

**Effects of catalysts and post-curing conditions in  
the polymer network of epoxy and phenolic resins: Preliminary results**

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**Abstract:** In the earlier study about polymer network of phenolic and epoxies resins mixed with linseed oil, only Phencat 15 was used as the catalyst for the phenolic resin. In this study, Phencat 382 and UH (a urea hydrochloride solution based on a 1 : 1 mole ratio of urea : hydrochloric acid 32%) will be used as catalysts to study their effects on the polymer network of phenolic and epoxy resins mixed with epoxidized linseed oil (ELO) (58%). The effect of each one of these catalysts on the curing and the properties of the formed network were investigated. It was discovered that Phencat 382 was the best catalyst for the composites. It was also discovered that ELO can play its role as plasticiser in the blends of epoxy and phenolic resins and does improve the flexural strength and other mechanical properties of the prepared resins. The storage modulus, flexural modulus, stress at peak and glass transition temperature decreased with increasing percentage by weight of ELO added irrespective of the catalysts used, while the strain yield increased. The cross-link density decreased with the increasing amount of ELO in the resins. The best properties were obtained for the 80/20 epoxy/phenolic resin blends after post-curing for 4 hours.

**Keywords:** flexural modulus, catalysts, epoxy resin, phenolic resin, cross link density and linseed oil.

## **Background**

Phenolic thermosetting materials were the first major plastic material used by industry. They are still among the most widely used thermosets because they are some of the lowest-cost engineering material on a cost-per-volume basis. Phenolics are formed from the condensation of polymerization reaction between phenol and formaldehyde. The condensation reaction for phenolics can be carried out under two different conditions,

resulting in two different intermediate materials. One of the intermediates is called resoles and the other novolacs [1-2].

Hyrez 202 is the name given to the epoxy resin made by a composite research centre in the University of Southern Queensland (USQ). It is a mixture between 'part A', which is a mixture of commercial epoxy resins and 'part B', which is a mix of different commercial hardeners. Previous study shows that the best proportion is 80% by weight of part A and 20% by weight of part B [3]. Hyrez 202 lowers the cost of epoxy. The emergence of the use of fibre composite materials and technologies in civil and structural engineering has created opportunities in the development of "smarter" new polymers and polymer additives. The research centre in USQ developed a polymer network of phenolic and epoxy resins mixed with epoxidised linseed oil (ELO) (58%), in which proportions by weight of epoxy and phenolic resins that will form interpenetrating polymer network were identified [3].

Linseed oil is a straw to amber in colour with a recognisable odour, fatty oil extracted from the cotyledons and inner coats of the seeds of flax (linseed). The raw oil is extracted from the seeds by pressing. In its raw form it is light in colour, but when boiled it turns darker and thicker. The oil polymerizes or oxidises more readily when heated [4]. The iodine value related to linseed oil is a measure of the unsaturation of the fats and the oils and is expressed in centigrams of iodine absorbed per gram of sample (% iodine absorbed) [5]. The epoxydized reaction consists of the opening of the C-C double bond and replacing it by a C-O-C cycle (oxirane ring). The epoxydized double bond is a pre-polymer way of synthesis.

In another study, Biobased neat epoxy materials containing varying percentage by weight of epoxydized linseed oil (ELO) were cured with MTHPA, an anhydride curing agent. The main

drawbacks of epoxy resins for industrial applications are their high cost and brittleness. By adding, epoxidized linseed oil, curing agent and additives, it is possible to obtain a tougher but lower cost epoxy based material. In this study, a defined amount of diglycidyl ether of bisphenol F (DGEBF) was replaced by ELO. The storage modulus, glass transition temperature, and the HDT decreased with increasing percentage by weight of ELO added. The cross-link density increased when more than 70% by weight of ELO was added. The Izod impact strength was constant up to 60 % by weight of ELO, after that the Izod impact strength decreased slightly. The fracture toughness behaved in a similar way with different percentage by weight of ELO [6].

Miyagawa et al., also cured biobased neat epoxy materials containing varying percentage by weight of epoxidized linseed oil (ELO) with POPTA, an amine curing agent. The purpose of this study is to produce a tougher but lower cost epoxy based material. A defined amount of diglycidyl ether of bisphenol F (DGEBF) was replaced by ELO. The thermo-physical properties of the amine-cured biobased neat epoxy were measured by dynamic mechanical analysis (DMA). The storage modulus, glass transition temperature, and cross-link density radically decreased with an increase in the amount of ELO added. On the other hand, the Izod impact strength sharply increased with an increase of ELO added [7].

Another researcher produced Matrix materials consisting of epoxidized linseed oils with various blend ratio of a commercial epoxy have been prepared and reinforced with woven glass mats. In most cases, photoinitiators containing  $\text{BF}_4^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$  or  $\text{SBF}_6^-$ , the strongest acids are employed. They can dissolve in various cationically polymerizable monomers to give stable solutions. The monomers used are derived from biorenewable sources. The resin, ERL (ERL 4221) was bisepoxide 3,4-epoxycyclohexylmethyl -3',4'-epoxycyclohexane

carboxylate. While unsaturated triglyceride oils are not directly polymerizable by cationic techniques, they can be epoxidized readily and thereby made polymerizable. Epoxidized soybean oil (ESO) was also used in place of ELO. The composites have reasonable stiffness, strength and toughness, and are extremely simple and inexpensive to fabricate [8].

The storage modulus at room temperature for the 100% ERL composite is about double that of the 100% ELO composite. The storage modulus decreased with increasing temperature. The peaks in dynamically obtained loss factor agreed reasonably well with glass transition temperatures of the neat resin mixtures measured using differential scanning calorimeter (DSC). The 100% ELO displays a dynamic glass transition temperature of 65 °C, which is too low for most applications. The glass transition temperature for matrix with 60% ELO and 40% ERL was 100 °C, which is enough for general applications. The unusually broad loss factor curves suggest that these composites have good toughness and this was confirmed by tensile tests. The Young's modulus of samples post-cured at room temperature for 7 days is higher than those immersed in water for 6 days, which in turn is higher than those post cured at 100 °C for 2 hours. The hydrophobic nature of ELO is exhibited by the less weight gain when the samples containing ELO were immersed in water for a longer time than those consisting of epoxies only. The samples post-cured at 100 °C darkened considerably, and suggest that oxidative degradation occurs at this temperature in the unstabilized ELO [8].

Yuan et al., employed epoxidized linseed oil (ELO) to modify phenolic resin to obtain high quality friction material. He also discovered the ELO became a portion of the phenolic resin structure, i.e. interpenetrating network polymer was formed. The heat resistant and heat stability of ELO modified phenolic resin are superior to those of neat phenolic resin. Tribological characteristics and mechanical properties of ELO modified phenolic based

composite indicate that the friction material have high coefficient of friction, stabilized friction property, low wear rate, high impact strength and mezzo hardness [9-10].

It can be argued that ELO in most cases increase the thermal and mechanical properties of the phenolic and epoxy based composites, provided, in some cases, the percentage by weight of ELO does not exceed 60%. This is similar to the discovery of this paper.

### **Curing of phenolic resin and the samples**

The polymer based on phenolic resin is Phenol-formaldehyde (PF). The PF resins are formed by the reaction of phenol with formaldehyde. By varying the reaction time, reaction temperature, catalyst type, and the ratio of formaldehyde to phenol, a number of adhesive systems with different characteristics can be produced.

A disadvantage of phenolic resins is that they are characterized by a complex process of polymerization (cure) with generation of water and formaldehyde, with consequent formation of voids. Therefore, the processing of phenolic materials requires careful temperature control and gradual heating to allow continuous elimination of volatiles and to reduce the number of defects in final components. Normally the time required for these operations is incompatible with common industrial process schedules.

Initially formaldehyde reacts with phenol to form hydroxymethyl derivatives preferentially at the aromatic ring carbon para to the phenolic hydroxyl as depicted in Figure 1.

As the reaction proceeds, reactions also take place between the hydroxymethyl groups and the aromatic ring carbons of phenol or another hydroxymethyl group to form methylene linkages. In this manner, the polymeric structure of the resin shown in Figures 2 and 3 is produced.

Samples were obtained by mixing different reagents together in plastic boxes. Weights of different reagents were carefully measured to ensure the right compositions and thicknesses (10 mm) were obtained. After curing the samples, they were cut into suitable pieces using a circular saw; they were then sanded to give them the accurate dimensions for analysis with the DMA and flexural testing machines. The dimensions of the sample must be more than 70mm in length, 4mm in width and 10mm in thickness. There were 5 or 6 samples for each combination of reactants.

### **Flexural test**

The flexural test measures behaviour of materials when subjected to simple beam loading. It is also called a transverse beam test with some materials. Maximum fibre stress and maximum strain are calculated for increments of load. Flexural strength is defined as the maximum stress in the outermost fibre. Flexural modulus is calculated from the slope of the stress against deflection curve [2]. Flexural test is often done on relatively flexible materials such as polymers, wood and composites. There are two types of the test: 3 point flexural test and 4 point flexural test. Three point bending test will be used in this project. In this test, the area of uniform stress is quite small and concentrated on the centre loading point. Consider a rectangular beam, on which a simple concentrated force is exercised in the centre of the beam with a load of  $P$  as depicted in Figure 4. The standard used is ISO 14125:1998(E) [11]. This

study uses a universal machine MTS Alliance RT/10 at 10kN couple with the software TESTWORK 4.

The equation used for calculating the flexural stress,

$$\sigma_f = \frac{3PL}{2bh^2} \quad (1)$$

The equation used for calculating the flexural strain,

$$\varepsilon_f = \frac{6Dh}{L^2} \quad (2)$$

The equation used for calculating the Young's modulus,

$$E_B = \frac{L^3 m}{4bh^3} = \frac{\text{Flexural strength}}{\text{Flexural strain}} \quad (3)$$

where:  $\sigma_f$ : stress in outer fibre at midpoint, MPa;

$\varepsilon_f$ : strain in the upper surface, %;

$E_B$ : modulus of elasticity in bending, MPa;

P: load at a given point on the load deflection curve, N;

L: support span, mm;

b: width of test beam, mm;

h: depth of test beam, mm;

D: maximum deflection of the centre of the beam, mm;

m: slope of the tangent to the initial straight line portion of the load deflection curve, N/mm.

### **Using different catalysts**

In general, there are three catalysts for phenolic resin: Phencat 15, Phencat 382 and UH.

Phencat 15 is a fast action acid catalyst. The reaction with phenolic resins is strongly

exothermic. It is toxic and causes burns with body contact. Its composition consists of xylenesulfonic acid, 70 to 90%, phosphoric acid, 10 to 20% and water, 1 to 10%. Phencat 382 is a slow action acid catalyst. The reaction with phenolic resin is exothermic. It is toxic and dangerous to body contact. Its composition consists of phosphoric acid, 40 to 80% and water 20 to 60%. Phencat 382 is similar to Phencat 15 but with slower reaction rate. UH is a urea hydrochloride solution based on a 1: 1 mole ratio of urea: hydrochloric acid 32%. The reaction with phenolic resins is strongly exothermic. It has a high toxicity and burns the skin. In the earlier study, it was found that Phencat 15 reacted very fast with the phenolic resin and provoked moss due to the presence of polysulfone; even with Phencat 382, moss was sometimes found for composites with more than 70% by weight of Hyrez 202 [1]. In order to understand the reactions of the latter better, Hyrez 202 with different proportions of parts A and B were mixed with phenolic resin and Phencat 382; the mixture were post-cured at 80 °C for 4 hours.

Composite 80/20 was then mixed with different percentages of epoxidised linseed oil (58%) and then post-cured differently: one was heated up to 80 °C and soaked at that temperature for 4 hours and the other was soaked at 80 °C for 4 hours followed by gradually increasing its temperature to 150 °C.

## **Results and discussions**

The results of mixing phenolic and Hyrez 202 (epoxy) resins with Phencat 382 were summarized in Table 1. It was observed that Phencat 382 cured epoxy resin (sample 1) but in a very much less rate than Phencat 15 did. In fact, only samples 1 and 5 (of Table 1) were cured. However, Phencat 15 cured nearly all combinations of part A and part B by weight as

shown in Table 2. However, when the percentage of epoxy resin increases, the reaction becomes too exothermic and fast, moses were given out. Moreover, there is another reaction taking place; Phencat 15 is composed of xylenesulfonic acid which reacts with epoxy resin to form another by product.

When the Hyrez 202 contained parts A and B, it was observed that the mixture was also cured by Phencat 382 (sample 6) but the network was smaller and was not a good material. Besides, when part B was added to the phenolic resin with a little or no catalyst, a rubbery material was obtained which was solid at room temperature and liquid when it was heated (samples 4 and 7). These results confirmed that part B broke the polymer network. So it would be better to change the hardener of epoxy or delete it. Sample 3 did not cure. There are two possibilities for this; phenolic J2027L was not a hardener for part A of Hyrez 202, or the proportion by weight was not enough to permit the polymerisation. Finally, the apparition of moss when a little phenolic resin was mixed in Hyrez 202 (sample5) confirmed that phenolic resin cured epoxy resin because the 2 reactions gave out a lot of energy, resulting in apparition of moss.

Another catalyst used for test was UH and after trying many combinations of phenolic and epoxy resins with epoxidised linseed oil (EPO), it was found that composite 80/20 (composite 80/20 means the proportion by weight for epoxy resin is 80 % and that of phenolic resin is 20%) with 40% of ELO gave the best properties. It was also observed that mist disappeared when the percentage by weight of ELO is more than 20%. The post-curing time was maintained at 4 hours at 80 °C. It was also noticed that ELO/Phenolic composites became solid at room temperature when they were cured with UH but not with Phencat 382. With UH, samples just jelled at room temperature or stayed soft. The difference in curing can

explain why Phenolic resins cured with UH have low peak flexural stress and strain at break. In the solid state, chemical reactions are much slower because molecules cannot move freely. Moreover, heating up to 150 °C weakened the material and this is in line with the work of Crivello et al. [8].

With UH and Phencat 382 as hardeners, it was found that the composite would not mix well if the percentage by weight of ELO was higher than 20%. When the ELO/phenolic composites were cured with UH, they became solid at room temperature; when the composites were cured with Phencat 382, the samples just jelled at room temperature or stayed soft. Figure 5 illustrates that the flexural modulus of the composites decreased with increasing percentage by weight of ELO irrespective of the catalysts used. The drop is most significant with 10% UH and least significant with 10% phencat 382.

Table 3 shows the mechanical properties of composite 80/20 cured by different hardeners. It is observed that, with 5 % by weight of hardeners, the values of the peak flexural stress, flexural modulus, storage modulus and glass transition temperature are highest with Phencat 382, followed by UH and Phencat 15. On the other hand, the values of strain at peak, strain at break, deflection at peak and deflection at peak are highest with Phencat 15, followed by Phencat 382 and UH. It is also discovered that, with 10 % by weight of hardeners, the values of the peak flexural stress, flexural modulus, storage modulus and glass transition temperature are highest with Phencat 382, followed by UH, and moss was obtained with Phencat 15. The values of strain at peak, strain at break, deflection at peak and deflection at peak are highest with UH followed by Phencat 382. With 10% by weight of UH, the strain at break was 4.46 %, which was the result required by most projects of the research centre.

However this composite had exceptional resistance to fire so it is useful to civil engineering applications.

Table 4 shows the degree of cure and mechanical properties of composite 20/80 cured by different hardeners. Two ways of curing were carried out; in one case, the phenolic was first mixed with part A of Hyrez followed by a catalyst; in the other, the phenolic was first mixed with catalyst followed by part A. Only 10% Phencat 382 was able to cure composite 80/20; on top of this, the values of peak flexural stress, strain at break and flexural modulus obtained were lower than those obtained in Table 2. The values of peak flexural stress, strain at break and flexural modulus obtained by mixing phenolic and part A first were higher than those obtained by mixing phenolic and catalyst first.

Figure 6 illustrates that the flexural modulus of composite 80/20 mixed with ELO (58%) and heat-treated differently. In both cases, the flexural modulus decreased with increasing percentage of ELO. It was found that the values of flexural modulus were lowered by raising the heat-treated samples to 150 °C after being soaked for 4 hours at 80 °C.

Figure 7 shows that the strain at break (%) of composite 80/20 mixed with ELO (58%) and heat-treated differently. In both cases, the strain at break initially increased with increasing percentage of ELO and peaked at 10% of ELO; it then decreased with increasing ELO. It was found that the values of strain at break were lowered by raising the heat-treated samples to 150 °C after being soaked for 4 hours at 80 °C.

Figure 8 shows that the peak flexural stress of composite 80/20 mixed with ELO (58%) and heat-treated differently. In both cases, the peak flexural stress decreased with increasing percentage of ELO as in the case of flexural modulus. It was found that the values of flexural modulus were lowered by raising the heat-treated samples to 150 °C after being soaked for 4 hours at 80 °C. It can therefore be argued that by raising the temperature to 150°C decreases the mechanical properties of the polymer network of phenolic and epoxies resins mixed with linseed oil (58%). In other words, soaking the composite for 4 hours at 80 °C is enough.

Hwang et al., studied the effects of the functionality of an epoxy monomer on the composite properties of anisotropic conductive films (ACFs) and found that as the crosslink density of the epoxy network increased, the composite properties such as coefficient of thermal expansion (CTE), modulus, and glass transition temperature ( $T_g$ ), were improved. The improved composite properties were increased in modulus and  $T_g$  and decreased in CTE of ACFs. The crosslink density is number of moles of chains per  $\text{cm}^3$  and is inversely proportional to the number of average molecular weight between crosslinks,  $M_c$ . Crosslink densities could be determined from the elastic modulus of the samples according to the modified rubber elasticity theory and the equation is as follows: [12-13]

$$\nu = \frac{E'}{3RT} \quad (1)$$

where  $\nu$  represents the crosslink density (number of moles of chains per  $\text{cm}^3$ ),  $R$  is the gas constant (8.314J/K.mole),  $T$  is the temperature in Kelvin and  $E'$  is the elastic modulus or the storage modulus at  $T_g + 50$  °C.

In this study, the crosslink densities of composites 80/20 (Epoxy/Phenolic) , 70/30 and 60/40 with different percentage by weight (up to 20%) of ELO and cured 5% Phencat 382 were

calculated using equation (1). The crosslink densities found were plotted against percentage by weight of ELO and is shown in Figure 9. As shown for the 60/40 and 80/20 resin blends, the crosslink densities decreases with increasing percentage by weight of ELO in the resins. In other words, the increasing inclusion of the epoxidized linseed oil in the resin system increases the toughness of the system by reducing the crosslink density of the cured network. This increases in toughness is demonstrated by the decrease in the stiffness of the resins due to the proportional decreases in the flexural modulus (see Figure 5) with increasing amounts of added ELO. On the other hand, a reduction of ELO will have the opposite effect, i.e. an increases in the crosslink density, which will result in a proportional increases in the mechanical modulus of the cured resin, as previously discussed by Hwang et al. [12]. These results strengthen the argument of this paper that the ultimate properties of the composites (modulus and yield stress) decreased with the increase of ELO while the toughness and associated properties (yield strain) increased.

## **Conclusion**

It was discovered that Phencat 382 was the best catalyst for the composites. On top of this, when the post-cured condition was changed and the temperature of the samples was slowly raised to 150 °C after being soaked for 4 hours at 80 °C. It was found that composite 80/20 was the best material obtained and the flexural modulus of the composites decreased with increasing percentage by weight of ELO irrespective of the catalysts used. The drop is most significant with 10% UH and least significant with 10% Phencat 382. By raising the samples to 150 °C after being soaked at 80 °C for 4 hours, the mechanical properties of the composite 80/20 were lowered; therefore the post-curing of soaking the composite for 4

hours at 80 °C is enough. The values of crosslink densities are good indicator of properties of polymer based composites

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## **Figure Captions**

Figure 1: Formation of the hydroxymethyl derivatives phenol

Figure 2: Condensation of the hydroxymethyl derivates of phenol

Figure 3: Creation of the PF adhesives by the base-catalyse polymerisation

Figure 4: A schematic diagram for three point bending test

Figure 5: Flexural modulus against percentage of ELO for different catalysts

Figure 6: Flexural modulus against different percentages of ELO

Figure 7: Strain at break against different percentages of ELO

Figure 8: Peak flexural stress against different percentages of ELO

Figure 9: Crosslink densities of Epoxy/Phenolic composites vs. wt% of ELO

## **Tables**

Table 1: Results of mixing Hyrez 202 with phenolic resin and Phencat 382.

Table 2: Mechanical properties of composite 80/20 cured by different catalysts

Table 3: Curing states of composite 20/80 cured by different catalysts

Table 4: Mechanical properties of composite 20/80 cured by different catalysts