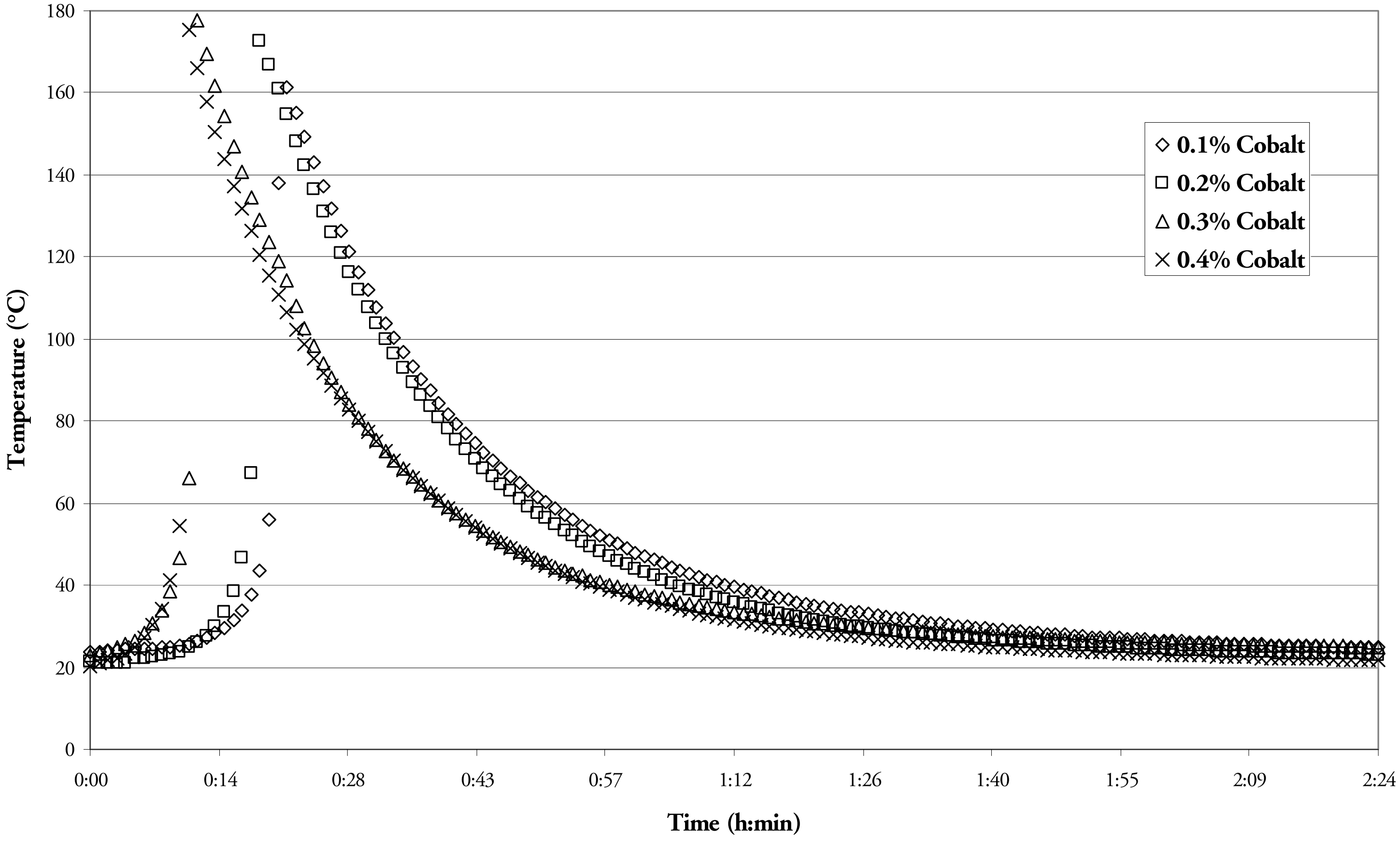

Figure A.13 Thermocouple scan of Hetron 914 vinyl ester cured with alternative levels of accelerator.

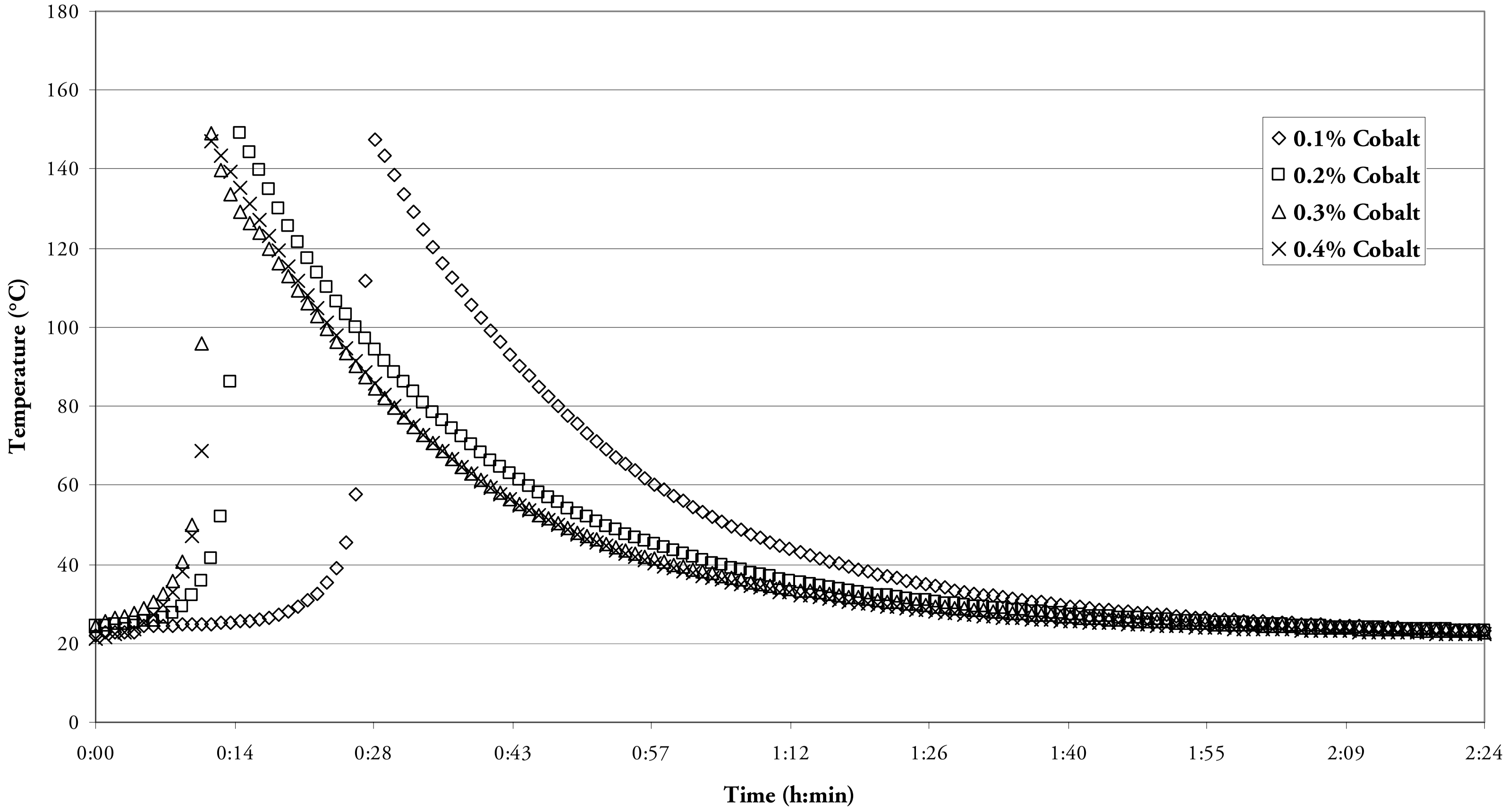

Figure A.14 Thermocouple scan of Hetron 914 vinyl ester with 40% filler cured with alternative levels of accelerator.

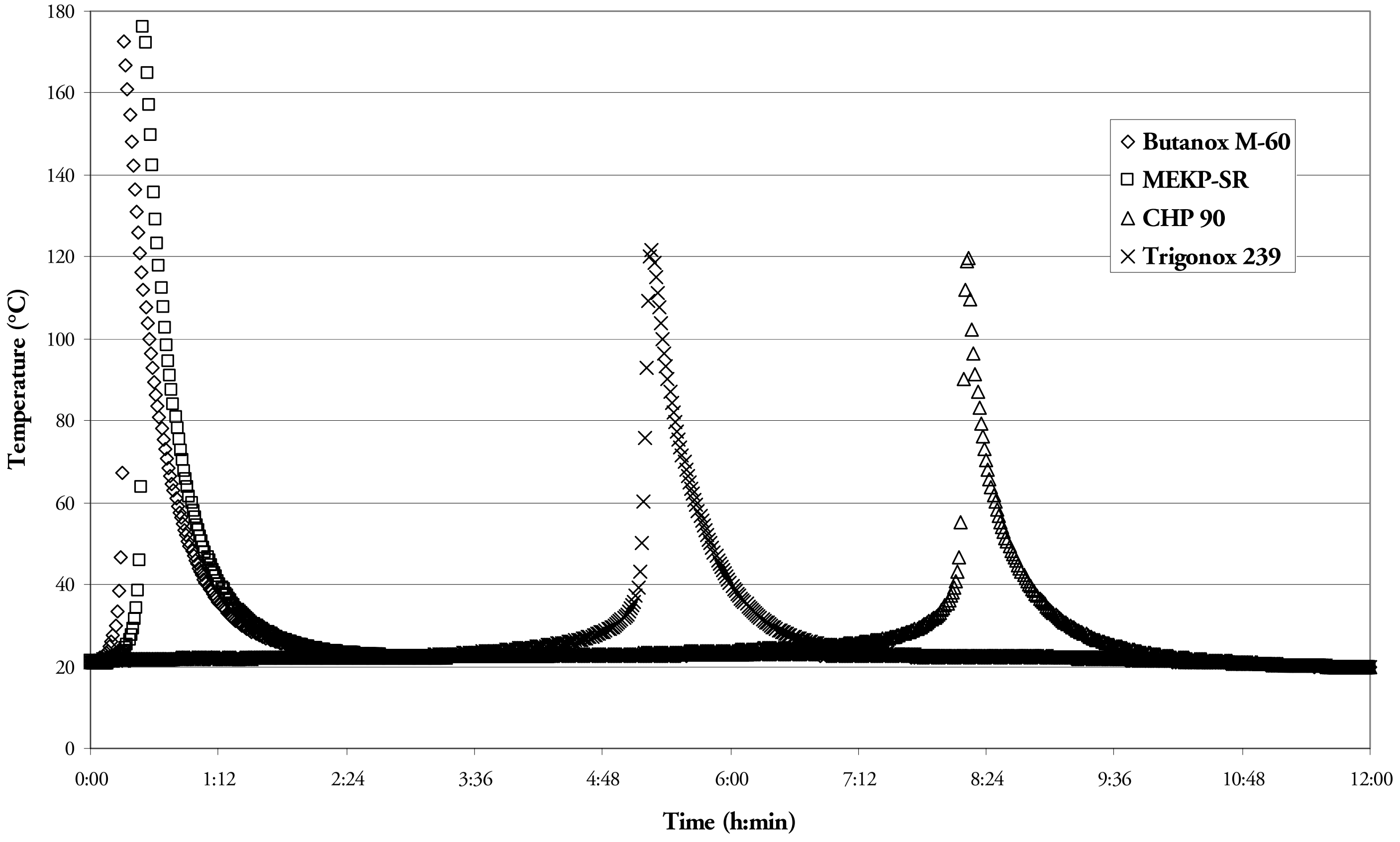

Figure A.15 Thermocouple scan of Hetron 914 vinyl ester cured with alternative initiator types.

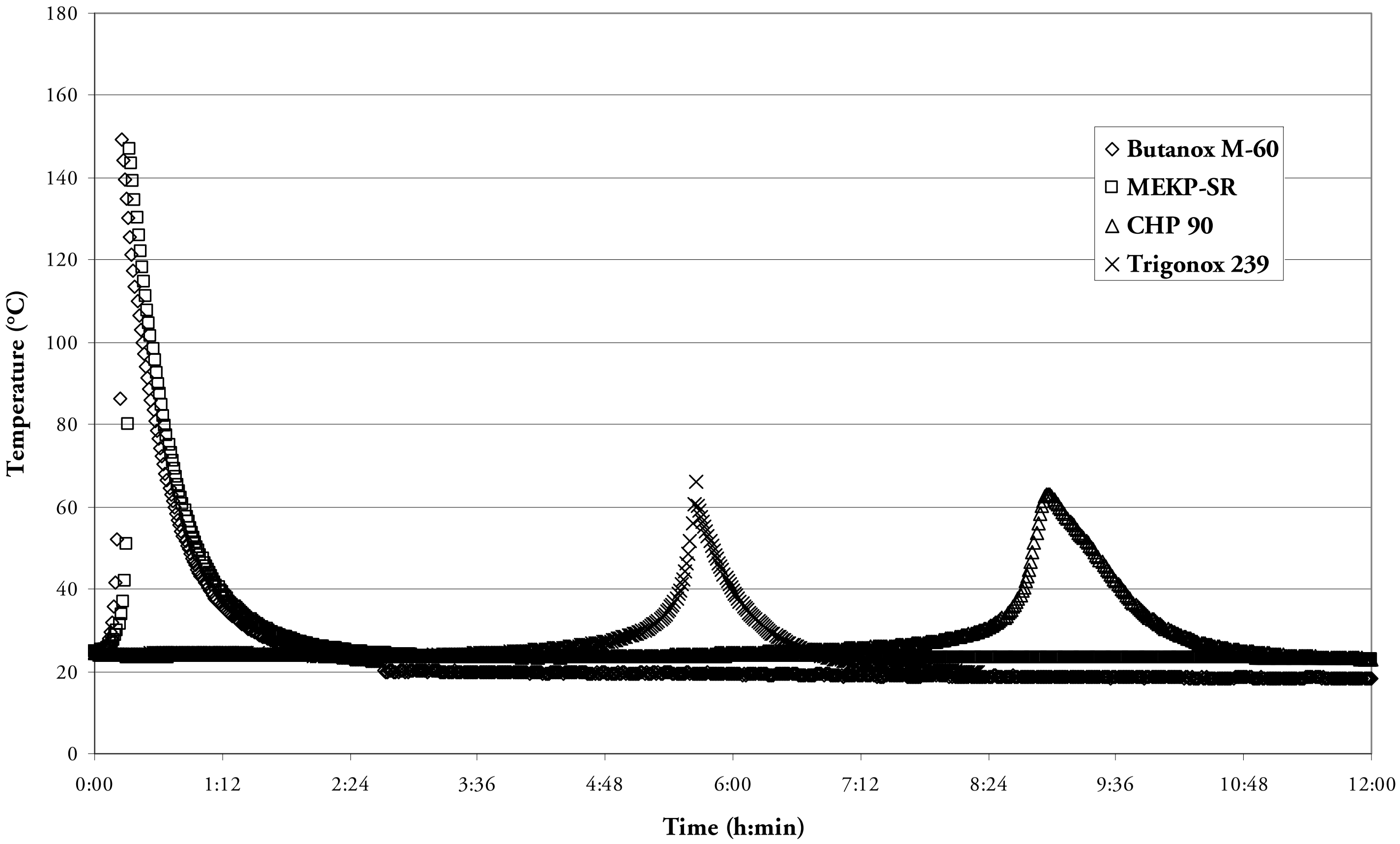

Figure A.16 Thermocouple scan of Hetron 914 vinyl ester with 40% filler cured with alternative initiator types.

APPENDIX B.

EXPERIMENTAL DATA AND RESULTS FOR THE DETERMINATION OF THE TENSILE PROPERTIES OF VINYL ESTER / CENOSPHERE COMPOSITES

This Appendix contains supplementary information relating to the characterisation of tensile properties presented in Chapter 5. The relationship of the sample ID and filler volume fraction are shown in Table B.1. The "USQI" of the sample ID numbers identifies the samples as internal USQ research and the "01" the year the research was initiated (eg: 2001). This system of sample identification was used throughout the characterisation program of mechanical properties.

Table B.1 Correlation of Sample ID with Filler Volume Fraction.

Sample ID	Filler Volume Fraction (%)	Sample ID	Filler Volume Fraction (%)
USQI-01-038-_	0	USQI-01-039-_	40
USQI-01-042-_	10	USQI-01-040-_	45
USQI-01-043-_	20	USQI-01-041-_	50
USQI-01-044-_	30		

Table B.2 presents the experimental result series details for tensile testing of the machined (T) and moulded specimens (DB). The "DE" suffix identifies the tests completed using the dual extensometer and the "SE" suffix the tests completed using the single extensometer. The experimental data and results corresponding with each series are presented overleaf. The mean, standard deviation (SD) and coefficient of variation (COV) were calculated for the data and results.

Table B.2 Tensile Testing Experimental Result Series Details.

Machined Specimens – "T"		Moulded Specimens – "DB"	
Test Type		Test Type	
Dual Extensometer	Single Extensometer	Dual Extensometer	Single Extensometer
038-T-DE	038-T-SE	038-DB-DE	038-DB-SE
042-T-DE	042-T-SE	042-DB-DE	042-DB-SE
043-T-DE	043-T-SE	043-DB-DE	043-DB-SE
044-T-DE	044-T-SE	044-DB-DE	044-DB-SE
039-T-DE	039-T-SE	039-DB-DE	039-DB-SE
040-T-DE	040-T-SE	040-DB-DE	040-DB-SE
041-T-DE	041-T-SE	041-DB-DE	041-DB-SE

Sample ID Number: USQI-01-038-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	11.48	4.23	48.54	258	0.15	0.051	0.347
2	10.98	4.25	46.72	228	0.14	0.058	0.390
3	10.96	4.27	46.80	252	0.15	0.057	0.373
4	11.11	4.23	47.05	275	0.15	0.054	0.364
5	11.22	4.13	46.34	238	0.14	0.052	0.358
6	10.93	4.19	45.83	243	0.15	0.057	0.378
Mean	11.11	4.22	46.88	249	0.15	0.055	0.368
SD	0.21	0.05	0.92	17	0.01	0.003	0.015
COV	1.9%	1.2%	2.0%	6.6%	3.5%	5.3%	4.1%

Sample ID Number: USQI-01-038-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	11.48	4.23	48.54	2998	62	2.14	3438
2	10.98	4.25	46.72	2748	59	2.00	3363
3	10.96	4.27	46.80	2813	60	1.97	3608
4	11.11	4.23	47.05	2726	58	1.96	3517
5	11.22	4.13	46.34	2925	63	2.26	3355
Mean	11.15	4.22	47.09	2842	60.4	2.07	3456
SD	0.21	0.05	0.85	117	2.1	0.13	107
COV	1.9%	1.3%	1.8%	4.1%	3.4%	6.3%	3.1%

Sample ID Number: USQI-01-039-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	10.44	4.24	44.28	355	0.14	0.048	0.336
2	10.37	4.25	44.05	336	0.15	0.046	0.313
3	10.21	4.11	41.93	300	0.14	0.047	0.321
4	10.37	4.20	43.52	339	0.15	0.048	0.313
5	10.33	4.18	43.14	330	0.15	0.046	0.308
6	10.40	4.22	43.84	331	0.15	0.051	0.328
Mean	10.35	4.20	43.46	332	0.15	0.048	0.320
SD	0.08	0.05	0.85	18	0.01	0.002	0.011
COV	0.8%	1.2%	2.0%	5.4%	3.5%	3.9%	3.3%

Sample ID Number: USQI-01-039-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	10.44	4.24	44.28	1241	28	0.80	4994
2	10.37	4.25	44.05	1256	28	0.87	5004
3	10.21	4.11	41.93	1237	29	0.96	4987
4	10.37	4.20	43.52	1258	29	0.87	4917
5	10.33	4.18	43.14	1249	29	0.89	5111
Mean	10.34	4.20	43.38	1248	28.6	0.88	5003
SD	0.08	0.06	0.93	9	0.55	0.06	70
COV	0.8%	1.3%	2.1%	0.7%	1.9%	6.5%	1.4%

Sample ID Number: USQI-01-040-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	10.27	4.20	43.18	336	0.15	0.047	0.321
2	10.18	4.20	42.74	353	0.15	0.047	0.314
3	10.16	4.20	42.69	361	0.15	0.047	0.320
4	10.30	4.21	43.38	341	0.15	0.045	0.316
5	10.22	4.21	43.06	342	0.15	0.048	0.317
6	10.26	4.15	42.53	340	0.15	0.043	0.308
Mean	10.23	4.20	42.93	346	0.15	0.046	0.316
SD	0.05	0.02	0.33	9	0.00	0.002	0.005
COV	0.5%	0.5%	0.8%	2.7%	0.0%	4.0%	1.5%

Sample ID Number: USQI-01-040-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	10.27	4.20	43.18	1152	27	0.75	5374
2	10.18	4.20	42.74	1116	26	0.80	5165
3	10.16	4.20	42.69	1125	26	0.64	5286
4	10.30	4.21	43.38	1137	26	0.66	5357
5	10.22	4.21	43.06	1131	26	0.62	5237
Mean	10.23	4.20	43.01	1132	26.2	0.69	5284
SD	0.06	0.01	0.29	14	0.4	0.08	86
COV	0.6%	0.1%	0.7%	1.2%	1.7%	11.1%	1.6%

Sample ID Number: USQI-01-041-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	10.14	4.24	42.96	343	0.14	0.042	0.296
2	10.20	4.18	42.62	350	0.14	0.045	0.313
3	10.31	4.19	43.20	369	0.15	0.043	0.287
4	10.09	4.15	41.84	339	0.15	0.045	0.304
5	10.19	4.18	42.64	320	0.15	0.045	0.307
6	10.19	4.27	43.48	345	0.15	0.047	0.308
Mean	10.19	4.20	42.79	344	0.15	0.045	0.303
SD	0.07	0.04	0.57	16	0.01	0.002	0.009
COV	0.7%	1.1%	1.3%	4.6%	3.5%	4.0%	3.1%

Sample ID Number: USQI-01-041-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	10.14	4.24	42.96	1006	23	0.52	5087
2	10.20	4.18	42.62	1027	24	0.61	5135
3	10.31	4.19	43.20	1030	24	0.53	5272
4	10.09	4.15	41.84	1010	24	0.62	4992
5	10.19	4.18	42.64	1027	24	0.60	5031
Mean	10.19	4.19	42.65	1020	23.8	0.58	5103
SD	0.08	0.03	0.51	11	0.4	0.05	109
COV	0.8%	0.8%	1.2%	1.1%	1.9%	8.2%	2.1%

Sample ID Number: USQI-01-042-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	10.79	4.23	45.63	272	0.15	0.054	0.353
2	10.73	4.18	44.89	282	0.15	0.054	0.357
3	10.71	4.20	45.00	266	0.15	0.057	0.372
4	11.00	4.15	45.70	277	0.15	0.057	0.359
5	10.79	4.21	45.46	271	0.15	0.052	0.356
6	10.90	4.18	45.56	257	0.14	0.051	0.358
Mean	10.82	4.19	45.37	271	0.15	0.054	0.359
SD	0.11	0.03	0.34	9	0.00	0.002	0.007
COV	1.0%	0.7%	0.8%	3.2%	2.8%	4.6%	1.8%

Sample ID Number: USQI-01-042-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	10.79	4.23	45.63	2379	52	2.02	3627
2	10.73	4.18	44.89	2241	50	1.91	3671
3	10.71	4.20	45.00	2159	48	1.75	3651
4	11.00	4.15	45.70	2238	49	1.81	3670
5	10.79	4.21	45.46	2318	51	1.98	3629
Mean	10.80	4.19	45.34	2267	50.0	1.89	3650
SD	0.12	0.03	0.37	84	1.6	0.11	21
COV	1.1%	0.7%	0.8%	3.7%	3.2%	6.0%	0.6%

Sample ID Number: USQI-01-043-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	10.60	4.25	45.01	291	0.15	0.051	0.338
2	10.53	4.15	43.68	282	0.15	0.059	0.343
3	10.74	4.17	44.80	295	0.15	0.052	0.329
4	10.54	4.24	44.70	301	0.15	0.049	0.336
5	10.60	4.27	45.21	290	0.15	0.054	0.352
6	10.80	4.28	46.24	299	0.15	0.057	0.368
Mean	10.64	4.23	44.94	293	0.15	0.054	0.344
SD	0.11	0.05	0.83	7	0.00	0.004	0.014
COV	1.0%	1.3%	1.8%	2.4%	0.0%	7.0%	4.0%

Sample ID Number: USQI-01-043-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	10.60	4.25	45.01	1867	41	1.78	4165
2	10.53	4.15	43.68	1837	42	1.77	4063
3	10.74	4.17	44.80	1875	42	1.73	4145
4	10.54	4.24	44.70	1857	41	1.77	4162
5	10.60	4.27	45.21	1925	42	1.74	4116
Mean	10.60	4.22	44.68	1872	41.6	1.76	4130
SD	0.08	0.05	0.59	33	0.5	0.02	42
COV	0.8%	1.3%	1.3%	1.7%	1.3%	1.2%	1.0%

Sample ID Number: USQI-01-044-T-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.99	4.23	42.24	292	0.15	0.050	0.337
2	10.37	4.24	44.00	309	0.15	0.048	0.322
3	10.15	4.26	43.24	311	0.15	0.054	0.353
4	10.27	4.26	43.72	309	0.15	0.052	0.340
5	10.24	4.16	42.56	310	0.15	0.049	0.338
6	10.11	4.17	42.12	286	0.15	0.050	0.340
Mean	10.19	4.22	42.98	303	0.15	0.051	0.338
SD	0.13	0.04	0.79	11	0.00	0.002	0.010
COV	1.3%	1.0%	1.8%	3.6%	0.0%	4.3%	2.9%

Sample ID Number: USQI-01-044-T-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.99	4.23	42.24	1416	33	1.21	4616
2	10.37	4.24	44.00	1506	34	1.33	4593
3	10.15	4.26	43.24	1382	32	1.04	4608
4	10.27	4.26	43.72	1505	34	1.44	4542
5	10.24	4.16	42.56	1450	34	1.37	4720
Mean	10.20	4.23	43.15	1452	33.4	1.28	4616
SD	0.14	0.04	0.75	55	0.9	0.16	65
COV	1.4%	1.0%	1.7%	3.8%	2.7%	12.3%	1.4%

Sample ID Number: USQI-01-038-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.76	4.28	41.77	233	0.15	0.056	0.367
2	9.81	4.26	41.81	221	0.15	0.058	0.386
3	9.73	4.33	42.08	223	0.14	0.050	0.360
4	9.76	4.24	41.36	213	0.14	0.053	0.366
5	9.81	4.27	41.87	214	0.15	0.053	0.370
Mean	9.77	4.28	41.78	221	0.15	0.054	0.370
SD	0.04	0.03	0.26	8	0.01	0.003	0.010
COV	0.4%	0.8%	0.6%	3.7%	3.8%	5.7%	2.6%

Sample ID Number: USQI-01-038-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain	Modulus (MPa)
1	9.76	4.28	41.77	1937	46	1.50	3212
2	9.81	4.26	41.81	1595	38	1.21	3228
3	9.73	4.33	42.08	1325	31	0.96	3339
4	9.76	4.24	41.36	1411	34	1.01	3538
5	9.81	4.27	41.87	1355	32	1.01	3290
Mean	9.77	4.28	41.78	1525	36.2	1.14	3321
SD	0.04	0.03	0.26	253	6.1	0.22	131
COV	0.4%	0.8%	0.6%	16.6%	16.8%	19.7%	4.0%

Sample ID Number: USQI-01-039-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.80	4.18	41.01	312	0.14	0.047	0.326
2	9.92	4.26	42.28	320	0.15	0.050	0.332
3	9.78	4.08	29.89	306	0.15	0.045	0.297
4	9.79	4.26	41.67	318	0.15	0.045	0.309
5	9.81	4.16	40.81	314	0.15	0.050	0.327
6	9.86	4.21	41.52	302	0.15	0.051	0.326
Mean	9.83	4.19	39.53	312	0.15	0.048	0.320
SD	0.05	0.07	4.75	7	0.00	0.003	0.014
COV	0.5%	1.6%	12.0%	2.2%	2.8%	5.6%	4.2%

Sample ID Number: USQI-01-039-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.80	4.18	41.01	943	23	0.47	5084
2	9.92	4.26	42.28	982	23	0.52	4812
3	9.78	4.08	29.89	1071	27	0.73	4892
4	9.79	4.26	41.67	1077	26	0.65	4966
5	9.81	4.16	40.81	1071	26	0.66	5003
Mean	9.82	4.19	39.13	1029	25	0.61	4951
SD	0.06	0.08	5.20	62	2	0.11	104
COV	0.6%	1.8%	13.3%	6.0%	7.5%	17.7%	2.1%

Sample ID Number: USQI-01-040-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.92	4.15	41.15	329	0.15	0.045	0.315
2	9.86	4.25	41.89	312	0.14	0.046	0.315
3	9.95	4.25	42.33	326	0.15	0.047	0.315
4	9.96	4.15	41.37	349	0.15	0.047	0.310
5	9.93	4.10	40.68	332	0.15	0.046	0.307
6	9.87	4.31	42.57	333	0.15	0.048	0.313
Mean	9.92	4.20	41.67	330	0.15	0.047	0.313
SD	0.04	0.08	0.73	12	0.00	0.001	0.003
COV	0.4%	1.9%	1.7%	3.6%	2.8%	2.3%	1.1%

Sample ID Number: USQI-01-040-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.92	4.15	41.15	978	24	0.55	5123
2	9.86	4.25	41.89	928	22	0.52	4846
3	9.95	4.25	42.33	932	22	0.52	4878
4	9.96	4.15	41.37	969	23	0.48	5238
5	9.93	4.10	40.68	1002	25	0.55	5260
6	9.87	4.31	42.57	1048	25	0.63	4736
Mean	9.92	4.20	41.67	976	23.5	0.54	5014
SD	0.04	0.08	0.73	45	1.4	0.05	222
COV	0.4%	1.9%	1.7%	4.6%	5.9%	9.3%	4.4%

Sample ID Number: USQI-01-041-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.97	4.08	40.63	318	0.15	0.045	0.298
2	9.94	4.27	42.40	335	0.15	0.047	0.311
3	9.96	4.20	41.81	337	0.15	0.044	0.300
4	9.96	4.23	42.14	359	0.15	0.047	0.305
5	9.95	4.21	41.89	312	0.15	0.042	0.291
6	9.93	4.28	42.52	331	0.14	0.047	0.316
Mean	9.95	4.21	41.90	332	0.15	0.045	0.304
SD	0.01	0.07	0.68	16	0.00	0.002	0.009
COV	0.1%	1.7%	1.6%	5.0%	2.8%	4.6%	3.0%

Sample ID Number: USQI-01-041-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.97	4.08	40.63	771	19	0.44	4718
2	9.94	4.27	42.40	822	19	0.43	4857
3	9.96	4.20	41.81	819	19	0.42	4942
4	9.96	4.23	42.14	939	22	0.51	5051
5	9.95	4.21	41.89	865	21	0.47	4972
6	9.93	4.28	42.52	802	19	0.41	4757
Mean	9.95	4.21	41.90	836	19.8	0.45	4883
SD	0.01	0.07	0.68	59	1.3	0.04	129
COV	0.1%	1.7%	1.6%	7.0%	6.7%	8.3%	2.6%

Sample ID Number: USQI-01-042-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.85	4.19	41.30	251	0.15	0.055	0.361
2	9.89	4.21	41.64	255	0.15	0.056	0.360
3	9.87	4.26	42.08	256	0.14	0.053	0.362
4	9.85	4.26	41.95	246	0.15	0.050	0.348
5	9.84	4.27	42.00	264	0.15	0.050	0.364
6	9.82	4.24	41.59	241	0.15	0.056	0.372
Mean	9.85	4.24	41.76	252	0.15	0.053	0.361
SD	0.02	0.03	0.30	8	0.00	0.003	0.008
COV	0.2%	0.8%	0.7%	3.2%	2.8%	5.3%	2.1%

Sample ID Number: USQI-01-042-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.85	4.19	41.30	1434	35	1.05	3923
2	9.89	4.21	41.64	1752	42	1.39	3897
3	9.87	4.26	42.08	1439	34	1.00	3857
4	9.85	4.26	41.95	1856	44	1.53	3776
5	9.84	4.27	42.00	1882	45	1.59	3803
6	9.82	4.24	41.59	1674	40	1.33	3577
Mean	9.85	4.24	41.76	1673	40.0	1.32	3806
SD	0.02	0.03	0.30	198	4.6	0.24	125
COV	0.2%	0.8%	0.7%	11.8%	11.5%	18.5%	3.3%

Sample ID Number: USQI-01-043-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.84	4.06	40.00	253	0.15	0.050	0.343
2	9.78	4.12	40.29	274	0.15	0.055	0.369
3	9.86	4.08	40.22	274	0.14	0.050	0.345
4	9.88	4.11	40.65	271	0.15	0.054	0.356
5	9.87	3.94	38.91	264	0.15	0.053	0.345
Mean	9.85	4.06	40.01	267	0.15	0.052	0.352
SD	0.04	0.07	0.66	9	0.00	0.002	0.011
COV	0.4%	1.8%	1.6%	3.3%	3.0%	4.4%	3.1%

Sample ID Number: USQI-01-043-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.84	4.06	40.00	1423	35	1.09	4596
2	9.78	4.12	40.29	1522	38	1.33	4508
3	9.86	4.08	40.22	1611	40	1.61	4146
4	9.88	4.11	40.65	1558	38	1.45	4480
5	9.87	3.94	38.91	1355	35	1.06	4436
Mean	9.85	4.06	40.01	1494	37.2	1.31	4433
SD	0.04	0.07	0.66	104	2.2	0.23	171
COV	0.4%	1.8%	1.6%	6.9%	5.8%	18.0%	3.9%

Sample ID Number: USQI-01-044-DB-DE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Axial Strain (%)	Transverse Strain (%)	Poisson's Ratio
1	9.89	4.19	41.45	287	0.15	0.050	0.328
2	9.73	4.20	40.86	290	0.15	0.049	0.337
3	9.89	4.27	42.20	293	0.15	0.052	0.361
4	9.88	4.26	42.04	301	0.15	0.049	0.337
5	9.96	4.17	41.52	289	0.15	0.048	0.327
6	9.83	4.29	42.12	288	0.15	0.052	0.333
Mean	9.86	4.23	41.70	291	0.15	0.050	0.337
SD	0.08	0.05	0.52	5	0.00	0.002	0.012
COV	0.8%	1.2%	1.2%	1.8%	0.0%	3.3%	3.7%

Sample ID Number: USQI-01-044-DB-SE

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	9.89	4.19	41.45	1355	33	1.06	4559
2	9.73	4.20	40.86	1271	31	0.87	4510
3	9.89	4.27	42.20	1351	32	1.20	4459
4	9.88	4.26	42.04	1219	29	0.76	4438
5	9.96	4.17	41.52	1288	31	0.92	4569
6	9.83	4.29	42.12	1315	31	1.02	4358
Mean	9.86	4.23	41.70	1300	31.2	0.97	4482
SD	0.08	0.05	0.52	52	1.3	0.15	80
COV	0.8%	1.2%	1.2%	4.0%	4.3%	15.9%	1.8%

APPENDIX C.

EXPERIMENTAL DATA AND RESULTS FOR THE DETERMINATION OF THE COMPRESSION PROPERTIES OF VINYL ESTER / CENOSPHERE COMPOSITES

This Appendix contains supplementary information relating to the characterisation of compressive properties presented in Chapter 5. The experimental result series details for compressive testing and the associated filler volume fraction of the series are shown in Table C.1. The adopted system of sample identification outlined in Appendix B was continued. The experimental data and results corresponding with each series are presented overleaf. The mean, standard deviation (SD) and coefficient of variation (COV) were calculated for the data and results.

Table C.1 Compressive Testing Experimental Result Series Details.

Sample ID	Filler Volume Fraction (%)	Sample ID	Filler Volume Fraction (%)
USQI-01-038-C	0	USQI-01-039-C	40
USQI-01-042-C	10	USQI-01-040-C	45
USQI-01-043-C	20	USQI-01-041-C	50
USQI-01-044-C	30		

Sample ID Number: USQI-01-038-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	74.62	36.91	1069.79	94942	88.75	5.39	2356
2	74.80	36.87	1067.67	93228	87.32	5.02	2383
3	74.07	36.94	1071.72	93753	87.48	5.49	2319
4	75.17	36.91	1070.18	94559	88.36	5.39	2332
Mean	74.67	36.91	1069.84	94121	87.98	5.32	2348
SD	0.46	0.02	1.45	671	0.60	0.18	24
COV	0.6%	0.1%	0.1%	0.7%	0.7%	3.4%	1.0%

Sample ID Number: USQI-01-039-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	74.03	36.83	1065.16	81140	76.18	3.50	3080
2	74.75	36.74	1059.96	81807	77.18	3.61	3022
3	74.57	36.91	1069.79	82163	76.80	3.63	3109
4	74.10	36.80	1063.62	81697	76.81	3.61	3051
Mean	74.36	36.82	1064.63	81702	76.74	3.59	3066
SD	0.35	0.07	4.07	424	0.41	0.06	37
COV	0.5%	0.2%	0.4%	0.5%	0.5%	1.6%	1.2%

Sample ID Number: USQI-01-040-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	74.83	36.38	1039.29	79166	76.17	3.27	3242
2	75.79	36.33	1036.81	77667	74.91	3.15	3268
3	74.81	37.07	1079.09	82365	76.33	3.48	3145
4	74.75	36.59	1051.51	79474	75.58	3.55	3207
Mean	75.05	36.59	1051.68	79668	75.75	3.36	3216
SD	0.50	0.34	19.37	1964	0.64	0.19	53
COV	0.7%	0.9%	1.8%	2.5%	0.9%	5.5%	1.7%

Sample ID Number: USQI-01-041-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	75.03	37.04	1077.34	74872	69.50	3.02	3162
2	74.61	37.74	1118.65	77142	68.96	3.08	3075
3	74.54	37.17	1085.11	73613	67.84	3.20	3005
4	74.78	36.20	1029.22	70239	68.24	2.79	3225
Mean	74.74	37.04	1077.58	73967	68.64	3.02	3117
SD	0.22	0.64	36.89	2882	0.74	0.17	97
COV	0.3%	1.7%	3.4%	3.9%	1.1%	5.7%	3.1%

Sample ID Number: USQI-01-042-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	75.18	36.45	1043.48	88562	84.87	4.84	2287
2	74.35	36.57	1050.56	87998	83.76	4.69	2551
3	74.37	36.31	1035.67	86738	83.75	4.62	2547
4	73.57	36.48	1045.20	86454	82.72	4.81	2176
5	74.84	36.64	1054.39	90623	85.95	4.62	2643
Mean	74.46	36.49	1045.86	88075	84.21	4.72	2441
SD	0.61	0.13	7.16	1670	1.23	0.10	199
COV	0.8%	0.3%	0.7%	1.9%	1.5%	2.2%	8.1%

Sample ID Number: USQI-01-043-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	74.55	36.64	1054.39	88918	84.33	4.56	2777
2	75.00	36.62	1053.24	88478	84.01	4.36	2838
3	74.90	36.37	1038.72	87540	84.28	4.47	2779
4	74.91	36.49	1045.96	86556	82.75	4.42	2792
Mean	74.84	36.53	1048.08	87873	83.84	4.45	2797
SD	0.20	0.13	7.27	1049	0.74	0.08	28
COV	0.3%	0.3%	0.7%	1.2%	0.9%	1.9%	1.0%

Sample ID Number: USQI-01-044-C

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Height (mm)	Diameter (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	73.85	36.18	1028.08	82254	80.01	4.20	2415
2	73.24	36.71	1058.23	85112	80.43	4.17	2838
3	72.75	36.35	1037.57	83405	80.38	4.38	2557
4	74	36.16	1026.94	81767	79.62	4.00	2925
5	73.78	36.63	1053.81	86205	81.80	4.13	2890
Mean	73.46	36.41	1040.93	83749	80.45	4.18	2725
SD	0.46	0.25	14.47	1882	0.82	0.14	226
COV	0.6%	0.7%	1.4%	2.2%	1.0%	3.3%	8.3%

APPENDIX D.

EXPERIMENTAL DATA AND RESULTS FOR THE DETERMINATION OF THE FLEXURE PROPERTIES OF VINYL ESTER / CENOSPHERE COMPOSITES

This Appendix contains supplementary information relating to the characterisation of compressive properties presented in Chapter 5. The experimental result series details for flexure testing and the associated filler volume fraction of the series are shown in Table D.1. The adopted system of sample identification outlined in Appendix B was continued. The experimental data and results corresponding with each series are presented overleaf. The mean, standard deviation (SD) and coefficient of variation (COV) were calculated for the data and results.

Table D.1 Flexure Testing Experimental Result Series Details.

Sample ID	Filler Volume Fraction (%)	Sample ID	Filler Volume Fraction (%)
USQI-01-038-F	0	USQI-01-039-F	40
USQI-01-042-F	10	USQI-01-040-F	45
USQI-01-043-F	20	USQI-01-041-F	50
USQI-01-044-F	30		

Sample ID Number: USQI-01-038-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	0

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.49	8.99	139.26	523.7	90.36	3.03	3458
2	15.34	9.18	140.82	465.1	77.72	2.50	3464
3	15.46	9.25	143.01	667.9	109.06	4.07	3108
4	15.31	9.25	141.62	525.6	86.66	2.90	3356
5	15.33	9.14	140.12	570.6	96.23	3.28	3148
Mean	15.39	9.16	140.96	550.6	92.01	3.16	3307
SD	0.08	0.11	1.44	75.5	11.66	0.58	169
COV	0.5%	1.2%	1.0%	13.7%	12.7%	18.5%	5.1%

Sample ID Number: USQI-01-039-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	40

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.44	9.18	141.74	293.8	48.77	1.16	4679
2	15.58	9.13	142.25	263.5	43.83	1.01	4737
3	15.65	9.22	144.29	270.9	43.99	0.97	4680
4	15.52	9.16	142.16	264.4	43.85	0.96	4705
5	15.44	9.16	141.43	287.2	47.89	1.12	4706
Mean	15.53	9.17	142.37	276.0	45.67	1.04	4701
SD	0.09	0.03	1.12	13.8	2.45	0.09	24
COV	0.6%	0.4%	0.8%	5.0%	5.4%	8.7%	0.5%

Sample ID Number: USQI-01-040-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	45

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.60	9.24	144.14	258.5	41.92	0.89	4975
2	15.60	9.16	142.90	247.1	40.78	0.84	4981
3	15.62	9.20	143.70	240.2	39.24	0.78	4997
4	15.65	9.08	142.10	235.7	39.45	0.80	4938
5	15.58	9.21	143.49	238.0	38.91	0.79	5046
Mean	15.61	9.18	143.27	243.9	40.06	0.82	4987
SD	0.03	0.06	0.79	9.2	1.26	0.05	39
COV	0.2%	0.7%	0.6%	3.8%	3.1%	5.5%	0.8%

Sample ID Number: USQI-01-041-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	50

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.62	9.20	143.70	219.1	35.79	0.71	5023
2	15.65	9.14	143.04	225.9	37.33	0.74	5004
3	15.68	9.14	143.32	190.5	31.42	0.62	4906
4	15.71	9.12	143.28	224.1	37.05	0.76	5029
5	15.78	9.25	145.97	229.3	36.68	0.74	5072
Mean	15.69	9.17	143.86	217.8	35.65	0.71	5007
SD	0.06	0.05	1.20	15.7	2.44	0.06	62
COV	0.4%	0.6%	0.8%	7.2%	6.8%	7.8%	1.2%

Sample ID Number: USQI-01-042-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	10

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.70	9.25	145.23	423.0	68.02	2.13	3566
2	15.63	9.19	143.64	426.5	69.79	2.18	3380
3	15.66	9.20	144.07	402.8	65.65	2.03	3651
4	15.56	9.15	142.37	426.0	70.64	2.16	3633
5	15.47	9.20	142.32	426.7	70.39	2.20	3695
Mean	15.60	9.20	143.53	421.0	68.90	2.14	3585
SD	0.09	0.04	1.22	10.3	2.08	0.07	124
COV	0.6%	0.4%	0.9%	2.4%	3.0%	3.1%	3.4%

Sample ID Number: USQI-01-043-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	20

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.23	9.31	141.79	409.6	67.02	1.99	4188
2	15.23	9.19	139.96	361.9	60.77	1.74	3837
3	15.19	9.09	138.08	386.1	66.44	1.96	4045
4	15.18	9.14	138.75	349.2	59.47	1.67	3979
5	15.17	9.21	139.72	338.7	56.86	1.59	3921
Mean	15.20	9.19	139.66	369.1	62.11	1.79	3994
SD	0.03	0.08	1.41	28.7	4.45	0.18	133
COV	0.2%	0.9%	1.0%	7.8%	7.2%	9.9%	3.3%

Sample ID Number: USQI-01-044-F

Resin:	Hetron 922 PAW
Initiator:	2.5% Butanox M-60
Filler:	E-Spheres SLG
Filler Volume Fraction:	30

Specimen No.	Width (mm)	Thickness (mm)	Area (mm^2)	Peak Load (N)	Peak Stress (MPa)	Peak Strain (%)	Modulus (MPa)
1	15.35	9.14	140.30	354.9	59.78	1.53	4375
2	15.18	9.13	138.59	324.8	55.45	1.40	4536
3	15.28	9.18	140.27	321.5	53.92	1.32	4491
4	15.43	9.21	142.11	332.4	54.85	1.44	4359
5	15.22	9.17	139.57	327.0	55.19	1.40	4525
Mean	15.29	9.17	140.17	332.1	55.84	1.42	4457
SD	0.10	0.03	1.29	13.3	2.28	0.08	84
COV	0.7%	0.4%	0.9%	4.0%	4.1%	5.4%	1.9%

APPENDIX E.

DYNAMIC MECHANICAL ANALYSIS (DMA) RESULTS

This Appendix contains the DMA curves and glass transition data from the first and second heating runs for the investigation of transition behaviour presented in Chapter 6. The investigation parameters are listed below and the results are presented overleaf.

Transition Behaviour of Unfilled Vinyl Esters

- Influence of Initiator Concentration
- Influence of Peroxide Initiator Type
- Influence of Accelerator Level
- Influence of Oligomer Molecular Weight
- Influence of Styrene Addition Level

Transition Behaviour of Filled Vinyl Esters

- Influence of Peroxide Initiator Type
- Influence of Oligomer Molecular Weight

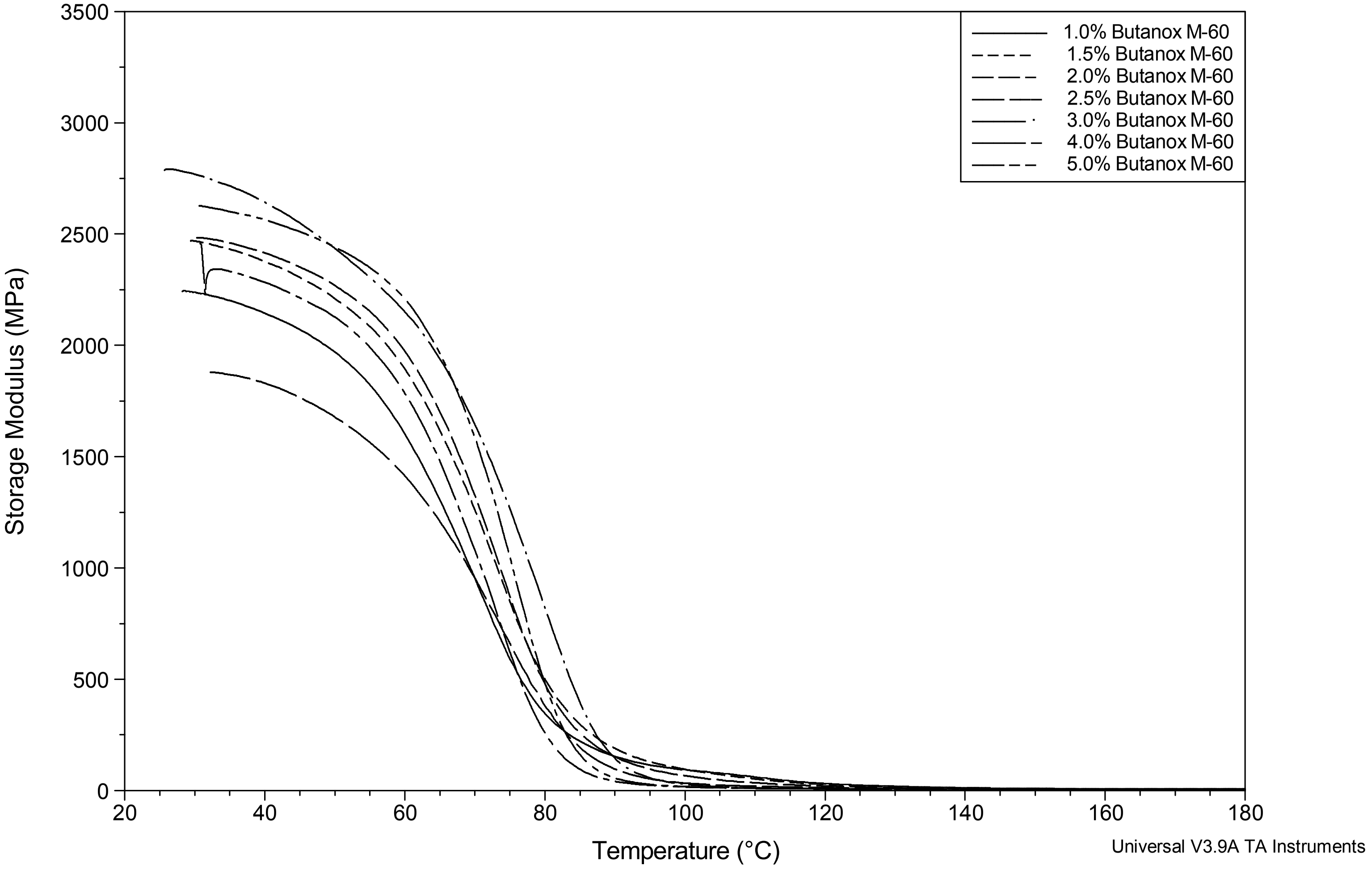

Figure E.1 **First DMA run for Hetron 922 PAW vinyl ester with varying levels of initiator.**

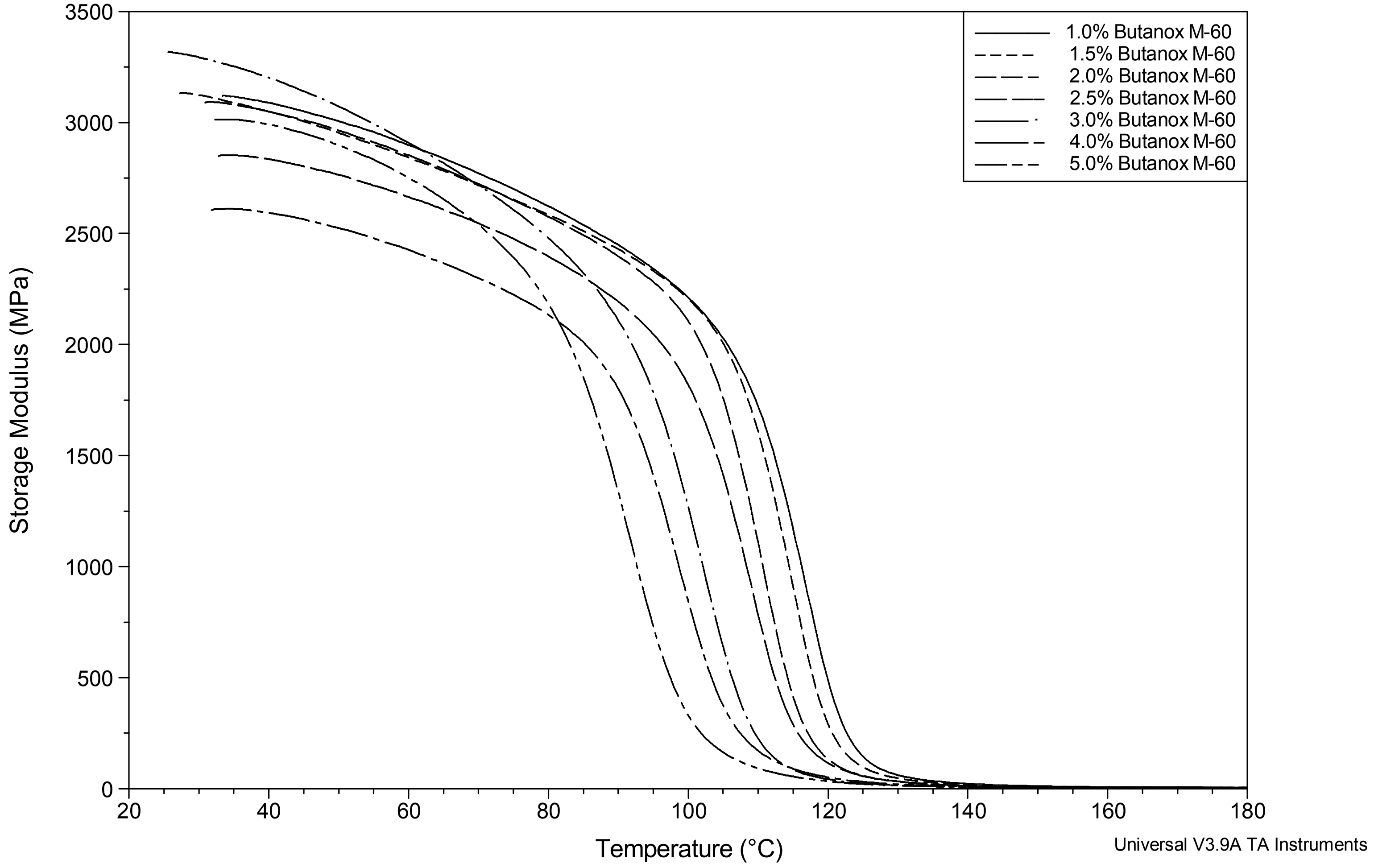

Figure E.2 Second DMA run of Hetron 922 PAW vinyl ester with varying levels of initiator.

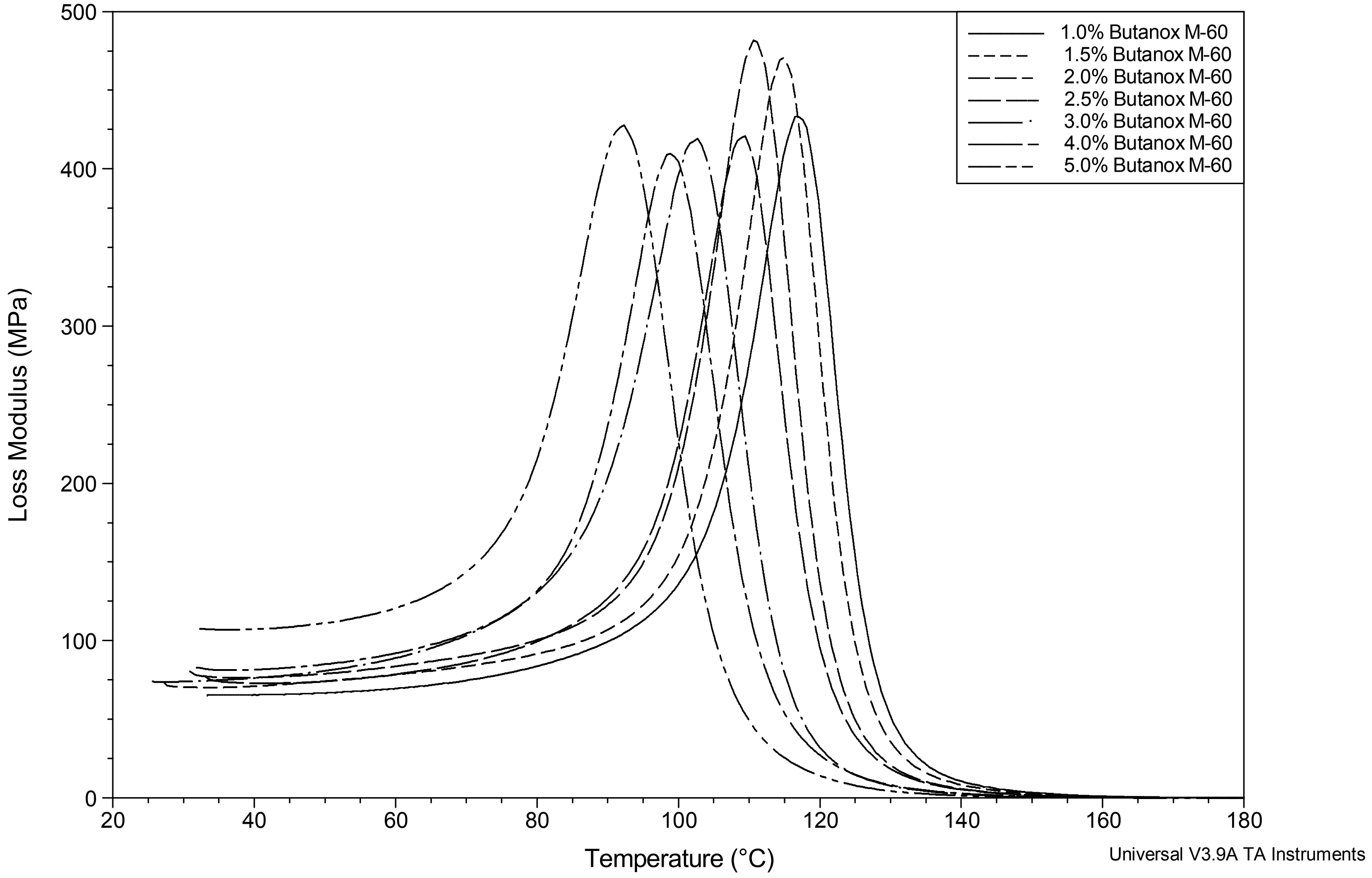

Figure E.3 Loss modulus relationships from the second DMA run of Hetron 922 PAW vinyl ester with varying levels of initiator.

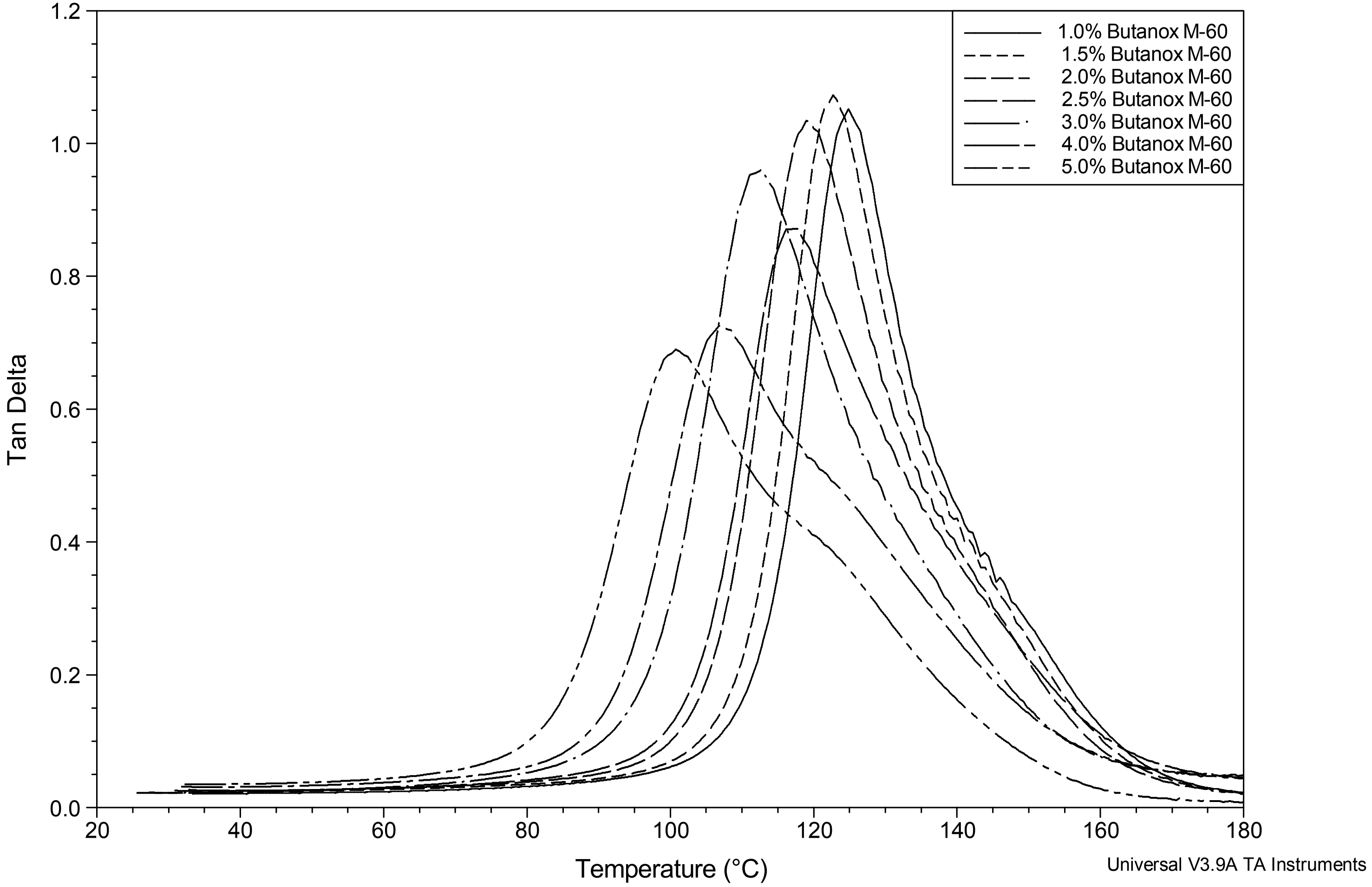

Figure E.4 Tan δ relationships from the second DMA run of Hetron 922 PAW vinyl ester with varying levels of initiator.

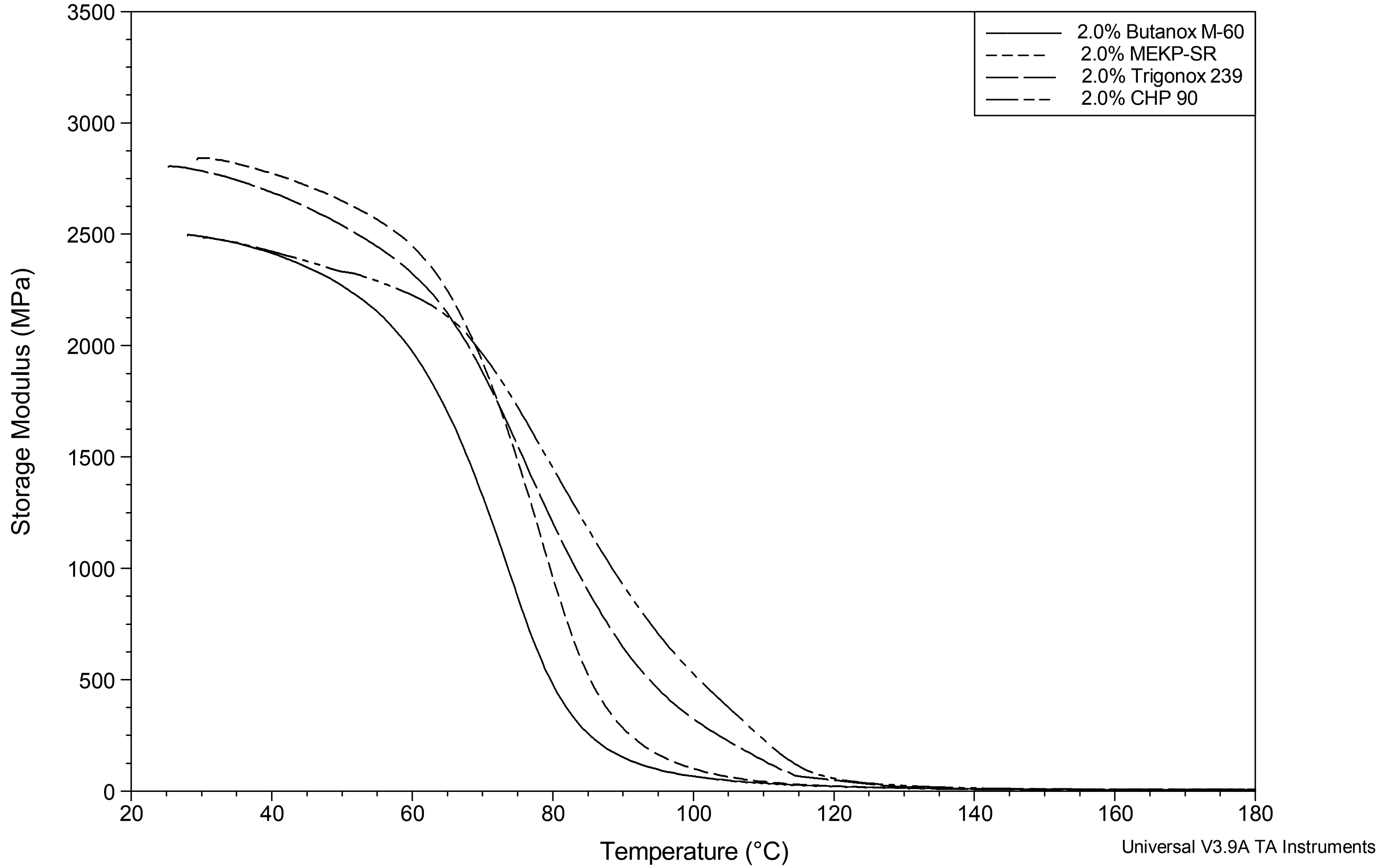

Figure E.5 **First DMA run for Hetron 922 PAW vinyl ester cured with alternative initiator types.**

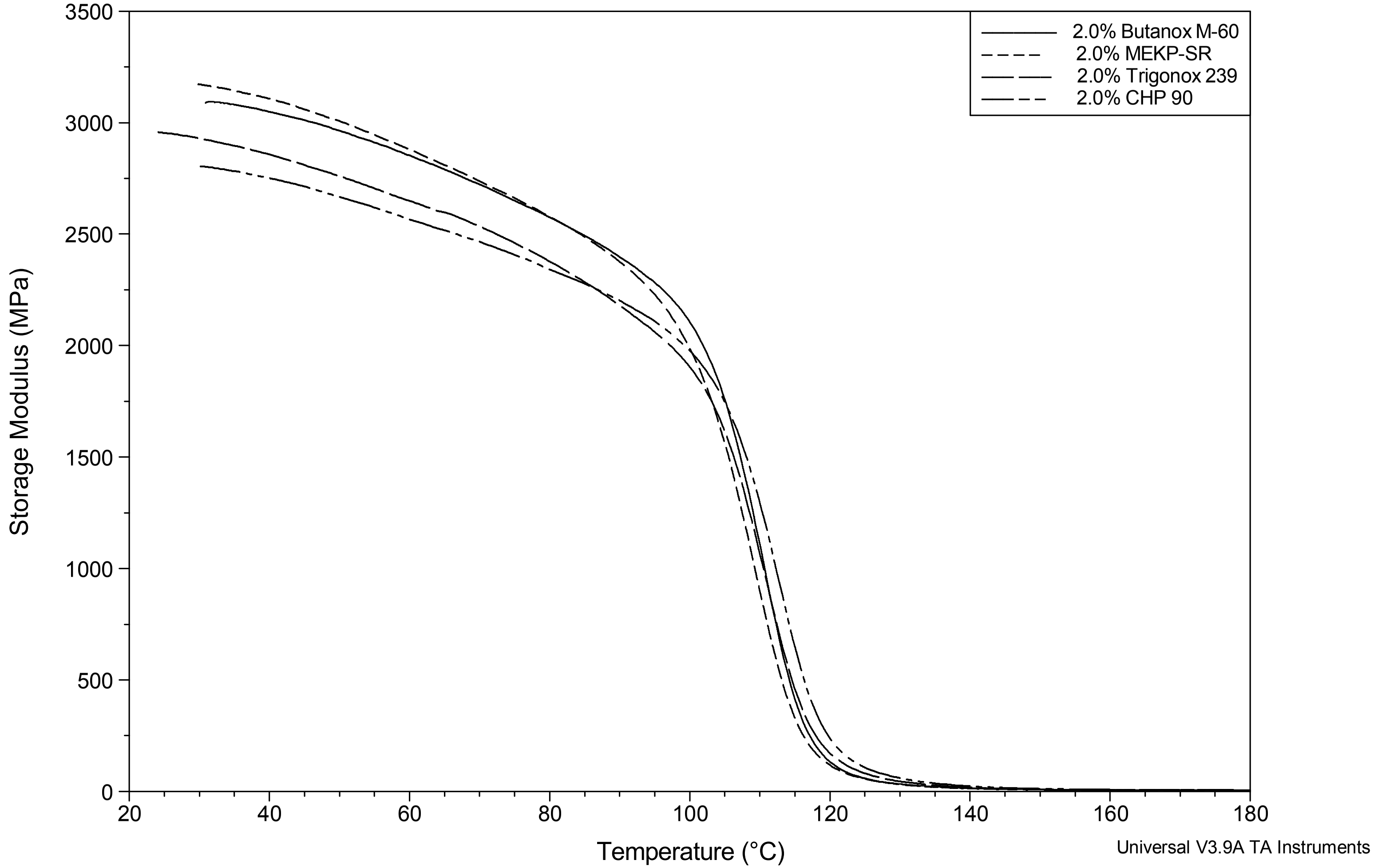

Figure E.6 **Second DMA run for Hetron 922 PAW vinyl ester cured with alternative initiator types.**

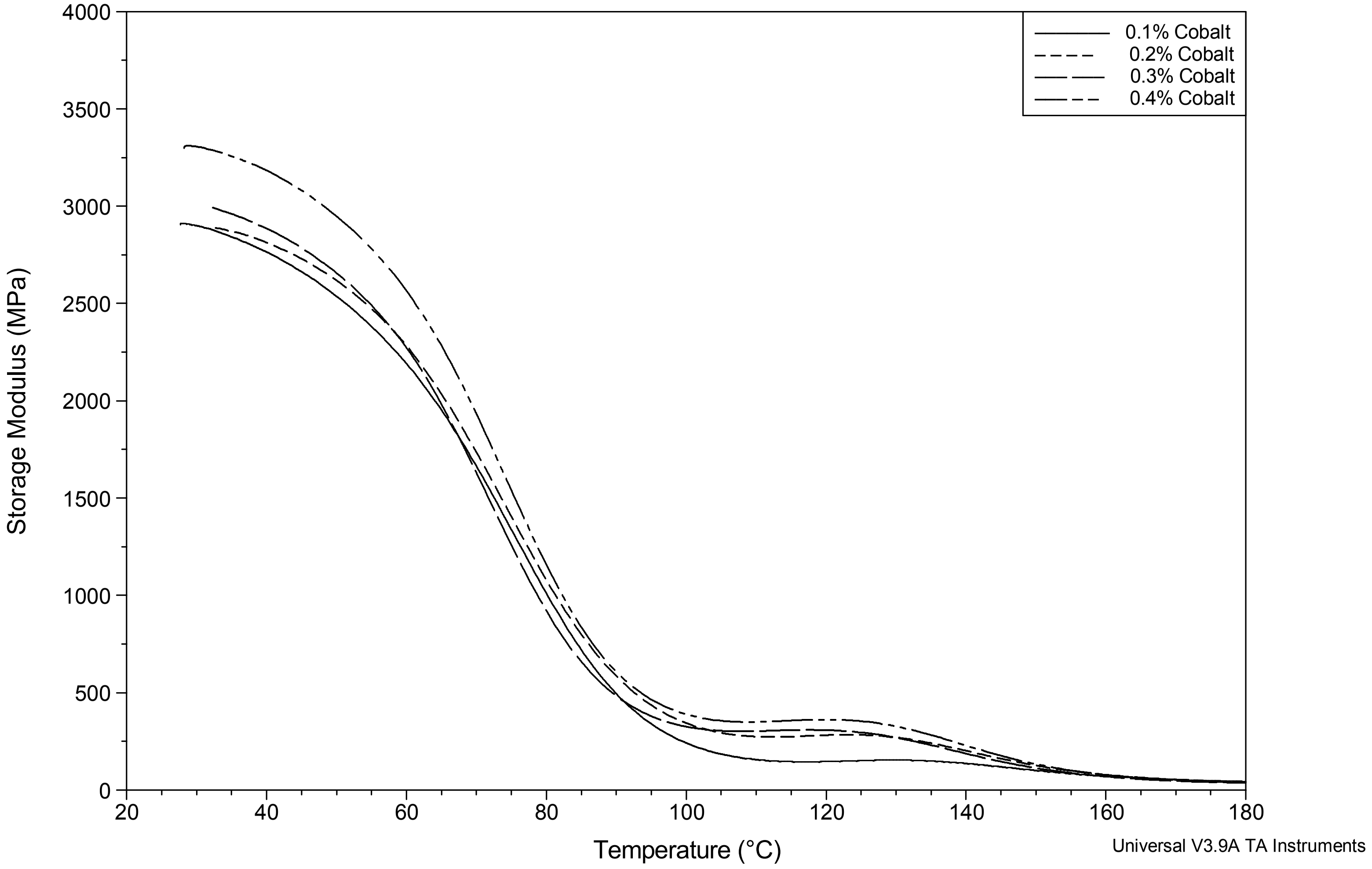

Figure E.7 **First DMA run for Hetron 914 vinyl ester with varying accelerator levels.**

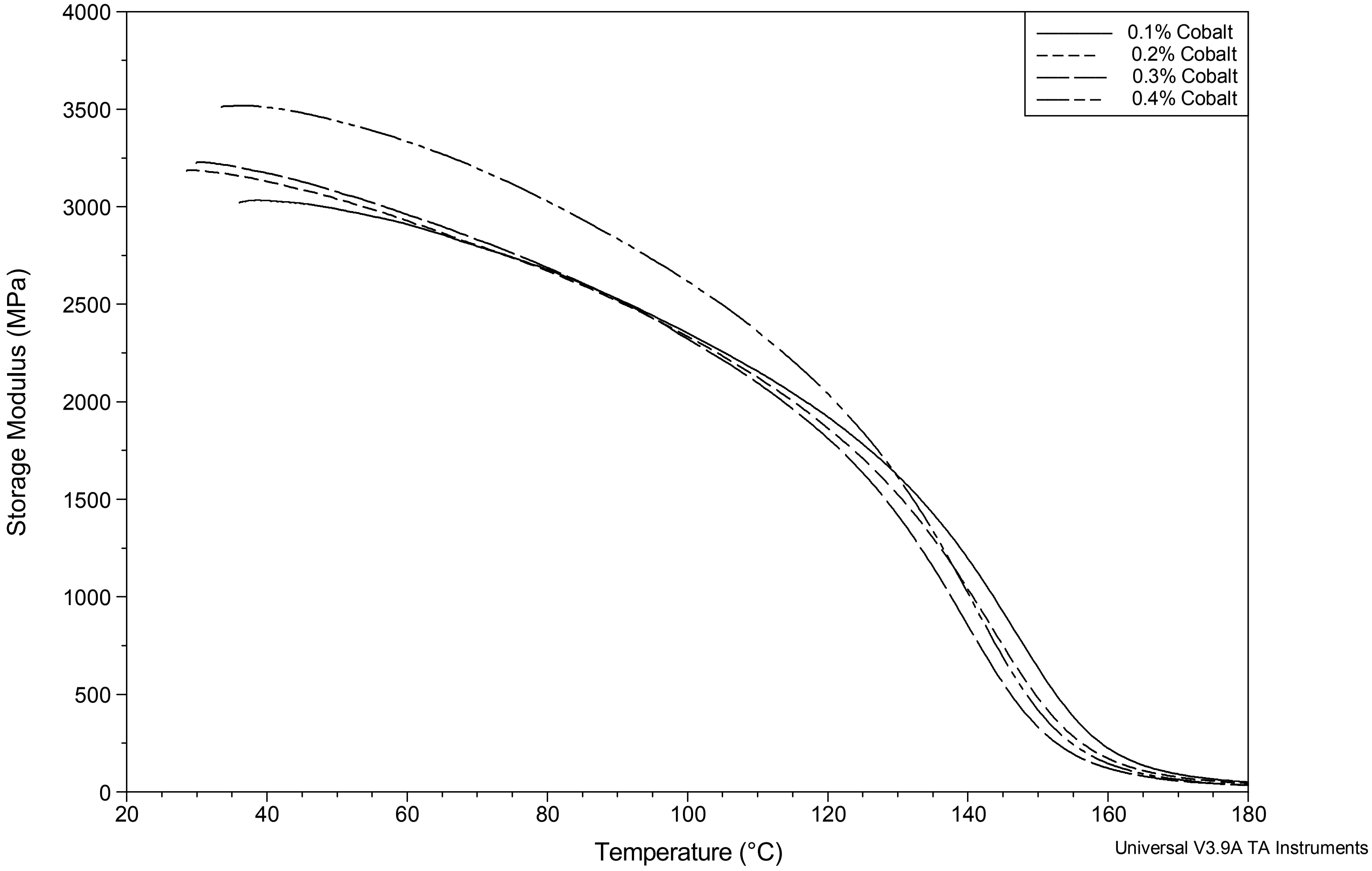

Figure E.8 **Second DMA run for Hetron 914 vinyl ester with varying accelerator levels.**

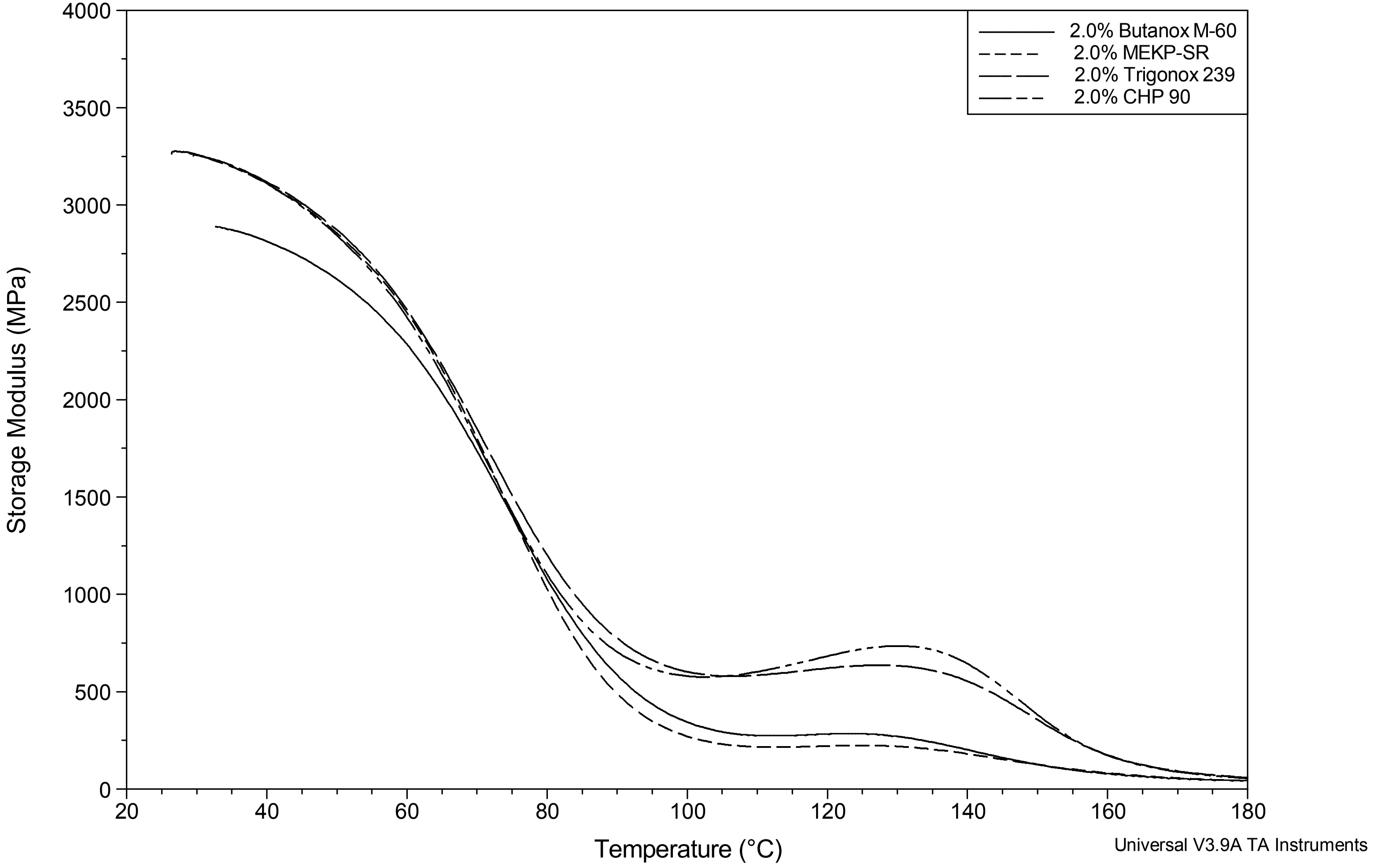

Figure E.9 First DMA run for Hetron 914 vinyl ester with alternative initiator types.

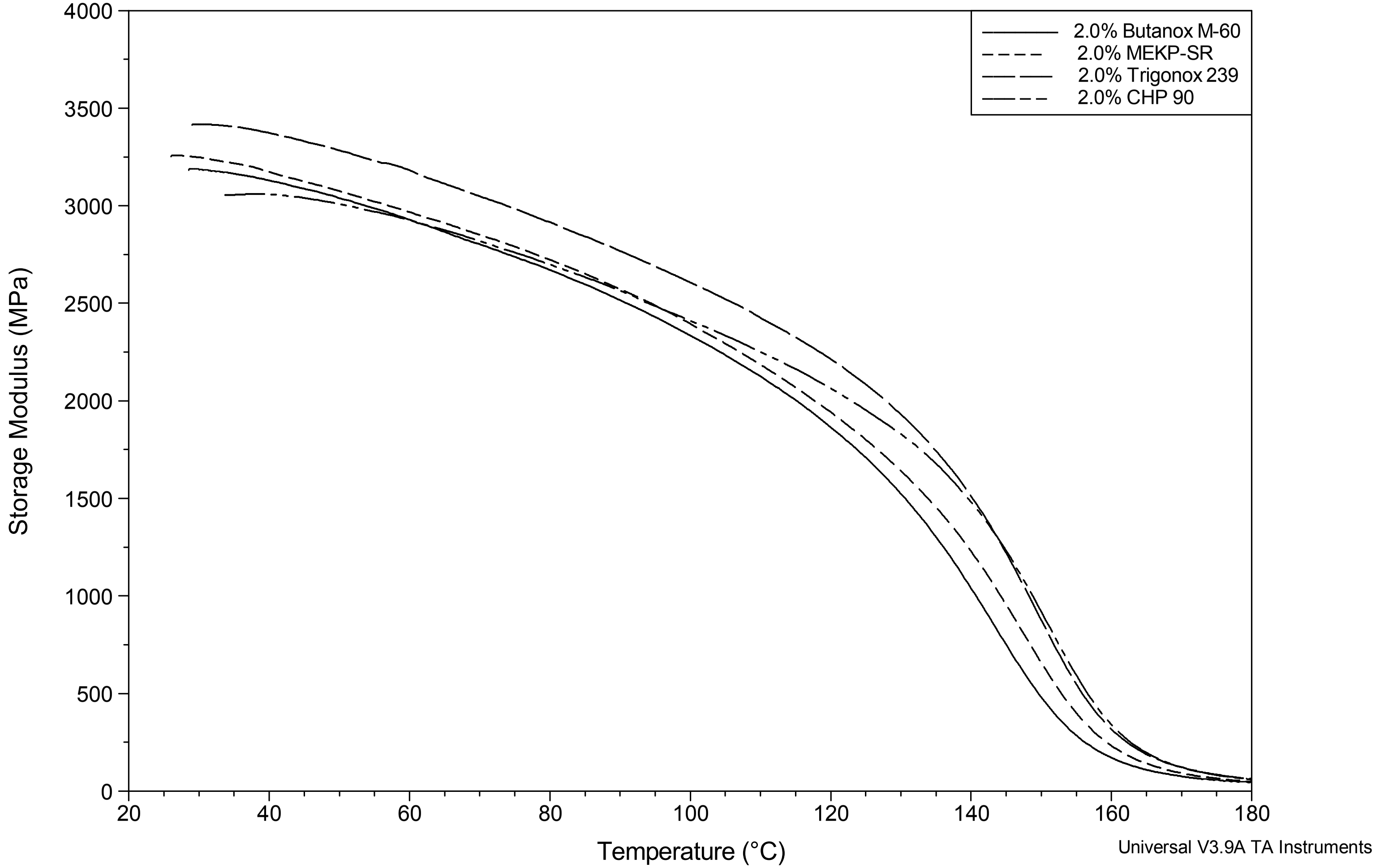

Figure E.10 Second DMA run for Hetron 914 vinyl ester with alternative initiator types.

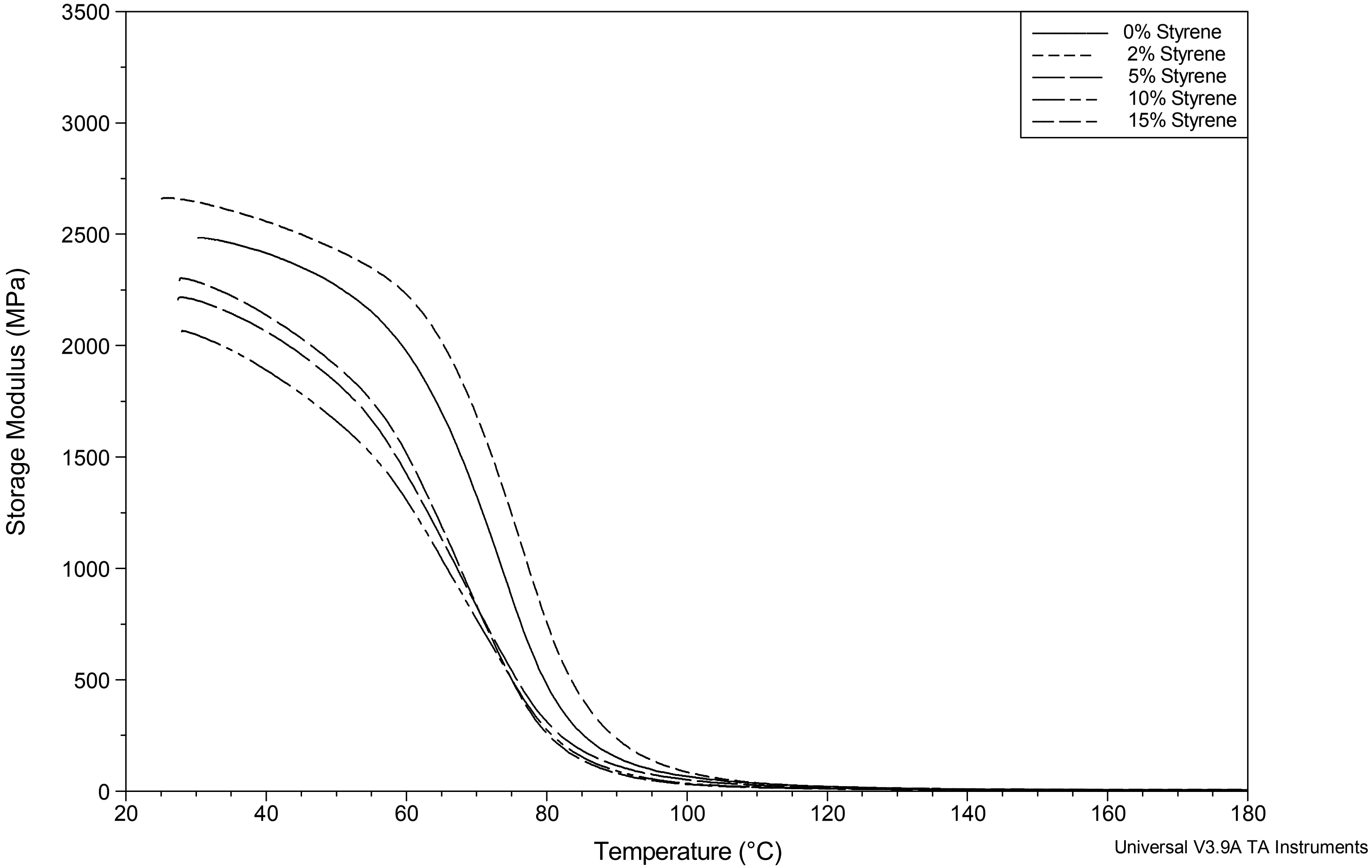

Figure E.11 **First DMA run for Hetron 922 PAW vinyl ester with varying levels of additional styrene.**

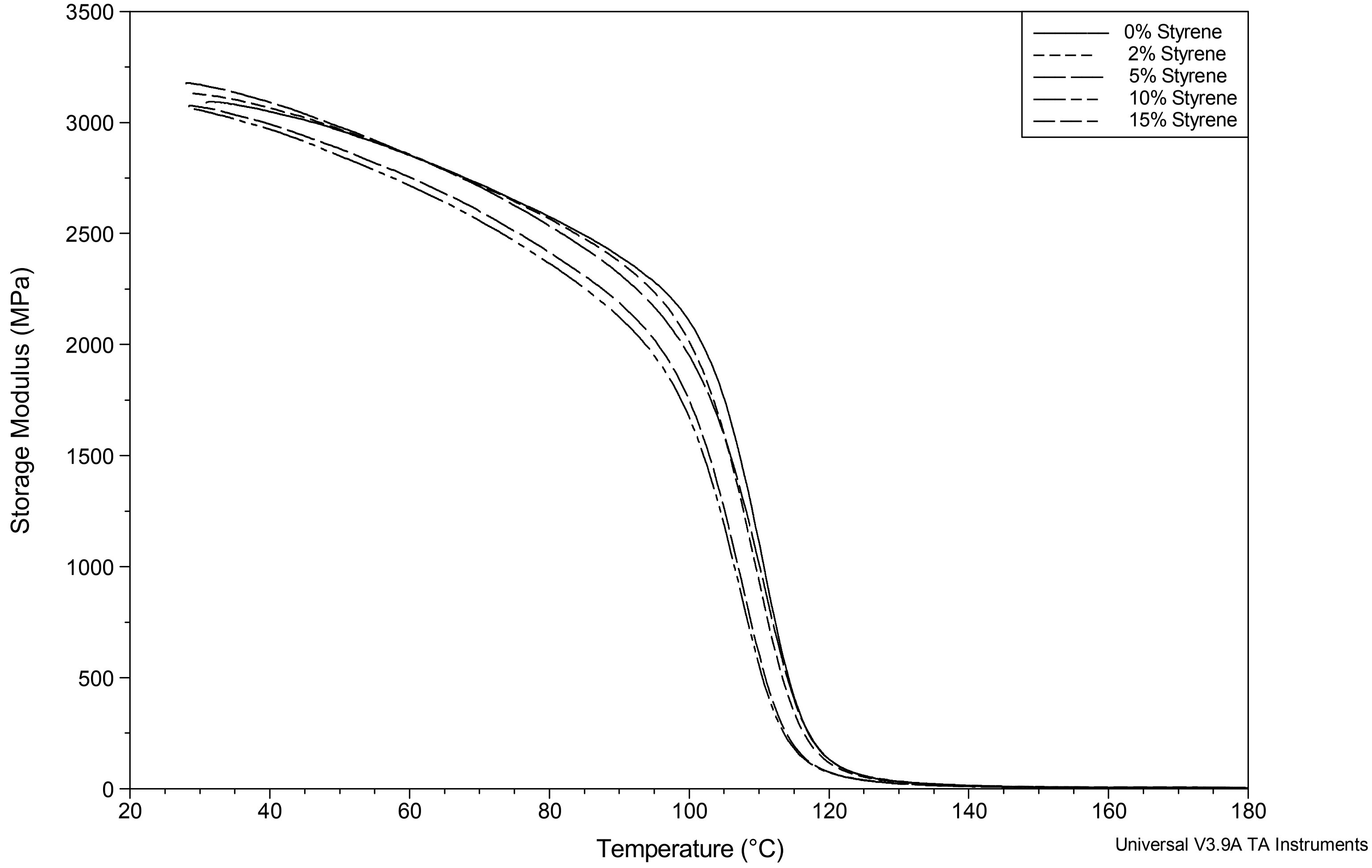

Figure E.12 Second DMA run for Hetron 922 PAW vinyl ester with varying levels of additional styrene.

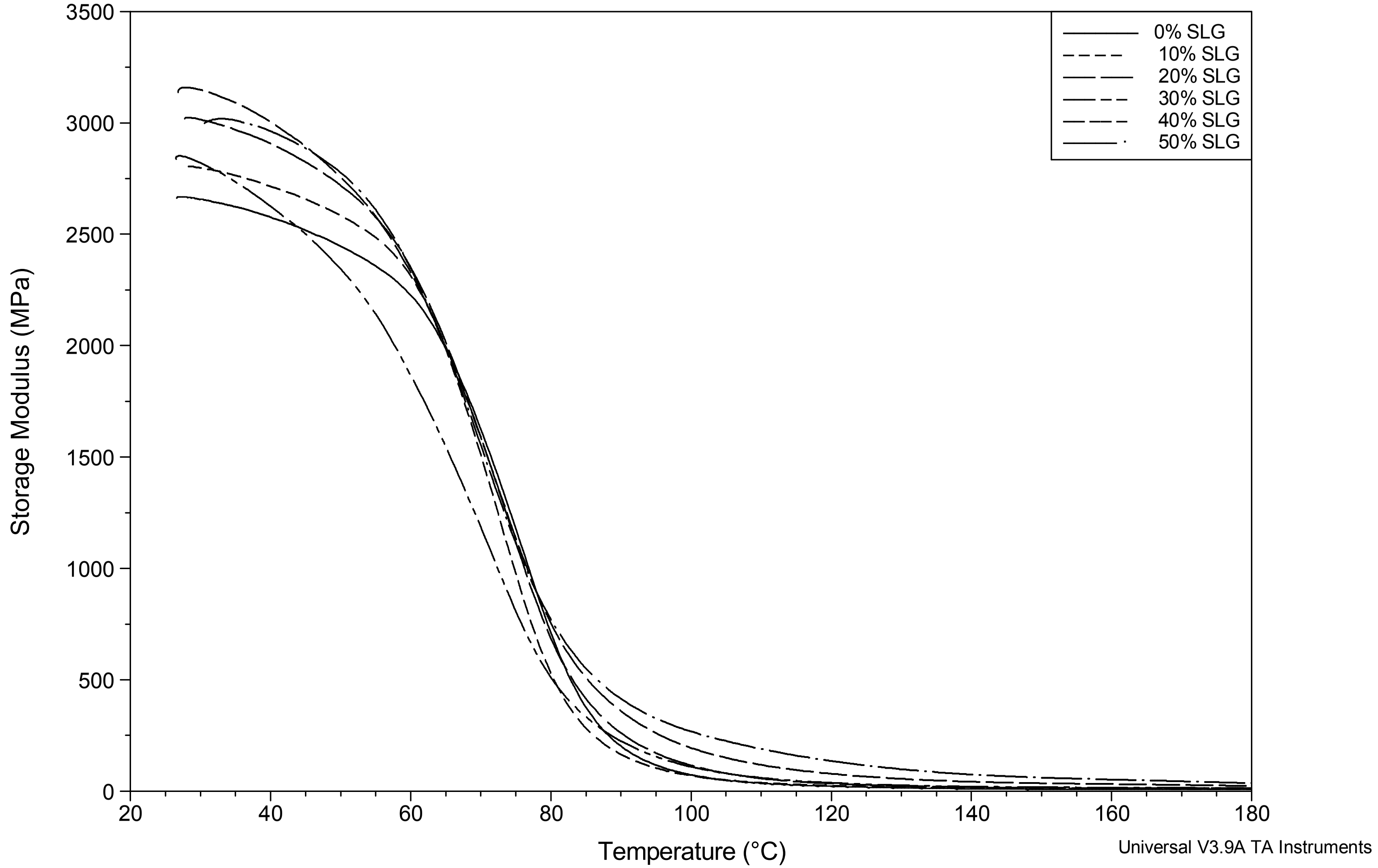

Figure E.13 **First DMA run for Hetron 922 PAW vinyl ester / cenosphere composites with varying volume fractions of filler.**

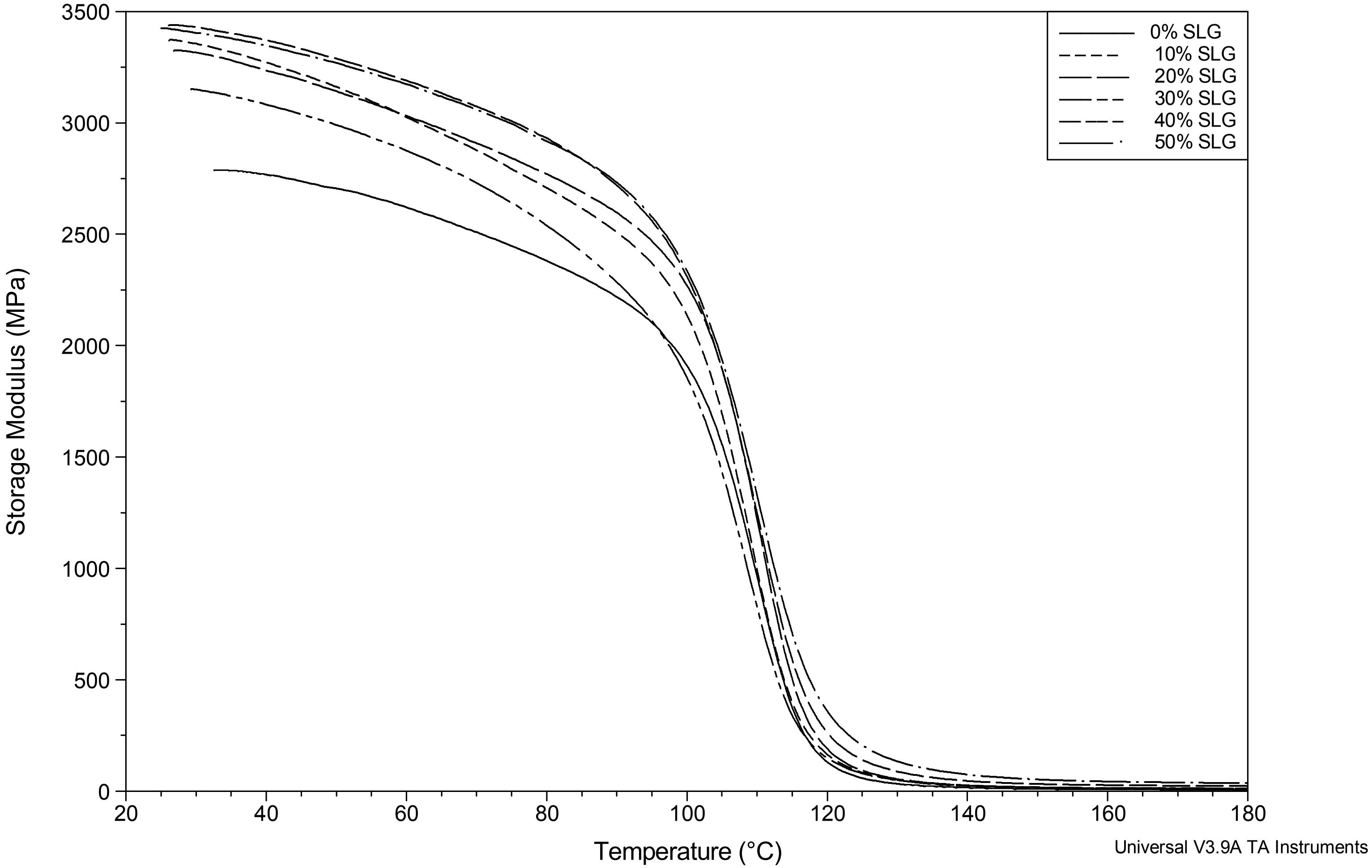

Figure E.14 Second DMA run for Hetron 922 PAW vinyl ester / cenosphere composites with varying volume fractions of filler.

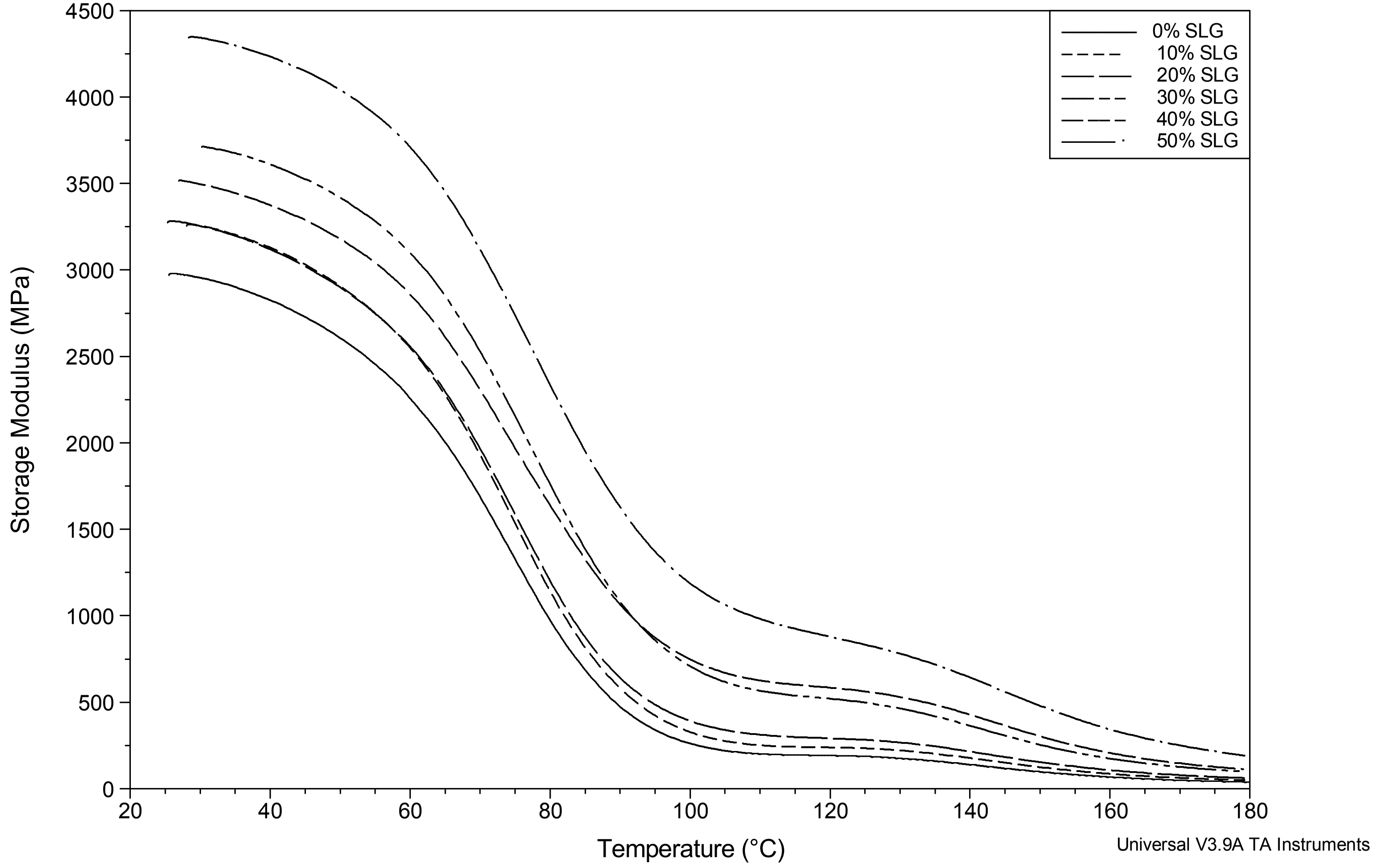

Figure E.15 **First DMA run for Hetron 914 vinyl ester / cenosphere composites with varying volume fractions of filler.**

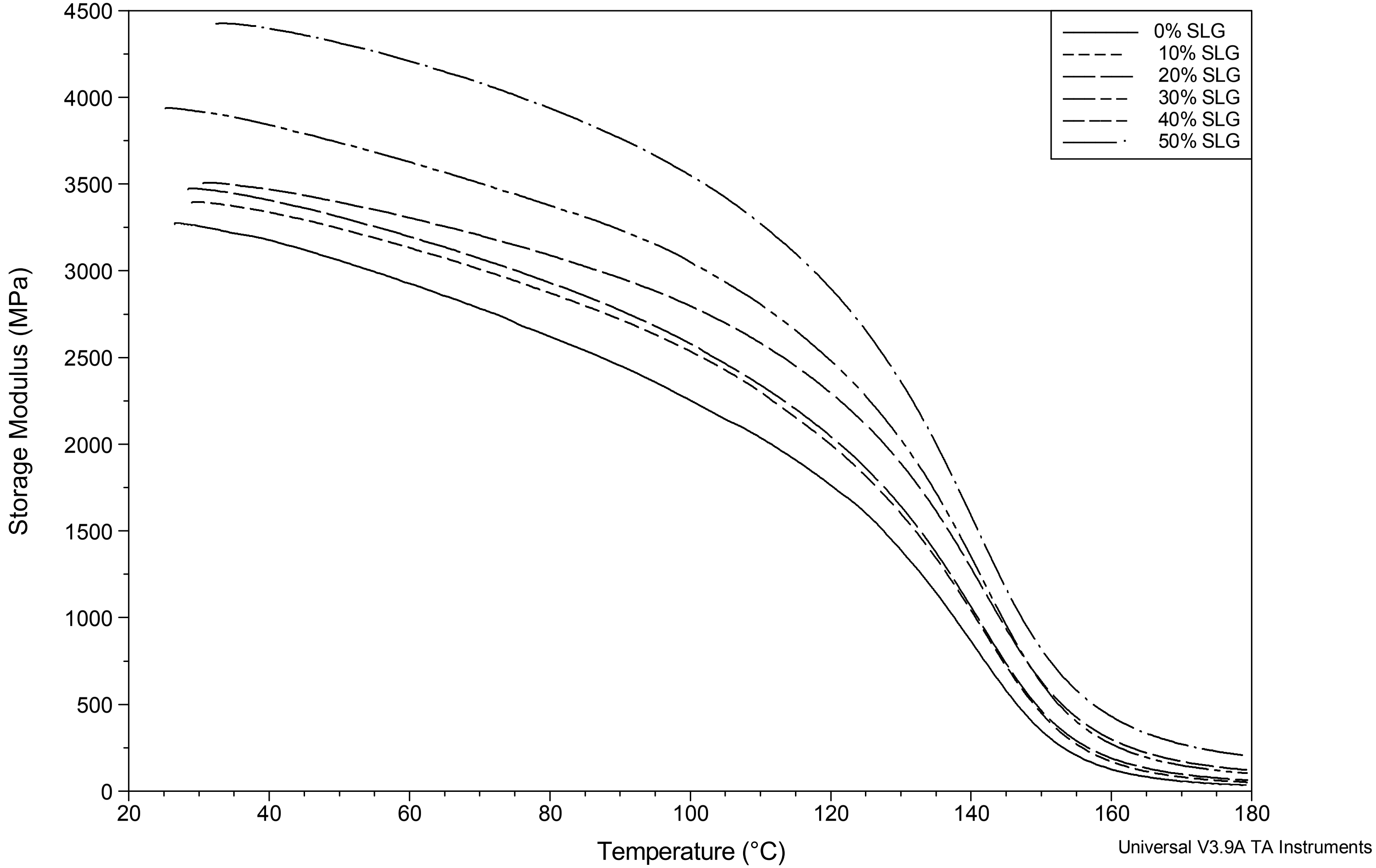

Figure E.16 Second DMA run for Hetron 914 vinyl ester / cenosphere composites with varying volume fractions of filler.

Table E.1 Glass Transition Temperatures of Hetron 922 PAW Vinyl Ester with Varying Initiator Levels using DMA.

Initiator Addition Level (%)	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
1.0	71	75	115	117	117	125
1.5	73	77	111	115	115	123
2.0	74	77	106	111	111	119
2.5	74	79	100	109	109	117
3.0	80	82	96	102	103	113
4.0	74	74	89	99	99	107
5.0	76	78	90	92	92	101

Table E.2 Glass Transition Temperatures of Hetron 922 PAW Vinyl Ester with Varying Initiator Types using DMA.

Initiator	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
Butanox M-60	74	77	106	111	111	119
MEKP-SR	79	81	108	109	109	118
Trigonox 239	76	86	115	111	111	119
CHP 90	79	94	117	113	113	120

Table E.3 Glass Transition Temperatures of Hetron 914 Vinyl Ester with Varying Accelerator Levels using DMA.

Accelerator Addition Level (%)	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
0.1	76	80	116	146	146	161
0.2	74	79	145	143	142	157
0.3	72	78	142	140	138	155
0.4	74	79	144	141	140	157

Table E.4 Glass Transition Temperatures of Hetron 914 Vinyl Ester with Alternative Initiator Types using DMA.

Initiator	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
Butanox M-60	74	79	145	143	142	157
MEKP-SR	74	78	109	147	146	160
Trigonox 239	71	80	156	149	148	161
CHP 90	71	78	156	151	151	163

Table E.5 Glass Transition Temperatures of Hetron 922 PAW Vinyl Ester with Varying Styrene Addition Levels using DMA.

Styrene Addition Level (%)	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
0	74	77	106	111	111	119
2	77	80	107	109	109	119
5	68	77	106	111	110	119
10	67	77	103	107	107	116
15	68	75	101	108	108	117

Table E.6 Glass Transition Temperatures of Hetron 922 PAW Vinyl Ester with Varying Filler Volume Fraction using DMA.

Filler Addition Level (%)	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
0	76	79	107	110	110	120
10	73	76	105	109	109	118
20	74	78	108	111	111	119
30	72	76	107	109	109	117
40	73	77	107	110	110	118
50	70	75	106	110	111	118

Table E.7 Glass Transition Temperatures of Hetron 914 Vinyl Ester with Varying Filler Volume Fraction using DMA.

Filler Addition Level (%)	Glass Transition Temperature					
	First Heating Run			Second Heating Run		
	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)	Point of Inflection (°C)	Peak Loss Modulus (°C)	Peak Tan δ (°C)
0	75	78	112	140	139	155
10	75	80	113	141	141	156
20	75	81	114	141	140	155
30	78	86	141	141	141	154
40	74	94	143	142	142	154
50	78	90	139	140	141	151