



LONG-TERM BEHAVIOUR OF PARTICULATE- FILLED EPOXY-BASED POLYMERS

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Mojdeh Mehrinejad Khotbehsara

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Abstract

Epoxy-based polymers are now widely used in civil engineering applications including bonding of structural elements, filling for structural repair, and coating for railway sleepers. Recently, different particulate fillers were introduced to reduce the cost of epoxy-based polymers. While the optimum amount of fillers was found to enhance the short-term properties of epoxy-based polymers, their effect on the long-term properties is still unknown. Understanding the long-term behavior of epoxy-based polymers is important as this material is subject to different environmental conditions, which can limit their application range.

This study systematically investigated the long-term durability through deep understanding of the mechanistic response of particulate-filled epoxy-based polymer coating containing fire retardant (FR) and fly ash (FA) fillers. It focused on the weathering effects of high moisture, elevated in-service temperature, and solar ultraviolet (UV) radiation, and the synergistic effects of these severe environmental conditions on the mechanical, physico-chemical and microstructure behavior of particulate-filled epoxy-based polymer. New empirical models were also developed to predict the changes in the mechanical characteristics of epoxy-based polymers when exposed to harsh environmental conditions.

The effect of in-service elevated temperature (from room temperature to 80°C) was evaluated as the first study. FR and FA filler materials were increased from 0% to 60% (with an increment of 20%) in the epoxy based matrix. The physical, mechanical and microstructure of particulate-filled epoxy polymers epoxy-based polymer matrix was examined. The results showed that sensitivity of epoxy resin against in-service temperatures can be significantly improved by the inclusion of fillers by up to 60% by volume. A simplified prediction equation based on power function showed a strong

correlation to the experimental strength properties of particulate-filled epoxy based resin at different levels of in-service elevated temperature.

The effect of the combined moisture and temperature (hygrothermal conditioning) on the durability of particulate-filled epoxy resin was investigated as the second study. The epoxy resin was conditioned for up to 3000 h at temperatures up to 60°C and a relative humidity of 98%. Inclusion of fillers was found to decrease the moisture absorption, increase the glass transition temperature and slightly reduce the mechanical properties after hygrothermal conditioning. Based on the Arrhenius model, the filled epoxy polymers can retain more than 70% of their mechanical properties at 100 years of service in the Australian environment.

The behaviour of the particulate filled epoxy polymer coating when exposed to UV was investigated as the third study. Epoxy-based resin system filled with FR and FA was exposed to UV for up to 2000 h. It was found that adding up to 60% by volume of FR and FA reduced the UV degradation to 0.5 mm, which is 5 times less than that of the neat epoxy resin. The developed prediction equation showed that providing a polymer coating of 11 mm will result in up to 100 years UV resistant materials.

Finally, the synergistic effect of temperature, moisture and UV on the long-term performance of the particulate filled epoxy polymer coating was evaluated. The polymer coating was conditioned at a relative humidity of 98% and temperature of 60°C for 2000 h (HG). These specimens were then exposed to UV for 2000 h. It was found that not all environmental conditions were detrimental to the properties of particulate filled epoxy, indicating its suitability as a protective coating material.

An in-depth understanding of the long-term behaviour of particulate filled epoxy polymer coating was the significant outcome of this study. The results from this

work provided a good representation and comparison of the long-term properties and durability performance of particulate filled epoxy polymer coating in different harsh environments. The experimental data, theoretical models and predictions equations derived from this study are critical for a safe mix design and use of epoxy-based polymers as coating for civil infrastructure.

Certification of Thesis

This Thesis is entirely the work of Mojdeh Mehrinejad Khotbehsara except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except w here acknowledged.

Principal Supervisor: Professor Allan Manalo

Associate Supervisor: Professor Thiru Aravinthan

Student and supervisors signatures of endorsement are held at the University.

Statements of Contributions

The articles produced from this study were a joint contribution of the authors. The details of the scientific contribution of each author are provided below:

Manuscript 1: Khotbehsara, M.M., Manalo, A., Aravinthan, T., Reddy, K.R., Ferdous, W., Wong, H. and Nazari, A., 2019. Effect of elevated in-service temperature on the mechanical properties and microstructure of particulate-filled epoxy polymers. *Polymer Degradation and Stability*, 170, p.108994. (Impact factor: 4.032 and SNIP: 1.591)

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The overall contribution of Mojdeh Mehrinejad was 60% related to the data collection, critical review of related literature, analysis and interpretation of data, drafting and revising the final submission. Allan Manalo, Thiru Aravinthan, Reddy Kakarla, Wahid Ferdous and Ali Nazari contributed to the structuring the manuscript, statistical analysis, analysis and interpretation of data, editing and providing important technical inputs.

Manuscript 2: Khotbehsara, M.M., Manalo, A., Aravinthan, T., Ferdous, W., Nguyen, K.T. and Hota, G., 2020. Ageing of particulate-filled epoxy resin under hygrothermal conditions. *Construction and Building Materials*, 249, p.118846. (Impact factor: 4.419 and SNIP: 2.217)

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Manuscript 3: Khotbehsara, M.M., Manalo, A., Aravinthan, T., Turner, J., Ferdous, W., and Hota, G. Effects of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating. *Polymer Degradation and Stability*, *PDST-D-20-00105R1*. (Impact factor: 4.032 and SNIP: 1.591).

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Abbreviations

FR	Fire retardant
FA	Fly ash
UV	Solar ultraviolet
HG	Hygrothermal aging
hr	Hour
GFRP	Glass fiber reinforced polymer
°C	Celsius
DGEBA	Bisphenol A diglycidyl ether
PFR	Particulate-filled epoxy polymer
T _g	Glass transition temperature
K	Degradation rate (1/time)
A	Constant relative
E _a	Energy of activation of reaction
R	Universal gas constant
T	Temperature in kelvin.
DMA	Dynamic Mechanical Analysis
TGA/DSC	Simultaneous Thermal Analysis
SEM	Scanning Electron Microscopy
FTIR	Fourier-transform infrared spectroscopy
γ_c	Crosslink density
\tilde{E}	Storage modulus
ANOVA	Analysis of variance

Chapter 1

Introduction

1.1 Background and motivation

Composite materials have been increasingly used in many applications such as the aerospace, aeronautical, marine and automobile industries. This use is due to their good properties including high specific tensile strength and stiffness, lower density, high fatigue endurance, high damping and low thermal coefficient (Azeez et al., 2013). These advanced materials are now also beginning to be used in civil engineering applications, wherein they are exposed to challenging environmental conditions, including high moisture, elevated in-service temperature and solar ultraviolet (UV) radiation. For example, Sirimanna et al. (2011) measured a surface temperature as high as 61°C for composite bridge decks, when exposed to the Australian summer which can have a negative effect on the mechanical properties of composites. In addition, a number of studies have been conducted to evaluate the durability of composite materials under different environmental conditions (Wang et al., 2018, Haque et al., 1991, Benmokrane et al., 2020, Ahmadi et al., 2020). Wang et al. (2018) found that after 120 days of hygrothermal aging (HG), carbon fibre/epoxy reduced the short-beam shear strength, in-plane shear strength and transverse flexural strength to 27.2%, 39.6% and 22.0%, respectively of their original strength. Mikami et al. (2015) observed a reduction in the adhesive strength of composite materials when they were exposed to a hygrothermal environment (HG), as the absorbed moisture induced swelling stress resulting in fibre-matrix debonding and matrix cracking. They concluded that the combination of high temperature and humidity was the most detrimental to bond strength. A study by Almeida et al. (2016) revealed that carbon

fibre/epoxy laminates, conditioned at 80°C and at a relative humidity of 90% for 60 days, exhibited a reduction in shear strength and modulus by about 70% and 60%, respectively. The reduction was due to a reversible plasticization of the matrix and induced stresses by the absorbed water. Further studies conducted by Bazli et al. (2020) found that the mechanical properties of pultruded GFRP tubes decreased after exposure to seawater conditions and at elevated temperatures. Up to 34% and 21% reduction on the compressive and tensile strengths, respectively were observed for 8-mm thick GFRP tubes after exposure to seawater for 6 months at 60°C. These studies showed that composite materials can be affected by severe environmental conditions and they should be protected to increase their service lives.

Epoxy-based polymers are currently being applied as protective coatings to minimise the environmental effects on the properties of fibre composites (Ferdous and Manalo, 2014). A number of studies have evaluated the sensitivity of polymers to hygrothermal conditioning (Xin et al., 2017, Manalo et al., 2020, Shamsuddoha et al., 2017) and found that the ingress of moisture can react with the epoxy polymer and impose internal stresses, causing a reduction in mechanical properties (Fiore et al., 2015). Elarbi and Wu (2017) found that moderate to high heat can significantly degrade the mechanical properties of epoxy resins; however, low to moderate heat can promote post curing resulting in enhanced flexural strength. Ghasemi-Khahrizangi et al. (2015) and Yusif and Haddad (2013) highlighted the harmful effects of UV exposure on the physical, mechanical and chemical properties of epoxy polymers. The photo-oxidative reaction caused by solar UV radiation reduces molecular weight and makes the polymer more brittle (Signor et al., 2003). When the UV rays are combined with other environmental factors such as atmospheric oxygen, moisture and temperature, the photo-oxidative degradation can be accelerated to break the

polymeric chains (Karbhari et al., 2003). The degradation is due to the energy of solar UV light being higher than the chemical bond strength, e.g., C–C, O–O, H–O, and C–N in polymers (Nikafshar et al., 2017). Rosu et al. (2012) also found that UV affects the polymer networks of epoxy resin and polyurethane. The processes of photodegradation and photo-oxidation during UV results in colour changes and mass losses in the exposed samples. In another study, Lu et al.(2018) concluded that UV degradation of polymeric surfaces was strongly dependent on UV wavelength, intensity and exposure time. Chin et al. (1997) observed surface erosion and cracking on thin polymer films made of vinyl ester and iso-polyester after exposure to a 1000-watt xenon arc source for 1200 h at 30°C in an Oriel solar simulator. These studies showed the significant effect of UV on the durability properties of epoxy polymers. Attempts to reduce the transparency of polymer coating are therefore necessary to minimise their degradation under solar UV radiation.

A number of studies have added particulate fillers to epoxy resin system and investigated their short term properties (Ferdous et al., 2016, Lokuge and Aravinthan, 2013, Shamsuddoha et al., 2013). Ferdous et al., (2016) showed that the addition of light-weight filler materials including fly ash (FA), fire retardant (FR) and hollow microsphere (HM) to the resin minimised the cost of an epoxy polymer matrix. Similarly, Lokuge and Aravinthan., (2013) added fly ash to increase the compressive strength of epoxy-based polymer concrete. Research on the effects of different filler materials such as fly ash and silica fume (Bărbuță et al., 2009, Rebeiz et al., 2004, Gorninski et al., 2004) on epoxy-based polymer concrete have also been investigated by other researchers, with the use of the former shown to improve the mechanical, chemical and durability properties of polymer concrete. Golestaneh et al., (2010) showed that a higher compressive strength can be achieved by adding fine or coarse

filler to epoxy-based polymer concrete. The improvement in strength using a blend of fine and coarse filler was also reported by Lim et al., (2009), where brittleness was reduced by optimising the filler contents. The addition of coarse filler is often recommended for structural repair to improve the curing and shrinkage performances in the epoxy grouts (Shamsuddoha et al., 2013). These studies have shown that in addition to minimising the cost, the introduction of fillers enhanced the physical and mechanical properties of epoxy-based polymer matrix. However, as epoxy polymers are exposed in the environment when used in civil engineering applications, their behaviour and long-term performance under different exposure conditions warrant detailed investigation.

Few studies have evaluated the long-term properties of epoxy matrices with fillers. Among these studies, He et al.,(2007) investigated the moisture absorption of DGEBA epoxy-based nanocomposites containing nano-calcium carbonate (nano-CaCO₃) and it was revealed that the moisture absorption decreased with increasing nano-CaCO₃ content. Chin et al.,(1997); Yan et al., (2015) and Peng et al., (2014) found that deterioration of the mechanical properties of polymeric composites due to UV radiation is caused by the surface oxidation resulting in surface erosion and cracking of the polymer matrix. Shamsuddoha et al. (2016) studied the long-term properties of epoxy polymers with different percentages (27%, 15% and 13%) and types of fillers under hot-wet conditioning for 1000 h at 70°C. Their results showed a reduction of up to 74% and 83% in the compressive and flexural strengths, respectively. These results indicated that composites are affected by hot-wet conditioning as the polymer resin absorbs and reacts with water, resulting in the weakening of the bond between the fibre and the matrix interface. To minimise the damaging effects of solar UV radiation on polymers, Tcherbi-Narteh et al. (2014)

incorporated nanoparticles in DGEBA epoxy resin. Their results showed that the addition of 1% by weight into polymer delayed the onset of destructive effects of UV due to partial curing of the epoxy and better dispersion of the nanoparticles. Cao et al. (1998) detected some enhancement in the properties of polymer coating systems after 2000 hrs of UV exposure with the addition of titanium dioxide (TiO₂) particles. In a recent study, Ferdous et al. (2016) evaluated the role of particulate fillers on the physical and flexural strength of epoxy polymers when exposed to simulated UV solar radiation. After 2000 h exposure, they found embrittlement, discolouration and reduction in weight in all the specimens. Lesser weight loss (0.15%) was measured for specimens with the highest amount of fillers (60%) than was observed for the neat epoxy resin (0.37%). These studies have shown that there is a benefit in introducing fillers to polymer coating in enhancing UV resistance. However, polymer coatings are exposed to a combination of environmental conditions in civil engineering applications and therefore a detailed understanding of their behaviour is needed. Although some studies have investigated the effect of environmental factors on fibre composites, a limited number of studies have investigated the synergistic effects of hygrothermal conditioning and ultraviolet solar radiation on the properties of particulate-filled epoxy polymer (PFR) coating.

In civil engineering applications, the particulate-filled epoxy-based polymer coating matrices are generally exposed to moisture, rain, frost, snow, hail and dew, which significantly contribute to the degradation of polymer composites. These harsh environmental conditions are known to affect the physical and mechanical properties of particulate-filled epoxy-based polymer coating systems and may limit their application range. Moreover, they are generally exposed to UV radiation and high temperature. Although a number of studies have focused on the effects of harsh

environments on the properties of composite materials, most of them have evaluated the materials resistance exposed to one weathering condition. In service, particulate-filled epoxy-based polymer coating are generally exposed to a combination of environmental conditions. It is necessary therefore to have a deep understanding of the long-term durability properties of epoxy-based polymer coating. This research focuses on understanding both the single and synergistic effects of different weather conditions such as high temperature, moisture, and ambient UV radiation on the durability of the particulate-filled epoxy-based polymers. The physical, mechanical, thermo-mechanical and microstructure behaviour of these materials are investigated (**Figure 1.1**). Empirical models that can predict the changes in the mechanical characteristics of particulate-filled epoxy-based polymer coating when exposed to harsh environmental conditions are also developed to predict the strength retention after 100 years of service in the Australian environment.

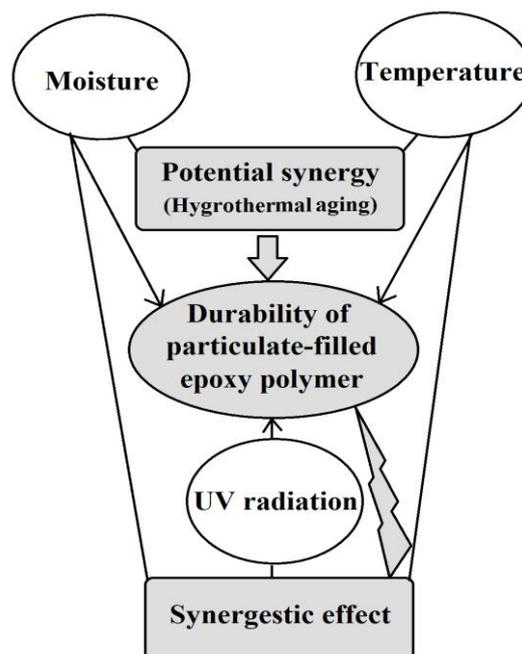


Figure 1.1: Diagram of environmental factors influencing the durability of the particulate-filled epoxy-based polymer coating with fillers

1.2 Objectives:

This study aims to investigate the long-term behaviour of epoxy-based polymers containing different percentages of fire retardant (FR) and fly ash (FA) fillers and to explain the interactions affecting their durability when exposed to different environmental conditions. The specific objectives of this study are:

1. Investigate the mechanical and microstructural properties of the particulate-filled epoxy-based polymer coating with light-weight fillers exposed to elevated temperature;
2. Assess the properties of particulate-filled epoxy-based polymer coating after exposure to high moisture and elevated temperature;
3. Evaluate the effects of ultraviolet (UV) radiation exposure on the properties of epoxy-based polymer coating with fillers;
4. Determine the synergistic effects of temperature, moisture and UV on the durability of epoxy-based polymers with fillers; and
5. Predict the long-term properties of the particulate-filled epoxy-based polymer coating with fillers when subjected to different environmental conditions.

1.3 Thesis organization

This dissertation comprises an **Introduction** that highlights the research theme, extensive **Review of Literature**, four major studies that addresses the five objectives, and a **Conclusion** that summarizes the findings and contributions of this study. Four high quality journal articles produced from this research are presented below:

Article from study 1:

Study 1 focused on the effect of in-service elevated temperature to address the first and fifth objectives of the study.

Article I: Khotbehsara, M.M., Manalo, A., Aravinthan, T., Reddy, K.R., Ferdous, W., Wong, H. and Nazari, A., 2019. Effect of elevated in-service temperature on the mechanical properties and microstructure of particulate-filled epoxy polymers. *Polymer Degradation and Stability*, 170, p.108994.

Article from study 2:

Study 2 focused on the effect of hygrothermal conditioning to address the second and fifth objectives of the study.

Article II: Mojdeh Mehrinejad Khotbehsara , Allan Manalo, Thiru Aravinthan, Wahid Ferdous, Kate T. Q. Nguyen, and Hota Gangarao. Ageing of particulate-filled epoxy resin under hygrothermal conditions. *Construction and Building Materials*, 249, p.118846.

Article from study 3:

Study 3 focused on the effect of UV exposure to address the third and fifth objectives.

Article III: Mojdeh Mehrinejad Khotbehsara: Allan Manalo, Thiru Aravinthan, Wahid Ferdous, Joanna Turner, and Hota Gangarao. Effects of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating. *Polymer Degradation and Stability*

Article from study 4:

Study 4 focused on the synergistic effect of temperature, moisture and UV to address the fourth and fifth objectives.

Article IV: Mojdeh Mehrinejad Khotbehsara: Allan Manalo, Thiru Aravinthan, Wahid Ferdous, Nguyen, K.T. and Benmokrane, B. Synergistic effect of hygrothermal conditioning and ultraviolet solar radiation on the properties of particulate-filled epoxy based polymers. *Construction and Building Materials*

The significant results of these research were also disseminated in technical posters and in national and international conferences as provided in **Appendices A and B**.

1.4 Summary

In civil engineering applications, particulate-filled epoxy polymer coating is exposed to moisture, in-service elevated temperature, and ultraviolet (UV) radiation. These harsh environmental conditions are known to affect the physical and mechanical properties of a construction and building materials. While a number of researchers have investigated the durability and long-term performance of epoxy resin systems under the effect of different environments, studies on the long-term performance of particulate-filled epoxy-based polymer coating are limited. Moreover, the synergistic effects of the combination of these harsh environmental conditions are still unknown. This is the main motivation of this research and will be addressed in the technical sections presented in Chapters 3 to 6. Moreover, an in-depth review of related literature is conducted to assess state-of-the-art in the field and to identify the gaps in knowledge in this area, which is presented in the next section.

Chapter 2

Literature review

This chapter discusses the applications of epoxy-based polymers and reviews their durability and long-term performance under different environmental conditions. It focuses on the effect of different environmental conditions, including high moisture, elevated in-service temperature and solar ultraviolet (UV) radiation on the behaviour of epoxy based polymers. It also provides a critical review of the different types of fillers and their effect on the overall behaviour of the epoxy based polymers. Moreover, the gaps in knowledge were identified to address the durability and long-term performance issue of epoxy polymers, when used as a coating materials in harsh environmental conditions.

2.1. Applications of epoxy-based polymers in civil engineering

The term ‘epoxy resin’ refers to both the reactive polymer and its cured resin/hardener system (Azeez et al., 2013). Generally, this reaction is exothermic (i.e., generates heat) and forms long polymer chains during the curing process which create the matrix’s flexibility and strength. This type of polymer system requires a certain curing time in order to develop sufficient strength and stiffness. As a matrix for composite fibres, epoxy resin can bind them together into a cohesive structural unit and play a significant role in composite performances. They also protect the reinforcing fibres from adverse environments and provide all the inter-laminar shear strength and resistance against crack propagation and damage (Kumar, 2016).

Despite the cost benefits of vinyl-ester and polyester compared to epoxy, they are not suitable if excellent mechanical and thermal properties, superior resistance to humidity, low shrinkage and high elongation are required in order to produce a durable and flexible polymer matrix (Loos, 2014). As a result, epoxy resins have been used in

a wide variety of applications in the automotive, construction and aerospace industries (May, 1987). Epoxy-based polymers are now also being used in civil engineering applications such as bonding of structural elements (Heshmati et al., 2015, Adhikarinayake et al., 2016), infill for structural repair systems (Karayannis and Sirkelis, 2008, Issa and Debs, 2007, Azraai et al., 2015, Shamsuddoha et al., 2013), and coating for railway sleepers (Van Erp and Mckay, 2013, Ferdous et al., 2016) as shown in **Figures 2.1 to 2.4**. Epoxy grouts have also proven effective for repairing metallic components and tubular pipes with corroded or gouged sections (Duell et al., 2008). Another development is the epoxy filled repair sleeve that can be used to repair high-pressure pipelines in moist or underwater conditions (Gibson, 2003, Seica and Packer, 2007, Palmer-Jones et al., 2011). Similarly, epoxy-based polymer concrete has sparked a growing interest in civil engineering owing to its great resistance to chemical aggression, by fast hardening, good adhesion with the aggregates and mechanical strength, in particular under tension, higher than the cement based concretes (ACI Committee, 2009). Epoxy polymers are also used as protective coating to composite materials and structures; wherein they are exposed to aggressive environmental conditions including moisture, in-service temperature and solar ultraviolet (UV) radiation (Ferdous and Manalo, 2014). Due to the increasing interest and applications of epoxy polymers, a good understanding of their short- and long-term properties is warranted for their wider use and acceptance in civil engineering applications.



Figure 2.1: Concrete crack repair- epoxy resin injection (www.strongtie.com.au)

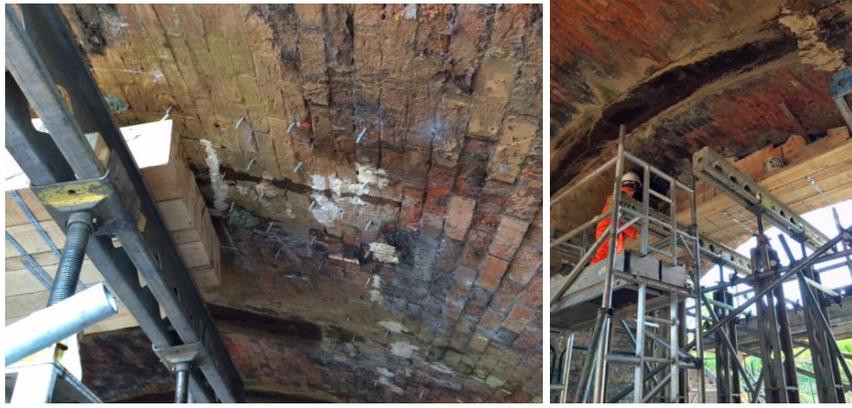


Figure 2.2: Bridge repairs to trough bearings using epoxy resin (www.h2ox.net)



Figure 2.3. Pipe exterior repair using infill and flexible wrap, filling defect with putty and wrapping epoxy wetted carbon fabric around the defect (Duell et al., 2008)



Figure 2.4. Sandwich panels coated by epoxy in railway sleepers (Ferdous et al., 2016, Van Erp and McKay, 2013)

2.2. *Properties of epoxy resin*

The choice of a particular resin for civil engineering applications depends mainly on its compressive and tensile properties, glass transition temperature, durability, ease of processing, material availability, and cost. In the past, researchers have investigated different resin systems in polymer concrete with the most commonly used resins

including epoxy (Elalaoui et al., 2012), vinyl-ester (Lokuge and Aravinthan, 2013) and polyester (Ferreira et al., 2000). Epoxies are known to have excellent balance between various properties such as mechanical and physical properties, high degree of adhesion properties to almost any adherends, humidity resistance and finally heat resistance. Epoxies also have moderately superior thermal stability than vinylesters and polyesters which makes them the preferred resin system in civil engineering applications (Carbas et al., 2013, Strong, 2008). Epoxy resins, along with high strength fibres like carbon, are also known for their anti-corrosive performance and durability even in moist or even underwater conditions (Seica and Packer, 2007). The advantages of epoxy resins compared to vinyl-esters and polyesters are shown in **Table 2.1**. However, the relatively high cost compared to hydraulic concrete and other type of polymeric resin systems, represent the main obstacles for the further use of epoxy-based resin systems (Elalaoui et al., 2012).

Table 2.1: Advantages of epoxy resin

Advantages	References
i. Wide range of adaptability	i. (Shamsuddoha et al., 2013, Loos, 2014, Kumar, 2016)
ii. Better compatibility with fibres	ii. (Ray, 2006, Seica and Packer, 2007)
iii. Good moisture and chemical resistance	iii. (Seica and Packer, 2007, Loos, 2014, Lokuge and Aravinthan, 2013)
iv. Superior physical and mechanical properties	iv. (ACI Committee, 2009, (Ferdous et al., 2016, Blaga and Beaudoin, 1985, Lokuge and Aravinthan, 2013)
v. Low cure shrinkage	v. (Lokuge and Aravinthan, 2013, Shamsuddoha et al., 2013, Loos, 2014)
vi. Better adhesion	vi. (Lokuge and Aravinthan, 2013, Shamsuddoha et al., 2013)

2.3. *Epoxy Resin with fillers*

Many researchers have introduced different kind of fillers to reduce the cost of epoxy and to further improved their physical, mechanical and durability properties. The choice of particular filler types depends upon factors like cost, desired properties, and

chemical/weather resistance (Kumar, 2016, Unnikrishnan and Thachil, 2006, Yang et al., 2005). Singh et al.,(2002) and Pinto et al. (2015) have shown that nanofillers (metallic or inorganic type) are excellent in improving the mechanical, thermal and electrical properties of epoxy resins. This is because nanofillers have large surface areas, which makes them chemically very active and helps them to bond with the matrix. Although the positive effects of nanomaterials on the performance of epoxy matrix have been proven, their high cost has limited their use in civil engineering applications.

Research into the effects of fly ash and silica fume on the physical and mechanical properties epoxy-based polymer concrete have been investigated by several researchers (Rebeiz et al., 2004, Bărbuță et al., 2009, Gorninski et al., 2004). Fly ash, a product of the coal burning in power plants, is used as filler because of its easy availability and relatively low price (Gorninski et al., 2004). Shamsuddoha et al. (2013) added fillers of different particle sizes to reduce the cost in addition to reduce the shrinkage of three epoxy grout systems. Most recently, Ferdous et al. (2016) added lightweight filler materials to minimise the cost of an epoxy polymer matrix.

The application of epoxy resin is limited by their inherent flammability. There has been a trend in recent years, driven principally by environmental and safety considerations, towards use of halogen free fire retardant systems, including intumescent formulations and dehydrated fillers. Several of the materials listed in **Table 2.2** are potentially suitable fire retardant fillers for polymers.

Table 2.2: Candidate fire retardant fillers (Hornsby, 2001)

Candidate material (common names and formula)	Approximate onset of decomposition, °C	Approximate enthalpy of decomposition, $\text{kJ g}^{-1} \times 10^3$	Volatile content, wt-%		
			Total	H ₂ O	CO ₂
Nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	70–100	1750	61	39	22
Alumina trihydrate, aluminium hydroxide $\text{Al}(\text{OH})_3$	180–200	1300	34.5	34.5	0
Basic magnesium carbonate, hydromagnesite $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	220–240	1300	56	20	36
Sodium dawsonite $\text{NaAl}(\text{OH})_2\text{CO}_3$	240–260	NA	43	12.5	30.5
Magnesium hydroxide $\text{Mg}(\text{OH})_2$	300–320	1450	31	31	0
Magnesium carbonate subhydrate $\text{MgO} \cdot \text{CO}_{2(0.96)}\text{H}_2\text{O}_{(0.30)}$	340–350	NA	56	9	47
Calcium hydroxide $\text{Ca}(\text{OH})_2$	430–450	1150	24	24	0

Substantial industrial use is made of the principal fire retardant fillers ATH, MH, and, to a lesser extent, hydromagnesite/huntite mixtures. They account for more than 50% by weight of worldwide sales of fire retardants. It is estimated that the current use of flame retardant fillers is over 400 kt/annum. Lower cost grades of Aluminum hydroxide ($\text{Al}(\text{OH})_3$), also known as ATH, is produced using the Bayer process from mineral bauxite using the Bayer process and mainly used in thermosetting resins. The heat capacity of these fillers and, in particular, the strong endotherm can strongly influence the input of heat required for polymer decomposition and release of combustible volatiles. At sufficiently high filler levels, hydrated fillers can also reduce the mass burning rate by inhibiting the rates of heat transfer from the flame to the underlying matrix (Hornsby, 2010).

The effects of the addition of different filler materials in the physical, mechanical, and durability properties of epoxy based polymers are discussed in the succeeding sections.

2.3.1. Physical properties of epoxy with filler

Shamsuddoha et al. (2013) showed that the shrinkage of viscous epoxy resin can be reduced by introducing fine and coarse aggregates as fillers to the resin. The results of their study showed a maximum shrinkage of only 2.77% for epoxy resin with 65% by weight of fine filler, which was seemed applicable for structural repair of steel pipelines. Ferdous et al., (2016) found that the amounts of voids and density of the

DGEBA epoxy polymer changes with the addition of fillers including FA, FR and HM. Their results showed that the densities of the solid specimens gradually increased from 1.093 g/cm³ to 1.458 g/cm³ with increases from 0% to 60% of filler volume. The increase of density was expected with the increase of filler as the density of filler (FR: 2.411 g/cm³, HM: 0.752 g/cm³ and FA: 2.006 g/cm³) was higher than that of the resin system (Part-A: 1.068 g/cm³ and Part-B: 1.183 g/cm³). On the other hand, the increase in the porosity from 0.02% to 4.37% with the increase in filler volume from 0% to 60% makes the polymer matrix less workable. The addition of fillers also increased the pore sizes which were less than acceptable in an ideal polymer matrix. They further concluded that the mixes containing 0 to 30% filler volumes were resin-rich or flowable which allowed the easy escape of voids whereas the addition of 40% or more basically produced filler-dominated mixes in which air bubbles usually became stuck. **Figure 2.5** shows the surfaces of the specimens containing different filler volume (0%, 40% and 60%), where the black spots represent void areas and the red solid surfaces. The relative porosity measured from the image analysis was used to evaluate requirements for the coating material. These results indicated the importance of investigating the effect of particulate fillers not only on the physical but also on the mechanical properties of epoxy-based polymers.

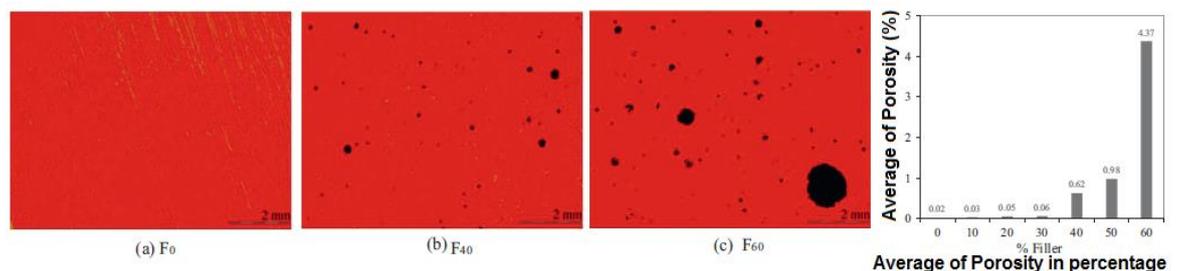


Figure 2.5. Effect of 0% (F₀), 40% (F₄₀) and 60% (F₆₀) on the porosity (Ferdous et al., 2016)

2.3.2. Mechanical properties of epoxy with fillers

The mechanical properties of epoxy matrices with different filler materials were investigated by a number of researchers. **Table 2.3** shows some a summary of the significant research and developments in using fillers in epoxy matrix.

Table 2.3: Research, development and practices in epoxy matrix

Reference	Description	Result
(Gojny et al., 2005)	Influence of carbon nanotubes on the mechanical properties of DGEBA-based epoxy matrix composites	Inclusion of CNT enhanced the tensile strength (with the maximum of 8% at 0.3 wt% amino-functionalised DWCNT)
(Bărbuță et al., 2009)	Effect of fly ash and silica fume in polymer concrete containing epoxy resin	With 10.4% silica fume, increased the compressive strength up for 51% and split tensile strength for 53%. 19% increase for addition of fly ash up to 12.8% in compressive strength and 40% increase in split tensile
(Lokuge and Aravinthan, 2013)	Effect of fly ash in polymer concrete	7% increase in compressive strength containing epoxy resin by addition of up to 10% Fly ash and 30% reduction in flexural strength
(Wan et al., 2014)	DGEBA-based epoxy resin composites filled with silane-functionalized graphene oxide	With 0.25 wt% silane-f-GO, the tensile modulus and strength increased by ~10% (3.45 ± 0.13 GPa) and ~48% (78.33 ± 2.73 MPa)
(Amaro et al., 2016)	Effect of nanoalumina on mechanical properties of D.E.R. TM 332 epoxy resin	1 wt.% of alumina nanoparticles 50% increased the bending strength (from 100MPa to 150 MPa)
(Ferdous et al., 2016)	Effect of Fly ash, Hollow microsphere and Fire retardant in DGEBA-based epoxy resin matrix	32% and 70% reduction in compressive and flexural strength, respectively by adding up to 60% fillers

The results of the work by Gojny et al. (2005) demonstrated that carbon nanotubes (CNTs) in general exhibit a certain potential to improve the mechanical properties of the epoxy matrix systems. Amaro et al. (2016) also studied the reinforcing effects of pretreated alpha alumina nanoparticles (with irregular shapes and with 100 nm maximum size) on the flexural and hardness properties of epoxy resin nanocomposites using Diaminodiphenylmethane (DDM) as hardener. They evaluated the effects of

several variables related to the nanofillers, such as size, shape, surface area, surface pretreatment type, particle size distribution and percentage of loading, as well as the used dispersion technique. **Figure 2.6** shows their findings that the neat sample presents a typical smooth surface, which can lead to brittle fractures, while the addition of nanoparticles made the surface rough, which resulted in increased mechanical properties.

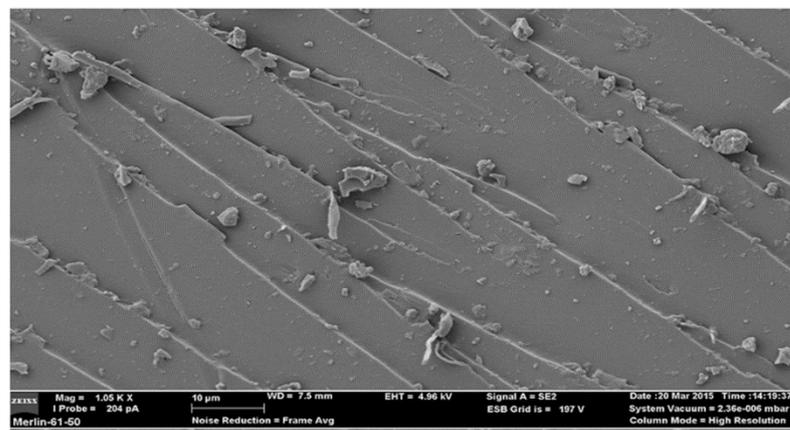
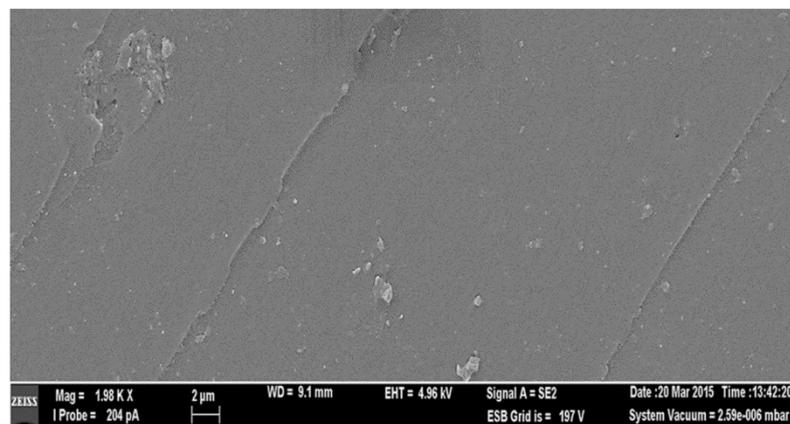
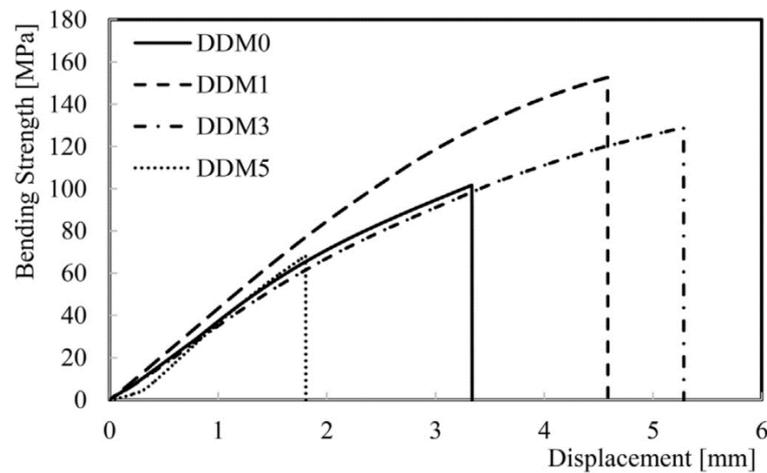
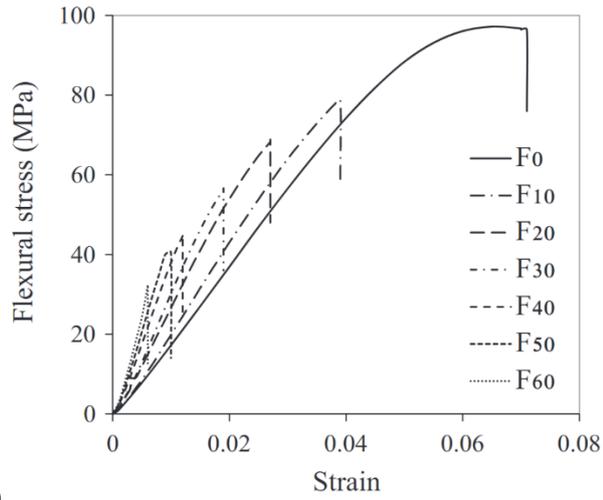
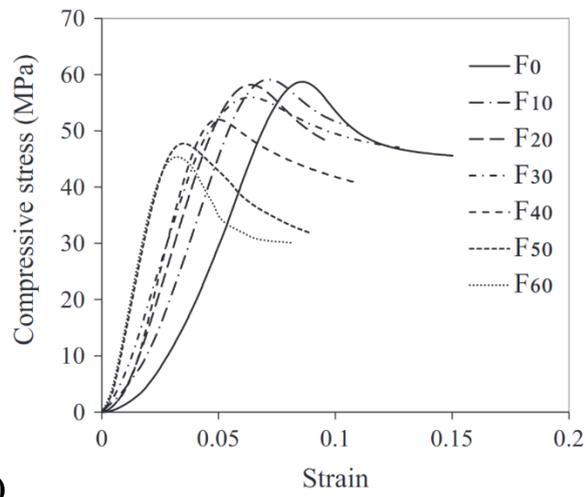


Figure. 2.6. a) Typical bending strength-displacement curves for 0, 1, 3 and 5wt.% of alumina nanoparticles and SEM images of fractured surface: b) 0wt.% nanoparticles c) 3wt.% nanoparticles (Amaro et al., 2016)

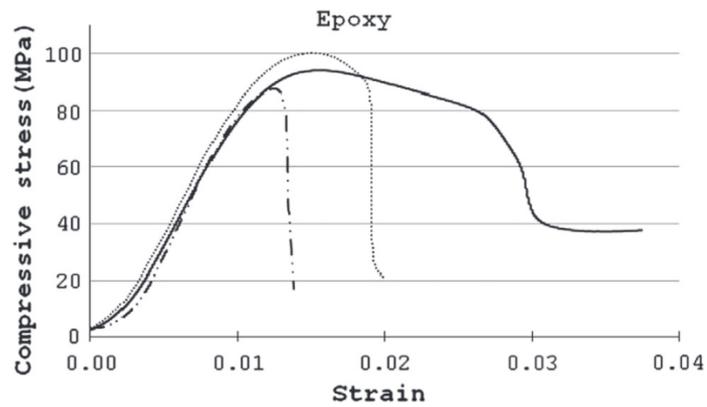
Wan et al.(2014) investigated the mechanical properties of the composites with both the as-produced graphene oxide (GO) and silane functionalized GO (silane-f-GO). Their microstructure analysis including FTIR, XPS, Raman, TGA and XRD demonstrated that the (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) coupling agent containing epoxy ended-groups was successfully grafted onto the surface of GO sheets. TOM, TEM and SEM analysis revealed that such silane covalent functionalization of GO produced improved dispersion and strong interfacial interaction with the epoxy matrix, which provided ameliorating effects in the improvement of thermal and mechanical properties of the silane-f-GO/epoxy composites. Bărbuță et al., (2009) found that the addition of fillers in small amounts such as nanofillers and mineral additives increased the mechanical properties of polymer concrete, while the further addition showed a reverse trend. Ferdous et al. (2016) also showed that the addition of more than 20% fillers to the DGEBA based polymer matrices reduced the mechanical properties, but to a level that could still satisfactorily meet the requirements for coating of composite railway sleepers (**Figure 2.7a and b**). A similar trend was reported by Lokuge and Aravinthan (2013) (**Figure 2.7c**) who revealed that when the epoxy content was increased beyond 20%, the split tensile, flexural and compressive strength of polymer concrete would be reduced.



a)



b)



c)

Figure 2.7: a) Flexural and b) compressive stress-strain behaviours (Ferdous et al., 2016), c) Compressive stress-strain behaviours (Lokuge and Aravinthan, 2013)

The above studies show that, while the optimum amount of fillers was found to enhance the short-term properties of epoxy-based polymers, their effect on the long-term properties is still limited. This information is very important as the epoxy-based polymer when used as a coating material is subject to different environmental conditions including high moisture, elevated in-service temperature, and solar UV radiation. These harsh environmental conditions may affect the physical and mechanical properties of epoxy-based polymer coating systems and should warrant a detailed investigation.

2.4. Durability of epoxy matrix with fillers

Epoxy-based polymers are applied as protective coatings to minimise the environmental effects on the properties of fibre composites in civil engineering infrastructures, wherein they are exposed to challenging environmental conditions, including high moisture, elevated in-service temperature and solar UV radiation. This section reviews the effects of these harsh environments on the durability and long-term properties of epoxy polymers.

2.4.1. Effect of elevated temperature

A significant consideration in the use of epoxy polymers is the threat of elevated temperature as it is an important durability property. Performance of epoxy-repaired concrete beams under thermal cycling was first investigated by Al-Mandil et al. (1990), who found that the alternate heating and cooling had a detrimental effect on the performance of the bond between epoxy and concrete as it imposes internal stress. The swelling stress induced by the moisture uptake can also cause matrix cracking and fibre-matrix debonding (Hayes et al., 2000). A high temperature and high humidity are particularly detrimental (Mikami et al., 2015). This adverse effect on the bond strength was more noticeable when the epoxy-concrete interface was subjected to tensile

stresses, as opposed to the case where the interface was subjected to combined compression and shear. However, El-Hawary and Abdel-Fattah (2000) showed a reverse trend. They carried out experiments on polymer concretes prepared using different resins (one polyester and two epoxies, for grouting and bonding applications) and aggregates constituted by sand and gravels. Different ratios of polymers (9%, 12% and 15% by weight) and exposure temperatures (20, 100, 150 and 200°C) were considered. They confirmed that the increase in the percentages of polymer in concrete increased the compressive strength up to approximately 200% between 20°C and 200°C for 12% of epoxy resin. Moreover, they explained that there was little change in the modulus of elasticity due to temperature exposure below 200°C. A reduction in tensile strength due to temperature exposure was observed for all polymer concretes while an increase in toughness and compressive strength were noticed. They explained that the heating and cooling cycles cause hardening in the polymer and increase in compressive strength. This effect is coupled, however, with the deterioration and loss of strength of the polymer concrete due to temperature, as is the case with any other type of concrete. The two factors together reduce the effect of temperature on polymer concrete.

It has been noted in the literature that when the polymers are exposed to high temperature the matrix will soften, and this can cause distortion, buckling and failure of load-bearing structures (Karbhari, 2007). For example, a sleeper made from polymeric materials can demonstrate two different mechanical behaviours below and above its glass transition temperature (T_g). T_g is one of the most important thermal properties for designs of polymeric composite materials (Michels et al., 2015). At a temperature below T_g , a polymeric material exhibits a high modulus and behaves like a glassy material. However, its modulus drops dramatically and it behaves in a rubbery

fashion when exposed to a temperature above its T_g . The effect of temperature is more significant in the case of turnout bearers that have a long length greater than 5.5 m each. Moreover, significant dimensional changes can occur in a plastic sleeper due to temperature variations (Cirko, 2014). High-temperature tests of the properties of a variety of fibre reinforced polymers (FRP) containing epoxy resin were conducted by a number of researchers. Fujisaki et al., (1993) reported a reduction of 40% in the tensile strength of glass-carbon FRP grids at a temperature of 100°C, probably due to changes in the properties of the polymer that forms the grid; however, no further reduction was seen for higher temperatures of up to 250°C. Ningyun and Evans (1995) reported a reduction of 75% in the flexural strength of FRP beams containing epoxy resin as the temperature was increased from room temperature to 300°C.

The simplest and usually most cost-effective way of increasing the heat resistance of polymers is the addition of fire retardant fillers. The filler particles are blended into the liquid resin during the final stage of processing and must be uniformly dispersed to ensure consistent fire retardant properties. Most polymers need a high loading of fillers and the average content in most resins is 40-60% (Karbhari, 2007). Wan et al. (2014) filled epoxy composites with silane-functionalized graphene oxide. Their DMA results showed that the glass transition temperature and thermal decomposition temperature shifted to a higher temperature after the silane functionalization (from 147.9 °C for neat epoxy to 149.5 °C for the epoxy composite with 0.5 wt% GO) (**Figure 2.8a**). Shamsuddoha et al.,(2016) also found that the inclusion of fillers increased the T_g from 53°C in grouts containing fine fillers to 60°C in grouts containing coarse fillers. Ferdous et al., (2016) conducted research on the thermal properties of DGEBA epoxy polymer matrix with fire retardant, fly ash and hollow microsphere. The exothermic reaction between the resin (Part-A) and hardener

(Part-B) could generate temperatures up to 75°C which were uncomfortable to handle and difficult to work with. The addition of a filler to the resin up to 60 % resulted in a temperature in a comfortable working range. They also showed that at room-temperature curing, the addition of filler increased the glass transition temperature obtained from storage modulus curve of DMA test up to 55°C, which was 5°C more than the neat epoxy resin (**Figure 2.8b**).

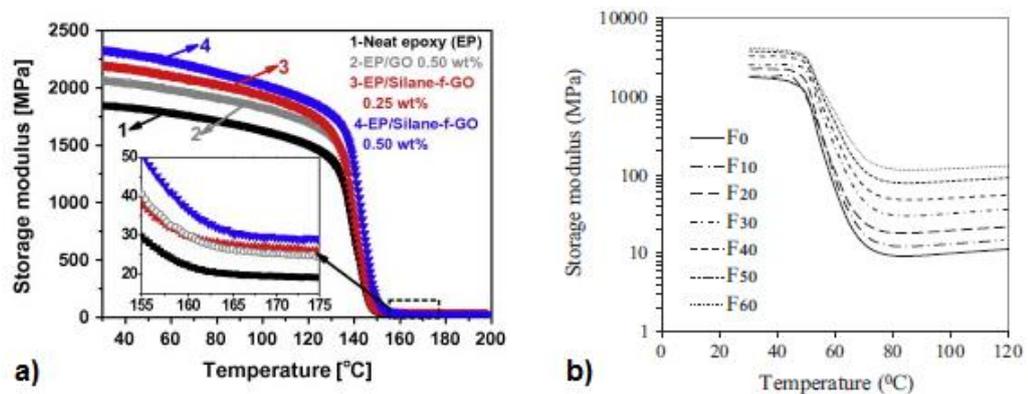


Figure 2.8: Storage modulus curve of a) neat epoxy and its nanocomposites (Wan et al., 2014) and b) neat epoxy and different percentages of fillers (Ferdous et al., 2016)

2.4.2. Effect of moisture

Exposure to the harsh climate can result in structures being subjected to stress, shrinkage cracking and deterioration. The harsh environmental conditions include alkalinity, and high humidity (hygrothermal environment), which significantly contribute to the degradation of a polymer composite as the ingress of moisture can weaken not only its polymer resin but also its reinforcing fibres. This absorption can react with the polymer matrix and impose internal stress, which causes reduction in a composite's overall mechanical properties (Fiore et al., 2015, Chou and Ding, 2000, Hayes et al., 2000). Generally, there are three absorption modes: i) bulk dissolution of water in the polymer network, ii) moisture absorption onto the surface of vacuoles which define the excess free volume of the glassy structure, and iii) hydrogen bonding between polymer hydrophilic groups and water (Apicella and Nicolais, 1985). Elarbi

and Wu (2017) investigated the flexural behaviour of epoxy-based FRP sheets and found that this composite is more sensitive to moisture under elevated temperature than at room temperature moisture. The combination of high humidity and long exposure time (1250 hrs) produced a strong negative effect. The literature shows that hygrothermal conditioning can increase the moisture absorption of epoxy resin from less than %0.05 to %2.5 in various time of conditioning (Masoodi et al., 2012; Soles et al., 1998; Leman et al., 2008). The maximum deflection of the specimens exposed at 0% humidity was two to four times higher than that of the specimens at 100% humidity. A study on using carbon/epoxy and glass/epoxy composites also suggested that interfacial adhesion was affected by hygrothermal ageing, especially at high conditioning temperature and long exposure time (Ray, 2006). As a result, a number of researchers tried to improve the moisture resistance of epoxy polymers by adding nanofillers (He et al., 2016, Amaro et al., 2016, Dittanet et al., 2017). For example, He et al. (2016) investigated the moisture absorption of DGEBA epoxy-based nanocomposites containing nano-calcium carbonate (nano-CaCO₃) and it was revealed that the moisture absorption decreased from 4.1% up to 2.8% with increasing nano-CaCO₃ content up to 4 wt% as shown in **Figure 2.9a**. This was due to a more uniform distribution of nano-CaCO₃ particles, which created a longer diffusion path for moisture in the nanocomposites.

The T_g of polymeric composites can be affected by moisture and becomes low when water is absorbed (Selzer and Friedrich, 1997). There are several factors, which can affect the T_g of a polymer, but the one of prime interest is associated with changes arising from the absorption of water into the cured epoxy structure. The T_g can be altered by changing the polymer's free volume at a given temperature. If a polymer were mixed with a miscible liquid that contains more free volume than the pure

polymer, then the T_g will be lowered. In particular, if it is further assumed that the free volumes are additives, then the polymer-diluent mixture will contain more free volume at a given temperature than would the polymer alone. As a result, plasticized polymers must be cooled to a lower temperature in order to reduce their free volume to 1/40 of the total volume of the polymer-diluent combination. This is the process, which is proposed to occur when moisture is absorbed into an epoxy resin (Browning, 1978).

The addition of nanofillers has been shown to decrease the moisture absorption and increase the performance of epoxy matrix. However, other studies have suggested the negative effect of the inclusion of other kinds of fillers to epoxy resin. Shamsuddoha et al. (2016) subjected different percentages of epoxy (27%, 15% and 13%) with various combinations of fillers: i) fine aggregates; ii) fine coarse aggregates; and iii) fine and coarse aggregates in hot-wet conditions for 1000 hrs. Their results showed a mild change in colour on the surface of the grout. **Figure 2.9b** shows that the average moisture absorption of the grouts was within a range of 0.5–2.7% after 1000 hrs. This moisture absorption reduced the bonding between the aggregate and matrix causing a reduction in tensile strength and modulus. Moreover, the mechanical properties were reduced as well as the T_g (30% reduction shown in **Figure 2.9b**) because elevated temperature moist curing limited their applicability in a submerged service condition. The lower resin content was related to higher moist absorption in epoxy modified mortar (Shamsuddoha et al., 2016).

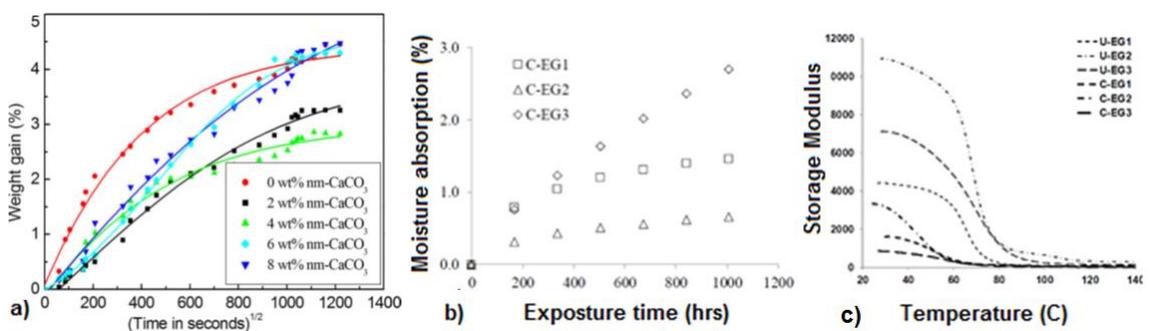


Figure 2.9: a) Effect of nano-CaCO₃ in moisture absorption (He et al., 2016), b) Moisture absorption and c) thermal plots to get T_g in conditioned and unconditioned grouts (Shamsuddoha et al., 2016)

From the results of the above studies, it can be concluded that different kind of fillers will have different effects on the durability of epoxy resin system in a high moisture environment. It is therefore important to understand the effect of fillers on properties of epoxy polymers exposed to other environmental conditions.

2.4.3. Effect of photochemical reactions from solar ultraviolet (UV)

Solar UV radiation is responsible for photolytic, photo-oxidative, and thermos-oxidative reactions that can cause degradation of polymeric materials. This photo-oxidative reaction reduces the molecular weight and makes the polymer more brittle (Signor et al., 2003). The UV rays caused by sunlight are frequently combined with atmospheric oxygen, moisture, temperature, wind-borne abrasives, freeze-thaw and other environmental factors, and their photo-oxidative degradation can break the polymeric chains (Karbhari et al., 2003). Due to photo-oxidation, the polymer matrix is greatly affected by UV radiation and can affect its physical and mechanical properties (Yan et al., 2015). To reduce the transparency of epoxy resin, non-transparent fillers like fly ash can be added (Ferdous et al., 2016). In addition to the degradation under UV radiation, epoxy resins also experience a significant degradation under elevated temperature.

The mechanism of the UV effects on silicone adhesives is shown in **Figure 2.10** (Isaacson et al., 2016). Tcherbi-Narteh et al. (2014) incorporated nanoparticles into polymer composites in order to improve the UV resistance of DGEBA epoxy resin. Their results showed that the addition of 1 wt. % nanoparticles will have a higher catalytic effect than neat resin after 2500 hrs of UV radiation exposure due to

dispersion of nanoparticles within the mix and partial curing. On the other hand, the combination of UV exposure time (500, 1000 and 1500 h) and water spraying on bidirectional woven flax fabric/epoxy composites as found by Yan et al., (2015) showed that the specimen surface became fuzzier with exposure time. The change in colour occurred immediately at the first 500 hrs. Up to 10% and 29% reduction in tensile and flexural properties, respectively, was then observed after 1500 h of UV exposure, which was mainly attributed to the degradation of the flax fibres and the fibre/matrix interfacial bonding. In the accelerated weathering chamber, the UV light and the high humidity (water spraying) cycles had a negative effect on the contents of the cellulose, hemicellulose, and lignin within the flax fibre. Compared to the pure epoxy, the tensile properties of the controlled composite (0 h) increased by 61.4%. Chin et al. (1997) investigated the UV radiation on thin polymer films exposed to a 1000 watt xenon arc source for 1200 h at 30°C in an Oriel solar simulator. They observed surface oxidation results surface erosion and cracking for both vinyl ester and iso-polyester samples. Peng et al. (2014) studied the accelerated weathering on polypropylene composites reinforced with wood flour, lignin and cellulose at different loading levels from 0 to 960 h. They observed large cracks and delamination of polypropylene layer after 960 h of UV exposure. However, composites containing lignin showed less loss of flexural strength and modulus, fewer cracks, and better hydrophobicity on weathered surfaces than other groups, confirming its functions of stabilization and antioxidation. Cao et al. (1998) investigated the degradation of polymer coating systems under 2000 h of UV exposure. Their study detected enhanced degradation due to the presence of TiO₂ and the subsequent loss of free-volume and hole fraction due to UV irradiation. Ferdous et al. (2016) investigated the role of fillers on the behaviour of polymer matrix exposed to 2000 h of simulated UV radiation.

Seven different mixes were prepared containing different amounts of particulate fillers, i.e. pure resin mix (0% filler) to a mix with 60% fillers (**Figure 2.11a and b**). They observed embrittlement, discolouration and an overall reduction in weight of the polymer matrix after UV exposure, with the loss of weight lower for the mix with higher filler volume (**Figure 2.11b**). This finding is comparable to that obtained for the loss of weight of carbon fibre-reinforced epoxy composites after 500 h of UV exposure by Kumar et al. (2002), wherein a minor 0.27% decrease in weight was measured. Ferdous et al. (2016) further observed that exposure to UV radiation for 2000 h reduced the flexural properties of neat polymer matrix by 48% with no significant change for the mix with 60% filler content (**Figure 2.11a**). These results showed that the addition of fillers could help to preserve structural performance by absorbing or blocking UV radiation before it reached the chromophores on which the colour of a polymer matrix is dependent.

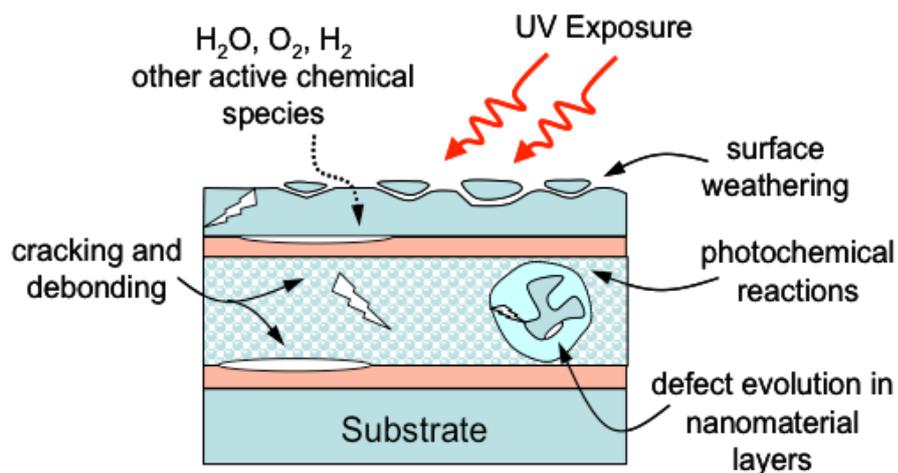
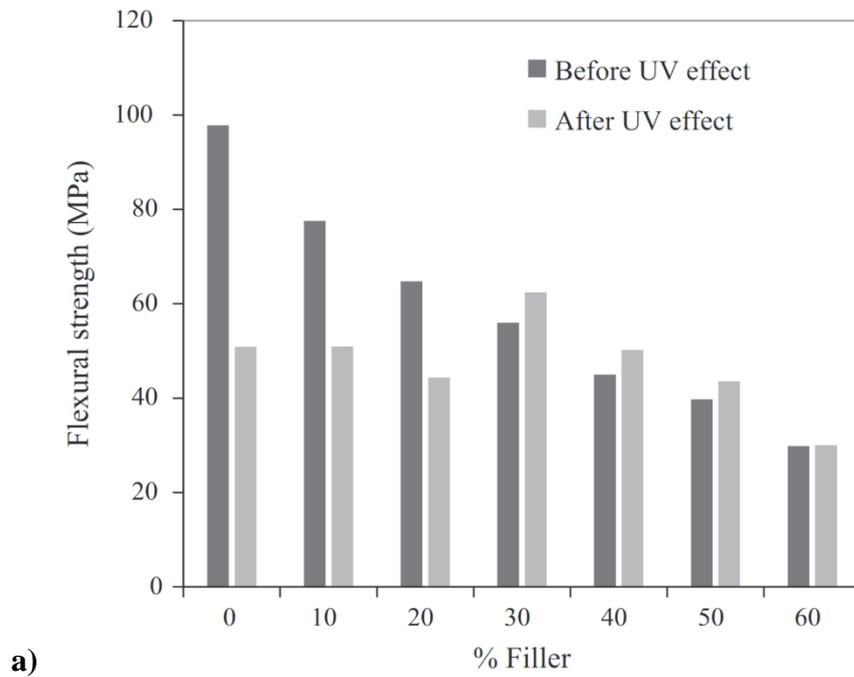
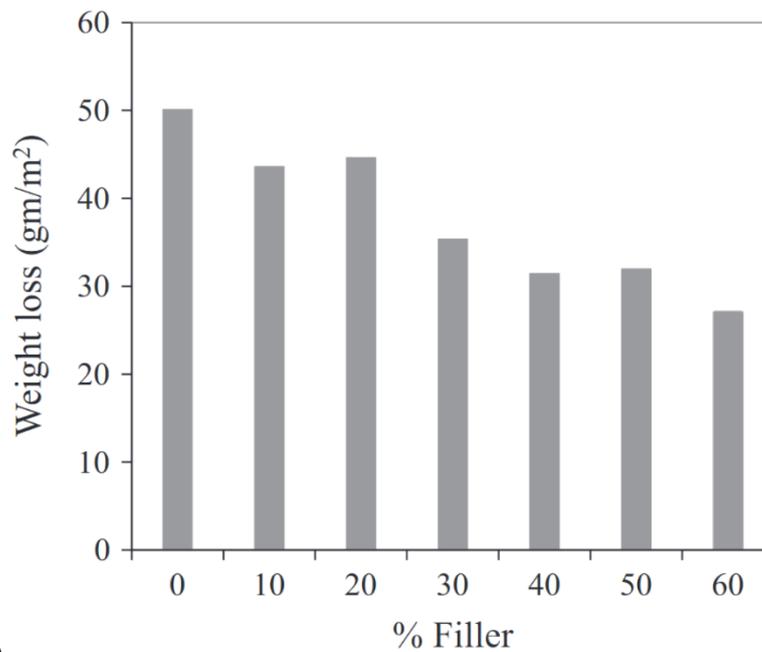


Figure 2.10: Mechanism of the effects of UV on silicone adhesives (Isaacson et al., 2016)



a)



b)

Figure 2.11: Effects of UV radiation on flexural strengths of polymer matrix and Loss of weight of polymer matrix after 2000 h of UV exposure (Ferdous et al., 2016)

The above experimental studies showed that epoxy polymers are affected by exposure to different environmental conditions. This long-term performance should be estimated using simple prediction equations that can reliably describe the durability and retention properties when subject to severe environments.

2.5. Long-term prediction

Many studies have been conducted to develop accelerated aging procedures and predictive models to evaluate long-term durability performance of polymers in harsh environments. These models are mostly based on the Arrhenius model in which materials will be aged at high rates using an accelerating factor, usually temperature (Nelson, 2009). Research on the effects of temperature on the durability of polymers indicates that an acceleration factor for each temperature difference can be defined using Arrhenius laws. Accelerating factors differ for each material, depending on the types of resin. In addition, these factors are affected by environmental conditions, such as surrounding solution media, temperature, pH, moisture, and freeze–thaw conditions. Predictive models based on Arrhenius laws make the implicit assumption that the elevated temperature will only increase the rate of degradation without affecting the degradation mechanism or introducing other mechanisms. Gerritse (1998) indicated that at least three levels of elevated temperatures were necessary to perform an accurate prediction based on Arrhenius laws shown in equation 1:

$$K=A \exp (-Ea/RT) \quad (1)$$

where K is the degradation rate (1/time), A is the constant relative to material and degradation process, Ea is the energy of activation of the reaction, R is the universal gas constant and T is the temperature in kelvin. Eq. (1) can be transformed into:

$$1/k = 1/A \exp (Ea/RT) \quad (2)$$

$$\ln (1/k)= Ea/RT-\ln(A) \quad (3)$$

From Eq. (2), the degradation rate k is expressed as the inverse of time needed for a material property to reach a given value. From Eq. (3) it can further be observed that the logarithm of time needed for a material property to reach a given value is a linear function of $1/T$ with the slope of Ea /R .

Porter et al. (1997) investigated the durability of FRP composite materials by exposing them to three different temperatures with a maximum of 60 degrees temperature for 3 months. Their research results indicate that the ultimate strength of materials decreases with aging in high temperatures. Robert and Benmokrane (2013) conducted predictions for tensile-strength retention as a function of time for immersions of GFRP reinforcing bars in saline solution and moist concrete over the long-term at 10°C and 50°C, and the general relation between the tensile-strength retention levels (PR) and the predicted service life at the average temperatures of 10°C and 50°C. **Figure 2.12c** shows the predicted time to reach the determined strength-property retention level (PR) for the GFRP bars at an isotherm temperature of 10°C is approximately 2 and 200 years for a PR of 90% and 75%, respectively. For the same bar immersed at an isotherm temperature of 50°C, the service-life predictions are approximately 0.75 and 35 years for a PR of 90% and 75%, respectively. These results show that the long-term tensile strength of the GFRP bars was more affected by the saline solution and moist concrete in a warm climate. They also calculated the property retention (PR) at three temperature (23, 40 and 50 °C) and four time of conditioning (60, 120, 210 and 365 d) (**Figure 2.12a**). **Figure 2.12b** also shows the property retention as a function of inverse absolute temperature for various chosen lifetimes. Based on the study by Chen et al. (2006) on the durability of FRP bars it was also indicated that FRP loses its strength when exposed to high temperatures, especially in solutions. In this case, the Arrhenius relationships were obtained by plotting the natural log of time to reach 50, 60, 70, and 80% tensile strength of GFRP bars versus $1/T$.

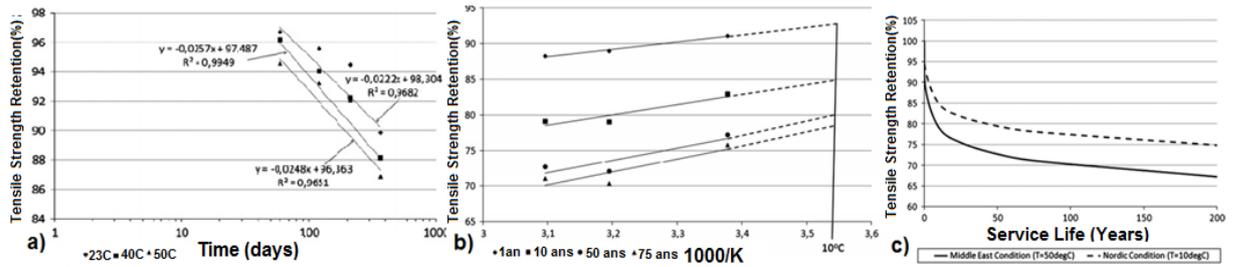


Figure 2. 12: a) Tensile retention as a function of time, b) property retention as a function of temp and service life, c) Relation between PR and the predicted service life (Robert and Benmokrane, 2013)

2.6 Research gaps

Composite materials have been employed extensively in civil engineering infrastructures, where they are exposed to challenging environmental conditions, including high moisture, elevated in-service temperature and solar ultraviolet (UV) radiation. Epoxy-based polymers are currently applied as protective coatings to minimise the environmental effects on the properties of these advanced materials. Recently, different particulate fillers were introduced to reduce the cost of epoxy-based polymers. While the optimum amount of fillers was found to enhance the short-term properties of epoxy-based polymers, their effect on the long-term properties is still unknown. This is important as the epoxy-based polymer, when used as a coating material, is subject to different environmental conditions, which are known to affect the physical and mechanical properties of materials. Although a number of studies have focused on the effects of harsh environments on the properties of composite materials, most of them have evaluated the resistance of materials exposed to one weathering condition. Therefore, it is very important to have a deep understanding of the following single and synergistic effects of different weather conditions on the long-term properties of particulate-filled epoxy-based polymer coating:

- Elevated in-service temperature

- High moisture
- Solar ultraviolet (UV) radiation
- Synergistic effect of temperature, moisture and UV radiation

The above is the main motivation of this work, which is addressed in Chapters 3 to 6.

An overview of the overall research was also presented in a technical poster in

Appendix A1.

Chapter 3

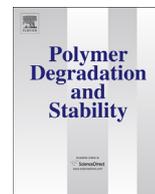
Article I: Effect of elevated in-service temperature on the mechanical properties and microstructure of particulate-filled epoxy polymers

Elevated in-service temperature is identified in Chapter 2 as one of the significant environmental factors that affect the long-term behaviour of polymeric materials. *Article I* examined the effect of in-service elevated temperature (from room temperature to 80°C) on the physical, mechanical and microstructure of particulate-filled epoxy-based polymer matrix. The fillers are composed of fire retardant, which was aluminium hydroxide (ATH) and fly ash, and they were increased from 0% to 60% by volume of the matrix in increments of 20%. In this study, two main components of the resin systems are low viscosity epoxy resin (Part-A) and Hardener (Part-B), which are common for coating applications. The resin producer furnished an Epoxy Equivalent Weight of 100 g for Part-A and Hardener Equivalent Weight of 25 g for Part-B which were manually mixed together in a bucket and stirred using a plastic spoon. Two different filler materials were mixed together and added to resin with 20% increase. The preparation of the particulate filled epoxy polymers coating in this study was conducted following the industry procedure in manufacturing composite railway sleepers wherein no post-curing is preferred to minimise cost of production. Based on the results of this research, the addition of fly-ash affects the physical (color and density) and mechanical properties depending on the volume content. It can be concluded that as long as the fly-ash has similar particle size and are well dispersed within the matrix, the particulate filled epoxy-based polymer coating will achieve the same properties and behaviour. The physical and mechanical properties were examined. Thermo-mechanical properties were investigated using dynamic Mechanical

Analysis (DMA) and simultaneous Thermal Analysis (TGA/DSC). Moreover, microstructure was examined via scanning Electron Microscopy (SEM). The results showed that increase in the filler content improved the matrices thermal properties. Result of DMA test showed that addition of fillers and further increase of fillers increased the storage modulus and increased the crosslinking density at in-service elevated temperature. In crosslinking reactions of DGEBA and hardener, the C–O bond within the epoxide group breaks and the carbon end of the opened epoxy group reacts with the nitrogen of the amine group in the curing agent molecule. Crosslink density (ν_c) is directly related to the storage modulus (E') in the rubbery plateau region. The crosslinking density rises as the functionality of crosslinkers increases, thus increasing the E and lowering failure strain. By varying chemistry and how the material is processed, E and crosslinking density, might be expected to change. Result of mechanical tests showed that with increase in the filler content particulate filled epoxy mixes retained the mechanical properties at in-service elevated temperature. Scanning electron microscopy images showed the formation of dense microstructures for particulate filled epoxy based resin at elevated temperatures, which resulted in better engineering properties. The proposed simplified prediction equation showed a good correlation with the experimental results at different levels of in-service elevated temperature. The significant findings from this work were also presented in international conferences with details provided in Appendices B1 and B2.

The results from this study showed that the sensitivity of epoxy resin against elevated in-service temperatures can be significantly improved by the inclusion of particulate fillers. Along with elevated in-service temperature, moisture is identified as another factor that can affect the long-term behaviour of epoxy polymer matrix. The effects of

hygrothermal environmental condition (combined moisture and temperature) are investigated and are presented in the Chapter 4.



Effect of elevated in-service temperature on the mechanical properties and microstructure of particulate-filled epoxy polymers



Mojdeh Mehrinejad Khotbehsara^a, Allan Manalo^{a,*}, Thiru Aravinthan^a, Kakarla Raghava Reddy^a, Wahid Ferdous^a, Hong Wong^b, Ali Nazari^c

^a Centre for Future Materials (CFM), School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD, 4350, Australia

^b Imperial College London, Department of Civil and Environmental Engineering, Kensington, London, SW7 2AZ, UK

^c Centre for Sustainable Infrastructure, Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia

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ABSTRACT

In civil engineering applications, epoxy-based polymers are subject to different environmental conditions including in-service temperature, which might accelerate their degradation and limit their application ranges. Recently, different particulate fillers were introduced to enhance the mechanical properties and reduce the cost of epoxy-based polymers. This paper addresses the effect of in-service elevated temperature (from room temperature to 80 °C) in particulate-filled epoxy based resin containing up to 60% by volume of fire retardant and fly ash fillers through a deep understanding of the microstructure and analysis of their mechanistic response. An improvement in the retention of mechanical properties at in-service elevated temperature was achieved by increasing the percentages of fillers. The retention of compressive and split tensile strength at 80 °C for the mix containing 60% fillers was 72% and 52%, respectively, which was significantly higher than the neat epoxy. Thermo-dynamic analysis showed an increase in glass transition temperature with the inclusion of fillers, while these mixes also experienced less weight loss compared to neat epoxy, indicating better thermal stability. Scanning electron microscopy images showed the formation of dense microstructures for particulate-filled epoxy based resin at elevated temperatures. This indicates that the particulate filled epoxy resin exhibits better engineering properties at in-service elevated temperatures, increasing their durability and therefore their suitability for civil engineering applications. A simplified prediction equation based on power function was proposed and showed a strong correlation to the experimental compressive and splitting tensile strength at different levels of in-service elevated temperature.

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1. Introduction

Epoxy resins are now commonly used as matrices in fibre reinforced polymer (FRP) composites as well as in coating, binding and adhesive materials [1,2]. This thermosetting resin is used for pavement overlays, wastewater pipes, hazardous waste containers, and decorative construction panels in aggressive environmental conditions [3–9]. They are also used as infill for structural repair systems [6,10,11] due to their superior properties including modulus and strain, tensile strength, strength development, resistance to chemical attacks and drying shrinkage compared to

ordinary Portland cement-based materials. Recent examples of structural applications of epoxy resins include as grout in the annulus between damaged pipe and outer FRP repair systems in underground and underwater pipelines [12], as infill material for pre-fabricated FRP jackets for damaged columns [13], and as coating and gluing sandwich panels for composite railway sleepers [14]. In these civil engineering applications, the epoxy-based polymer can be subjected to aggressive environmental conditions including in-service elevated temperatures, which can degrade this material. For example, Sirimanna et al. [15] measured a surface temperature as high as 61 °C for FRP composite bridge decks exposed to Australian weather conditions. In such conditions, the main concern was the decrease of the mechanical properties due to material degradation from elevated temperatures.

The sensitivity of mechanical and physical properties of

* Corresponding author.

E-mail address: manalo@usq.edu.au (A. Manalo).

particulate-filled epoxy based resin to elevated temperatures is one of the major concerns in civil engineering and construction applications [16]. The continuous service temperature is generally known to be in the range of sub-ambient to 120 °C [17]. Asset owners and engineers remain cautious about accepting epoxy matrices in civil infrastructure out of concern about their structural performance in the applications exposed to elevated temperatures. Manalo et al. [8] mentioned that the most important reason for this concern is the incomplete and limited information about the temperature dependence of composites for their application, particularly in hot areas. Polansky et al. [18], found that exposing epoxy-based FRP laminates to temperatures ranging from 170 °C to 200 °C and for a duration of 10–480 h will rapidly decrease the material's glass transition temperature (T_g) due the decrease in reaction to thermal stress. Their microscopic observations also showed degradation of epoxy resin (changing colour intensity) especially between the glass fibres and the matrix interface which led to gradual deterioration of electrical and mechanical properties. Anderson [19] further showed that the T_g of epoxy resin could remain constant for a short time, but rapidly decreased at elevated temperatures because they experienced network degradation as evidenced by mass loss. The mechanical properties of polymers are also noted to be significantly dependent on time and temperature [20,21]. When exposed to high temperature, the epoxy polymer will soften and this can cause mechanical failures [22]. Ray [23] noted a high moisture absorption for glass and carbon fibre-reinforced epoxy composites with an increase in temperature. The high temperature during hygrothermal ageing also modified the local stress threshold required for delamination nucleation and reduced the interlaminar shear strength of epoxy-based composite laminates. Therefore, there is a need to explore methods to enhance the performance of epoxy resin under elevated temperatures.

Different additives were introduced to epoxies to improve their properties at an elevated temperature including nanocomposites with carbon-family materials and metal hydroxides [24,25]. Koh et al. [20] found that the fracture toughness and failure mechanisms of bisphenol A epoxy resin and cyclohexanedicarboxylic anhydride (hardener) at an elevated temperature can be enhanced by filling with silica particulates. Recent developments have also shown that the application of filler materials such as fly ash (FA), fire retardant (FR) fillers, hollow microsphere (HM), and silica can improve certain mechanical properties and at the same time, reduce the cost of epoxy-based polymer matrix and provide environmental benefits [26,27]. The mechanical behaviour of particulate filled epoxy resin is the result of complex interplay between the characteristics of the constituent phases: filler, resin, and interfacial regions [28]. The result of research by Bărbuță et al. [29], Rebeiz et al. [30], and Gorninski et al. [31], have shown that the inclusion of fillers could improve chemical, thermo-mechanical, mechanical, and durability properties of epoxy-based polymer concrete. Lokuge and Aravinthan [32] also noted an increase in compressive strengths as high as 100 MPa for epoxy-based polymer concrete

with the addition of 10% FA by volume. Ferdous et al. [9], showed that the addition of light-weight fillers up to 60% by volume could increase flexural modulus around three times as the fillers provide a larger surface area that promotes rigid bonding with the resin. While these studies have shown that the addition of particulate fillers can improve mechanical properties of epoxy resin, very limited information exists on the effects of elevated temperatures to which civil infrastructures are normally subjected. A better understanding of the performance of particulate-filled epoxy based resin under an elevated in-service temperature must be achieved to further the safe use and adoption of this material in various construction applications.

In this study, experimental investigations were conducted to determine the effect of in-service temperatures on the durability of particulate-filled epoxy based resin containing FA and FR fillers. It focuses on understanding the effect of in-service elevated temperature on physical, mechanical, and physico-chemical properties as well as the microstructure of epoxy-based polymer matrix. The results of this research are expected to provide critical information to advance the application and development of durable cost-effective epoxy-based coating matrix through a comprehensive understanding and evaluation of their mechanical properties and degradation mechanism.

2. Materials and methods

2.1. Materials

Fig. 1 shows the materials employed in this study including epoxy resin and lightweight fillers. The two main components of the epoxy resin system were Bisphenol A diglycidyl ether (DGEBA) type epoxy resin (Part-A) and an amine-based curing agent (Part-B). This type of epoxy system was previously studied by Ferdous et al. [4] and found suitable for composite railway sleeper application. The epoxy resin was supplied by ATL Composites Pty Ltd (Gold coast, Australia). Part A as unreactive and part B as reactive components were mixed together based on the Amine Hydrogen Equivalent Weight (AHEW) of 60 g for Part-B and Epoxy Equivalent Weight (EEW) of 190 g for Part-A as furnished by the supplier. One equivalent weight quantity of the amine curative and one equivalent weight quantity of DGEBA epoxy resin were required in order to make the resin mix reactive. Thus, 100 g of Part-A with density of 1.064 g/cm³ were used to mix with 32 g of Part-B with density of 1.182 g/cm³ to maintain the mixing ratio. Two different fillers including FR (hydrated alumina powder) with a density of 2.411 g/cm³ and FA with a density of 2.006 g/cm³, were mixed together. Railway sleepers are often subjected to fire from thermite welding of rail joints, elevated temperature and UV radiation from sun. This is why hydrated alumina powder and fly ash have been used together [33,34]. The FR used was non-toxic and had low abrasiveness, chemical inertness, acid resistance, smoke suppression and electric arc resistance, and was supplied by Huber Engineered

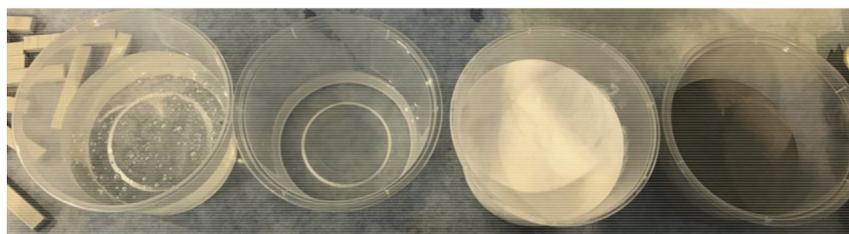


Fig. 1. From left: Epoxy resin (Part-A), amine-based curing agent (Part-B), FR and FA.

Table 1
Mix proportion of polymer matrices.

Resin/Filler (by volume)	F0	F20	F40	F60
Part A (g)	1000	737	552	368
Part B (g)	320	236	177	118
FR (g)	0	397	794	1192
FA (g)	0	119	239	358

Materials (HEM), while Cement Australia Pty Ltd supplied FA. The fillers were round with a diameter of 0.1–30 μm for FA and 75–95 μm for FR [14].

2.2. Mixture proportions

Four mixes with different amounts of filler were prepared, and the mix with no filler was considered to be the control sample. Filler amounts of up to 60% by volume of the matrix were added in increments of 20%, as more than 60% by volume filler in the mix was found unworkable, as was also confirmed by Ferdous et al. [9]. The mixing ratio of FR-to-FA was kept constant for all mixes. This ratio was adopted from the previous study [9] where it was finalised after several trials. Since the main purpose of this study is to investigate the effect of temperature on the mechanical and microstructure properties and ensure the cost is minimised, therefore, the total amount of filler was considered as a variable rather than the ratio of FR-to-FA. The mixes were denoted according to the amount of filler by volume, e.g., F20 indicates a mix containing 20% filler and 80% resin, as detailed in Table 1.

2.3. Specimen preparation

The preparation of samples and characterisation of the physical, mechanical, thermo-mechanical and microstructural properties of the epoxy polymer matrices were performed according to appropriate ASTM test standards. Table 2 summarises the different test methods and the number of specimens tested for each type of test. The epoxy resin materials and the particulate filler materials were first mixed separately. This ensured consistent mixing and allowed the epoxy resin to become completely mixed and reactive before the filler was added, then they were all mixed together until the matrix had a uniform consistency. The specimens were cast in: i) sealed-bottom cylindrical PVC pipes with a diameter of 25 mm and height of 25 mm – suitable for measuring the density, porosity, compressive strength and split tensile strength; ii) non-stick sheets to be cut to 60 mm length, 10 mm width and 5 mm depth – suitable for measuring the T_g . The samples were cured in moulds for 2 days at room temperature, demoulded and then tested after 7 days.

Table 2
Summary of the test methods and number of specimens.

Properties	Test Method	Number of specimens			
		F0	F20	F40	F60
Physical properties					
Density	ASTM C905 [35]	4	4	4	4
Porosity		5	5	5	5
Thermo-mechanical properties					
Dynamic Mechanical Analysis (DMA)	ASTM D7028 [36]	2	2	2	2
Simultaneous Thermal Analysis (TGA/DSC)		1	1	1	1
Mechanical properties					
Compressive strength	ASTM C579 [38]	15	15	15	15
Split tensile strength	ASTM C579 [38]	15	15	15	15
Microstructure					
Scanning Electron Microscopy (SEM)		5	5	5	5
Micro-focused Fourier Transform Infrared Spectroscopy (FTIR)		5	5	5	5

3. Test procedure

3.1. Physical properties

3.1.1. Density

The hardened density of different mixes with dimensions of 25 mm high and 25 mm in diameter was measured using an electronic balance (MonoBloc-AB204-S) with sensitivity of 0.0001 g according to the ASTM C905 [35]. The weight and volume of demoulded samples were measured. The hardened density then was calculated according to the standard.

3.1.2. Pore size

The size of the pores of different polymer matrices tested under various temperatures was measured using an optical microscope from the cut slices of 25 mm by 25 mm surface. A total of 60 images were taken, 3 from each sample exposed to various temperatures and with different percentages of fillers.

3.2. Thermo-mechanical properties

3.2.1. Glass transition temperature

To measure the T_g of different mixes, dynamic mechanical tests (DMA) were carried out according to the ASTM D7028 [36]. T_g is one of the main thermal properties in polymeric composite materials. T_g is the temperature at which the state of polymeric material is changed from hard or glassy to rubbery and soft [18,37]. A Q800 type TA instrument was used, wherein the samples were clamped by using a dual-cantilever system and the DMA multi-frequency strain of 1 Hz was applied. The temperature between 30 °C and 120 °C and increments of 5 °C during temperature scans was set. At least two samples with dimensions of 60 mm \times 10 mm \times 5 mm were tested for each series to determine the T_g of the epoxy-polymer matrix. The surfaces of the samples were prepared straight, flat, clean and dry to prevent them slipping from the dual cantilever grips.

3.2.2. Loss of weight

A calibrated simultaneous DSC/TGA (SDT 650) (Simultaneous Thermal Analysis) manufactured by TA Instruments was used for measuring the percentages of weight loss. Dry nitrogen gas at 200 ml/min was used during the experiments to purge the SDT cell. Samples between 10 and 25 mg were enclosed in the standard SDT aluminium sample pans. Dynamic scans were performed at a heating rate of 5 °C/min from room temperature to 120 °C. The moisture contents in the specimens were determined by SDT analysis as the difference in the weight loss between the reference matrix and the material under investigation and dried up to 120 °C.

3.3. Mechanical properties

The compressive and splitting tensile strength of polymer filled epoxy matrix were evaluated at five different temperatures (23, 40, 50, 60 and 80 °C) to coincide with in-service temperatures for epoxy thermosets as suggested by Ref. [16]. In order to achieve the required test temperature, Instron 3119 environmental chamber mounted on a 100 kN servo-hydraulic MTS machine was used. Before testing, a smooth surface had been prepared for the cylindrical samples to facilitate the uniform distribution of load. The environmental chamber was firstly set for 30 min at the required temperature before testing. Meanwhile, the other samples were placed in an oven set at the desired temperature while the testing of samples at a lower test temperature was being conducted. This was in addition to the 30 min soaking period in the chamber. The splitting tensile and compressive strength of the samples were obtained in accordance with the test procedure in the ASTM C579 [38] using 100 kN universal testing machine with a loading rate of 2 mm/min.

3.3.1. Scanning electron microscope

The scanning electron microscope (SEM) observation was carried out to investigate the microstructural characteristics of the different polymer mixes tested under different temperatures by using (SEM, JEOL JXA 840A). The samples were carefully prepared by cutting into small pieces (dimensions <1 cm) and then coated by gold using a sputter deposition machine. Afterward, the SEM was performed on the various small gold-coated pieces.

3.3.2. Fourier-transform infrared spectroscopy

Microfocused Fourier-transform infrared spectroscopy (FTIR) was conducted in order to determine the functional groups presented in the particulate filled epoxy base resin. FTIR spectra were recorded on a Nicolet 6700 FTIR spectrophotometer with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were then achieved by averaging 16 scans at a resolution of 4 cm^{-1} .

4. Results and discussion

4.1. Effect of percentage of fillers and temperature on physical properties

Fig. 2 shows the hardened densities of all epoxy mixes. It can be

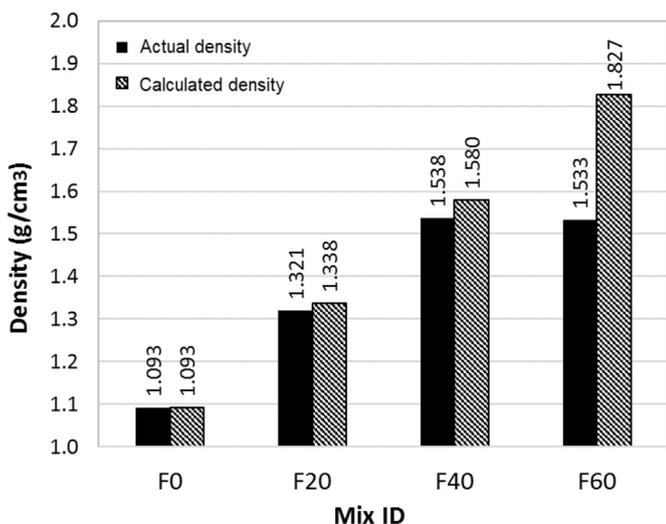


Fig. 2. Density of different epoxy mixes.

seen that the density increased (from 1.093 g/cm^3 to 1.538 g/cm^3) with an increase in filler content. This increase was up to approximately 40% in F40 compared to F0. The increase in density of the particulate filled resin can be explained by the replacement of lighter epoxy resin with fillers. This is to be expected as the density of filler (FR with a density of 2.411 g/cm^3 and FA with a density of 2.006 g/cm^3) was higher than that of the resin system (1.193 g/cm^3). However, the mix with 60% filler resulted in a slight reduction in the density of mixes compared to that of the F40 because the decrease in flowability of the mix resulted in the creation of more pores and voids than the mixes with a lower amount of fillers. The densities of the polymer-filled epoxy based matrix with different components were also calculated (Fig. 2). From the combined densities of the components in the mix, it was found that the densities of the mixes increased from 1.093 g/cm^3 to 1.827 g/cm^3 with increase in the filler volume from 0% to 60%. Based on the experimental results, it was observed that the variation between the calculated and the measured densities increased with the increase in the amount of fillers. This variation was almost 16% for F60. This further shows that the mix containing 20% filler volumes was flowable, which was due to low viscosity of epoxy resin. However, the inclusion of 40% or more fillers produced filler-dominated matrices.

The variations in density of the particulate-filled resin can be explained by the measured porosity of the mix. Fig. 3 shows that the pore sizes and number of the samples increased with increments of filler percentages from 0% to 60%. These pores were small for the mixes with 20% filler but relatively big for 60% filler. These findings were in agreement with the variations in density in Fig. 2, where differences between the densities of the solid and ingredients samples were higher in mixes including higher volume of fillers. Based on the results of Ferdous et al. [9], the inclusion of particulate fillers not only led to an increase in density to the peak of 1.458 g/cm^3 in F60, which is close to that of the timber railway sleepers, but also increased the porosity from 0.02% in F0 to 4.37% in F60. This showed the effect of fillers in the pore structure of epoxy based polymer matrix. Fig. 4 also shows the porosity of the surfaces of samples without fillers tested at 60 °C and 80 °C. Compared to Fig. 3a which showed the porosity of the F0 at room temperature, it is obvious from Fig. 4a that by increasing the temperature to 60 °C, the volume and size of the pores reduced. The size of the pores of F0 further reduced at 80 °C as shown in Fig. 4b (from 60 μm at room temperature to 18 μm at 80 °C). The trend was similar for F60 as can be seen in Fig. 5, wherein the increase of temperature showed a significant decrease on the volume and size of the pores compared to that at room temperature (Fig. 3d) (from 402 μm at room temperature to 73 μm at 80 °C). This can be due to softening and increasing of the mobility of the epoxy resin molecules at higher temperatures and decreasing the pore size in the samples including fillers. It has been reported that an increase in temperature can lead to a decrease of pores in the mix [39]. Lin and Ritter [40] also conducted a study on the effect of temperature on the pore structure of carbon xerogels derived from resorcinol–formaldehyde resins. They found that increasing the carbonisation temperature caused a reduction in the number of micropores, and it also had effect on the mesopore size distribution.

4.2. Effect of percentage of fillers and temperature on thermo-mechanical properties

The effect of percentage of fillers and temperature on thermo-mechanical properties of the particulate filled epoxy resins was evaluated using the Dynamic Mechanical Analysis (DMA). In addition, the Simultaneous Thermal Analysis (SDT) was conducted to measure weight loss at elevated temperatures to characterise the

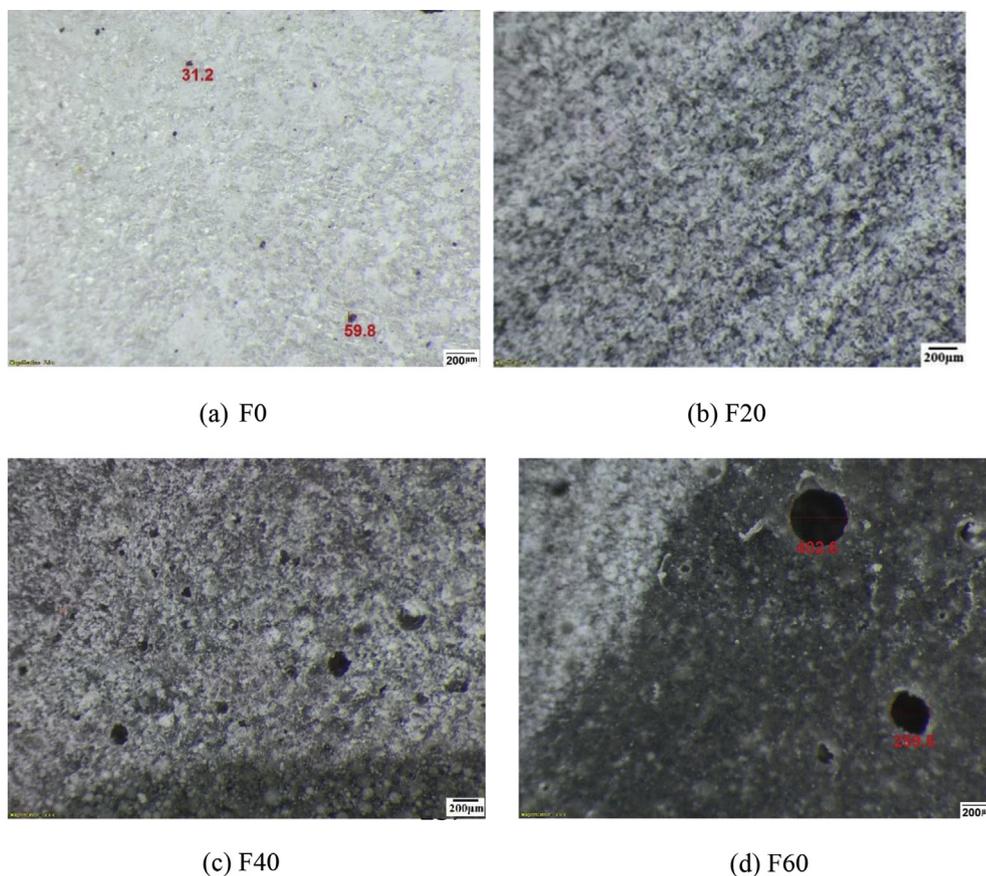


Fig. 3. Porosity of epoxy based resin with different amount of fillers.

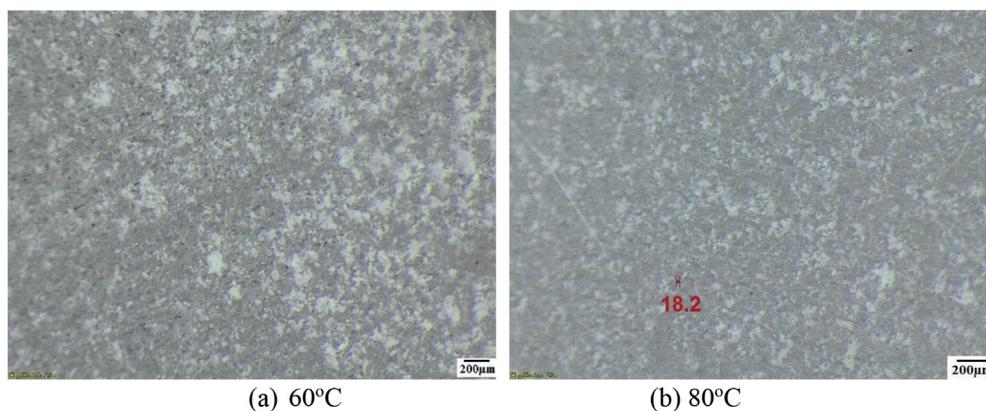


Fig. 4. Porosity of F0 at elevated temperature.

thermal stability of the particulate filled epoxy resin. The DMA results in Fig. 6a revealed three different temperature zones that affect the storage modulus of the polymer matrices: i) a reference plateau between 30 °C and 55 °C, where stiffness remained almost stable; ii) a zone that caused considerable decreases in between 55 °C and 65 °C, where temperatures were near T_g ; and iii) a zone that caused slight decreases in storage modulus between 85 and 120 °C, where the temperature was above the T_g of the polymers. In zone (i), since the temperature was below T_g , the molecular chain mobility of the polymer did not change, as also indicated by Ashrafi et al., [41]. By increasing the temperature to 55 °C and reaching the T_g in zone (ii), the molecular bonds began breaking and caused the

ductility of the material to increase, resulting in a significant reduction in the storage modulus of the samples. In the last zone (iii), there was a gradual decrease in the storage modulus.

From the storage modulus curve in Fig. 6a, it can be seen that the T_g of F0 is at 57 °C while that of F60 is at 63 °C. On the other hand, the measured T_g from the tan delta curve in Fig. 6b for F0 is 65 °C while that of F60 is 70 °C. This result indicated that adding up to 60% of filler to the polymer matrix increased the T_g by 5–6 °C. This enhancement in the thermo-mechanical properties of epoxy resin is directly related to the higher capability of a polymer matrix with fillers to store energy under high temperatures due to high thermal resistance of the used fillers [9]. The T_g of the polymer mixes

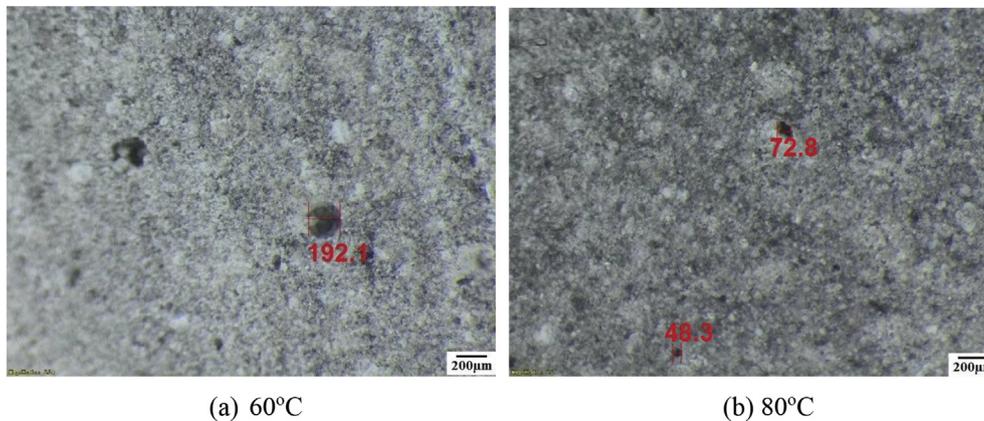


Fig. 5. Porosity of F60 at elevated temperature.

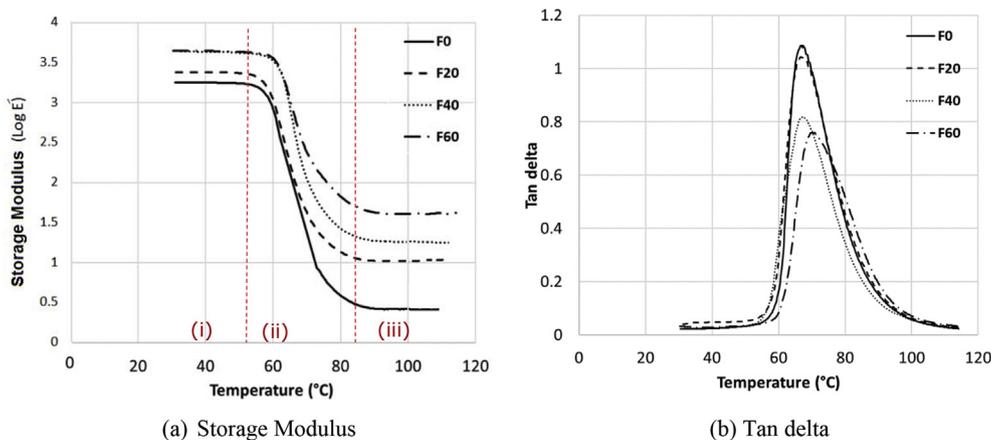


Fig. 6. Variations in dynamic mechanical properties with temperature.

depended basically on the resin system, while the type of resin was the same for different mixes. However, when the fillers with higher degradation points (Epoxy resin–340 °C, FA–800 °C and FR–980 °C) were included in the matrix, it led to an increase in the T_g as well. Shamsuddoha et al. [42] also showed that the incorporation of coarse aggregates could increase the storage modulus and T_g . In their research it was found that the T_g for the mix containing 45% epoxy resin and 32% fine filler (0.06–350.0 µm) with 23% hardener, was around 38 °C, while with the incorporation of 60% coarse aggregates (40.45 µm–2.36 mm), it was boosted to 60 °C. Ferdous et al. [9] also revealed that the T_g was increased with the increase of FA, FR and HM percentages, where in different mixes, the magnitude of T_g ranged from 50 °C to 55 °C using the storage modulus. Moreover, Fig. 6b shows that the magnitude of the peak of the tan delta as a function of temperature decreased from 1.05 to 0.76 with the increases in the filler percentage to 60%. These results indicated that F0 with tan delta peak of 1.05 has more potential for energy dissipation than the mixes with higher amount of filler as tan delta represents the ratio of the dissipated energy (loss modulus) to the energy stored (storage modulus) per cycle sample deformation. Energy dissipation is the result of an irreversible process in which energy is transformed from initial form to final form, while the capability of the final form in term of mechanical resistance is less than the initial form. Crosslink is a covalent bond formed when epoxy molecules react with curing agent molecules. In crosslinking reactions of DGEBA and hardener, the C–O bond within the epoxide group breaks and the carbon end of the opened epoxy group reacts

with the nitrogen of the amine group in the curing agent molecule [43]. Crosslink density (ν_c) is directly related to the storage modulus (E') in the rubbery plateau region according to the following equation [44]:

$$E' = \nu_c RT \quad (2a)$$

where T is the temperature (K) and R is the gas constant. As shown in Fig. 7, the crosslinking density increased with further inclusion of fillers. F60, which has the highest amount of fillers, has the highest storage modulus and consequently crosslink density is increased.

The temperature at which the rapid loss of weight occurs can be also defined as the decomposition temperature. It is the temperature, under which the thermoset loses its weight most rapidly during the whole degradation process [45]. In many applications, adhesive strength loss is a significant variable, which leads to ambiguity in how loss of weight measurements is related to loss of adhesive strength at the anticipated in-service temperature. Table 3 shows the weight loss of different mixes which was evaluated by SDT from the room temperature to 120 °C, similar to the temperature range for the DMA test. Neat epoxy resin exhibited a minor loss of weight of around 0.02% at lower temperature and then a rapid weight loss of around 0.63% at 120 °C, possibly due to loss of water or unreacted volatiles, which come from amine-based organic compound of hardener as indicated by Preghenella et al. [46]. As a measure of the extent of degradation, the extent of weight loss is usually applied. Volatile degradation species that are

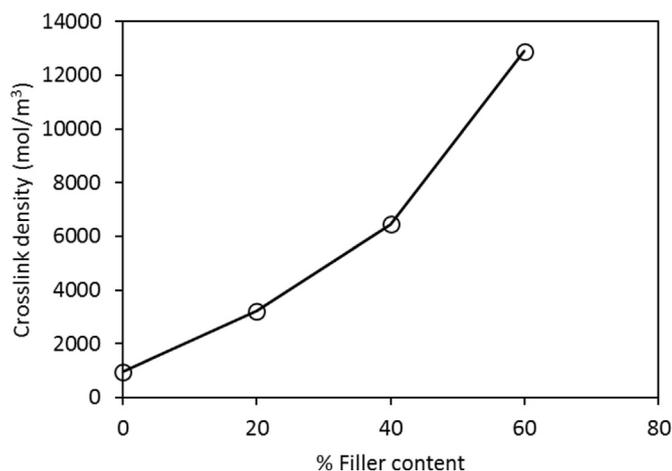


Fig. 7. Crosslinking density of particulate filled epoxy polymer.

Table 3
Weight losses after SDT scan.

Mix ID	(40 °C) %	(60 °C) %	(80 °C) %	(100 °C) %	(120 °C) %
F0	0.0202	0.0814	0.1789	0.4230	0.6238
F20	0.0240	0.0755	0.1573	0.2894	0.4486
F40	0.0183	0.0689	0.1122	0.1611	0.2045
F60	0.0009	0.0093	0.0331	0.0656	0.0765

released from the material when network bonds break, can lead to weight loss. It is worth noting that the extent of degradation definition is not implying 100% loss of weight at an extent of degradation of unity. The ultimate weight of the sample, which is asymptotically approached over a long time is referenced by the extent of reaction [17]. Thus, this significant weight loss for F0 is predicted to be followed at higher temperatures due to the thermal degradation of the resin matrix, which will result in a considerable weight loss of the epoxy resin. However, F40 and F60 showed significantly less weight loss of only around 0.2% and 0.07%, respectively at 120 °C. This phenomenon can play an important role in improving the retardant properties of the epoxy polymer due to their higher ability to store the energy under high temperatures as was already indicated in Fig. 6a.

The result of weight loss is in agreement with the measured T_g result. T_g and weight loss are two important properties showing the influence of degradation, and demonstrate that the inclusion of fillers can help to reduce the degradation rate under elevated temperatures. Thus, the thermal stability of the epoxy at high temperatures was improved, as the percentages of resin was

reduced by inclusion of FA and FRA in the mixes due to the higher melting temperature of the particulate fillers compared to that of the epoxy resin.

4.3. Effect of percentage fillers and temperature on mechanical properties

The mechanical properties of the epoxy-based polymer with different percentages of fillers and at elevated temperature were assessed under compression and split tensile testing. Table 4 summarises the results of the mechanical tests. In order to have a fair comparison of strength among the mixes with different densities, the specific strength also has been provided. The values listed within parentheses are the standard deviation of the test results.

Fig. 8 shows the typical failure mode of particulate-filled epoxy resin in compression at elevated temperature. As shown in Fig. 8, despite the creation of micro cracks, which were not easy to see with the naked eye, specimens F0 and F20 were deformed without crushing even after reaching their ultimate strengths (Fig. 8 a and b). These samples behaved like elastic materials as they resumed their original shape when the load was released, even though they retained some of their bulged shape. On the other hand, at lower temperatures, micro cracks followed by a shear cracks were observed for specimen F40. It is interesting to note that for F60, noticeable failures with a huge sudden shear crack at ultimate strength was observed, showing a brittle fracture. The stiffness of fillers can be attributed to the mechanisms of this phenomenon for those mixes containing higher percentages of filler, particularly F60 as was also reported by Ferdous et al., [9]. Indeed, the behaviour of polymer matrices changed from flexible to relatively rigid with an increase in the volume of filler, which is also indicated by the abrupt drop in the stress strain curve in the next paragraph. The failure mode could be also related to pore size and volume. The increase of porosity with the increase of fillers also affected the transfer of stresses from one part to another that may increase stress concentration and lead to premature failure. High-porosity mixes (F40 and F60) have larger pores randomly distributed through a matrix and failed in a brittle manner. However, the crack along the direction of the compressive stress rather than along the interface between the resin and the fillers, indicates the excellent adhesion of fillers to the epoxy matrix. Similarly, Ferdous et al. [9] found that epoxy-based polymer containing up to 30% of FA, FR and HM exhibited an elastic failure mode without visible cracks under compression at room temperature while the samples including 40%, 50% and 60% failed by cracking. One can observe that the failure modes for resin-rich mixes at higher temperatures are similar to those at room temperature, indicating flexible matrices. However, it was also apparent that the failure mode in F40 became

Table 4
Mechanical properties of epoxy polymer matrices under elevated temperature.

Property	Temperature										
	Room		40 °C		50 °C		60 °C		80 °C		
Mix ID	Density	strength	Specific strength								
Compressive strength (MPa)											
F0	1.093	92.0 (3.3)	84.2	51.2 (1.4)	46.8	25.2 (2.5)	23.1	3.1 (0.6)	2.8	1.4 (0.7)	1.3
F20	1.321	85.7 (2.9)	64.8	52.8 (1.8)	39.9	33.4 (2.2)	25.3	7.3 (1.6)	5.5	5.3 (0.6)	4.0
F40	1.538	82.4 (2.3)	53.6	58.7 (0.1)	38.2	45.1 (3.8)	29.3	37.0 (2.1)	24.1	34.4 (0.0)	22.3
F60	1.533	59.4 (6.7)	38.7	47.4 (0.2)	30.9	44.3 (6.4)	29.0	43.5 (1.7)	28.4	43.1 (3.7)	28.1
Splitting tensile strength (MPa)											
F0	1.093	33.9 (1.4)	31.0	15.8 (1.3)	14.4	3.8 (1.6)	3.5	1.0 (0.7)	0.9	0.7 (0.2)	0.6
F20	1.321	27.1 (0.8)	20.5	19.3 (1.2)	14.6	10.3 (3.8)	7.8	3.7 (3.4)	2.8	3.2 (1.9)	2.4
F40	1.538	25.3 (1.7)	16.5	17.9 (1.3)	11.6	14.8 (3.2)	9.6	10.3 (5.4)	6.7	9.5 (1.5)	6.1
F60	1.533	20.4 (0.7)	13.3	15.7 (0.7)	10.2	12.3 (1.0)	8.0	12.1 (2.1)	7.9	10.8 (0.7)	7.0

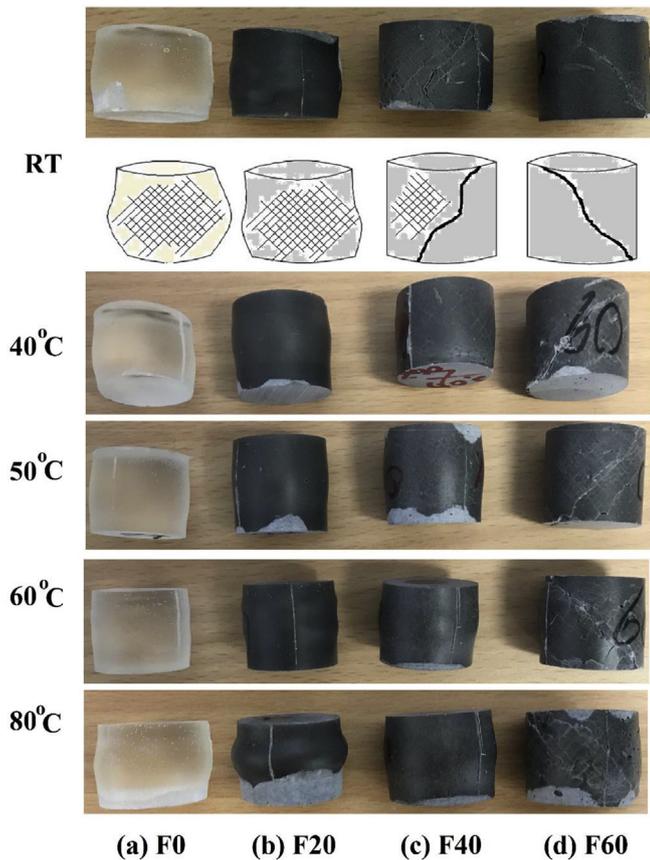


Fig. 8. Failure modes of particulate-filled resin under compression at different temperatures.

flexible under elevated temperature and it was followed by microcracks and bulged shape. For F60, a semi-ductile failure can be observed at higher temperatures; the failure was initiated as a microcrack, then propagated as a shear failure that resulted in multiple fracture, then propagated as a shear failure that resulted in multiple fracture and crushing under ultimate load. With an increase in the temperature, as T_g was reached, the epoxy resin became very ductile. Meanwhile, the inclusion of fillers could hinder the mobility of the polymer's molecular chains, and provide some stiffness too. The strength retention at this temperature, which will be discussed in the last paragraph, proves that the softening of the matrix allowed the fillers to move freely in the direction of the loading, and their porosity decreased, resulting in a better stress transfer [39]. The reduction in porosity might

consequently result in a decrease of brittleness.

The compressive stress and strain behaviour of F0 as reference and F60 as the mix containing the highest percentage of filler at room temperature to 80 °C are plotted in Fig. 9. For F0, slightly non-linear stress-strain behaviour is observed due to its nature of rubber-like material. The non-linearity then gradually reduced with an increment of filler content and became almost linear for the mix containing 60% fillers (Fig. 9b). It is noticeable that at room temperature F60 has a lower failure strain compared to F0. This is caused by the introduction of particulate fillers in the epoxy with larger surface area and the creation of a rigid bond with the resin [9]. This consequently demonstrated an inflexible polymer matrix due to gradual increases in the volume of higher-modulus materials exhibiting a lower failure strain (Fig. 9b) as it is also comparable in Table 4. However, with the increase of temperature in addition to retaining the properties, F60 exhibits a significant decrease in stiffness with an increase in failure strain. At high temperature, it showed more ductility due to the softening of the epoxy resin which led to an increase in bonding to fillers resulting in retaining strength at higher temperatures.

Fig. 10 shows the strength retention in compression of particulate filled epoxy-based resin at elevated temperature. In general, the compressive strength of epoxy-based polymers decreased with increasing temperature. This reduction in strength was caused by the softening of the epoxy matrix with the increase in temperature. Generally, higher strength retention was observed for the mixes containing filler compared to the neat epoxy due to the better filler and matrix interaction, which could be due to the reorientation of the fillers during the softening of the resin. Moreover, the softening of the resin and reduction in porosity resulted in the bonding between the filler and the resin being slightly enhanced. This result was supported by higher T_g and cross linking density of mixes with higher amount of fillers. As shown in Fig. 10 for samples without or with low amount of fillers (F0 and F20), there was a significant drop in the strength retention capacity at 60 °C due to exceeding the T_g of polymer. When the temperature increased to 60 °C (about their T_g), epoxy reached the heat distortion temperature (HDT), and it began to deform. The continued increase in temperatures to 80 °C led to more ductile and elastic behaviour and yield point and strength loss. At this level of temperature, F0 and F20 retained only 3.4% and 8.5% respectively of their compressive strength at room temperature. The low compressive strength retention of mixes with low amount of particulate fillers can be directly linked to the softening of epoxy resin at a temperature near or above T_g and losing its adhesive and cohesive strength, as was also found by Bajracharya et al. [47]. On the other hand, F40 and F60 could retain 44.9% and 73.3% respectively of their compressive strength at 60 °C, and 41.7% and 72.6% respectively at 80 °C. The higher compressive strength

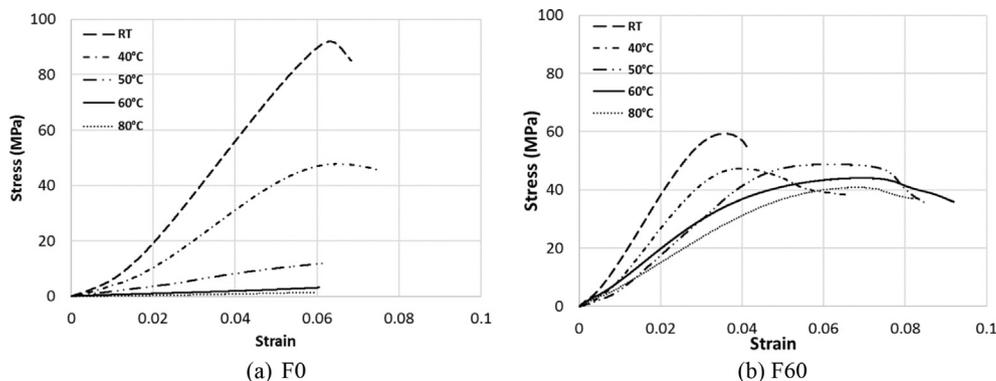


Fig. 9. Compressive stress and strain behaviour at in-service elevated temperature.

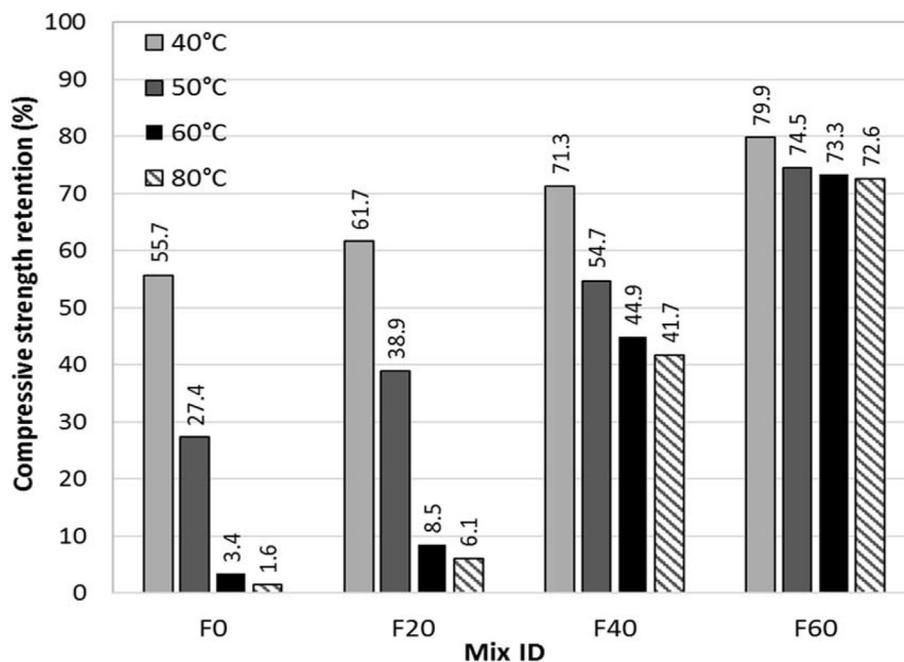


Fig. 10. Compressive strength retention at in-service elevated temperature.

retention for F40 and F60 was firstly due to the better thermal properties of the fillers including higher T_g and higher thermal stability as was discussed in previous sections. Thus, the polymer filled epoxy can continue to support a load in higher temperatures. This could be due to the softening of epoxy resin at higher temperatures, which led to a reduction in the size and amount of pores in the mixes with higher percentages of fillers as is shown in Fig. 8.

Fig. 11 shows the failure mode of various mixes after a splitting

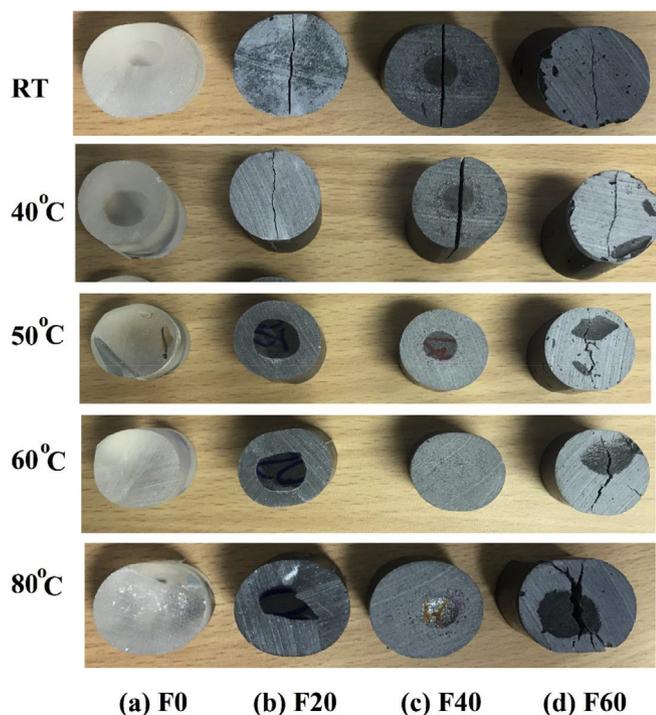


Fig. 11. Failure modes of particulate-filled resin under tension at different temperatures.

tensile test at room temperature and at the maximum temperature of 80 °C. As can be seen in Fig. 11, in the same way as the samples tested under compression strength, F0 samples behave like elastic material and they deformed without visible cracks even after reaching their ultimate strengths; the samples resumed their original shape when the load was released. However, mixes containing 20%, 40% and 60% fillers failed primarily at a single cross section along the diameter by brittle fracture, which was followed by the abrupt drop in the stress-strain curve at peak load. This was due to the poor filler/matrix adhesion. At 80 °C, although F0 showed the same failure mode as room temperature, F20 and F40 showed ductile failure, which is due to the softening of epoxy resin at higher temperatures. The softening of the matrix allowed fillers to have better bonding with epoxy resin through the matrix, resulting in the increase in failure strength and flexibility of the matrix. F60, however, showed a semi-brittle fracture with inclined failure surface along the width of the sample tested at maximum temperature of 80 °C. The resin transfers stress however, as the temperature increased, caused the resin to become malleable and soft, thus, better interlocking between resin and fillers was achieved.

From Fig. 12, stress-strain graphs show that at lower temperatures, F60 was completely brittle, while F0 was ductile. Moreover, split tensile results at Table 4 show the reduction of strength with increasing filler volumes at room temperature due to gradual increases in the amount of higher stiffness filler materials. This result is in agreement with the trend reported by Lokuge and Aravinthan [32], who revealed that when the epoxy content was further increased (20%), in addition to flexural strength and compressive strength, split tensile strength also reduced. However, as the temperature reached 80 °C, not only could F60 retain more than 50% of the peak stress but also the tensile failure strain of F60 increased by the rise in temperature. This phenomenon happened while neat epoxy resin was deformed under minimal stress of less than 2–3 MPa at maximum temperatures of 60 °C and 80 °C. The significant variations in strength for F0 and F20, which was observed with an increase in the temperature was due to the softening of epoxy resin and a loss of the properties in resin-rich mixes. The split

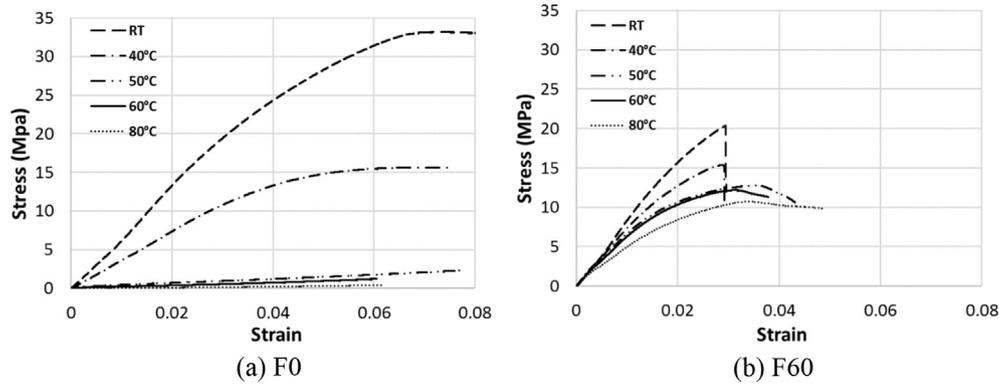


Fig. 12. Tensile stress and strain behaviour at in-service elevated temperature.

tensile retention results given in Fig. 13 revealed that the inclusion of higher percentages of fillers to the matrix could significantly help to retain the strength by almost 41% and 37% for F40, and 59% and 53% respectively for F60 at 60 °C and 80 °C. Resin-rich samples (F0 and F20) significantly lost their strength particularly after 60 °C. F0 experienced a significant reduction of 97% and 98% respectively in its strength at 60 °C and 80 °C.

4.4. Microstructure of particulate-filled epoxy resin at elevated temperature

When materials are combined, their properties are governed not only by the characteristics of individual components, but also by the interface between them [48]. Moreover, the mechanical characteristics of a particulate filled polymer depend on the type of distribution of particles, which can be characterized by SEM [49].

From this study, the SEM revealed that the microstructure of F0 and F60 specimens has a direct correlation on the physical, thermo-mechanical and mechanical properties of epoxy-based polymer exposed to in-service elevated temperatures (Fig. 14). Specimen F60 was chosen since it exhibited the highest property retention at 80 °C. The FTIR of specimen F0 was also analyzed and presented for comparison. As can be seen in Fig. 14a–c, there are remarkable differences in the texture and form of the particulate-filled epoxy resin compared to the neat epoxy samples. Dense microstructures with small pore sizes were formed in samples without filler (F0), while the mix containing 60% FA and FR (F60) showed various pores and weak interfacial bond between different fillers and the resin through the matrix due to pores and voids in the matrix (Fig. 14c). This subsequently decreased the mechanical performance of the polymer matrix at room temperature. Ahmad et al. [50] pointed out that the presence of fused silica resulted in inhomogeneous

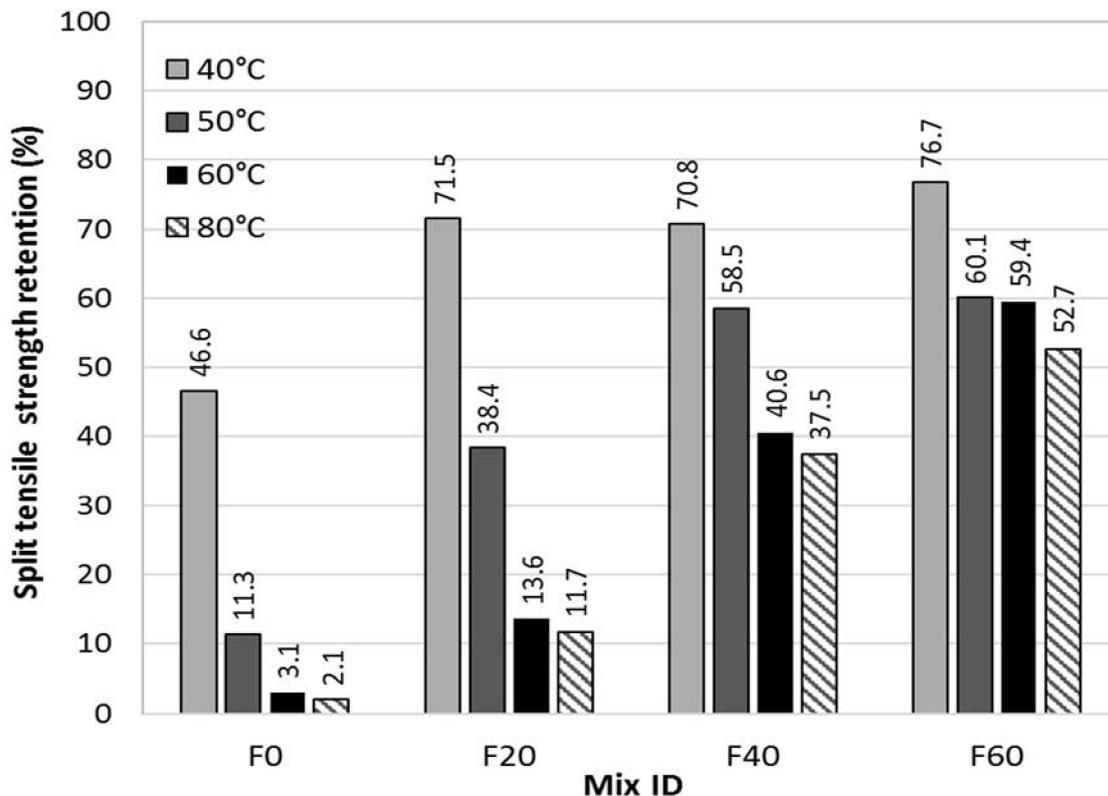


Fig. 13. Tensile strength retention at in-service elevated temperature.

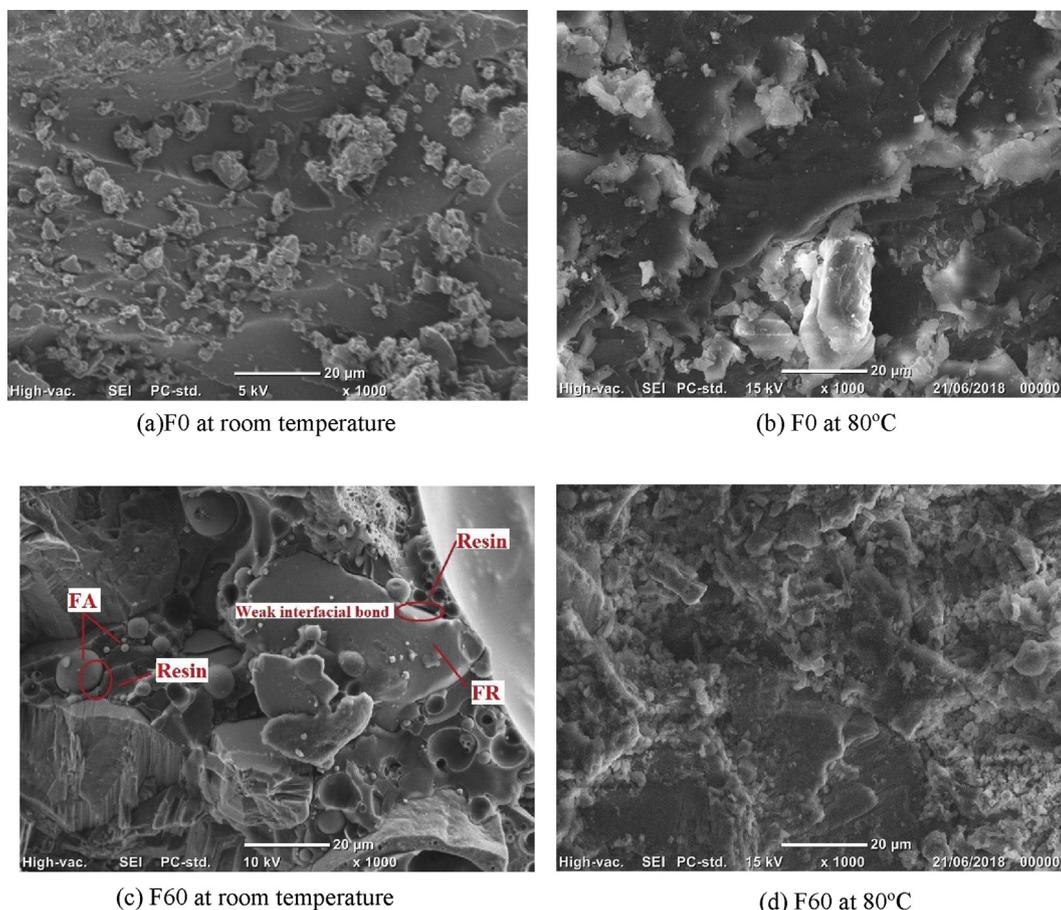


Fig. 14. SEM micrographs of particulate filled epoxy resins.

distribution and weakened the interaction between the matrix and the filler due to the defect in the matrix caused by the voids between the particles, and led to undesirable material properties.

As shown in Fig. 14a, F0 samples at room temperature have a compact but relatively rough surface even after the application of the load while after testing at 80 °C, the roughness of fracture surface of epoxy samples was reduced (Fig. 14c). On the other hand, a close inspection of Fig. 14c–d revealed that the exposure of F60 to 80 °C not only reduced the amount of pores but also improved the interfacial bond between the fillers and resin compared to room temperature (Fig. 14c). For FR and FA as spherical inclusions, the packing arrangement defines the quantity of fillers and the distribution of particles. Thus, when the temperature increased, it enabled a better distribution of particles and consequently a dense microstructures with lower pores or voids formation. This then helped to retain the mechanical strength and increase the strain failure. This was in agreement with the results reported in the physical section, wherein the increase of temperature led to a significant decrease on the number and size of the pores (Figs. 3b–5b).

4.5. FTIR results of particulate filled resin subjected to elevated temperature

FTIR spectra was performed after the mechanical tests to determine functional groups presented in the particulate filled epoxy base resin. The mixing of epoxy resin produced carboxylic and carbonyl acid by-products due to the reaction of the curing agent and epoxy resin [51]. The solid particulate-filled epoxy resin composite was formed through the ring opening polymerisation

reaction in the presence of DGEBA, amine-based hardener and fillers (FA and FR). During the reaction, the carboxyl groups or hydroxyl groups were produced that presented as a pendant in part A. From the spectrum, the characteristic bands of F0, F20, F40 and F60 were observed at various wavenumbers as shown in Fig. 15. C–H and C–O were found to be major phases for all specimens. The band observed at $\sim 3800\text{ cm}^{-1}$ for different mixes corresponded to O–H stretching band. The second group of the bands, which were located at 2904 cm^{-1} and 2870 cm^{-1} were attributed to the stretching vibration of C–H group of epoxy [52,53]. However, the intensity of these wavenumbers decreased with further increase of fillers (F40 and F60). Instead of the wavenumber of 2000 cm^{-1} , the third group of bands were detected. The band at 1703 cm^{-1} and 1718 cm^{-1} was due to the stretching vibration of C=O in ester [3]. The bands at wavenumber 1508 cm^{-1} was the characteristic band for the aromatic ring stretching of C=C, characteristic of DGEBA epoxy systems [54]. The band at 1508 cm^{-1} may also represent nitro deformation from the cycloaliphatic amine curing agent. The bands corresponding to epoxide ring ($\sim 817\text{ cm}^{-1}$) wavenumbers at 1024 and 1234 cm^{-1} were characteristic bands for C–O stretching of saturated aliphatic primary alcohols [48,55], unlike the bands observed at C–O for F0 and F20 (resin-rich mixes), where a restrictive stretching with further inclusion of filler was observed (Fig. 15c and d). This was due to the decrease in the amount of resin by increasing the percentages of fillers. As shown in Fig. 15, mixes of all of the functional groups have the same peak values at their lowest and highest temperatures except for the shifting bands by increasing the temperatures, particularly for resin-rich samples (F0 and F20). A small shift of bands to higher wavenumbers by

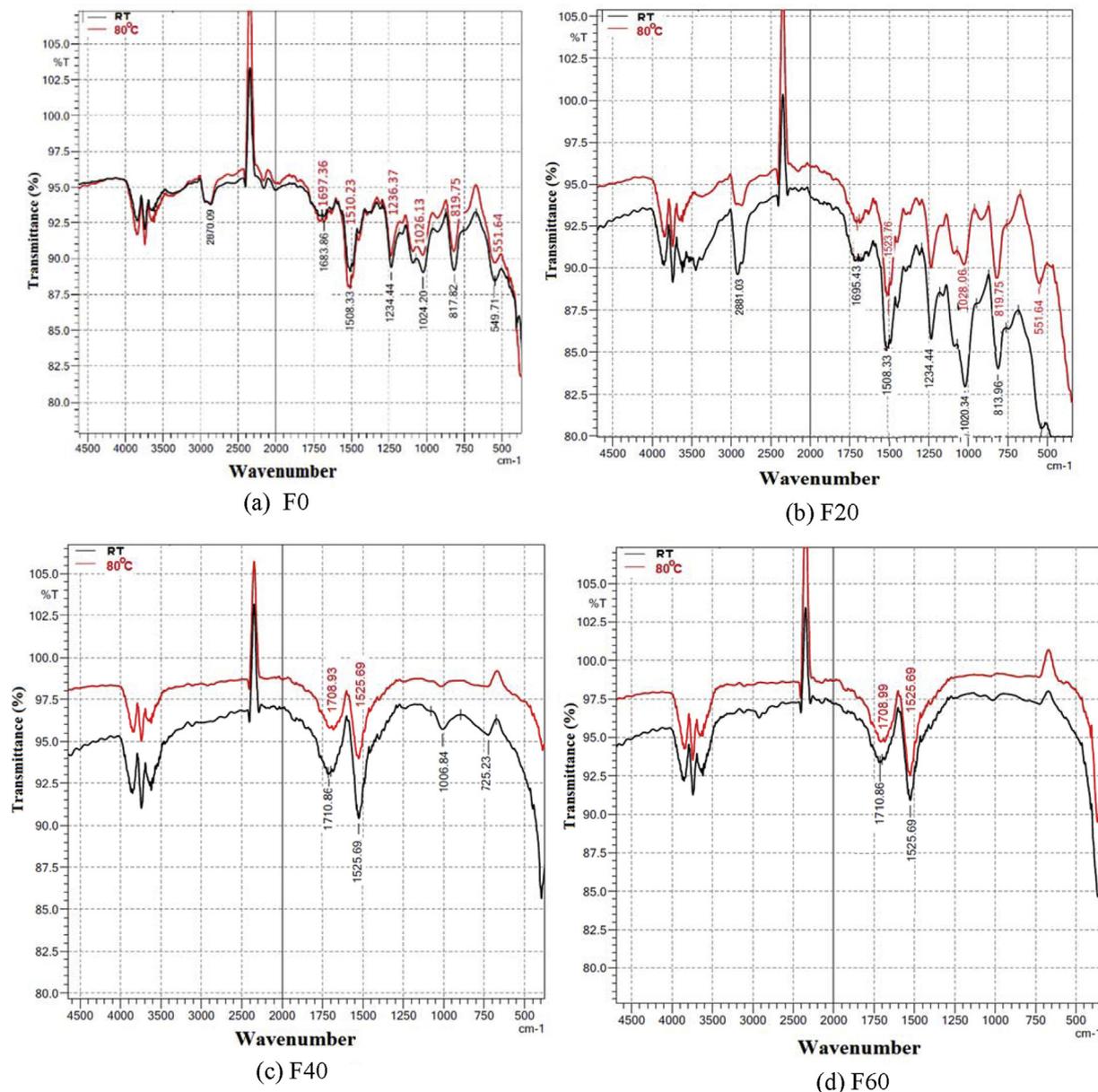


Fig. 15. FTIR graphs at room temperature and at 80 °C.

5–15 cm⁻¹ was observed in the spectra with the inclusion of fillers due to the interaction between epoxy and fillers (FA and FR). FTIR results demonstrate that the curing reaction completed and the formation of polymeric epoxy structures in all the particulate composites was done. These results are in accordance with SEM images showing the formation of solid resin after the curing reaction. (Fig. 14). These results showed that the sensitivity of epoxy resin against in-service temperature can be sufficiently reduced by the inclusion of fillers. This further indicates that the particulate filled epoxy resin will exhibit better engineering properties against in-service elevated temperature, as the fillers provide protection against thermal conditioning increasing their durability and suitability in civil engineering applications.

5. Simplified prediction model for particulate-filled epoxy based resin

The results from this study showed that the mechanical

properties of particulate-filled epoxy resin were very much affected by the in-service temperature while the percentages of fillers played a major role in retaining its mechanical properties. This section presents the development of a prediction model that describes reliably the mechanical properties of particulate-filled epoxy resin with different percentages of fillers and subjected to in-service elevated temperature.

5.1. Development of prediction model

Saberian et al. [56,57] and Mohajerani et al. [58] proposed a power function for predicting the resilient modulus of recycled pavement material containing different percentages of fine and coarse rubber. In the development of the model, they used the regression coefficients of the relationship between the resilient modulus, confining stress, deviator stress, and stiffness of recycled pavement mixes from the results of their experimental works. Following this approach, in this study, the compressive strength

Table 5

Equations of the prediction model of the particulate-filled epoxy based resin based on the relationships among the experimental values, percentages of fillers, and temperature.

Equation	R ²
$Y_{Comp} = 222.910 \times (\text{Filler content})^{0.719} \times (\text{Temp})^{-1.1379}$	0.72
$Y_{Split_tensile} = 183.088 \times (\text{Filler content})^{0.413} \times (\text{Temp})^{-1.090}$	0.80

and splitting tensile strength were presented as a function of the in-service elevated temperature along with the amount of fillers, to estimate the strength of the particulate-filled epoxy resin using a power function. Eq. (2) showed the general form to evaluate the relationship between the predicted values (Y), mechanical strength, temperature, and percentage fillers.

$$Y = K_1 \times (X_1)^{K_2} \times (X_2)^{K_3} \tag{2b}$$

where X_1 is percentage amount of fillers, X_2 is the level of in-service elevated temperature, and K_1, K_2, K_3 are regression parameters.

The regression equations to predict the compressive strength (Y_{Comp}) and the splitting tensile strength ($Y_{Split_tensile}$) are presented in Table 5. The regression parameters of the different samples were calculated based on the experimental results fitted against the power function model using Excel, where the strength properties, amount of fillers and different levels of temperature were given as input. The regression parameters were achieved as product of matrix calculations. The coefficient of determination, R^2 for the prediction models has also been provided in Table 5, while the relationship between the experimental and predicted values has been provided in Fig. 16. In both equations, K_1 and K_2 are positive values, implying that the outputs increased with an increase in the amount of filler while K_3 is negative indicating that by increasing the temperature, the mechanical properties will decrease.

5.2. Correlation between compressive strength and splitting tensile test results

The compressive strength test of epoxy-based resin, incorporating different percentages of fillers tested under in-service elevated temperature were presented against splitting tensile strength in Fig. 17 in order to understand the interdependence between these strength properties. It can be observed in the figure that there is a significant linear relationship between the compressive strength and the splitting tensile strength, with the

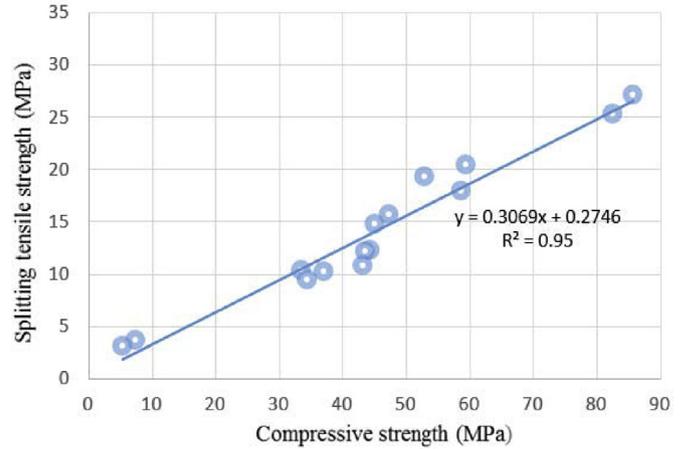


Fig. 17. Relationship between the compressive strength and splitting tensile strength.

coefficient of correlation of 0.95. This coefficient of correlation is very high and reflects a strong relationship between two different tests. This result also showed that the splitting tensile strength, $UCS_{Split_tensile}$ of the particulate-filled epoxy resin with different percentages of fillers and subjected to in-service elevated temperature can be predicted from its compressive strength, which is given as Eq. (2). It is recommended however that the reliability of this proposed equation be validated against percentages of fillers and in-service elevated temperature outside the levels investigated in this study.

$$Y_{Split_tensile} = 0.3069(Y_{Comp}) + 0.2746 \tag{2c}$$

6. Conclusions

In this study, the physical, thermo-mechanical, and micro-structural properties of epoxy-based polymers with different percentages of particulate fillers composed of fly-ash and fire retardant fillers were evaluated at elevated temperatures. From the results, the following conclusions are drawn:

- The density of particulate-filled epoxy-based polymer resin increased with increasing amount of fillers. However, a higher discrepancy between the actual and calculated densities was

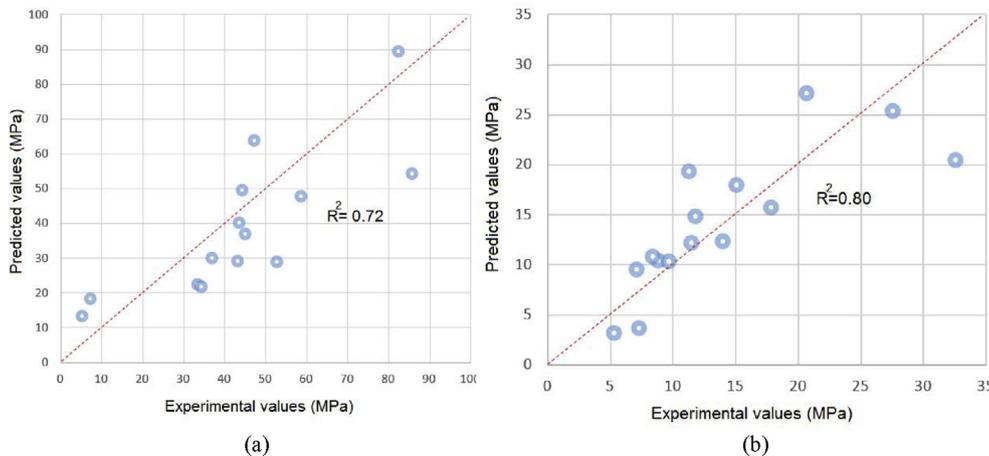


Fig. 16. Relationship between the experimental and predicted values a) compressive strength and b) splitting tensile strength.

noted for mixes with higher amount of fillers than those with lower amount of fillers due to an increase in the amount and size of pores in these samples.

- The size and number of pores of the particulate-filled epoxy-based polymer resin decreased with increasing temperature due to softening of the epoxy resin.
- Thermo-dynamical analysis from DMA test showed that adding 0–60% of filler to the polymer matrix could increase the T_g by at least 5 °C. Furthermore, results of SDT showed that the thermal stability of epoxy-based resin at high temperatures was improved by the inclusion of FA and FR.
- Large increases in ductility (strain to failure) and reduction in ultimate strength were observed at elevated temperatures. Nevertheless, the addition of fillers led to retention of compressive and tensile strengths by up to 72% and 52%, respectively for F60 at the maximum test temperature of 80 °C. This high mechanical strength retention was due to the high thermal stability of particulate fillers.
- SEM images showed the formation of dense microstructure with utilizing fillers in the mixtures at high temperatures. This resulted in higher compressive and split tensile strength retention in epoxy with fillers under elevated temperature.
- FTIR analysis indicated that C–H and C–O were found to be major phases for all specimens. However, there was restrictive stretching with the addition of filler up to 60%. The curing reaction was completed and the formation of polymeric epoxy structures in all the particulate-filled resins was performed. All of the functional group mixes had the same peak values at their lowest and highest temperatures and except for shifting of band by increasing of temperatures, particularly for resin-rich samples, which shows the in-service temperature, did not lead to significant changes in the spectra of different mixes.
- A simplified prediction equation based on power function was developed to predict the mechanical properties of the epoxy resin system with different percentages of particulate fillers at in-service elevated temperatures. Comparison between the predicted values and experimental results showed a strong correlation and the coefficient of correlation is at least 0.72.

The above results showed that the sensitivity of epoxy resin against in-service temperatures can be significantly improved by the inclusion of particulate fillers. This type of polymer matrix is suitable for manufacturing infrastructures exposed to the environment such as polymer railway sleepers, chemical storage tanks, and bridge girders. Continued efforts should be made towards understanding the behaviour of these new materials when exposed to other environmental factors such as moisture and photochemical reactions from solar ultraviolet (UV) and their synergetic effect in the presence of in-service temperatures.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymdegradstab.2019.108994>.

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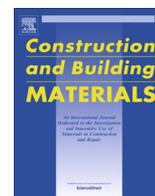
Chapter 4

Article II: Ageing of particulate-filled epoxy resin under hygrothermal conditions

The results of the investigation in Chapter 3 showed that the inclusion of hydrated alumina powder and fly ash as fillers improved the resistance of epoxy polymers under elevated in service temperature. In Chapter 2, moisture was identified to affect the long-term performance of polymeric materials. *Article II* investigated the effect of combined moisture and elevated temperature (hygrothermal conditioning) on the durability and service life of particulate-filled epoxy resin. To fulfil this objective, epoxy-based coating containing fire retardant and fly-ash was conditioned for 1000, 2000 and 3000 h at temperature up to 60 °C and a relative humidity of 98%, and the physical, mechanical, thermo-mechanical and microstructural properties were evaluated. Moisture absorption measurements were not made on the two fillers separately. This is due to the dryness of the fillers and their significantly higher melting point compared to epoxy resin. The relative humidity is dependent on air temperature. If the water vapor content stays the same and the temperature drops, the relative humidity increases. If the water vapor content stays the same and the temperature rises, the relative humidity decreases. In this study, an environmental chamber is used to ensure that the level of humidity is kept constant at 98% in different levels of exposure temperatures (Room temperature, 40°C and 60°C). With this approach, a direct comparison on the changes in the conditioned specimens can be made. In this study 3 different set of conditioning temperature (Room temperature, 40°C and 60°C) and 3 different exposure time (1000 h, 2000 h and 3000 h) were applied to generate data needed to predict the service life of particulate filled epoxy polymer using Arrhenius laws after 50 and 100 years. The results showed that the inclusion of fillers can

decrease the moisture absorption, increase the glass transition temperature and reduce slightly the mechanical properties of polymer coating. Based on the Arrhenius model, the particulate filled epoxy polymers are expected to retain more than 70% of their mechanical properties after 100 years of service at an annual average temperature of 30 °C in the Australian environment. These findings were also presented in a technical poster with details provided in Appendix A2.

The results of this study highlighted the beneficial effects of adding particulate fillers in improving the long-term properties of epoxy-based polymers exposed to moisture and elevated temperature. These results are also presented in a technical poster in Appendix A2. An understanding of the performance of this coating material when exposed to the photochemical reactions from solar ultraviolet (UV) is investigated and presented in Chapter 5.



Ageing of particulate-filled epoxy resin under hygrothermal conditions

Mojdeh Mehrinejad Khotbehsara^a, Allan Manalo^{a,*}, Thiru Aravinthan^a, Wahid Ferdous^a, Kate T.Q. Nguyen^b, Gangarao Hota^c

^a Centre for Future Materials (CFM), School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia

^b School of Engineering Cluster, RMIT University, Melbourne, VIC, Australia

^c Department of Civil and Environmental Engineering, West Virginia University, Morgantown, WV 26506, USA

HIGHLIGHTS

- Properties and microstructure of particulate-filled epoxy resin at hygrothermal conditions.
- Strength retention of particulate filled epoxy polymer after 100 years of service.
- Fillers make epoxy resin to have a dense microstructure after hygrothermal conditioning.
- FTIR analysis revealed no chemical changes in the epoxy after hygrothermal conditioning.

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ABSTRACT

This paper investigated the physical, mechanical, thermo-mechanical and microstructural properties of an epoxy-based resin system containing fire retardant and fly-ash under accelerated hygrothermal ageing. The particulate-filled epoxy resin was conditioned for 1000, 2000 and 3000 h at temperatures up to 60 °C and a relative humidity of 98%. Inclusion of fillers was found to decrease the moisture absorption, increase the glass transition temperature and slight reduce the mechanical properties after hygrothermal conditioning. The prediction using the Arrhenius model suggested that the particulate-filled epoxy resin will retain at least 70% of its strength after 100 years of service in the Australian environment.

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1. Introduction

In recent years, epoxy polymer resin systems have been increasingly used in the manufacture of polymer railway sleepers [1], structural repair[2], pavement overlays[3], waste-water pipes[4], decorative construction panels, hazardous waste containers, and structures built to withstand aggressive environmental conditions [5–10]. Epoxy resin is the preferred choice for civil engineering applications due to its superior mechanical properties compared to other resin systems [11–13]. As a component in civil engineering structures, the resin system is generally exposed to aggressive environments including elevated temperatures and high moisture, which may accelerate the physical and mechanical degradation of these materials. Therefore, an in-depth understanding on the effect of these environmental conditions is deemed necessary for their widespread acceptance and applications.

When exposed to high humidity, the susceptibility of polymers has been taken into consideration as an important durability property [14,15]. The ingress of moisture can react with the epoxy polymer and impose internal stresses, which causes a reduction in mechanical properties [16]. In addition to moisture, civil infrastructures are also subject to elevated in-service temperatures from the heat of the sun. For example, Sirimanna et al. [17] measured a surface temperature as high as 61 °C for composite bridge decks exposed to Australian weather conditions where the main concern was the decrease of the mechanical properties due to material degradation after long-term exposure to elevated temperatures. Manalo et al. [7] found that the flexural strength of sandwich composites consisting of glass fiber reinforced polymer (GFRP) skins and a phenolic core decreases by 20% when tested at 80 °C. Similarly, the full-composite action between the skin and core was lost due to the disintegration of the phenolic core at 150 °C and retained only 40% of their flexural strength. In another study, Manalo et al. [18] showed that the strength and stiffness of pultruded GFRP composite laminates significantly reduced by

* Corresponding author.

E-mail address: manalo@usq.edu.au (A. Manalo).

between 100 °C and 150 °C which corresponded to due to the glass transition of the vinyl ester resin. Unfortunately, elevated temperatures can also facilitate the moisture absorption of epoxy resin systems [19]. The damaging process caused by the combined moisture and temperature may result in additional weight gain and faster diffusion of water along with the samples' exposure to hydrothermal cycling conditions. Prolonged hydrothermal ageing can lead to irreversible damages of the resin such as oxidation, microcavity growth, cracking and debonding and polymer network relaxation [20]. For example, cracking and blistering can cause exceptionally high uptake [21]. Ray [22] noted that the high temperature during hygrothermal ageing reduced the interlaminar shear strength of epoxy-based composite laminates. Almeida et al., [23] showed that carbon fiber/epoxy laminates after conditioning at 80 °C and a relative humidity of 90% for 60 days reduced the shear strength and modulus to about 30% and 38% because the water absorbed by epoxy-based composites caused a reversible plasticization of the matrix and induced stresses that were detrimental to the fiber–matrix interface. Mohamed Elarbi and Wu [24] showed that epoxy samples were more sensitive to the combined effect of moisture under elevated temperatures compared to those exposed to moisture. Moderate to high heat can significantly degrade epoxy resins. However, low to moderate heat may initially accelerate post curing. For example, FRP system exposed to synergistic effect of moisture and temperature cycles is expected to exhibit lower durability, because of the deterioration of the bond between FRP and concrete. When moisture is penetrated in the resin can weaken the Van der Waals force between polymer chains. This subsequently can lead to a significant decrease in bond strength. The moisture uptake can induce the swelling stress, which can cause fiber–matrix debonding and matrix cracking [25]. Haque et al. [26] reported that the strength degradation of GFRP at temperatures below 100 °C was not noticeable. They also found that the moisture degradation was less severe than temperature degradation. Birger et al. [27] also revealed that carbon/epoxy composites at 95% humidity and 50 °C did not show degradation in the mechanical properties. Therefore, there is a need to explore methods to enhance the performance of epoxy resin under hygrothermal environments.

Shamsuddoha et al. [28] studied different percentages of epoxy (27%, 15% and 13%) with various combination of fillers in hot-wet conditions for 1000 h at 70 °C (around 10–20 °C more than their T_g). Their results showed a significant reduction of up to 74% and 83% in their compressive and flexural strengths, respectively. Research on silica filled epoxy resin under hot-wet conditioning confirmed the decrease in elastic modulus and strength. Results by Brun et al [29] showed that silica filled epoxy resin under hot-wet conditioning underwent a reduction in the elastic modulus and strength due to the absorbed water causing hydrolysis or after the debonding of the filler–matrix interface. When water molecules break the physical bond between the resin and silica grains and form H-bonds with the polymer some water accumulates between the two phases, might react with the resin. Recent developments have also shown that the application of filler materials such as fly ash (FA), fire retardant (FR) fillers, at the same time can reduce the cost of epoxy-based polymer matrix and provide environmental benefits [30–32]. While some studies have shown that the elevated temperature and moisture can affect the properties of epoxy resin, the influence of hygrothermal conditioning on the durability and long-term performance of particulate filled epoxy resin is not known. A better understanding of the performance of particulate-filled epoxy based resin under the synergistic effects of these harsh environmental conditions must be achieved in order to further advance the safe use and adoption of this material in various construction applications and predict their service life.

In this study, the accelerated aging program aimed at simulating exposure conditions due to synergistic effect of temperature and moisture on the particulate-filled epoxy resin with fly ash (FA) and flame retardant (FR) was implemented to correlate and predict the performance of these materials in actual field condition. This paper focuses on understanding the effect of hygrothermal conditioning on physical, mechanical and thermo-mechanical properties and the microstructure of an epoxy-based polymer matrix as well as their predicted service life based on the Arrhenius relation. The results of this research is expected to provide critical information to support the application and development of a durable cost-effective epoxy-based coating matrix through a comprehensive understanding and evaluation of their mechanical properties and degradation mechanism.

2. Materials and methods

2.1. Materials

A two-part resin of Bisphenol A diglycidyl ether (DGEBA) type epoxy resin (Part-A) and an amine-based curing agent (Part-B) was used in this study. The Epoxy Equivalent Weight (EEW) for Part-A is 190 g while an Amine Hydrogen Equivalent Weight (AHEW) for Part-B is 60 g. Thus, 100 g of Part-A with a density of 1.064 g/cm³ were used to mix with 32 g of Part-B with density of 1.182 g/cm³ to maintain the mixing ratio. FR was a hydrated alumina powder with density of 2.411 g/cm³ and FA was fly ash with density of 2.006 g/cm³. Both FR and FA were round in shape with a diameter of 75 to 95 μm, and 0.1 to 30 μm respectively [33].

2.2. Mix proportions

Fillers of up to 60% of the matrix's volume were added in 20% increments, where the mix with more than 60% fillers was found to be unworkable [30]. Mixes were named based on the volume percentage of the fillers. For example, F40 indicates a mix containing 40% filler and 60% resin and hardener, as detailed in Table 1. The ratio of FR:FA was kept constant.

2.3. Specimen preparation

The specimens were prepared on the same day at room temperature to minimise variation. All specimens were prepared in two different moulds: i) sealed-bottom cylindrical PVC pipes with diameter of 25 mm and height of 25 mm suitable for measuring the density, porosity, compressive strength and split tensile strength; and ii) non-stick metal sheets to be cut and prepared according to the recommendation of the test standards – suitable for measuring the glass transition temperature and flexural test (with the dimensions of 60 mm length × 10 mm width × 5 mm depth). The samples were kept in moulds for 48 h at room temperature and demoulded after another 7 days at room temperature curing.

2.4. Hygrothermal conditioning and testing

Accelerated ageing has been carried out in an environmental chamber (Votsch technik) to simulate a hygrothermal environment of particulate filled epoxy polymers. A total of 108 cylindrical and 45 rectangular samples were kept in the chamber at 98% relative humidity and at three levels of temperatures of 23 °C (RT), 40 °C and 60 °C, and were removed from the environmental chamber after 1000h, 2000 h and 3000 h. The temperature of the chamber was set to the required exposure temperature and the accuracy of exposure temperature was checked using a thermometer

Table 1
Mix proportion of polymer matrices.

Resin/Filler (by volume)	F0	F20	F40	F60
Part A – resin (g)	1000	737	552	368
Part B – hardener (g)	320	236	177	118
FR (g)	0	397	794	1192
FA (g)	0	119	239	358

installed inside the chamber. To avoid any thermal degradation, the maximum conditioning temperature used in this research was 60 °C. The chart given in Fig. 1 illustrates the appropriate ASTM test methods as well as the number of specimens tested for each type of test to evaluate the combined effect of elevated temperature and moisture on the properties of particulate filled epoxy resin.

3. Results and discussion

3.1. Physical properties

The weight of different mixes before and after conditioning was measured using an electronic balance (MonoBloc-AB204-S) with sensitivity of 0.0001 g. The hardened density was then calculated according to ASTM C905 [34]. The moisture absorption of different mixes was measured at 1000, 2000 and 3000 h according to the ASTM D570 [35]. Before weighing each sample, the surface water was wiped off and the percentage weight gain versus time was calculated according to the below equation:

$$\text{Weight gain ratio (Wr)} = (Wt - Wd) / Wd \times 100 \tag{1}$$

where *Wt* is the weight of sample at immersion time *t*, and *Wd* is the weight of dried sample.

3.1.1. Density

Fig. 2 shows the hardened densities of epoxy mixes. The results showed an increase from 1.093 g/cm³ to 1.533 g/cm³ with the increase in filler content from 0% to 60%. This increase in density was expected as the density of the FR and FA fillers was higher than that of epoxy resin (1.193 g/cm³). However, the mix with 60% filler had a slightly lower density than the F40 mix. The densities of the polymer-filled epoxy based matrix with different components were also calculated (Fig. 2) and were found to increase from 1.093 g/cm³ to 1.827 g/cm³ for mixing with 0% to 60% fillers. The variation between the calculated and measured densities for mixes with fillers is due to the mix becoming more viscous and less flowable, creating voids to the hardened mix as also found in the previous study by Khotbehsara et al. [33].

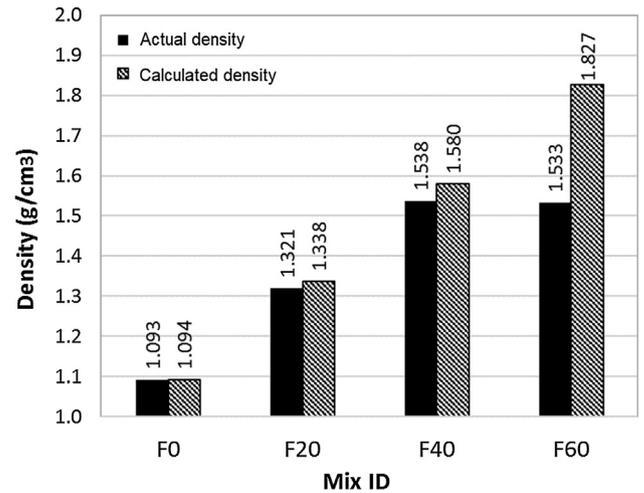


Fig. 2. Density of different mixes.

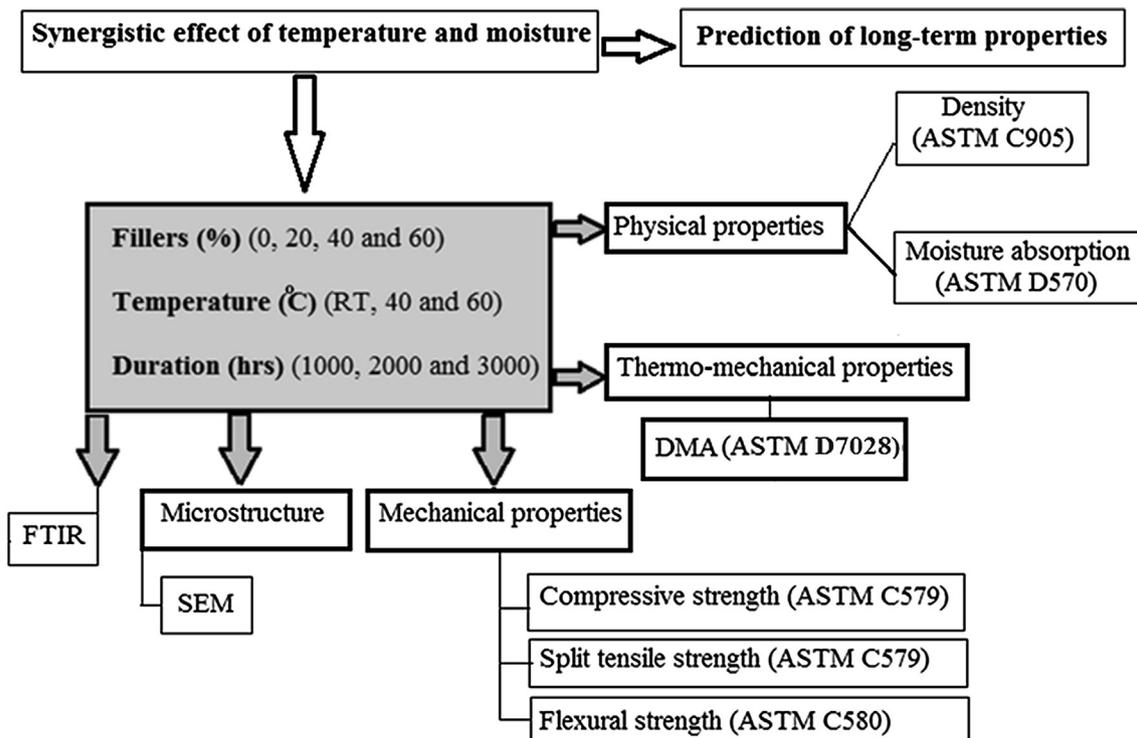


Fig. 1. Summary of test methods.

3.1.2. Water absorption

Fig. 3 shows the water absorption of all mixes after hygrothermal conditioning. All bars reported the average value measured from six nominally identical samples with the standard deviation less than 4% of the respective average weight. The results showed a minimal water uptake at RT (only around 0.3%) but increased with increasing temperature. Moreover, a higher water uptake was measured for neat epoxy (F0) than the mixes with particulate fillers. The significant high moisture absorption of F0 (up to 2.3% at 60 °C) indicates the sensitivity of neat epoxy to high temperatures. The hydroxyls and amines present in epoxy resin are known to have high affinity with water [39]. Water first interacts with epoxy surfaces. Water absorption can disrupt the hydrogen bonds among polymer segments which opens the polymeric network and causes the polymer to swell [40]. With temperature increase, the DGEBA network becomes more sensitive to the increased kinetics of water absorption and the molecular mobility [41], which explains the high water absorption of epoxy at elevated temperature. Shamsudoha et al. [28] showed an increase in the moisture absorption within a range of about 0.5–2.7% after 1000 h of conditioning epoxy grouts with calcium and silica-based fillers in hot-wet conditioning at 70 °C. They reported that the inclusion of fillers decrease the moisture absorption from 2.7% to almost 0.8%. In a similar way to our study, the inclusion of fillers reduced the moisture absorption from almost 2.3% to 0.5% after 3000 h of hygrothermal conditioning at 60 °C. The smaller weight gain of the mixes containing fillers at higher temperatures can be related to higher crosslinking density of these mixes resulting in less free volume [42,43]. The slightly higher water uptake of F60 than F40 can be considered to be due to the pores and voids [33].

3.2. Effect on thermo-mechanical properties

The thermo-mechanical properties were investigated by measuring the glass transition temperature (T_g) of the samples before and after conditioning in accordance with the ASTM D7028 [36] using a Q800 type of TA instruments. The samples were clamped in a dual-cantilever system, where the DMA multi-frequency strain was applied as the test mode. The temperature with increments of 5 °C during temperature scans was set to between 30 °C and 120 °C. T_g of the particulate filled epoxy resins before and after hygrothermal conditioning were summarised in Table 2. The T_g obtained from the storage modulus of the unconditioned samples is around 60 °C with almost 3 to 5 °C difference between F0 and F60. This enhancement in the thermo-mechanical properties of

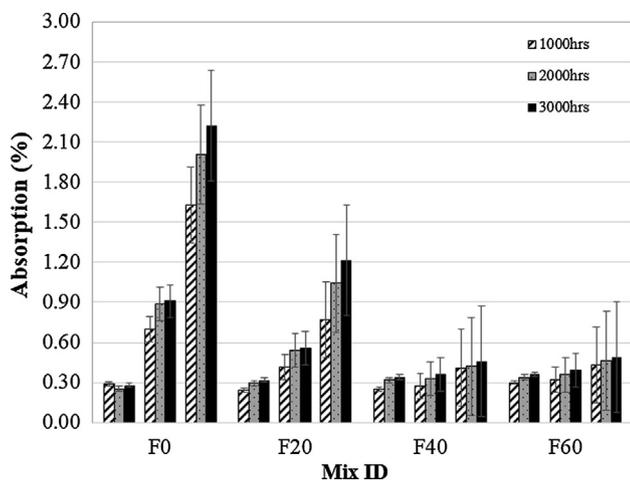


Fig. 3. Weight gain of epoxy mix at RT, 40 °C and 60 °C.

epoxy resin is directly related to the higher capability of a polymer matrix with fillers to store energy under high temperature due to high thermal resistance of the used fillers. The T_g of the polymer mixes depended basically on the resin system. While the type of resin was same for all mixes, the addition of fillers with higher degradation temperature (Epoxy resin ~ 340 °C, FA ~ 800 °C and FR ~ 980 °C) led to an increase in T_g values. Ferdous et al. [30] also revealed that the T_g increased from 50 °C to 55 °C with the addition of FA, FR and hollow microspheres (HM). Similarly, Shamsudoha et al. [28] showed that the incorporation of coarse aggregates increased the storage modulus and T_g . This result indicated that the coarse filler could improve the capability of polymer matrix to store energy under high temperatures. The results in Table 2 show that there were no significant changes in the T_g of epoxy polymers after 3000 h conditioning at RT, demonstrating that the epoxy are thermally stable at 23 °C. However, conditioning the samples at elevated temperature (60 °C) significantly increased the T_g values to around 80–85 °C. This implies that the exposure to elevated temperature during the initial stage enhanced the curing reaction of the sample leading to an increase in cross-link density as suggested by Marouani et al. [41]. This result was verified by the considerable increase in T_g of epoxy after 24 h post-curing at 40 °C (P40) and 60 °C (P60). From a T_g of 56 °C for F0 and from 61 °C for F60, this increased to 81 °C and 84 °C, respectively. An increase in T_g due to accelerated aging at elevated temperatures have also been observed in previous studies for epoxy and other type of composites. Patel and Case [44] and Marouani et al. [41] suggested that the increase in T_g is related to an increase in cross-link density of the network structure of the material (post-crosslinking). This causes an increase in T_g due to the progress of crosslinking reaction (this could also explain the darkening of the resin). Consequently, the material with a high cross-link density will have a low moisture content as there will be less free volume available for moisture absorption [38]. This explains the smaller weight gain of F40 and F60 after conditioning at high temperature, compared to F0. Crosslink is a covalent bond and is formed during the reaction of curing agent molecules and epoxy molecules. In crosslinking reactions of DGEBA and hardener, when the C–O bond within the epoxide group is breaking, the carbon end of the opened epoxy group is reacting with the nitrogen of the amine group in the hardener molecule [45]. Crosslink density (ν_c) is directly related to the storage modulus (E') in the rubbery plateau region according to the following equation [33,46]:

$$E' = \nu_c RT \quad (2)$$

where T is the temperature (K) and R is the gas constant. As shown in Fig. 4, the crosslinking density increased with further inclusion of fillers. F60, which has the highest amount of fillers, has the highest storage modulus and consequently crosslink density is increased.

3.3. Effect of hygrothermal conditioning on mechanical properties

The compressive and splitting tensile strengths of the samples were determined following the test procedure described in the ASTM C579 [37] using a universal testing machine with a capacity of 100 kN with a loading rate of 2 mm/min. The flexural strength of the samples was tested under 3-point static bending following the ASTM C580 [38]. Table 3 summarises the average strength in compression, split tension and flexure of epoxy-based polymer samples before and after hygrothermal conditioning. Results suggest a slight increase in the mechanical strength of samples after 1000 h of hygrothermal conditioning compared to the unconditioned samples due to post-curing resulting in better crosslinking density of polymer mixes as was also observed by Barbosa et al. [47].

Table 2
Variations in glass transition temperature (T_g) in °C from the storage modulus curve.

MIX ID	Un-Conditioned			Conditioned								
	Con+trol	Post-cured		RT			40 °C			60 °C		
		P40	P60	1000	2000	3000	1000	2000	3000	1000	2000	3000
F0	58.2	70.1	81.3	58.1	57.5	56.7	73.4	71.8	68.5	78.9	78.5	76.3
F20	59.6	71.0	82.4	58.2	57.2	56.4	76.3	73.1	71.1	79.8	78.9	77.6
F40	60.2	74.5	82.7	60.7	59.5	58.9	78.3	75.2	74.5	82.4	80.9	80.4
F60	61.6	75.2	84.5	61.2	60.4	59.9	79.9	76.2	75.1	84.7	83.7	82.9

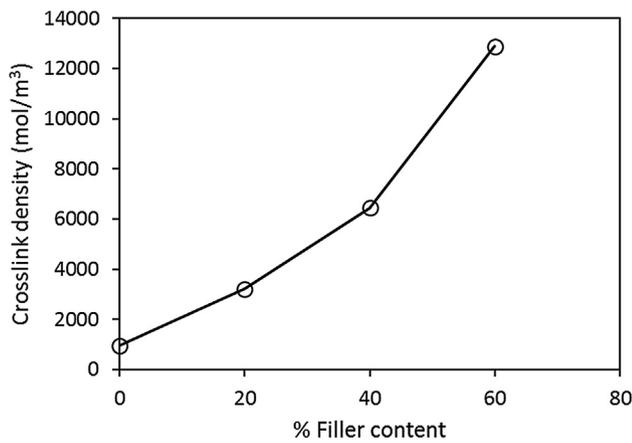


Fig. 4. Crosslinking density of particulate filled epoxy polymer.

3.3.1. Effect of hygrothermal conditioning on compressive strength

Fig. 5 shows the typical failure mode of conditioned and unconditioned particulate-filled epoxy resin samples in compression. As shown in the figure, F0 and F20 were deformed without crushing even after reaching their maximum compression strength. These samples behaved like elastic materials, as they resumed their original shape when the load was released, even though they retained some of their bulged shape. On the other hand, micro cracks followed by shear cracks were observed for unconditioned F40. For unconditioned F60, noticeable failures with huge sudden shear crack at ultimate strength was observed showing a brittle fracture. The high stiffness of fillers has caused this failure behaviour, particularly for those mixes containing higher percentages, as also reported by Ferdous et al. [30,48]. The brittle failure mode could

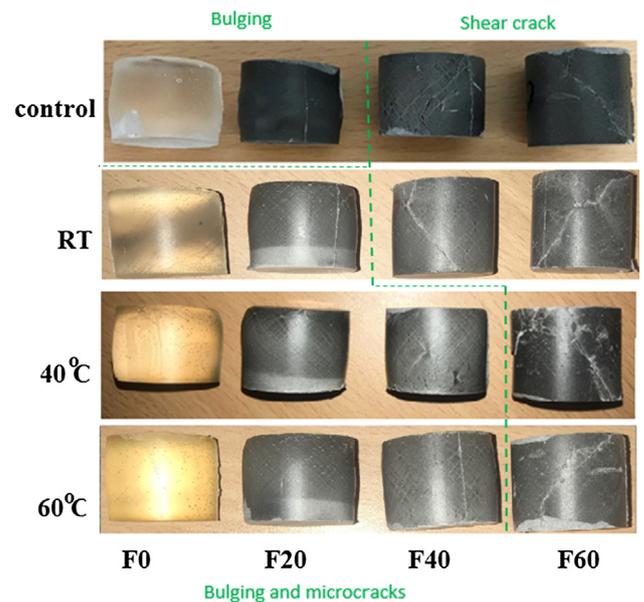


Fig. 5. Failures observed after compression test in different mixes unconditioned, and 3000 h conditioned at RT, 40 °C and 60 °C.

be also related to pore size and volume. The increase of porosity with the increase of fillers affected the transfer of stresses from one part to another that may increase stress concentration and lead to premature failure. High-porosity mixes (F40 and F60) have larger pores randomly distributed through a matrix and failed in a brittle manner. However, the crack along the direction of the compressive stress rather than along the interface between the resin

Table 3
Mechanical properties of epoxy polymer matrices under elevated temperature.

MIX ID	Un-Conditioned			Conditioned								
	Control	Post-cured		RT			40°C			60°C		
		P40	P60	1000	2000	3000	1000	2000	3000	1000	2000	3000
Compressive strength (MPa)												
F0	88.3	89.9	87.2	91.4	89.6	87.9	89.2	88.1	85.8	86.8	84.8	83.3
F20	85.7	86.3	87.7	89.9	87.3	86.3	88.2	86.1	84.9	87.0	85.4	83.3
F40	84.6	88.0	88.9	89.2	88.5	87.2	88.0	87.2	86.4	87.1	86.1	85.1
F60	61.5	62.8	65.7	70.1	68.5	67.5	69.6	67.7	66.9	68.2	67.0	65.5
Split tensile strength (MPa)												
F0	35.5	37.4	38.9	38.1	37.2	36.4	37.2	36.6	35.5	36.0	35.5	34.2
F20	27.9	29.1	29.2	28.9	28.0	27.8	27.8	27.6	26.8	27.3	26.8	26.3
F40	26.9	27.5	28.1	28.6	28.1	27.4	27.67	27.2	26.6	27.1	26.3	26.1
F60	20.4	20.5	21.9	20.7	20.4	20.0	20.1	19.5	19.42	19.6	19.1	18.9
Flexural strength strength (MPa)												
F0	97.8	104.1	103.6	108.8	105.9	102.2	107.3	103.2	99.9	104.2	101.1	96.7
F20	48.8	50.6	52.5	51.9	49.6	49.0	51.1	49.6	48.1	49.5	48.2	46.2
F40	26.8	36.1	42.7	42.4	41.3	40.2	42.2	40.1	39.9	41.1	39.9	38.4
F60	13.2	30.1	33.4	31.7	30.5	30.1	31.1	30.0	29.8	30.2	29.9	28.9

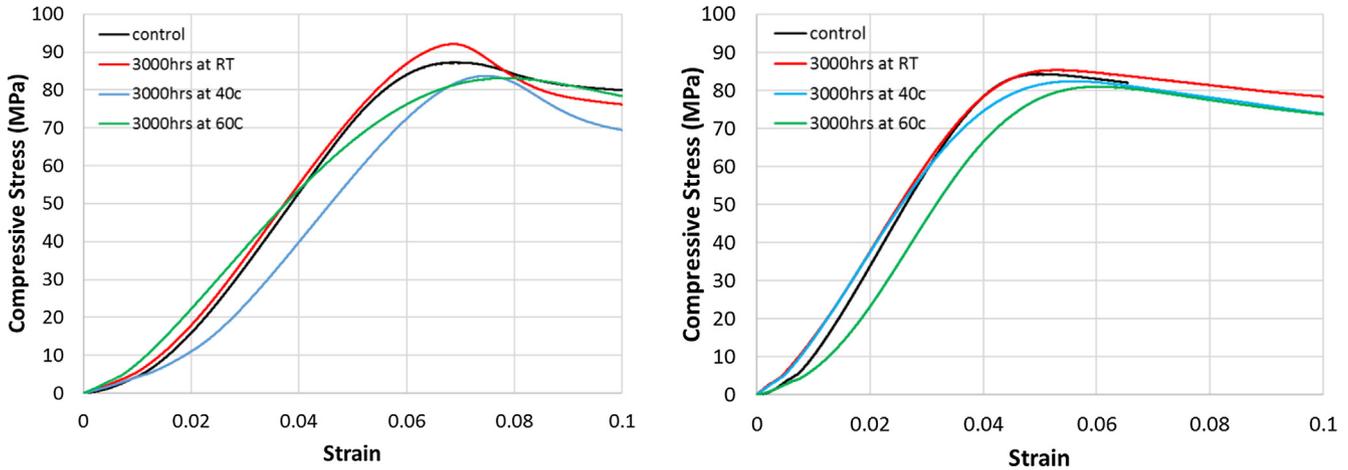


Fig. 6. Typical compressive stress and strain curves for F0 (left) and F40 (right) before and after conditioning.

and the fillers, indicates the excellent adhesion of fillers to the epoxy matrix. Similarly, Ferdous et al. [30] found that epoxy-based polymer containing up to 30% of FA, FR and HM, exhibited an elastic failure mode without visible cracks under compression at room temperature while the samples including 40%, 50% and 60% failed by cracking. One can observe that the failure modes for conditioned resin-rich mixes (F0 and F20) are similar to those of unconditioned, indicating flexible, matrices. The conditioned resin rich samples (F0 and F20) failed by bulging and microcracks which might be due to the moisture uptake and the interaction between water molecules and resin. While, for F40 unconditioned and conditioned at RT micro-cracks followed by a shear cracks were observed, the failure mode was more of micro cracks with bludged shape at 40 °C and 60 °C. This could be due to the softening of resin at high temperatures and reorientation of fillers resulting in better interlocking between different particles. It is also interesting to note that for F60, unconditioned and conditioned samples at RT showed noticeable shear failure at ultimate strength.

Fig. 6 shows the typical stress-strain curve for F0 and F40 as examples tested in compression after conditioning to various hydrothermal environments for 3000 h. It can be observed that as the conditioning temperature increased, the specimens slightly became more ductile and failed at a higher strain. This is because of the softening of the epoxy matrix at higher temperatures. This mechanism also explains the observed bulging on the tested samples at elevated temperature. With increasing the temperature, and being close to T_g , the particle filled epoxy polymers become slightly more ductile and the stiffness is decreased. Meanwhile, the inclusion of fillers hindered the mobility of the polymer's molecular chains, and provided some stiffness too. Moreover, the softening of the matrix might allow the fillers to be pulled in the direction of the loading, and their porosity to be decreased for better stress transfer. Fig. 7 shows the compression strength retention of particulate filled epoxy-based resin after hydrothermal conditioning. It can be seen that all mixes decreased its strength with exposure temperature and duration. After 3000 h of conditioning

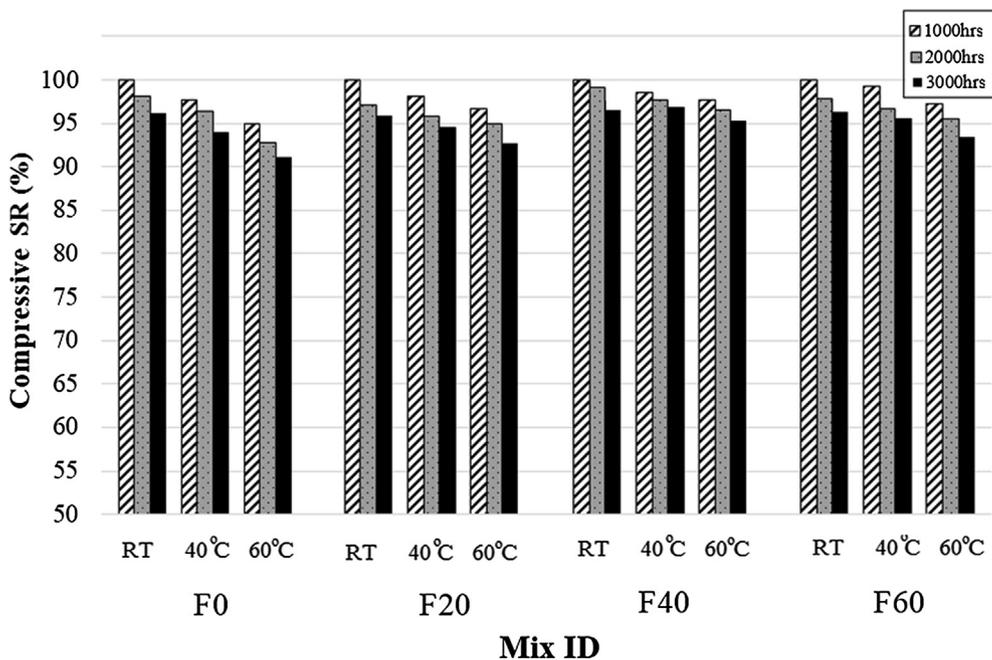


Fig. 7. Compressive strength retention (SR) of particulate filled epoxy polymers in different hydrothermal environments.

at 60 °C and relative humidity of 98%, the F0 mix retained up to 91% of its compressive strength while F20, F40 and F60 mixes retained at least 92% of their compressive strength. One possible explanation for this high retention is the effect of post-curing process of the resin at the initial stage of the hygrothermal conditioning. However, the retention of F0 was less than mixes containing fillers. As discussed in previous section, neat epoxy matrix absorbed more water than the mixes containing fillers resulting in the interaction between water molecules and the matrix particularly at higher temperatures of conditioning. Moreover, with temperature increase, the DGEBA network became more sensitive to the increased kinetics of water absorption [39] and the molecular mobility [40], which explains the high water absorption of epoxy at elevated temperature resulting in decrease of strength. Moreover, with increase of exposure time, the ingress of moisture reacted with the polymer matrix which could cause further reduction in the polymer's overall mechanical properties [49] while the higher retention for the F40 and F60 could be related to the hydrophilic nature of the fillers resulting in less absorption and consequently higher mechanical properties compared to neat epoxy. Another possible explanation would be the decrease in free volume due to higher crosslinking density of mixes containing fillers resulting in decrease of moisture uptake and increase of strength retention.

3.3.2. Effect of hygrothermal conditioning on splitting tensile strength

Fig. 8 shows the failure mode of unconditioned and conditioned samples under splitting tensile tests. The F0 samples deformed and bulged without visible cracks even after reaching their maximum strengths. They behaved like an elastic material and resumed their original shape when the load was released. However, the mixes containing 20%, 40% and 60% fillers failed primarily at a single cross section along the diameter by brittle fracture. This was due to the lower filler/matrix adhesion resulting in the failure of the matrix at the ultimate load because the fillers provide discontinuous links to the epoxy matrix. A similar mode of failure was observed for samples with fillers after hygrothermal conditioning.

All mixes retained most of their tensile strength as shown in Fig. 9 after hygrothermal conditioning. A lower strength retention

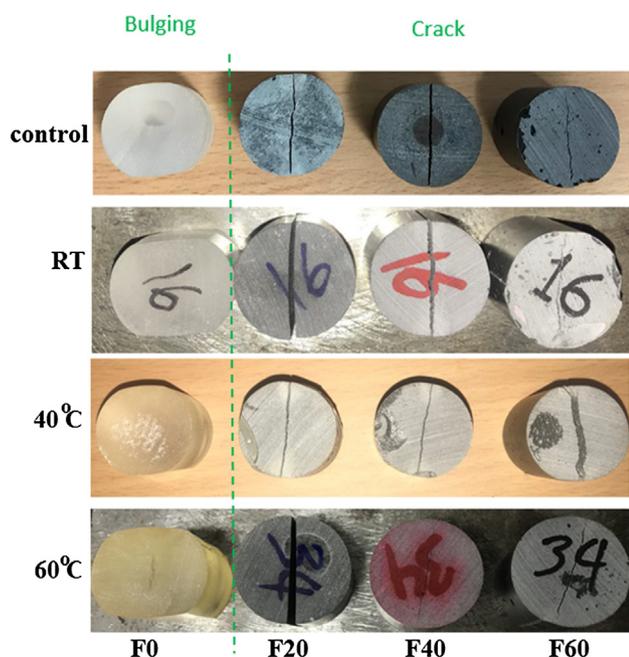


Fig. 8. Failures observed after splitting tensile test in different mixes unconditioned, 3000 h conditioned at RT, 40 °C and 60 °C.

was observed at higher exposure temperature and duration. The F0 mix retained up to 89% of its strength after 3000 h at 60 °C while the mix with fillers retained at least 91% of their splitting tensile strength. The high retention of the tensile strength of particulate filled epoxy could be due to effect of post-curing which resulted in the mixes absorbing less moisture and having higher crosslinking density than F0.

3.3.3. Effect of hygrothermal conditioning on flexural strength

For the unconditioned samples, flexural strength of mixes was significantly reduced from 97 MPa to 13 MPa by an increase in percentage of fillers. This phenomenon could be attributed to reduction in the resin content that the strength of a polymer matrix is primarily depended. Thus, lower flexural tensile strength was achieved, and the behaviour of mixes changed from flexible to rigid with increase in the percentages of fillers. F0 deformed without sudden crack, while the samples with fillers failed when a large vertical flexural crack occurred at the mid-span as shown in Fig. 10. F0 behaved like an elastic material with non-linear stress-strain behaviour due to its nature, being like rubber-like material. However, this behaviour changed with the inclusion of fillers and became rigid with almost linear behaviour. An increase in the amount of filler and consequent larger surface area, a rigid bond with the resin was created. This resulted in an inflexible polymer matrix with lower failure strain. Although the similar failure mode was observed for the conditioned and unconditioned F0 samples, creation of microcracks probably due to the effect of moisture uptake was also observed in the conditioned samples. For the samples containing filler, the failure mode of conditioned samples changed from relatively rigid to more flexible failure with the creation of microcracks before a large vertical flexural crack. Furthermore, as shown in Fig. 11, F60 and F40 could retain more than 91% and 92% of their flexural strength after exposure to hygrothermal conditioning, while F0 could retain only 88%. Moreover, as was also shown in Table 3 the flexural strength of F40 and F60, even after 3000 h conditioning to hygrothermal environment (29 and 38 MPa, respectively), was still much higher than the control samples (26 and 13 MPa for F40 and F60, respectively). Uniform dispersion of filler and better interlocking between resin and fillers in the aged particulate filled epoxy polymers led to higher strength and excellent strength retention. This was supported by the flexural results of post-cured samples at 40 and 60 °C for 24 h and moisture uptake, showing that F40 and F60 absorbed less moisture at high temperatures compared to resin rich mixes (F0 and F20).

4. SEM scanning electron microscope (SEM) and Fourier-Transform infrared spectroscopy (FTIR) observations

The microstructural characteristics of the particulate filled epoxy resin was observed using a scanning electron microscope (SEM, JEOL JXA 840A). The samples were cut and prepared into dimensions or around 1 cm then coated with gold using a sputter deposition machine. Microfocused Fourier-transform infrared spectroscopy (FTIR) also was also conducted to determine the functional groups present in the particulate filled epoxy base resin. FTIR spectra were recorded using a Nicolet 6700 FTIR spectrophotometer with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were then achieved by averaging 16 scans at a resolution of 4 cm^{-1} .

4.1. Microstructure of particulate filled epoxy resin systems

To form a composite, when some materials are mixed together, not only their properties are governed by the characteristics of

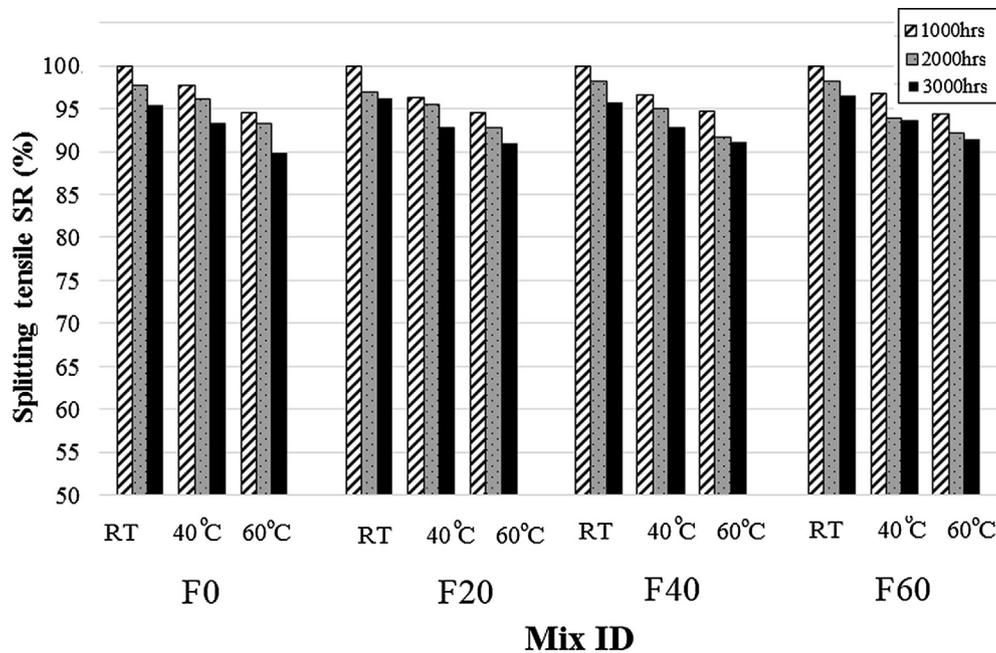


Fig. 9. a) Splitting tensile strength retention of particulate filled epoxy polymers in different hygrothermal environments.

each component, but also by the interface between them [50]. Moreover, the mechanical properties of a particulate filled polymer depend on the type of distribution of particles, which can be characterized by SEM [51]. From this study, the SEM revealed that the microstructure of unconditioned and conditioned F0 and F40 samples has a direct correlation on the physical, thermo-mechanical and mechanical properties of epoxy-based polymer exposed to a hygrothermal environment (Fig. 12). F40 was chosen since it had the highest strength retention after hygrothermal conditioning. As it can be seen in Fig. 12a and c, there are remarkable differences in the texture and form of the particulate-filled epoxy resin compared to the neat epoxy samples. Dense microstructures with small pore sizes were formed in samples without filler (F0), while the mix containing 40% FA and FR (F60) showed various pores and weak interfacial bonds between different fillers and the resin through the matrix due to the creation of pores and voids in the matrix (Fig. 12c). This subsequently decreased the mechanical performance of the polymer matrix of control samples. Ahmad et al. [52] pointed out that the presence of fused silica resulted in inhomogeneous distribution and weakened the interaction between the matrix and the filler. It could cause a defect to the matrix because of the presence of a void between the particles and led to undesirable material properties. As shown in Fig. 12a, the surface in the SEM image of the unconditioned neat resin shows that F0 samples have a compact but relatively rough surface. Although the surface of epoxy samples after conditioning to hygrothermal environment at 60 °C is much smoother, more pores were created due to the penetration of water molecules into the mix due to the increase of mobility at 60 °C which is close to the T_g of F0 (Table 2). This result is in agreement with the result in the physical section, where with the increase of temperature in hygrothermal conditioning there is a significant increase in the water absorption of F0 (Fig. 3). On the other hand, a close inspection of Fig. 12c and 12d revealed that the exposure of F40 to a hygrothermal environment improved the interlocking between the fillers and resin compared to the control sample (Fig. 12c). For FR and FA as spherical inclusions, the packing arrangement defines the quantity of fillers and the distribution of particles. As indicated in Fig. 12c, the surface of the particulate filled epoxy resin with 40% fillers shows a

two-phase morphology with a dispersed phase of isolated spherical particles (FA and FR) and a rigid continuous phase (resin). Thus, when the temperature increased the distribution of particles, improved due to increase of mobility and reorientation of fillers and consequently dense microstructures were formed. This could be due to the post curing of the mix and increase the interlocking between the resin and different filler particles, which could help to retain the mechanical strength, while increasing the strain failure capacity. This was also in agreement with the result reported and failure mode of mixes.

4.2. FTIR spectra before and after conditioning

FTIR spectra were at the outer surface and inner portion of the samples to determine functional groups present in the particulate filled epoxy resin. From the spectrum, the characteristic bands of mixes were observed at various wavenumbers as it is shown in Fig. 13 for comparison. The spectra of F0 and F40 have been presented as examples. Here, the spectrum of surface has been plotted as there were no changes in the central parts of conditioned samples. C-H and C-O were found to be major phases for all samples. The band observed at $\sim 3800\text{ cm}^{-1}$ for different samples corresponded to the O-H stretching band. The second group of the bands, located at 2904 cm^{-1} and 2870 cm^{-1} is attributed to the stretching vibration of the C-H group of epoxy [53]. However, the intensity of these wavenumbers decreased with the increase of fillers at F40. The band at 1703 cm^{-1} and 1718 cm^{-1} is due to the stretching vibration of C=O in ester [54]. The bands at wavenumber 1508 cm^{-1} is the characteristic band for the aromatic ring stretching of C=C, characteristic of DGEBA epoxy systems [54]. The band at 1508 cm^{-1} may also represent nitro deformation from the cycloaliphatic amine curing agent. The bands corresponding to the epoxide ring ($\sim 817\text{ cm}^{-1}$) wavenumbers at 1024 and 1234 cm^{-1} are characteristic bands for C-O stretching of saturated aliphatic primary alcohols [50]. However, this is unlike the bands observed at C-O for F0, where a restrictive stretching with further inclusion of filler was observed (Fig. 13 c and d). This is due to the decrease in the amount of resin by increasing the percentages of fillers. As shown in Fig. 13, all of the functional groups in both

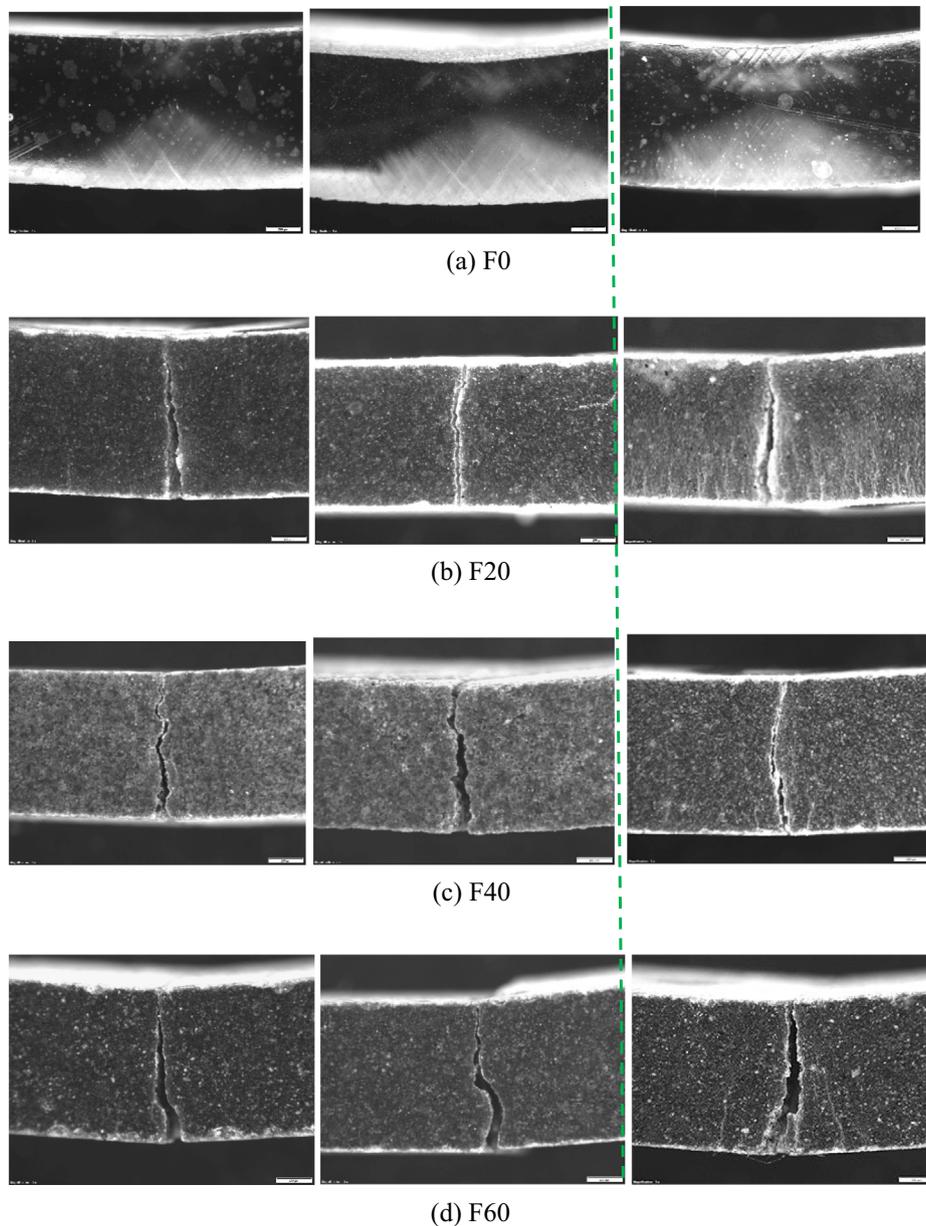


Fig. 10. Failures observed after flexural test in different mixes (From left: Unconditioned, Conditioned at RT, Conditioned at 40 and 60 °C).

unconditioned and conditioned samples have the same peak values except for some shifting of bands. FTIR results demonstrate that the curing reaction was completed, as was the formation of polymeric epoxy structures in all the particulate composites. These results were in accordance with SEM images showing the formation of solid resin after the curing reaction (Fig. 12). These results showed that the sensitivity of epoxy resin against hygrothermal conditioning can be sufficiently reduced by the inclusion of fillers. This further indicates that the particulate filled epoxy resin will exhibit better engineering properties, as the fillers provide protection against hygrothermal conditioning increasing their durability and suitability in civil engineering application.

5. Determination of influential design parameters using two-way ANOVA

The influence of filler content, exposure duration and temperature on the flexural strength and glass transition temperature of

the polymer matrix was determined by a two-way Analysis of Variance (ANOVA) using SPSS statistical analysis software [55,56]. The analysis was run with the variation of filler contents for 0%, 20%, 40% and 60%, exposure durations for 1000 h, 2000 h and 3000 h, and the curing temperature for 20 °C, 40 °C and 60 °C. Correlation graph with data points used in SPSS are given in Fig. 14, and the univariate analysis of tow-way ANOVA results are shown in Table 4. The correlation graphs plotted the data points used in SPSS analysis and showed how the amount of fillers, level of temperature and exposure time affecting the flexural and Tg properties of particulate filled resin.

The p-values (significance level) in Table 4 indicates that the flexural strength and glass transition temperature were affected significantly due to the variation of filler content, exposure duration and curing temperature as the p-values were obtained below 0.05 (i.e., 95% confidence level). However, the level of influence of each independent variable (filler content, exposure duration and curing temperature) on the dependent variables (flexural strength

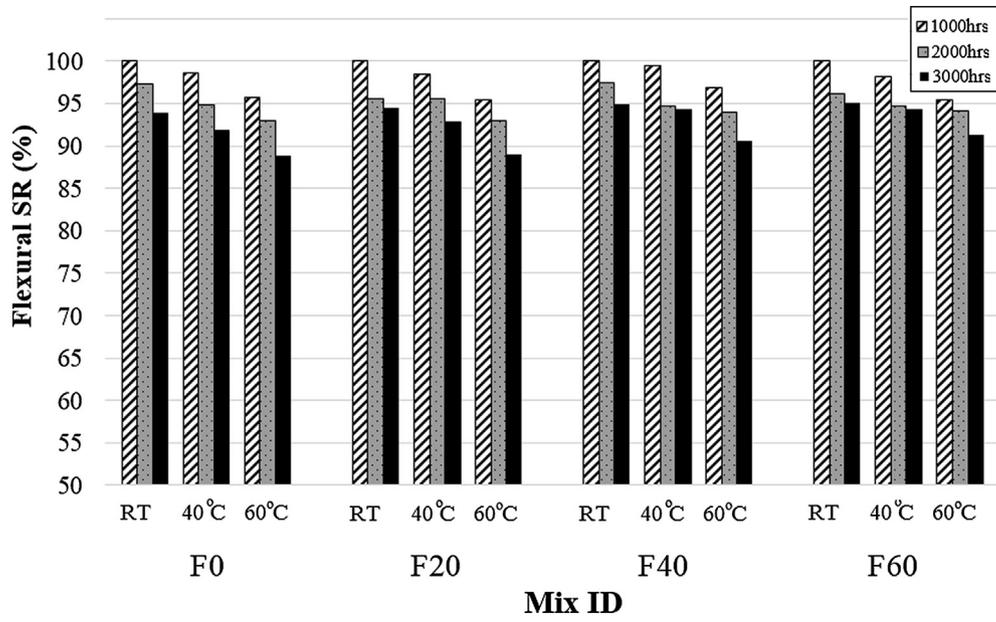


Fig. 11. a) Flexural strength retention of particulate filled epoxy polymers in different hygrothermal environments.

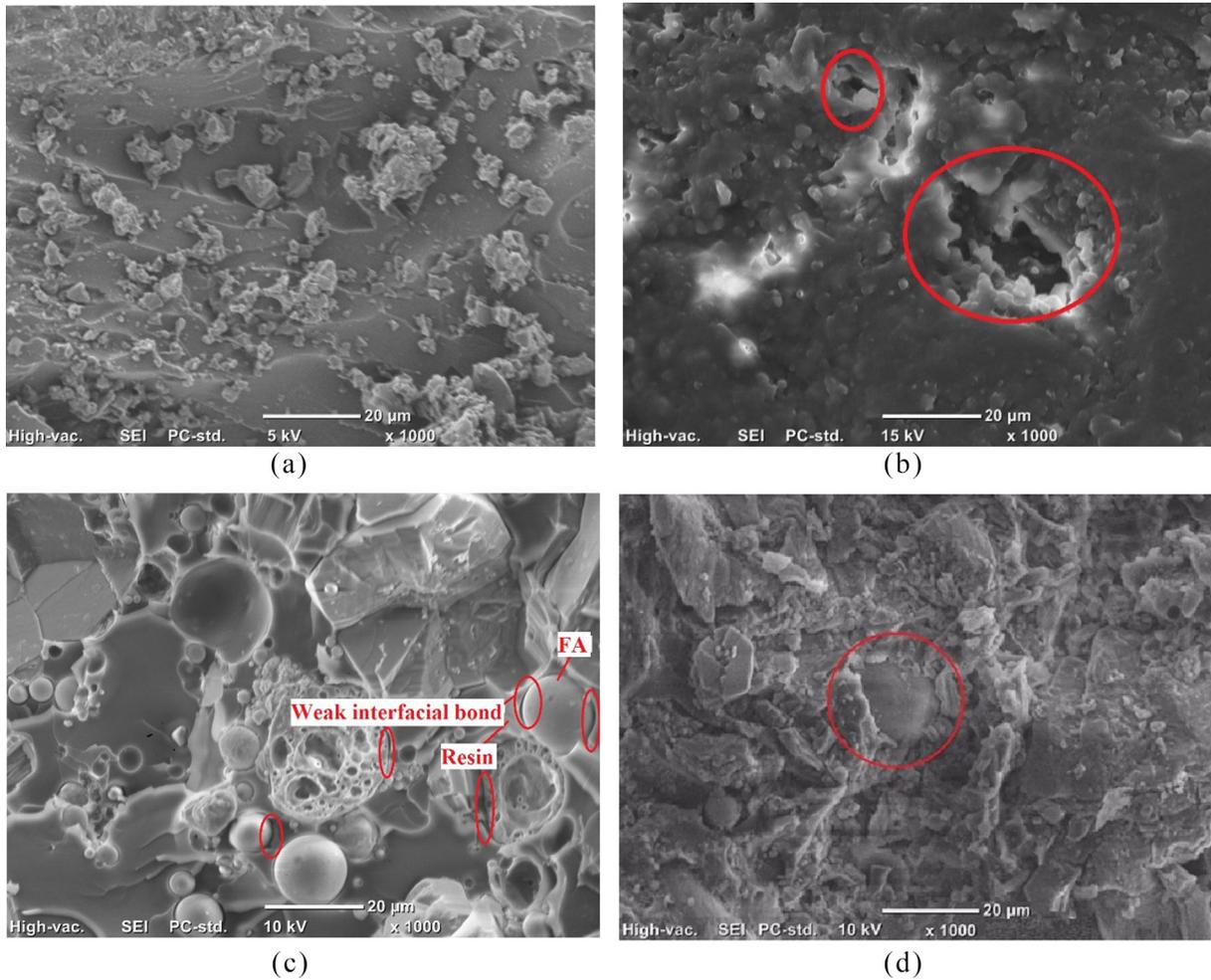


Fig. 12. SEM micrographs of particulate filled epoxy resins a) unconditioned F0, b) 3000 h Conditioned F0 at 60 °C, c) unconditioned F40, d) 3000 h Conditioned F40 at 60 °C.

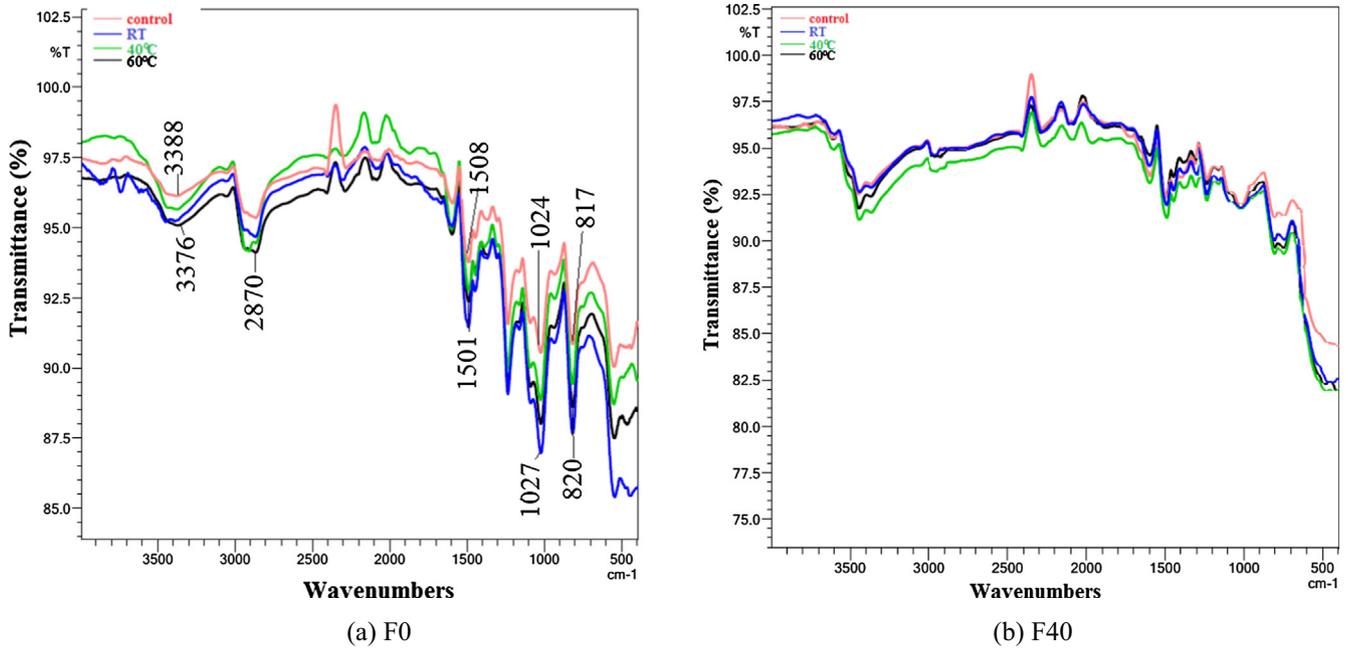


Fig. 13. FTIR spectra of conditioned and unconditioned samples at RT, 40 °C and 60 °C a) F0 and b) F40.

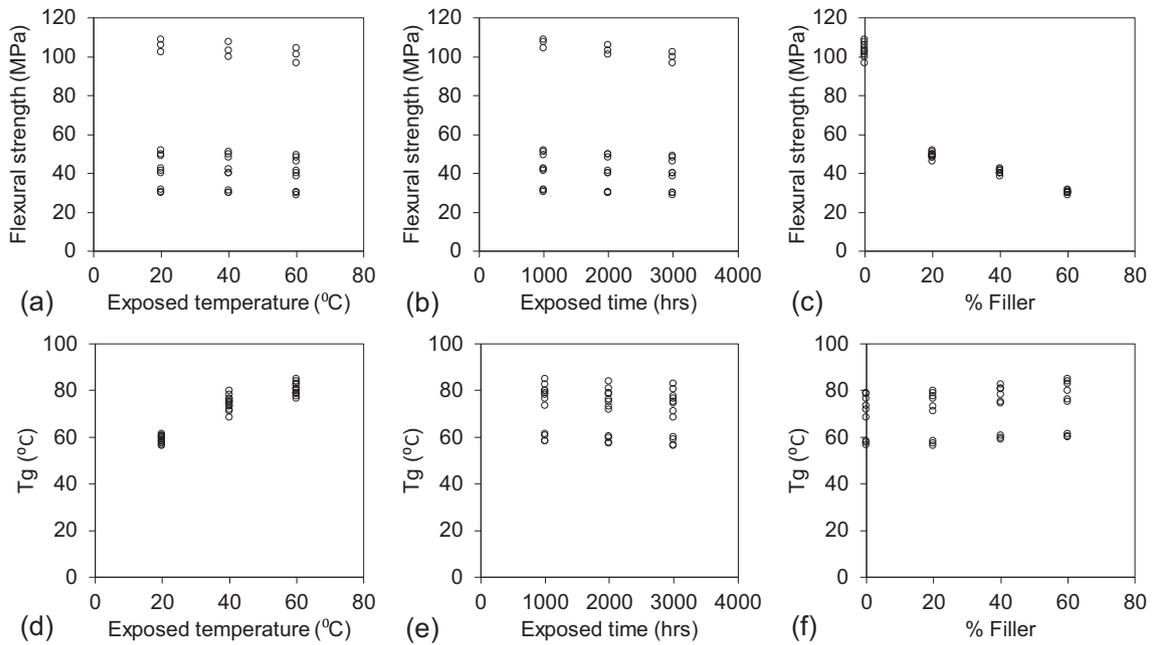


Fig. 14. Correlation graphs with data points used in SPSS.

Table 4
Two-way ANOVA using SPSS.

Dependant variable	Independent variable	F-value	p-value	Partial eta squared
Flexural strength	Filler content	5920.9	0.000	0.998
	Exposure duration	22.9	0.000	0.621
	Curing temperature	11.3	0.000	0.447
Glass transition temperature	Filler content	48.8	0.000	0.839
	Exposure duration	25.3	0.000	0.644
	Curing temperature	1611.6	0.000	0.991

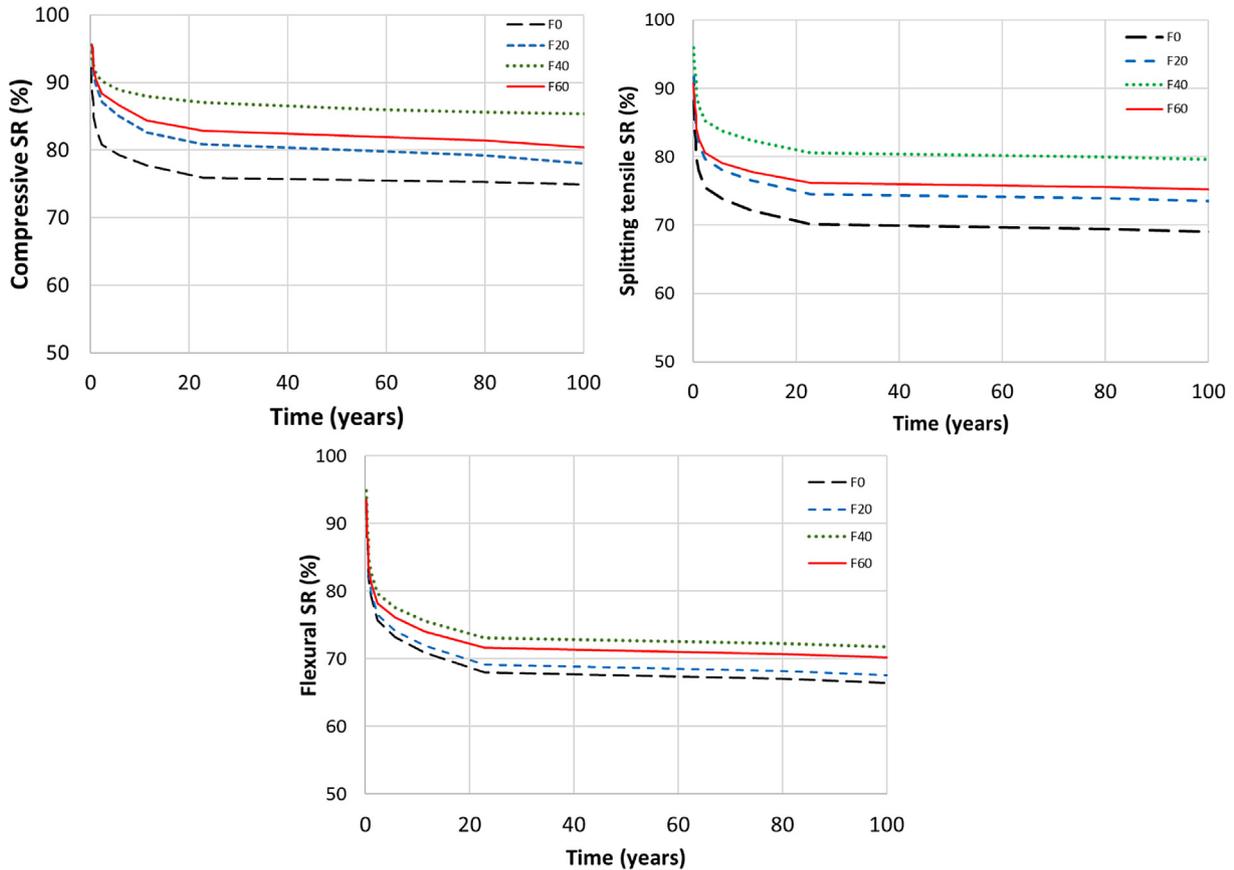


Fig. 15. Service life of particulate filled epoxy resin at 30 °C a) Compressive strength, b) Splitting tensile strength, c) Flexural strength.

and glass transition temperature) were different as reflected by partial eta squared values. The higher the value of partial eta squared, the greater the influence of the parameter. This concludes that the addition of fillers in polymer matrix has the highest influence on flexural strength followed by exposure duration and curing temperature. On the other hand, the greatest effect on glass transition temperature is coming from curing temperature followed by filler content and exposure duration.

6. Prediction of long-term strength properties

Engineers design civil structures with service lives of 75–150 years, thereby require information on the long-term performance of the new polymer matrices. Aiello et al. [57] indicated that a reliable prediction of a long-term behaviour of new materials are determined from accelerating ageing through hygrothermal exposure and the Arrhenius method can be used to predict the long-term performance of materials. A number of study [58,59] has used the Arrhenius relation to predict the service life and correlate with the real world situation through data obtained from the accelerated aging tests in the laboratory. This approach was used in this study to predict the mechanical strength of four different aged mixes under the combined moisture and temperature. The procedure provides a predicted service life for the epoxy matrix at a desired level of strength retention. Three levels of elevated temperatures were applied to perform an accurate predication based on Arrhenius laws shown in equation (2):

$$K = A \exp(-E_a/RT) \quad (3)$$

where K is the degradation rate ($1/\text{time}$), A is the constant relative to degradation process and material, E_a is the energy of activation of

the reaction, R is the universal gas constant and T is temperature in kelvin. Eq. (2) can be transformed into:

$$1/k = 1/A \exp(E_a/RT) \quad (4)$$

$$\ln(1/k) = E_a/RT - \ln(A) \quad (5)$$

From Eq. (4), the degradation rate, k is expressed as the inverse of time, which is needed for a material property to reach a given strength. The logarithm of K is a linear function of $1/T$ with the slope of E_a/R as shown in Eq. (4).

The Arrhenius method is characterized by activation energy, which causes a long-term chemical degradation in epoxy materials [60]. According to the Arrhenius law, the change in mechanical properties is measured as a function of conditioning time and elevated temperatures is used as accelerating factors of the degradation of epoxy. From the averages of mechanical results, the property retention (PR) values at different exposure time (t) were divided by the average property value for the control specimen ($t = 0$). These data were used to get the activation energy using linear regression with a line fitted through each set of data (one for each temperature of conditioning: (23, 40 and 60 °C) through a graph where the property retention value was on the vertical axis using a linear scale and time was on the horizontal axis using a logarithmic scale as a function of the reciprocal of the absolute temperature (1000 K^{-1}). The time to reach various levels of property retention at different aging temperatures was then calculated. These times were determined by substituting different values of mechanical strength retention (95%, 90%, 85% and 80%) into the regression equations. Finally, service life times were substituted into the regression equations (plot of the mechanical strength retentions as a function of time) to find the mechanical strength

retention at a various times at each of the aging temperatures. Graphically, these were represented up to 100 years, and horizontal lines from the intersection between these lines and the regression lines for the different temperatures. For each chosen lifetime, the mechanical strength retention in percentage was plotted as a function of the inverse temperature (1000 K^{-1}). Fig. 15 presents the equivalent service life of F0, F20, F40 and F60 at an annual temperature of 30 °C. A temperature of 30 °C was considered, as this is the average annual temperature in Australia. It was interesting that the mixes containing fillers had higher strength retention in their service life, as in F0 the matrix degradation due to the combination effect of moisture uptake and elevated temperature could lead to further reduction of its mechanical properties. This was also supported in the physical properties section where inclusion of fillers led to less moisture uptake after hygrothermal conditioning. As a summary, F40 can retain 85% of its compression (Fig. 15a), 81% of split tensile (Fig. 15b) and 70% of flexural strength (Fig. 15c) when exposed to humidity of 98% after 100 years of service. When the samples were tested under compression, the degraded surface did not significantly affect the failure, as it was initiated from the centre of the samples. However, samples tested under splitting tensile experienced failure initiation from the degraded surface followed by the failure in the centre of samples. The less retention of flexural strength can be related to degradation on the surface of the particulate filled epoxy polymers. These were very critical for the specimens subjected to the flexural test as this location is subjected to higher levels of flexural stress. Benmokrane et al., [61] in their study on the durability of glass-fiber-reinforced-polymer (GFRP) bars conditioned in alkaline solution for three months at 60 °C revealed that the decrease in the flexural properties of the bars can be explained by the high probability of defects on the edges.

7. Conclusion

In this study, the physical, thermo-mechanical, and microstructural properties of epoxy-based polymers with different percentages of particulate fillers composed of fly-ash and fire retardant fillers were evaluated in a hygrothermal environment. From the results, the following conclusions are drawn:

- The density of particulate-filled epoxy-based polymer resin increased with increasing amount of fillers. However, a higher discrepancy between the actual and calculated densities was noted for mixes with a higher amount of fillers than those with a lower amount of fillers due to an increase in the amount and size of pores in these samples. The addition of particulate fillers reduced the water uptake of epoxy resin at high temperatures due to the higher crosslinking density.
- Hygrothermal conditioning promoted the post-curing and increased the T_g of the particulate filled epoxy-based polymers. At least a 5 °C increase in T_g was measured with the introduction of 60% fly-ash and fire retardant fillers.
- Hygrothermal conditioning changed the failure behaviour of particulate filled epoxy resin from brittle to semi-ductile in both compression and splitting tensile. Moreover, less than 10% reduction in compressive and tensile strength was observed due to the post-curing of the resin at the initial stage of the hygrothermal conditioning.
- The flexural strength of highly filled epoxy resin mixes was significantly improved at the early stage of hygrothermal conditioning and increased the flexibility of the polymers. This is due to the better interlocking between resin and fillers that resulted in almost 70% strength retention after hygrothermal conditioning.
- SEM images showed that the exposure of particulate filled epoxy polymer to the hygrothermal environment improved the interlocking between the fillers and resin and increased the density of the section mode.
- FTIR analysis showed C–H and C–O in major phases for all specimens and with restrictive stretching with the addition of filler indicating that the hygrothermal conditioning did not change the chemical composition of particulate filled epoxy.
- Based on the Arrhenius model, the particulate filled epoxy polymers are expected to retain more than 70% of their mechanical properties after 100 years of service at an annual average temperature of 30 °C. This demonstrates that the particulate filled resin is a suitable coating material for civil infrastructure to protect it from the adverse effects of moisture and elevated temperature.

Continued efforts should be conducted towards understanding of these new materials on their behaviour when exposed to the synergistic effect of temperature and moisture and also the photochemical reactions from solar ultraviolet (UV).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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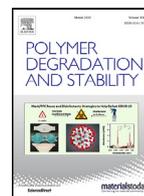
Chapter 5

Article III: Effects of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating

Chapters 3 and 4 identified the effect of elevated in-service temperature and hygrothermal conditioning on the properties of particulate-filled epoxy resin, respectively where it was demonstrated that the particulate filled resin was a suitable coating material for civil infrastructure. *Article III* investigated the effect of the photochemical reactions from solar ultraviolet (UV) on the durability of particulate-filled epoxy resin coating. Epoxy-based resin system containing up to 60% by volume of fire retardant and fly-ash fillers was exposed to 1000 and 2000 h of UV radiation and at a temperature of 60°C. The physical, mechanical, thermo-mechanical and microstructural properties of these coating materials were then evaluated. The effect of UV radiation was simulated by a Xenon arc lamp at a temperature of 60°C for 2000 h, which appeared to produce an output that could easily equate to approximately 5 years of UV exposure in the field. From the results of the experimental studies, no reduction in the flexural strength was observed for polymer coating containing at least 40% fillers. A thickness of at least 11 mm of epoxy-based coating with 60% by volume of particulate fillers can provide UV protection for 100 years. This thickness is only 20% of the required thickness if neat epoxy resin is used as a coating material. This significant reduction of required thickness for filled coating system is due to the particulate fillers blocking the penetration of UV radiation and reducing the surface degradation of the polymer coating.

In actual environment, moisture, elevated temperature and solar UV radiation are acting at the same time and affecting the properties of epoxy-based polymer coatings.

Chapter 6 investigated the synergistic effect of temperature, moisture and UV on their physical and mechanical behaviour.



Effects of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating

Mojdeh Mehrinejad Khotbehsara^a, Allan Manalo^{a,*}, Thiru Aravinthan^a, Joanna Turner^b, Wahid Ferdous^a, Gangarao Hota^c

^a Centre for Future Materials (CFM), School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia

^b Faculty of Health, Engineering and Sciences, University of Southern Queensland, Toowoomba, QLD 4350, Australia

^c Department of Civil and Environmental Engineering, West Virginia University, Morgantown, WV 26506, United States

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ABSTRACT

Exposure to solar ultraviolet (UV) radiation causes photochemical damage near the exposed surface, which results in the degradation of composite reinforcing elements. To minimise the UV degradation, epoxy polymers are being applied as protective coatings to composite materials to retain properties during their design service life. In this study, the effects of UV exposure on the physical, mechanical, and thermo-mechanical properties, including the microstructure particulate-filled epoxy-based polymer coating, were investigated. The polymer coating contains up to 60% by volume of hydrated alumina powder fire retardant (FR) and fillers such as an industrial waste like fly ash (FA) and is exposed to simulated UV conditions either 1000 h or 2000 h. Physical observations showed yellowing at the surface of neat epoxy coating after UV exposure but the presence of particulate FR and FA fillers minimised fading and weight loss. Similarly, no reduction in the flexural strength was observed for polymer coating containing at least 40% fillers, indicating that the FR and FA retained the structural performance of the coating. SEM observation revealed formation of microcracks in the surface of the neat epoxy resin but a dense microstructure in particulate filled epoxy resin after exposure to UV radiation. FTIR analyses indicated that photo-degradation due to UV radiation was limited only on the thin surface of the coating. From the results of this study, a coating thickness of at least 11 mm is required for epoxy based polymer coating with 60% by volume fillers, which is 5 times thinner than neat epoxy resin, to provide 100 years of UV resistance.

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1. Introduction

Composite materials and structures are now extensively utilised in civil engineering and construction where they are exposed to solar ultraviolet (UV) radiation. Exposure to UV radiation causes photochemical damage near the exposed surface, which results in the degradation of composites [1]. To minimise or prevent this effect, epoxy polymers are being applied as protective coatings to composite materials [2,3]. Despite several excellent properties of epoxy resins including high failure strength and strain, good chemical resistance, low shrinkage, and being curable at low temperatures, this type of resin system is susceptible to UV damage [4]. Ghasemi-Kahrizangi et al., [5] and Yousif and Haddad [6] highlighted the harmful effects on the physical, mechanical and chemical properties of epoxy polymers of photo-degradation caused by UV exposure. This is due to the energy of solar UV light

being higher than the chemical bond strength e.g., C–C, O–O, H–O, and C–N in polymers [4]. Moreover, exposure to UV reduces the molecular weight and makes the polymer more brittle, which can lead to an overall reduction in the physical and mechanical properties [7]. Thus, an investigation into the effect of solar UV radiation into polymeric composite materials is critical.

A number of studies have been implemented to determine the effect of UV solar radiation on the short and long-term properties of polymeric composites by exposing the materials in a simulated UV solar light [8–13]. Rosu et al. [14] investigated the effect of UV on semi-interpenetrating polymer networks based on epoxy resin and polyurethane. The presence of the processes of photodegradation and photo-oxidation resulting in colour changes and mass losses was identified in all samples. Chin et al. [15] investigated the effects of UV radiation on thin polymer films made of vinyl ester and isopolyester by exposing them to a 1000-watt xenon arc source in an Oriel solar simulator. They observed surface erosion and cracking in both samples after 1200 hrs at 30 °C. In another study, Shahzad., [16] found that hemp fibre reinforced unsaturated polyester composites lost weight and reduced their tensile proper-

* Corresponding author.

E-mail address: manalo@usq.edu.au (A. Manalo).

ties after UV exposure for 1000 h. In the study by Lu et al., [17] it was found that UV degradation of polymeric surfaces was strongly dependant on UV wavelength, intensity and exposure time. The effect of different UV exposure times (500, 1000 and 1500 hrs) on bidirectional woven flax fabric/epoxy composites was studied by Yan et al., [18]. They found a change in colour of the samples immediately after 500 hrs of exposure. Moreover, up to 10% and 29% reduction in tensile and flexural properties, respectively was observed after 1500 hrs of UV exposure due to the degradation of the flax fibres and the fibre/matrix interfacial bonding. These studies showed the damaging effects of solar UV radiation on polymeric composites.

A small number of researchers have introduced different particulate-type fillers to enhance the UV resistance of polymeric materials. Tcherbi-Narteh et al. [19] incorporated 1% by weight of nanoparticles into DGEBA epoxy resin and found that nanoparticles delayed the onset of deleterious UV effects. Moreover, the addition of nanoparticles resulted in partial curing of the epoxy after 2500 hrs of UV radiation exposure. Peng et al. [20] studied the accelerated weathering caused by UV solar radiation on polypropylene composites reinforced with lignin, cellulose, and wood flour at different loading levels. These researchers observed large cracks and delamination on the polypropylene layer after 960 hrs of UV exposure. However, the composites containing lignin showed lesser modulus and flexural strength loss and narrower cracks than the other samples due to its hydrophobic surface. In a recent study, Ferdous et al. [21] evaluated the role of particulate fillers on the physical and flexural strength of polymeric matrix exposed to simulated UV solar radiation. After 2000 hrs exposure, they found embrittlement, discolouration and reduction in weight in all the specimens. However, lesser weight loss (0.15%) was measured for specimens with the highest amount of fillers (60%) than was observed for the neat epoxy resin (0.37%). Furthermore, the epoxy resin with fillers retained most of its flexural strength. However, the mechanisms of the way particulate fillers helped in preserving the structural performance of polymeric matrices are not explained in detail. Thus, a more detailed investigation is needed to gain a better understanding on how the properties of epoxy resin filled with particulates is affected by UV solar radiation in order to further advance the safe use and adoption of this material in various engineering applications. This is particularly important in countries with an extreme UV index such as Australia, where the peak daily values are usually in excess of 12–14 in summer, and they can reach 16–17 at northern latitudes.

In this research, experimental investigations have been carried out to determine the effect of UV solar radiation on the durability and long-term performance of particulate-filled epoxy based resin containing fire retardant (FR) and fly ash (FA) fillers. This research will explore important aspects related to the effects of UV solar radiation on physical, mechanical, and physico-chemical properties and the microstructure of epoxy-based polymer coating. These results will contribute to the scientific knowledge in the field and the development of durable cost-effective coating material through an evaluation of their degradation mechanism and a comprehensive understanding of their behaviour. Moreover, conversion of UV exposed time to equivalent sunlight time is calculated to provide practical information on the time during which the UV affects the materials' properties and to determine the coating thickness of particulate-filled epoxy based polymer for 100-year UV exposure.

2. Materials and methods

2.1. Materials

Epoxy resin system made from Bisphenol A diglycidyl ether (DGEBA) type epoxy resin as Part-A and an amine-based curing

Table 1
Mix design of particulate-filled epoxy resins.

Resin/Filler (by volume)	F0	F20	F40	F60
Part A (g)	1000	737	552	368
Part B (g)	320	236	177	118
FR (g)	0	397	794	1192
FA (g)	0	119	239	358

agent as Part-B was used in this study. 100 g of Part-A with a density of 1.064 g/cm³ were mixed with 32 g of Part-B with a density of 1.182 g/cm³. Hydrated alumina powder as FR with a density of 2.411 g/cm³ and FA with a density 2.006 g/cm³, which were investigated previously by Ferdous et al. [21] and Khotbehsara et al., [22] were mixed together in approximate percentages as particulate fillers. FA was used due to its performance in decreasing the permeability of aggressive chemicals and water while FR was chosen due to its low abrasiveness, smoke suppression, acid resistance, chemical inertness, electric arc resistance, fire resistance and non-toxic behaviours. These fillers were round in shape with the diameter of 75 to 95 μ m for FR, and 0.1 to 30 μ m for FA. Filler amounts of up to 60% of the volume of the matrix were added in 20% increments, as more than 60% filler in the mix was unworkable [21]. In addition, neat epoxy resin mix was prepared as the control sample. The mixes were denoted according to their volumes of filler, e.g., F20 indicates a mix containing 20% filler and 80% resin, as given in Table 1.

2.2. Sample preparation

Non-stick sheets were used for casting the rectangular specimens suitable for measuring the glass transition temperature (T_g) and flexural tests of the particulate-filled epoxy based polymer coating. On the other hand, bottom-sealed cylindrical polyvinyl chloride (PVC) pipes were used in preparing specimens for measuring the density and porosity. The specimens were kept in moulds for 48 h at room temperature. They were then demoulded and cured for another 7 days at room temperature.

2.3. Simulated uv exposure

UV solar radiation was simulated using the Xenon 2200 watt air cooled lamp in the Sunset XLS UV chamber. A Xenon arc lamp was used as this is the most popular artificial light source for photo-degrading materials that can emit a similar type of harmful radiation caused by solar UV radiation [4]. The specimens were then subjected to 1000 h and 2000 h of UV radiation in an ambient atmosphere, temperature of 60 °C, simulating extreme summer conditions in Australia [23]. After 1000 hrs and 2000 hrs of UV exposure, the specimens were taken out from the chamber, weighed, examined under the microscope, mechanically and thermo-mechanically tested. Table 2 summarises the test methods as well as the number of samples for each type of test, and also the ASTM tests adopted to conduct this research.

3. Test procedure

3.1. Physical properties

The discolouration of the particulate-filled epoxy based polymer coating was noted and weight loss was measured after exposure to 1000 hrs and 200 hrs of UV radiation. Visual observations together with the use of an optimal microscope (OLYMPUS XC10) were implemented to appraise the discolouration of all the specimens (magnified by 100 times). On the other hand, an electronic balance (MonoBloc-AB204-S) with sensitivity of 0.0001 g was used

Table 2
Summary of number of specimens and the test methods.

Properties	Test Method	Number of specimens			
		F0	F20	F40	F60
<i>Physical properties</i>					
Discolouration		6	6	6	6
Weight loss		9	9	9	9
<i>Thermo-mechanical properties</i>					
Dynamic Mechanical Analysis (DMA)	ASTM D7028 [24]	6	6	6	6
Differential scanning calorimetry (DSC)	ASTM D3418 [25]	4	4	4	4
<i>Mechanical properties</i>					
Flexural strength	ASTM C580 [26]	9	9	9	9
<i>Microstructure</i>					
Scanning Electron Microscopy (SEM)		3	3	3	3
Micro-focused Fourier Transform Infrared Spectroscopy (FTIR)		3	3	3	3

to measure the weight loss immediately after the samples were taken out from environmental UV chamber.

The changes in colour of epoxy samples due to the UV exposure were evaluated. The gloss, colour attributes (L^* , a^* , b^*) and total colour difference (ΔE^*) were measured using a D65/2°-Erichsen model 565/45 spectrometer by CIE 1976 formula (Eq. (1)) as follows [27]:

$$\Delta E^* = \left((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{0.5} \quad (1)$$

where L^* is lightness, a^* and b^* are red–green and yellow–blue colour coordinates, respectively and ΔE represent the difference in corresponding parameters before and after UV exposure.

3.2. Mechanical properties

The 3-point static bending test was conducted using rectangular samples with dimensions of 60 mm length \times 10 mm width \times 5 mm depth following ASTM D580 [26] using a universal testing machine (ALLiance RT/10) with a capacity of 10 kN and a loading rate of 2 mm/min.

3.3. Thermo-mechanical properties

T_g of the samples before and after UV exposure was measured from the dynamic mechanical analyser (DMA), which was conducted in accordance with ASTM D7028 [24]. The samples were clamped in a dual-cantilever system, where the DMA multi-frequency strain was applied as the test mode using A Q800 type TA instrument. The temperature scans with increments of 5 °C were set between 30 °C and 120 °C. At least two samples with dimensions of 60 mm \times 10 mm \times 5 mm were tested for each mix (2 for Control-2 for 1000 hrs UV exposed and 2 for 2000 hrs UV exposed). The temperature corresponding to the storage modulus curve peak was used as the value of T_g . The T_g on the surface and inside the various mixes was also assessed with differential scanning calorimetry (DSC) in accordance with ASTM D3418 [25] to determine if there was a difference in the glass transition temperature in the exposed surface and inside the specimens after UV exposure.

4. Result and discussion

4.1. Effect of uv exposure on physical properties

Fig. 1 shows the surface discolouration after exposure to 1000 h and 2000 h of UV solar radiation, where samples tend to be yellowish. The discolouration is due to interaction between the photons from UV radiation and epoxy molecules on the exposed surface causing photo-oxidative reactions [28]. While the changes in colour were significant in resin-rich samples (F0 and F20), fading

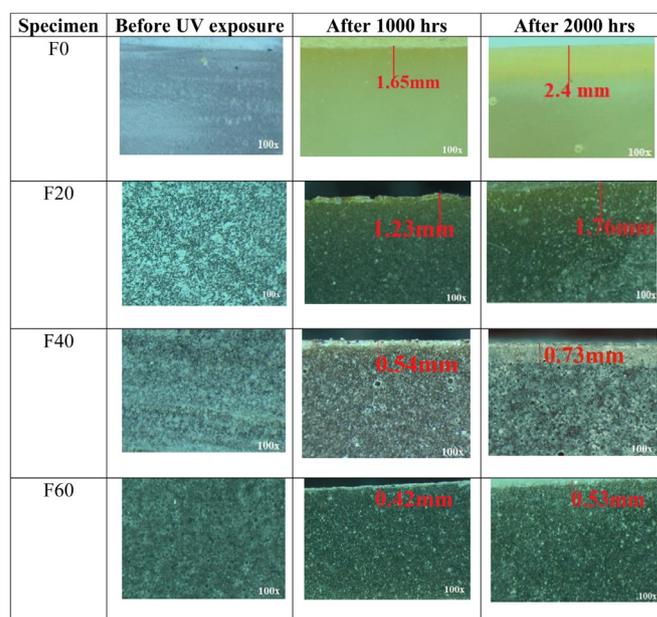


Fig. 1. Discolouration and affected depth in mm after 1000 and 2000 hrs of UV exposure.

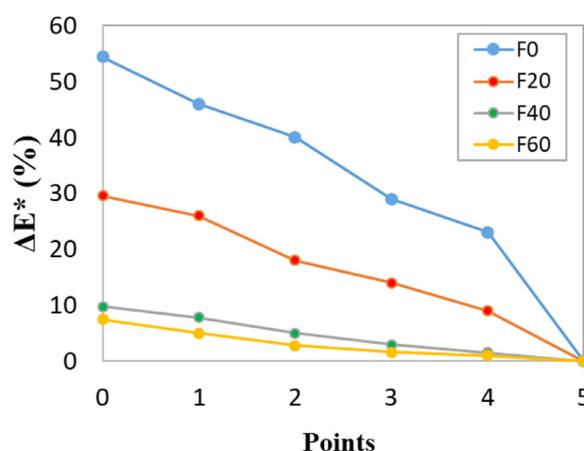


Fig. 2. Variation of ΔE^* for particulate filled epoxy polymers exposed to 2000 hrs UV exposure in different points.

was barely noticeable for F40 and F60 (Fig. 2). This was due to the decrease in the transparency of the epoxy resin due to the greyish colour of FA. This dark colour of the fillers blocked the UV rays from penetrating the samples. However, minor changes in surface roughness of all UV exposed specimens were visible to the naked

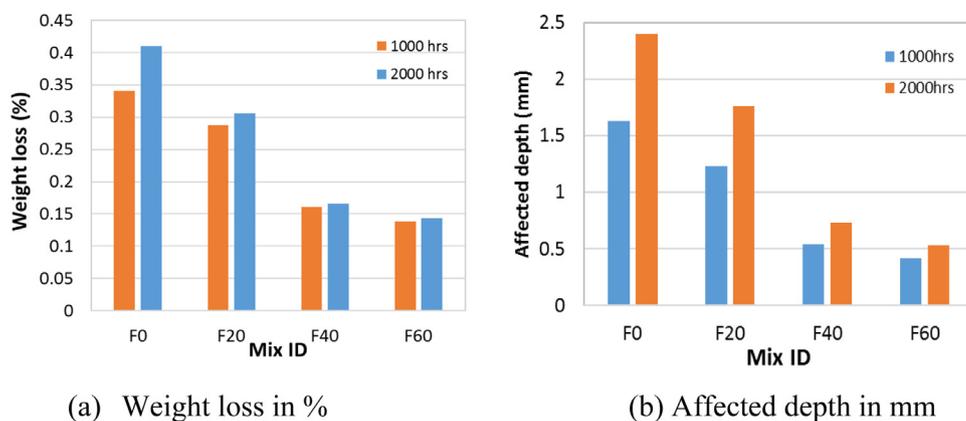


Fig. 3. Weight loss and affected depth of particulate filled epoxy after UV exposure.

eye. The Gwyddion program using the microscopic images showed that roughness in the surface of F0 increased from 6.81 μm to 8.21 μm and 8.57 μm after 1000 and 2000 hrs of UV exposure, respectively. This increase in surface roughness for F40 was from 19.62 μm to 21.59 μm and 21.94 μm . The increased roughness during irradiation could be due to chalking caused by the accumulation of photo degradation products on the UV exposed surfaces.

The colour change on the affected depth was described by CIELAB colour coordinate system, which is a similar method implemented by Navarro et al. [29] and Ghasemi-Kahrizsangi et al. [5]. The CIELAB colour space is based on the concept that colours can be considered as combinations of red and yellow, red and blue, green and yellow, and green and blue. To determine the exact combination of colours of a sample, coordinates of a three dimensional colour space were assigned including L^* , a^* and b^* coordinates. Fig. 2 shows the variations of colour difference values (ΔE^*) in 5 equal sections of the affected depth for different mixes after 2000 h of UV exposure with taking point 0 as the surface of exposed samples and point 5 as the start of the unaffected depth. After UV exposure, the colour of neat resin (F0) became yellow and then brown showing degradation of neat epoxy resin. This change in colour resulted in ΔE^* of around 50% at the exposed surface compared to the unaffected depth, the colour of the latter is similar to that of unconditioned specimens. Moreover, it was observed that ΔE^* reduced significantly with increasing percentages of fillers, which clearly shows that the fillers minimised the colour difference of the polymer samples exposed to UV. For instance, the colour changes of F40 and F60 samples are approximately 10% along its affected depth but is more than 30% for F20 at the exposed surface. The lower values of ΔE^* in polymer coating containing fillers also shows that the incorporation of fillers could minimise the discolouration of epoxy polymer coating caused by solar UV radiation. The lower colour differences of particulate filled samples than neat resin can be related to black pigments provided by the fly ash which makes the polymer coating less transparent. The beneficial effects of fillers with the dark grey colour arise from their UV stability characteristics, which also signify the importance of uniform dispersion of fillers in the matrix that can promote the UV resistance properties [5].

Fig. 3a shows the weight loss of specimens after UV exposure for 1000 hrs and 2000 hrs. A decreasing trend in weight loss could be observed in the polymer mixes with the increase in the amount of fillers. Moreover, the percentage weight loss was higher for the resin-rich mixes (F0 and F20) than F40 and F60. This lower weight loss for F40 and F60 mixes can be explained by the affected depth of only around 0.5 mm after 1000 hrs and 2000 hrs exposure while for F0 and F20 it was up to 2.5 mm, which is almost 50% (2.5 mm) of the total thickness of the samples. The extent of depth affected

by the UV exposure was measured by microscopic observations and the averaged affected depth of different mixes are given in Fig. 3b. It is expected that the expulsion of residual moisture and volatiles in the epoxy resin occurred only at this affected depth (Fig. 1 and Fig. 3b). This percentage weight loss for particulate filled resin is comparable with the measured weight loss for carbon fibre reinforced epoxy composites of 0.27% after 500 hrs of UV exposure as measured by Kumar et al., [28], which is attributed to the expulsion of volatiles and residual moisture. This shows that the addition of fillers in the epoxy polymer matrix can increase the UV resistance as the fillers block the penetration of UV radiation and only the thin resin surface is affected. Most of the weight loss occurred in the first 1000 hrs, with a slight increase after 2000 hrs. This can be related to the affected depth in Fig. 3b, where 65–80% of the affected depth occurred in the first 1000 h of UV exposure and increased slightly after that. This phenomenon can be considered as being due to the degraded surface of the specimen acting as a protective coating which impedes the penetration of UV radiation.

4.2. Effect of uv exposure on thermo-mechanical properties

Table 3 summarises the average thermo-mechanical and mechanical properties of particulate filled epoxy resin before and after 1000 hrs and 2000 hrs of UV exposure. Results suggest an increase in the properties of the UV exposed specimens containing fillers compared to the unconditioned specimens, possibly due to post-curing resulting in an increase of cross-linking density [30]. Thermosets undergo changes in different properties following post-crosslinking resulting in increase in the T_g , which explain the improvement of mechanical properties of the mixes containing fillers as they experienced higher crosslinking density, as will be presented in the next section.

The T_g of the particulate filled epoxy resins before and after UV exposure reported in Table 3 was measured using DMA and DSC. This table enables a comparison between post cured samples as well as a comparison between different ageing conditions for each mix. It was measured that the T_g obtained from storage modulus of the unconditioned polymer matrices is around 60 $^{\circ}\text{C}$ with almost 3 to 5 $^{\circ}\text{C}$ difference between F0 and F60. The table also indicated that UV exposure for up to 2000 hrs significantly increased the T_g to between 82 $^{\circ}\text{C}$ and 87 $^{\circ}\text{C}$. This result can be due to the higher temperature during the simulated UV exposure which enhanced the curing reaction of the epoxy polymers leading to post-crosslinking of the network structure of the epoxy, as was also observed by [31]. This result is supported by the considerable increase in T_g of specimens post-cured for 24 h at 60 $^{\circ}\text{C}$ wherein the T_g increased from 56 $^{\circ}\text{C}$ to 81 $^{\circ}\text{C}$ for mix F0 and from 61 $^{\circ}\text{C}$ to 84 $^{\circ}\text{C}$ for mix F60. This result further indicates that epoxy resin

Table 3
Mechanical and thermo-mechanical properties of particulate-filled epoxy polymer matrices.

Specimen	Unconditioned		Exposed to UV			
	Control	Post-cured	1000hrs		2000 hrs	
Glass transition temperature (T_g) (°C)			Inside	Surface	Inside	Surface
F0	58.2	81.3	84.8	72.1	82.6	68.9
F20	59.6	82.4	85.9	72.8	85.4	70.8
F40	60.2	84.5	86.2	73.9	86.5	73.1
F60	61.6	85.1	86.9	74.4	87.7	74.2
Flexural strength (MPa)						
F0	97.8	103.6	69.4		59.4	
F20	48.8	52.5	34.5		32.8	
F40	26.8	42.7	45.8		47.2	
F60	13.2	33.4	39.4		41.1	

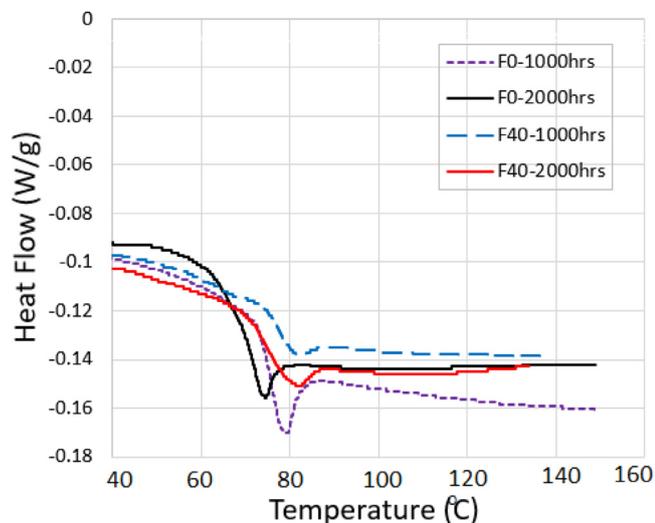


Fig. 4. DSC scans on the surface of F0 and F40 after 1000 and 2000 hrs UV exposure.

with particulate fillers can retain most of its storage modulus after UV exposure. The storage modulus can be an indication of the polymer's ability to store deformation energy which can be related to the degree of cross-linking of the polymers. In crosslinking reactions of hardener and DGEBA, the C–O bond within the epoxide group is broken and the carbon end of the opened epoxy group reacts with the nitrogen from the amine group in the curing agent molecule [32]. UV radiation exposure can create a condition for much needed post curing of the epoxy molecules [5,28]. However, the DSC results of the exposed surface shows a lower T_g when compared to the inner portion. The lowest T_g at the exposed surface of UV exposed samples was measured at mix F0 where a T_g of only 72 °C was measured while the inner surface of the specimen had a T_g of 85 °C. Moreover, increasing the UV exposure from 1000 hrs to 2000 h resulted in a further decrease in the T_g of the surface as shown in Fig. 4. This deleterious effect is more in resin rich samples (F0 and F20) where up to 16 °C lower T_g was measured compared to the inner part of the specimens. In contrast, the difference in the measured T_g at the exposed surface and inner portion of F40 and F60 after 2000 h is 13 °C. This result further showed that the particulate fillers can assist in reducing the surface degradation of epoxy polymers as they help in blocking the penetration of UV radiation.

4.3. Effect of uv exposure on flexural strength

The flexural characteristics of the particulate filled epoxy resins were determined by placing the specimens with the UV exposed

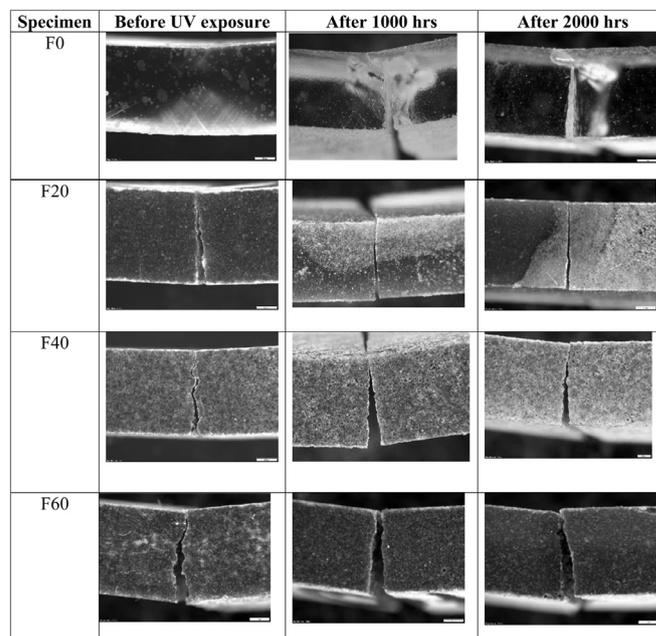


Fig. 5. Failures observed after flexural test in different mixes.

surface at the top during testing. The results showed that the control neat resin specimens (F0) deformed significantly under flexural load and with only microcracks observed at the bottom at midspan (Fig. 5a). Unconditioned F0 samples showed a non-linear stress-strain graph indicating the flexibility of the epoxy resins. While, the F0 specimens exposed to UV for 1000 h and 2000 h failed because of a flexural crack at mid-span and the behaviour changed from restively ductile to brittle. On the other hand, specimens F20, F40 and F60 failed because of a large vertical flexural crack at the mid-span of the samples (Figs. 5b, 5c and 5d, respectively) both for unconditioned and UV-exposed specimens. The brittle failure mode can be attributed to the micro-cracks in the surface of the specimens caused by the photo-oxidation during UV exposure. It is interesting that the flexural strength of filler dominant mixes was significantly improved when post-cured at various temperatures for 24 hrs (Table 3). Post curing in UV-exposed specimens also increased the flexural strength of resin dominant samples from almost 27 MPa with a 75% increase to approximately 47 MPa for F40 (Fig. 6). Moreover, as shown in Fig. 6, flexural strength of F60 could significantly increase to more than three times after exposure to UV, while for F0 the strength reduced by almost 29% and 55% after 1000 and 2000 h UV exposure, respectively. The significant reduction in flexural strength for specimen F0 can be related to the highest level of surface degradation, which is critical for materials

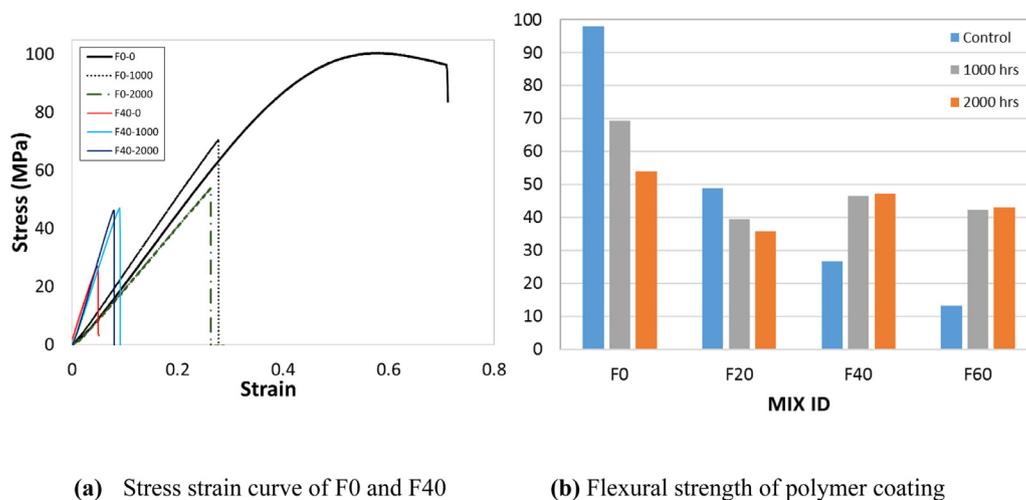


Fig. 6. Flexural behaviour of polymer coatings before and after UV exposure.

subject to the flexural test as the topmost and bottommost layers are subjected to the highest levels of flexural stress. On the other hand, the degraded surface of the specimens with a high amount of fillers acts as a protective coating impeding the penetration of UV radiation and resulting in retaining the flexural strength when the UV exposure time increased from 1000 h to 2000 h. This is supported by the results of weight loss and depth of UV affected in Fig. 2, where the affected depth was reduced by increase in the percentages of fillers and was less affected by an increase of exposure time in filler dominant mixes.

4.4. Scanning electron microscope (SEM) and fourier-transform infrared spectroscopy (FTIR) observations

The microstructure of the particulate filled epoxy resin before and after UV exposure was observed under the SEM using SEM, JEOL JXA 840A. Small samples (dimensions <1 cm) were taken from the UV exposed surface of specimens, and were prepared and coated with gold using a sputter deposition machine. FTIR was also performed to determine the functional groups of the epoxy polymers before and after UV exposure. FTIR spectra was recorded on a Nicolet 6700 FTIR spectrophotometer with KBr pellets. Then, spectra in the optical range of 400–4000 cm^{-1} was achieved by averaging 16 scans at a resolution of 4 cm^{-1} .

4.4.1. SEM

The SEM revealed that the microstructure of F0 and F40 (as an example of filler included specimens) has a direct correlation on the physical, mechanical and thermo-mechanical properties of particulate-filled epoxy polymers exposed to UV solar radiation. As it can be seen in Figs. 7a and d, there are noticeable differences in the form and texture of the control samples with fillers compared to the neat epoxy. Dense microstructures with smaller pore sizes can be observed in F0 while the specimen F40 showed larger pores and weak interfacial bond between the resin and different fillers through the matrix due to the creation of voids and pores in the matrix shown by circles (Fig. 7). Khotbehsara et al. [2] found that the presence of fillers can result in homogeneous distribution and weakened the interaction between the filler and the matrix. This has caused defects to the matrix in the form of a void between the particles and has led to undesirable material properties. Furthermore, the surface in the SEM image of the 1000 and 2000 h UV exposed F0 specimens showed micro-cracks due to the photo oxidation. It is shown in Figs. 7b and 7c with arrows and circles that the cracks were increased in F0 with an increase in exposure

time from 1000 to 2000 h. This result agrees with the flexural tests, wherein the specimens exposed to UV exhibited significant brittleness. A close inspection of a Fig. 7d and comparison with Figs. 7e and Fig. 7f on the other hand, revealed that the exposure of specimens F40 to UV improved the interlocking between the resin and fillers compared to the control specimens. For FA and FR as spherical inclusions, the packing arrangement defines the quantity of fillers and the distribution of particles. Given in Fig. 7d, the surface of the particulate filled epoxy resin with 40% fillers shows a two-phase morphology with a dispersed phase of isolated spherical particles (FA and FR) and a rigid continuous phase (resin). The dense microstructure after 1000 and 2000 h of UV exposure could be due to the post curing of the mix and increase the interlocking between the resin and different filler particles, which could help to retain the mechanical strength.

4.4.2. FTIR

Thermo- and photo-oxidation in polymeric materials can lead to the formation of alkyl radicals, which can interact with polymer molecules to form hydro peroxides by causing chain scission and other forms of degradation mechanisms [33–36]. In order to establish the effect of UV radiation on the thermal degradation and photo-oxidation, FTIR studies were conducted at the outer surface and inner portion of the particulate filled epoxy resin. From the spectrum, the characteristic bands of mixes were observed at various wavenumbers as shown in Fig. 8 for comparison. Here, the spectrum of the surface has been plotted as there were no significant changes in the central parts of the specimens before and after UV exposure. C–O and C–H bands were found to be major phases for all samples. The bands corresponding to the epoxide ring (around 817 cm^{-1}) wavenumbers at 1024 and 1248 cm^{-1} are characteristic bands for C–O stretching of saturated aliphatic primary alcohols [37]. However, unlike the bands observed at C–O for specimens F0, a restrictive stretching was observed with the inclusion of fillers (Figs. 8). This is due to the reduction in the amount of resin by increasing the percentages of fillers. The band at wavenumber 1508 cm^{-1} is the characteristic band for the aromatic ring stretching of C = C, characteristic of DGEBA epoxy systems [38]. The band at 1508 cm^{-1} may also represent nitro deformation from the cycloaliphatic amine curing agent. The band at 1703 cm^{-1} and 1718 cm^{-1} on the other hand is due to the stretching vibration of C–O in the ester [38]. The group of the bands, located at 2904 cm^{-1} and 2870 cm^{-1} is attributed to the stretching vibration of the C–H group of epoxy [39]. However, the intensity of these wavenumbers was reduced with an increase in

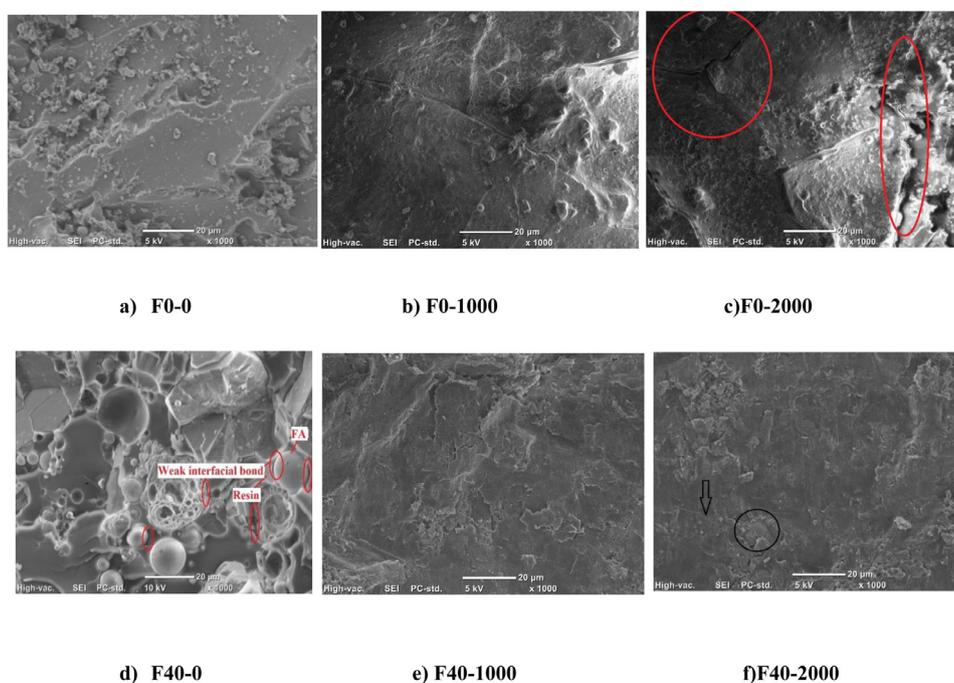


Fig. 7. SEM micrographs of epoxy polymers.

the percentages of fillers to 40%. The band observed at around 3400 cm^{-1} for different samples corresponds to the O–H stretching band. From Fig. 8, it is evident that after exposure to UV, the peak at 1604 cm^{-1} shifted slightly to wavenumbers $1618\text{--}1621\text{ cm}^{-1}$ indicating the presence of NH_2^+ radicals from primary amine deformation and was present in all exposed specimens [40]. The peaks around wavenumber 1234 and 1248 cm^{-1} shifted to 1251 and 1252 cm^{-1} and the intensity was reduced. This peak can be characteristic of stretching of epoxide ($-\text{C}-\text{O}$) bonds [33,41]. There were reductions in the peaks around 1250 and 1507 cm^{-1} , which might indicate an increase in the cross-link density of the epoxy [42,43]. This increased crosslinking can lead to excessive brittleness and result in microcracking as it was observed in SEM images (Fig. 7). Given in Fig. 8, all of the functional groups in both control and UV-exposed specimens have the same peak values except for some shifting of bands. These FTIR results shows that the formation of polymeric epoxy structures and the curing reaction in all the particulate filled mixes is complete. This is in accordance with SEM observations indicating the formation of solid resin after the curing reaction. The results revealed that the sensitivity of neat epoxy resin against UV can be decreased with the inclusion of the fillers. This shows the suitability of particulate-filled epoxy based polymer coating in a civil engineering application as the fillers provide protection against UV increasing their durability and engineering properties.

5. Conversion of uv exposed time to equivalent of sunlight time

5.1. Spectral reflectance measurement

Spectral irradiance measurements were made using the same instrumentation as Turner et al. [44] to determine the absolute irradiance of the UV lamp. The total irradiance (sensor directed towards the light's position in the UV chamber) was measured (Fig. 9). Only the data from 300 nm upward were used as the signal to noise ratio below 300 nm for the spectrometer was poor. The UV irradiance measurements were made using

Table 4

The values of irradiance ratio and ratio of one hour lamp exposure to one day solar exposure in various months.

Month	Irradiance ratio	Ratio of one hour lamp exposure to one day solar exposure
January	4.19	0.60
February	3.69	0.73
March	4.32	0.74
April	4.12	0.83
May	5.15	0.92
June	8.94	1.03

a USB4000 Plug-and-play Miniature fibre optic spectrometer with a cosine corrected (input diffuser (Ocean Optics, Inc., USA) [44]. This USB4000 spectrometer has a blaze wavelength of 400 nm and an opening slit width of $25\text{ }\mu\text{m}$ with a bandwidth of 200 nm to 850 nm and a 600 line blazed grating. The spectrometer measures (on average) integrated steps of 0.2 nm . The spectrometer was set with an integration time of 20 ms and averaged over 20 scans.

5.2. Solar uv irradiance and uv lamp irradiance calculation

The solar irradiance comparison were performed by analysing the solar spectrum using a scanning spectroradiometer (model DTM300, Bentham Instruments, Reading, UK) located at the University of Southern Queensland (Toowoomba, Australia). The Bentham scanning spectroradiometer takes a solar scan between 280 nm and 400 nm between 5 am and 7 pm every day, with steps

Table 5

Predicted coating thickness to provide 50- and 100-year UV resistance.

Mix	Equation of the line	R^2	Thickness, mm	
			50 years	100 years
F0	$y = 0.480x + 0.1433$	0.959	24.1	48.2
F20	$y = 0.352x + 0.1167$	0.949	17.7	35.4
F40	$y = 0.147x + 0.575$	0.931	7.4	14.8
F60	$y = 0.106x + 0.0517$	0.897	5.4	10.7

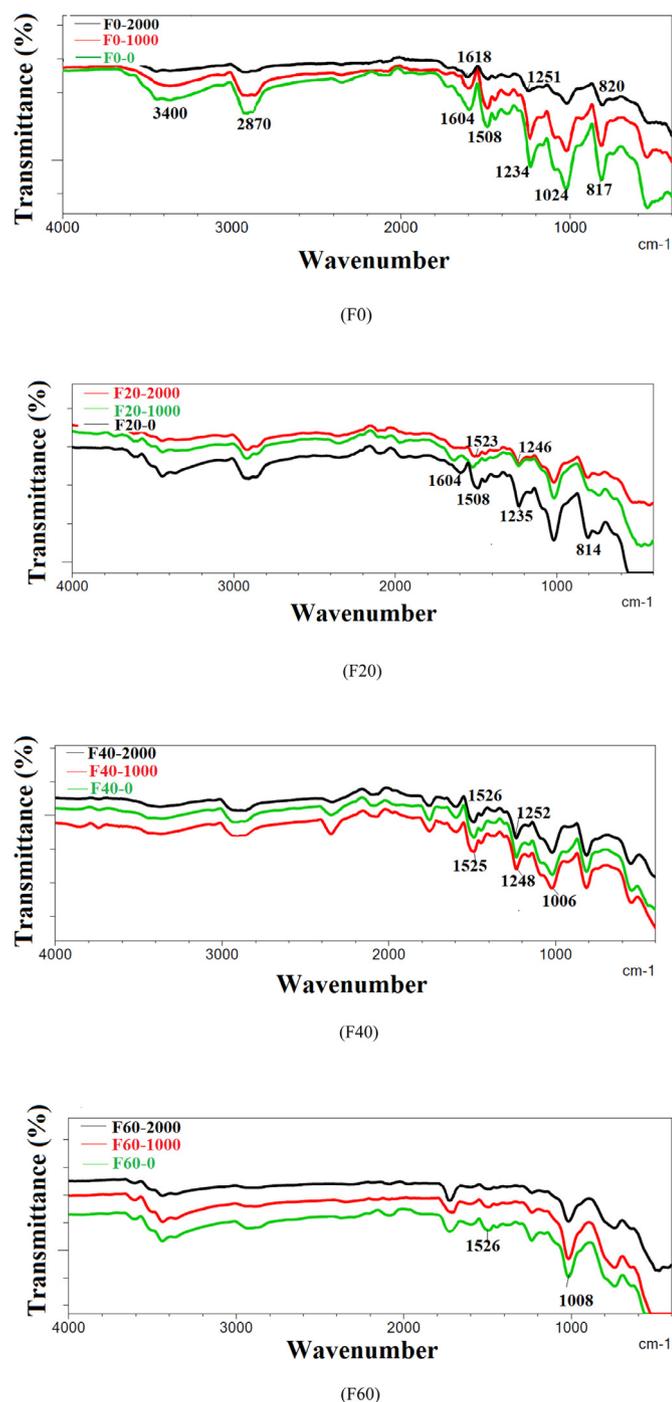


Fig. 8. FTIR spectra of control and UV-exposed specimens.

of 0.5 nm. Measurements are taken every ten minutes as suggested in [44]. The integrated solar irradiance for any single measurement can be expressed as:

$$I_{solar} = \int_{280nm}^{400nm} S d\lambda \quad (2)$$

where S is the irradiance at any one instant, and $d\lambda$ is the step size in nm

The average energy density is calculated by taking the average solar irradiance either side of the 10 min interval then multiplied by the time period (t).

$$E_{solar} = I_{solar} t \quad (3)$$

Six months of data from the Bentham scanning spectroradiometer were calculated this way. From the available days of data (160 days) a total of $1.18 \times 10^8 J/m^2$ solar irradiance was calculated for the six month period. The UV lamp irradiance is calculated only for 300 nm to 400 nm as the signal to noise ratio between 280 nm and 300 nm is poor. The measurements are taken manually every ten minutes for an hour. Analysis of the scans shows that there was very little variation between each scan over the hour. Therefore the total irradiance was averaged for the obtained data. The average energy density was then calculated for the relevant time period.

The lamp is designed to last for 2000 h. The subsequent energy density for the lifetime of the lamp was calculated. This resulted in an energy density of $1.16 \times 10^9 J/m^2$. However the 6 months interval was considered impractical for equivalence calculation and was thus doubled to produce a yearly equivalent:

Lampequivalence

$$= \frac{E_{lamp}/2000hours}{E_{solar}/1year} = \frac{1.16 \times 10^9 J/m^2}{2 \times (1.18 \times 10^8 J/m^2)} = 4.91 \quad (4)$$

The values of irradiance ratio in various months were calculated using the below equation and have been given in Table 4.

$$Irradiance\ ratio = \frac{I_{lamp}}{I_{solar}} \quad (5)$$

It was also found that the order of magnitude of energy density output by the lamp over one hour was in the same order of magnitude as the solar UV energy density for a day. This calculation used the number of hours the Bentham measures per day (14 h), with the daily average energy density per month, in comparison to hourly lamp energy density. Depending on the season the ratio of equivalence between lamp and seasonal exposure also changes (Table 4). From the analysis of the results, it was found that the UV chamber produces an output average irradiance that is approximately 4 times the average irradiance of the solar UV irradiance at local noon in summer (Toowoomba, Queensland, Australia), which was approximately 9 times the average irradiance of the solar UV irradiance at local noon in winter (Toowoomba) (Fig. 10). The UV lamp appeared to produce an output that could easily equate to UV exposure for approximately 5 years of exposure. This result was then used to predict the affected depth of UV exposure to the different particulate fillers investigated in this study. This is an estimated simplistic calculation, and may not be completely accurate, but and shows that the UV chamber can provide an estimate that equates to a few years of solar exposure. The issues that may change how materials are affected are to do with the rate of exposure. Damage from a higher intensity exposure, may overestimate the issues of a material, compared to a lower exposure carried out over a longer period of time.

5.3. Determination of coating thickness for 50-year and 100-year uv exposure

The affected depth of the polymer coating presented in Fig. 3 and the calculated equivalent of sunlight time in the previous section was plotted in Fig. 11. The equation of the best-fit linear line was determined and reported in Table 5 to predict the thickness of the polymer coating to provide 50-year and 100-year UV resistance using the three exposure durations. The R^2 of the regression line is at least 0.89 showing good correlation of the test results. A better correlation can be achieved by measuring the UV effect at more exposure durations. In the equation of the trend line, y represents the thickness of the epoxy coating while x is the time in years. Based on the results, the UV affected depth of neat epoxy resin after 50 and 100 years is predicted to be 24 mm and

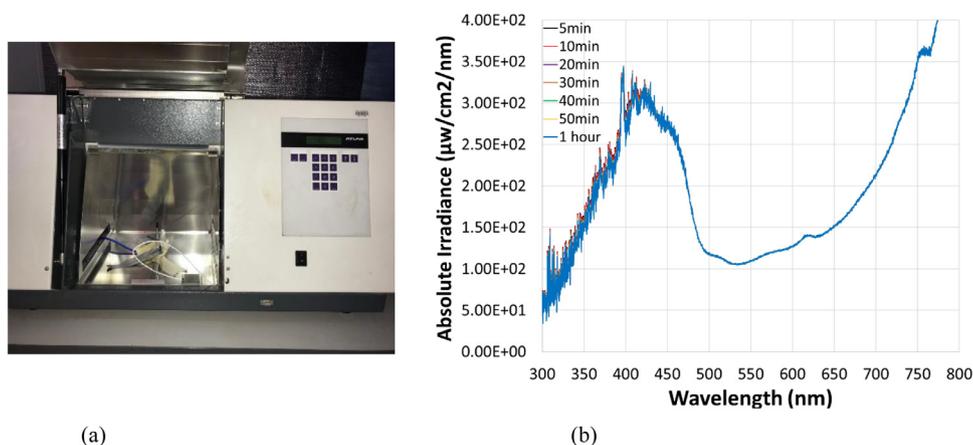


Fig. 9. a) Sensor direction for irradiance measurements, b) absorbance irradiance at different exposure time.

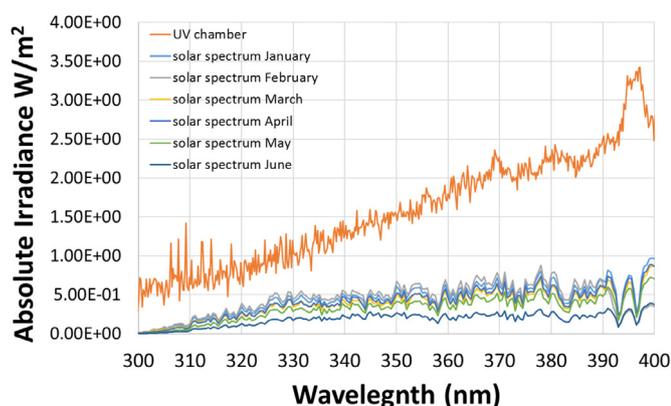


Fig. 10. Solar irradiance spectra vs UV chamber.

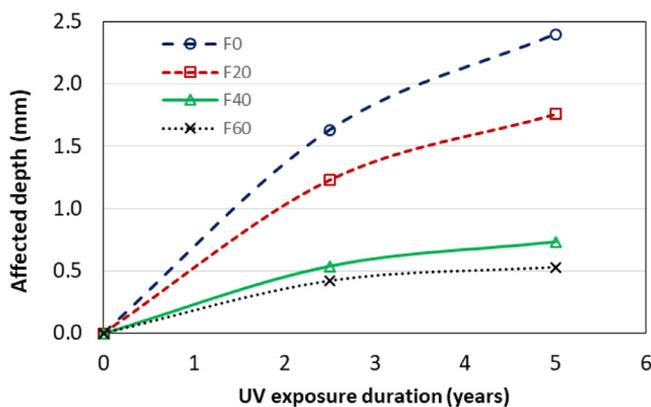


Fig. 11. The calculated equivalent of sunlight time.

48 mm, respectively. However, inclusion of fillers up to 60% could reduce the depth of the affected layer by almost 5 times, where the affected depth after 100 years is expected to reach only 10–14 mm in F40 and F60. This result shows that the addition of particulate fillers can reduce significantly the required coating thickness to protect structures from the deleterious effects of solar UV radiation and to achieve their design service lives.

6. Conclusion

In this research, the physical, mechanical, thermo-mechanical, and microstructural characteristics of particulate-filled epoxy polymers with different percentages of fly-ash and fire retardant ex-

posed to UV were evaluated. The following conclusions can be drawn:

- The addition of hydrated alumina powder and fly ash can significantly improve the UV resisting properties of epoxy resin. Adding up to 60% by volume of these fillers affected only 0.5 mm of the surface of the coating after 2000 h UV exposure, which is 5 times less than that of the neat epoxy resin. The presence of particulate fillers also reduced the discolouration compared to the neat epoxy resin where the surface became yellowish in colour.
- The fillers minimised the UV effect on the glass transition temperature (T_g) of epoxy based polymer coating. The T_g at the exposed surface of the coating with fillers (F40 and F60) is only 3 °C lower than the inner part but up to 15 °C lower for resin rich samples (F0 and F20).
- Exposure to UV changed the failure behaviour of the particulate filled epoxy polymers from ductile to brittle. This also decreased the flexural strength of neat epoxy resin but increased the strength of highly filled epoxy resin mix.
- SEM images showed the creation of micro-cracks in neat resin but an improved interlocking between the fillers and epoxy resin and a dense microstructure in particulate filled epoxy resin after exposure to UV radiation. This showed that the particulate fillers can assist in reducing the surface degradation of polymer coating by blocking the penetration of UV radiation.
- FTIR analysis showed stronger carbon-hydrogen and carbon-oxygen bonds for particulate filled resin than neat epoxy resin after exposure to UV radiation. Also, the UV affected only the thin surface of the specimens and there were no signs of chemical changes beyond the affected depth.
- Exposure to a Xenon arc lamp at a temperature of 60 °C for 2000 h appeared to produce an output that could easily equate to approximately 5 years of UV exposure in Australian environment.
- A thickness of at least 6 mm and 11 mm of epoxy-based coating with 60% by volume particulate fillers are required to protect from UV radiation for 50 years and 100 years, respectively. These thicknesses are only 20% the required thickness if neat epoxy resin is used as a coating material in outdoor applications.

Credit author statement

This is to confirm that all authors, Mojdeh Mehrinejad Khotbehsara, Allan Manalo, Thiru Aravinthan, Joanna Turner, Wahid Ferdous, and Gangarao Hota have contributed and agreed with the

content of submitted manuscript entitled “Effects of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating”.

Declaration of competing interest

There is no conflict of interest in the submitted manuscript entitled “**Effect of ultraviolet solar radiation on the properties of particulate-filled epoxy based polymer coating**”. All authors have approved the manuscript and agree with its submission to this journal. We guarantee that the contribution is an original material, has not been published previously and is not under consideration for publication elsewhere. All the materials and information contained in the paper are not restricted and are available to all.

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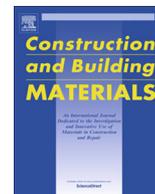
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Chapter 6

Article IV: Synergistic effects of hygrothermal condition and ultraviolet solar radiation on the properties of particulate-filled epoxy polymer coating

Chapters 3 and 4 identified that particulate fillers can enhance the performance of epoxy-based polymers when exposed to elevated in-service temperature and hygrothermal conditioning. Moreover, the results of Chapter 5 showed better UV performance for epoxy-based polymers with fillers than neat epoxy resin. *Article IV* investigated the synergistic effects of UV solar radiation, moisture and in-service temperature on the thermal, mechanical and physical properties and microstructure of particulate-filled epoxy-based polymer coating containing up to 60% by volume. Due to the application of particulate filled epoxy polymers as coating materials in railway sleepers wherein the main loading actions is in flexure, only flexural strength was chosen as main mechanical test conducted in this study. Moreover, considering limitation related to small space in UV chamber, only limited number of samples could be exposed to UV (60 mm in length \times 10 mm in width \times 5 mm in thickness, suitable for measuring the glass transition temperature (T_g) in DMA instrument. Based on the relevant standards 2 samples were tested to measure T_g , the result did not show any significant difference between various samples of each mix. Physical observations showed yellowing on the surface of neat epoxy coating after hygrothermal (HG) and UV exposure but the presence of fillers minimised fading and weight loss. There was no reduction in the flexural strength for polymer coating containing at least 40% fillers. ANOVA analyses showed that the combined HG and UV negatively impacted the flexural properties of coating with up to 20% fillers but enhanced the properties of

coating with fillers above 40%. This was due to the UV resisting and heat absorbing properties of fillers where the flexural strength can be preserved at high level of filler content. The results from this chapter provides a good representation and evaluation of the long-term properties and durability performance of particulate filled epoxy polymer coating in different harsh environments. It is interesting that not all environmental conditions are detrimental to the properties of particulate filled epoxy, indicating the suitability of this material as a protective coating materials and other construction and building materials. The major findings from this works are highlighted in the Conclusion and a number of recommendations for further studies to gain a detail understanding on the long-term performance of particulate filled polymers are presented in Chapter 7.



Synergistic effects of hygrothermal conditions and solar ultraviolet radiation on the properties of structural particulate-filled epoxy polymer coatings



Mojdeh Mehrinejad Khotbehsara^{a,*}, Allan Manalo^a, Thiru Aravinthan^a, Wahid Ferdous^a, Brahim Benmokrane^b, Kate T.Q. Nguyen^c

^a Centre for Future Materials (CFM), School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia

^b Department of Civil Engineering, University of Sherbrooke, Canada

^c School of Engineering, RMIT University, Melbourne, VIC, Australia

HIGHLIGHTS

- Properties of filled epoxy coating exposed to moisture, elevated temperature and UV.
- Durability of particulate-filled epoxy polymer coatings.
- Surface microcracks after UV exposure that were wider with hygrothermal conditioning.
- Environmental conditioning enhanced the properties of coatings with at least 40% filler content.

GRAPHICAL ABSTRACT

Mix	Environmental condition			
	Control	HG	UV	HG+UV
F0				
F20				
F40				
F60				

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ABSTRACT

The synergistic effects of solar ultraviolet (UV) radiation, moisture, and in-service temperature on the properties of structural particulate-filled epoxy-based polymer coatings were investigated. The coatings contained up to 60% by volume of hydrated alumina powder and fly ash as fillers. Four sets of coating specimens (20 samples per set) with dimensions of 60 mm × 10 mm × 5 mm were prepared. Two sets were conditioned at a relative humidity of 98% and temperature of 60 °C for 2000 hrs (HG). One of these sets was then exposed to simulated UV conditions for 2000 hrs with the other set evaluated for the effect of HG conditioning. One set was unconditioned and served as control specimens with another set exposed to UV. Physical observations showed yellowing on the surface of neat epoxy coating after HG or UV exposure, but the presence of fillers minimized fading and weight loss. Regardless of conditioning environment, there was no reduction in the flexural strength for the polymer coatings containing at least 40% fillers. HG or UV exposure promoted post-curing, increased the glass transition temperature, and enhanced cross-linking density. Microscopic observation revealed the formation of surface microcracks

* Corresponding author. Centre for Future Materials (CFM), School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia
E-mail address: Mojdeh.Mehrinejad@usq.edu.au (M.M. Khotbehsara).

after UV exposure that were wider with HG conditioning. ANOVA showed that the combination of HG and solar UV radiation negatively impacted the flexural properties of the coatings with up to 20% filler content but enhanced the coating properties with filler contents above 40%.

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1. Introduction

Epoxy-based polymers are currently being applied as protective coatings to minimise the environmental effects on the properties of composite structures [1,2]. In this application, the structural polymer coatings are exposed to aggressive environmental conditions including solar ultraviolet (UV) radiation, moisture, and in-service elevated temperature. A number of studies have evaluated the sensitivity of polymers to hygrothermal conditioning [3–5] and found that the ingress of moisture can react with the epoxy polymer and impose internal stresses, causing a reduction in mechanical properties [6]. Elarbi and Wu [7] found that moderate to high heat could significantly degrade the mechanical properties of epoxy resins, but that low to moderate heat could promote post-curing resulting in enhanced flexural strength. Douglas et al. [8] suggested that fiber-reinforced polymer (FRP) bond is vulnerable to combined effects of high temperature and humidity/water. Ghasemi-Khahrizangi et al. [9] and Yusif and Haddad [10] highlighted the harmful effects of UV exposure on the physical, mechanical and chemical properties of epoxy polymers. The photo-oxidative reaction caused by solar UV radiation reduces molecular weight and makes the polymer more brittle [11] and can break the polymeric chains [12]. The degradation is due to the energy of solar UV light being higher than the chemical bond strength, e.g., C–C, O–O, H–O, and C–N in polymers [13]. Rosu et al. [14] also found that UV affects the polymer networks of epoxy resin and results in colour changes and mass losses in the exposed samples. Rezig et al. [15] investigated the relationship between chemical degradation and thickness loss of an unpigmented, non UV-stabilized, crosslinked amine-cured epoxy coating exposed to UV conditions and found that the rate of chemical degradation for an amine cured epoxy coating is always greater than that of the thickness loss. In another study, Lu et al. [16] concluded that UV degradation of polymeric surfaces was strongly dependent on UV wavelength, intensity and exposure time. Sung et al. [17] showed that intensity of Fourier-transform infrared spectroscopy (FTIR) peaks related to the CH stretching band at 2960 cm^{-1} (mass loss), NH bending and CN stretching at 1520 cm^{-1} (chain scission), and the C = O band at 1726 cm^{-1} in the epoxy coatings decreased as exposure time increased, indicating that degradation is an ablation process taking place in the outer surface. Chin et al. [18] observed surface erosion and cracking on thin polymer films made of vinyl ester and iso-polyester after exposure to a 1000-watt xenon arc source for 1200 h at $30\text{ }^{\circ}\text{C}$ in an Oriel solar simulator. They found that deterioration of the mechanical properties of polymeric composites due to UV radiation is caused by the surface oxidation resulting in surface erosion and cracking of the polymer matrix. These studies showed the significant effect of UV on the durability properties of epoxy polymers. Attempts to reduce the transparency of polymer coating are therefore necessary to minimise their degradation under solar UV radiation.

A number of studies have added particulate fillers to epoxy resin system and investigated their short-term properties [19–21]. Ferdous et al. [20,22] showed that the addition of lightweight filler materials including fly ash (FA), fire retardant (FR) and hollow microsphere (HM) to the resin minimised the cost of an epoxy polymer matrix. Similarly, Lokuge and Aravinthan [21]

added fly ash to increase the compressive strength of epoxy-based polymer concrete. Research on the effects of different filler materials such as fly ash and silica fume on epoxy-based polymer concrete [21–23] have shown to improve their mechanical, chemical and durability properties. Golestaneh et al. [23] showed that a higher compressive strength can be achieved by adding fine or coarse filler to epoxy-based polymer concrete. The improvement in strength using a blend of fine and coarse filler was also reported by Lim et al. [24] where brittleness was reduced by optimising the filler contents. These studies have shown that the introduction of fillers enhanced the physical and mechanical properties of epoxy-based polymer matrix. However, the behaviour and long-term performance of structural epoxy coatings under different exposure conditions warrant detailed investigation.

Few studies have evaluated the long-term properties of epoxy matrices with fillers. Among these studies, Khotbehsara et al. [25] investigate the effect of in service elevated temperature on the mechanical properties and microstructure of particulate filled epoxy polymer including fly ash (FA) and hydrated alumina powder (FR). In another study, Khotbehsara et al. [26] investigated the effect of HG conditioning (1000, 2000 and 3000 h (hrs) at temperature up to $60\text{ }^{\circ}\text{C}$ and a relative humidity of 98%) on the durability and service life of particulate-filled epoxy resin. The results showed that the inclusion of FA and FR fillers decreased the moisture absorption, increased the glass transition temperature and slightly reduced the mechanical properties of polymer coating. He et al. [27] found that the moisture absorption of DGEBA epoxy-based nanocomposites containing nano-calcium carbonate (nano- CaCO_3) decreased with increasing nano- CaCO_3 content. Shamsuddoha et al. [28] studied the long-term properties of epoxy polymers with different percentages (27%, 15% and 13%) and types of fillers (fine and coarse aggregates) under hot-wet conditioning for 1000 h at $70\text{ }^{\circ}\text{C}$. Their results showed a reduction of up to 74% and 83% in the compressive and flexural strengths, respectively. Tcherbi-Narteh et al. [29] incorporated nanoparticles into DGEBA epoxy resin to minimize the damaging effects of solar UV radiation on polymers. Their results showed that the addition of 1% by weight to the polymer delayed the onset of deleterious effects of UV due to partial curing of the epoxy and better dispersion of the nanoparticles. Cao et al. [30] detected some enhancement in the properties of polymer coating systems after 2000 hrs of UV exposure with the addition of titanium dioxide (TiO_2) particles. In a recent study, Ferdous et al. [20] evaluated the role of particulate fillers including FA, HM and FR in the physical and flexural strength of epoxy polymers when exposed to simulated solar UV radiation. After 2000 hrs of exposure, they found embrittlement, discoloration, and weight loss in all the specimens. The weight loss (0.15%) was, however, lower in the specimens with the highest amount of fillers (60%) compared to neat epoxy resin (0.37%). These studies show that incorporating fillers in polymer coatings enhances UV resistance. Similar findings was observed by Khotbehsara et al. [31] wherein they found no reduction in the flexural strength for polymer coating containing at least 40% FA and FR fillers after 2000 hrs UV exposure. They also indicated that a thickness of at least 5 mm of epoxy-based structural coating with 60% by volume of particulate fillers could provide UV protection for 50 years. These studies show that incorporating fillers in polymer coatings enhances the durability of epoxy-based coating. However,

these studies have focused on evaluating the long-term properties of polymeric materials exposed only to one weathering condition. In service conditions, materials are generally exposed to a combination of environmental conditions. It is necessary therefore to have a deep understanding on the synergistic effects of harsh environmental conditions on the long-term durability properties of particulate-filled epoxy polymer (PFR) coating.

This study presents an experimental investigation to determine the effect of solar UV radiation and hygrothermal conditioning on the properties of an epoxy-based coating system containing fire-retardant (FR) and fly-ash (FA) fillers. The significance of this study is to understand the degradation mechanisms related to the synergistic effects of solar UV radiation, elevated in-service temperatures, and high moisture levels on the physical, mechanical, and physicochemical properties and the microstructure of epoxy-based polymer coatings. Analysis of variance (ANOVA) was also conducted to statistically determine the synergistic effects of exposure to UV and HG environments as well as to evaluate which of the environmental conditions had the greatest effect on the properties of the epoxy-based polymer coatings.

2. Materials and methods

2.1. Materials

Particulate-filled epoxy polymers were prepared by mixing resin and fillers. Part A of the resin system was DGEBA epoxy (bisphenol A diglycidyl ether) and Part B was an amine-based curing agent. Part A and part B were mixed together based on the Epoxy Equivalent Weight (EEW) of 190 g for Part-A and Amine Hydrogen Equivalent Weight (AHEW) of 60 g for Part-B as furnished by the supplier. The particulate fillers were fly ash (FA) and hydrated alumina powder (FR). The FA was supplied by Si Powders Pty Ltd, Australia and the epoxy resin by ATL Composites Pty Ltd. (Gold Coast, Australia). Huber Engineered Materials (HEM) supplied the FR. FR was chosen due to its low abrasiveness, smoke suppression, acid resistance, chemical inertness, electric arc resistance, fire resistance and non-toxic behaviours. FA was used due to its performance in decreasing the permeability of aggressive chemicals and water [20,32,33]. Railway sleepers are usually subjected to fire from thermite welding of rail joints, and elevated temperature and UV radiation from sun. This is the reason why FA and FR were used together [20]. Both the FR and FA were round in shape with diameters of 75 to 95 μm and 0.1 to 30 μm, respectively. The study involved four coating mixes: one of neat epoxy resin as the control sample, and three with particulate-filler contents of 20%, 40%, and 60%, labelled F0, F20, F40, and F60. The mixing ratio of FA-to-FR was kept constant for all mixes. The ratio was adopted from the previous study by Ferdous et al. [20]. Since the main aim of this research is to investigate the synergistic effect of HG and UV on the mechanical and microstructure properties of PFR and ensure the cost is minimised, therefore the total amount of filler was considered as a variable rather than the ratio of FA-to-FR. Table 1 lists the density of individual materials and mixture compositions.

Table 1
Mix design for particulate-filled epoxy polymer coatings.

Materials	Density (g/cm ³)	Mixes			
		F0	F20	F40	F60
Part A (g)	1.064	1000	737	552	368
Part B (g)	1.182	320	236	177	118
FR (g)	2.411	0	397	794	1192
FA (g)	2.006	0	119	239	358

2.2. Sample preparation

Four mixes with filler contents of 0%, 20%, 40%, and 60% by volume of the matrix were produced (total of 80 samples). The FR-to-FA ratio, which was adopted from a past study [9], was constant for all mixes. The polymer coating mixes were poured into rectangular nonstick molds measuring 60 mm in length × 10 mm in width × 5 mm in thickness, suitable for measuring the glass transition temperature (T_g) using DMA instrument and for flexural tests. The specimens were kept in molds for 48 hrs at room temperature before being demolded and cured for 7 days at room temperature.

2.3. Environmental conditioning

One set of unconditioned samples (total of 20 samples) was prepared, kept at room temperature with 35% relative humidity (RH) and tested at 14 days as control specimens. Two sets were conditioned at 98% RH and 60 °C for 2000 hrs (Fig. 1a). One of these sets was then exposed to simulated UV conditions for another 2000 hrs with one set of samples characterized for the effect of HG conditioning. At the same time, a set of unconditioned polymer coating mixes was exposed to UV conditions for 2000 hrs with a Xenon 2200-watt air-cooled lamp in the Sunset XLS UV chamber and the wavelength ranged from approximately 300 nm to approximately 800 nm. A Xenon arc lamp was used, as many researchers have used this type of lamp to simulate solar UV radiation for photodegrading of materials [13]. The solar UV radiation chamber was set in an ambient atmosphere, and at 60 °C to simulate the extreme summer conditions in Australia as measured by Sirimanna et al. [34] on FRP composite bridge decks. The simulated UV exposure appeared to produce an output corresponding to approximately 5 years of solar UV irradiance in Toowoomba, Queensland, Australia as found by Khotbehsara et al. [31]. All the specimens were weighed, examined under microscope, and mechanically and thermo-mechanically tested. The chart in Fig. 2 summarizes the test methods as well as the number of samples tested for each type of test.

2.4. Procedures for material characterization

The discoloration of the particulate-filled epoxy-based polymer coating was noted, and the weight loss was measured after exposure to 2000 hrs of UV radiation. Visual observations, together with the use of an optimal microscope (OLYMPUS XC10) with 100x magnification, were implemented to assess the discoloration and depth of penetration of all the specimens following the approach implemented by Khotbehsara et al. [31]. An electronic balance (MonoBloc-AB204-S) with sensitivity of 0.0001 g was used to weigh samples before and after being taken out of the environmental and UV chambers.

The glass transition temperature (T_g) of the unconditioned and conditioned samples before and after exposure to HG and UV was measured with a dynamic mechanical analyzer (DMA) in accordance with ASTM D7028 [35]. The samples were clamped in a dual-cantilever system in which the DMA multifrequency strain was applied as the test mode with a Q800 from TA Instruments. The temperature scans were set between 30 °C and 120 °C in 5 °C increments. The temperature corresponding to the storage modulus curve peak was used as the T_g value. The difference in the T_g at the exposed surface and inner portion of the conditioned samples cannot be measured by the DMA, thus DSC was implemented as this only requires small portion of samples extracted from the conditioned samples. Thus the difference in T_g between the exterior and interior of the specimens was also assessed with

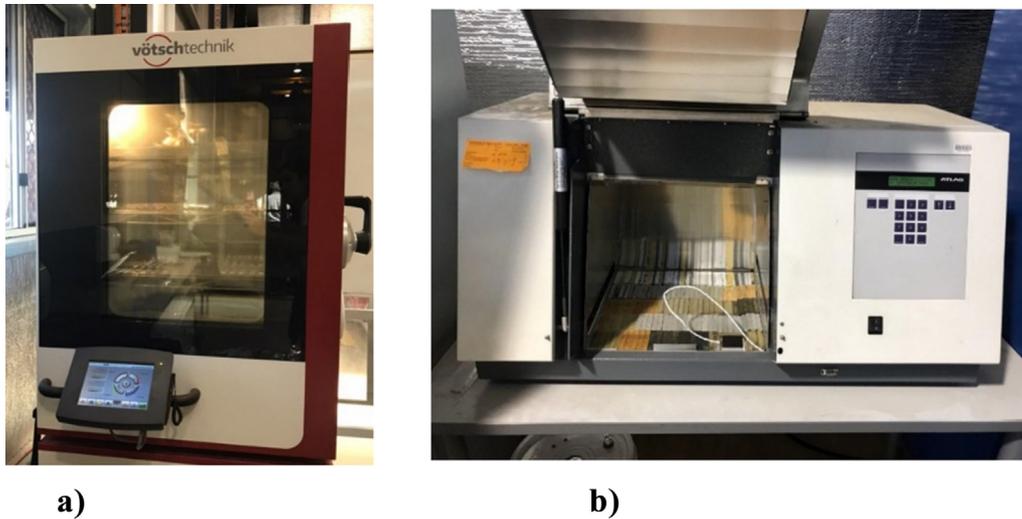


Fig. 1. a) Samples in the environmental chamber b) samples in UV chamber.

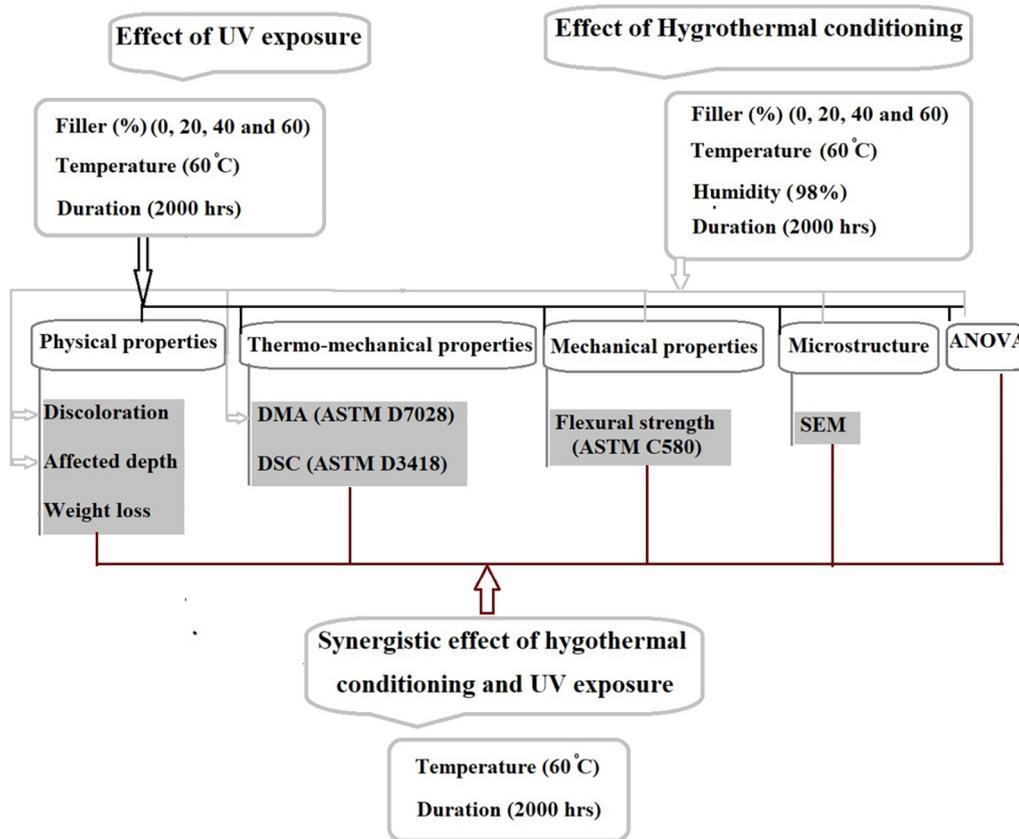


Fig. 2. Summary of the test methods of the conditioned specimens.

differential scanning calorimetry (DSC) according to ASTM D3418 [36] after HG conditioning and UV exposure.

The flexural properties of the particulate-filled epoxy resins were determined by placing the specimens in a 3-point static bending testing machine (ALLiance RT/10) with a capacity of 10 kN and a loading rate of 2 mm/min, according to ASTM C580 [37].

The microstructure of the particulate-filled epoxy resin before and after HG and UV conditioning was observed with a JEOL JXA 840A scanning electron microscope. Small samples (less than 1 cm) were taken from the UV-exposed surface of the specimens. They were prepared and coated with gold using a sputter deposition machine

3. Results and discussion

3.1. Physical properties of the Epoxy-Based coatings

Fig. 3 shows the surface discoloration after exposure to 2000 hrs of HG conditioning and exposure to solar UV radiation. The first column (control samples) shows that the polymer coatings turned darker as the filler content increased, which would be expected due to the dark grey color of the fly ash. The second column shows that, after 2000 hrs of HG exposure, the F0 samples tended to be yellowish, but there were no significant changes in the samples with higher filler content. The discoloration of samples F0 and F20 can be explained by physicochemical reactions in which the tertiary amines changed in hue from whitish to yellowish. These results are in agreement with the findings of Chen and Wu [38] on the color stability of nanocrystallite-treated and silicate-treated fillers of calcium phosphate composite resin. These researchers found that specimens with lower amounts of silica-treated fillers exhibited more variations in color than specimens with larger amounts of fillers after 1 to 16 days of aging. That would indicate that fillers with nanocrystal treatment could stabilize color variations. The change in color between F0 and F20 samples indicates that there might have been some physical or chemical reactions occurring in the epoxy resin due to thermal oxidation. The color depth, however, shows that the ageing was limited to thin surface layers and decreased as the filler content increased. In the HG conditioned specimens, the affected depth was less than 1.0 mm for F0 and F20 and less than 0.5 mm for F40 and F60. Discoloration was more noticeable for the samples with UV or HG + UV conditioning than for those with HG conditioning, as shown in columns 3 and 4. The discoloration at this

stage was due to interaction between the photons from UV radiation and epoxy molecules on the exposed surface, causing photooxidative reactions [39]. While the color change was significant in the resin-rich samples (F0 and F20), fading was barely noticeable in the filler-rich samples (F40 and F60; see Fig. 3). This was due to the decrease in the transparency of the epoxy resin caused by the greyish color of FA, which blocked the UV rays from penetrating the samples. The beneficial effects of fillers with the dark grey color derive from their UV stability characteristics, which also signify the importance of uniform dispersion of fillers in the matrix to promote UV-resistance properties [9]. Moreover, the surface of all the specimens exposed to UV radiation was rougher than the controls and HG-conditioning specimens based on visual observation. The increased surface roughness during solar irradiation could be due to chalking because of the accumulation of photodegradation products [18].

Fig. 4a shows that the weight loss of specimens exposed to UV or HG + UV conditioning decreased as the filler content increased. Moreover, the percentage weight loss was higher for samples exposed to combined UV + HG conditioning than to UV exposure alone. This could be explained by the epoxy polymer coating absorbing water during HG conditioning, which was extracted during the UV exposure. The lower weight losses of F40 and F60 compared to F0 and F20 can be explained by the thinner affected depth (only around 0.75 mm) after 2000 hrs of exposure. The depth of the resin-rich samples was up to 2.8 mm, which is almost 50% of the total sample thickness. The depth affected per hour of UV exposure was measured microscopically for the different mixes (see Fig. 4b). As the figure shows, UV exposure affected F0 at a rate of 0.0012 mm per hour, which is almost three times faster than F40. The HG conditioning had greater impact on increasing the

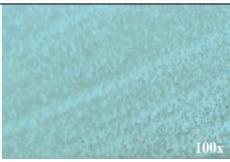
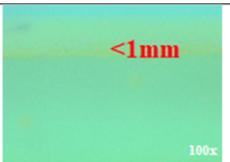
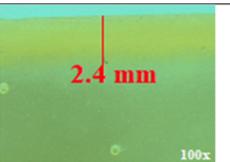
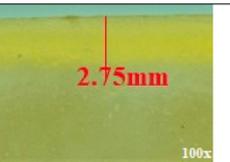
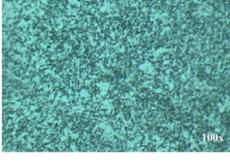
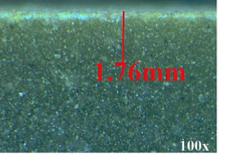
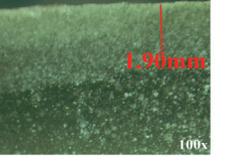
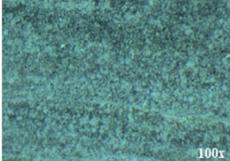
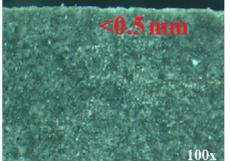
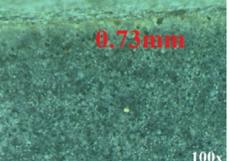
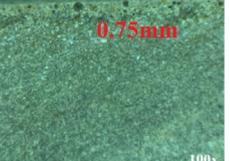
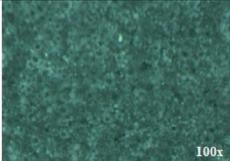
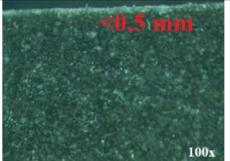
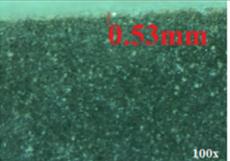
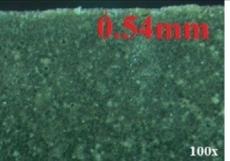
Mix	Environmental condition			
	Control	HG	UV	HG+UV
F0				
F20				
F40				
F60				

Fig. 3. a) Discoloration and b) affected depth of conditioned samples in mm.

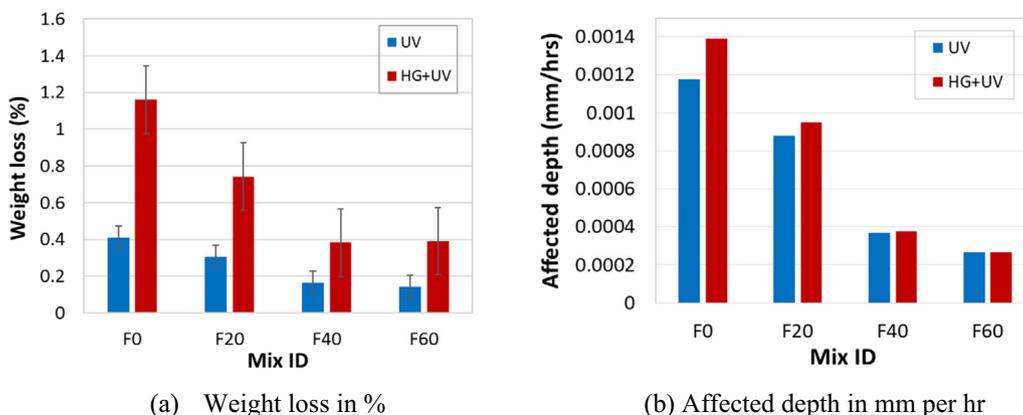


Fig. 4. Weight loss and affected depth of particulate-filled epoxy after UV exposure.

affected depth at low filler concentrations (F0 and F20), while this effect was marginal with F40 and F60. It could be expected that the expulsion of residual moisture and volatiles in the epoxy resin occurred mainly in this affected depth (Figs. 3 and 4b). The measured percentage weight loss for particulate-filled resin is comparable to the measured weight loss for carbon-fiber reinforced epoxy composites (0.27%) after 500 hrs of UV exposure, as determined by Kumar et al. [39]. This shows that adding fillers to an epoxy polymer coating has an effect similar to carbon fibers in increasing UV resistance. This is because the fillers block the penetration of UV radiation, leaving only the thin exposed surface affected.

3.2. Thermomechanical and mechanical properties of Epoxy-Based coating

Table 2 summarizes the average thermomechanical and mechanical properties of particulate-filled epoxy resin before and after 2000 hrs of HG (HG), UV exposure (UV), or combined HG and UV (HG + UV) conditioning. The values listed within parentheses are the standard deviation of the test results. Results suggest that the specimens containing fillers and exposed to HG or UV conditioning had enhanced mechanical properties compared to the unconditioned specimens, This could be due to post-curing, resulting in an increase of cross-linking density [40]. The post-curing cross-linking also increased T_g , which explains the improvement of the mechanical properties for the polymer coatings containing high amounts of fillers.

3.2.1. Effect on glass transition Temperature, T_g

Table 2 shows the measured T_g of the control and post-cured samples as well as a comparison of the different conditioning

environments. The T_g obtained from the storage modulus of the control samples was around 60 °C with a difference of almost 3 °C to 5 °C between F0 and F60. UV exposure significantly increased the T_g of the inner part of the samples to around 82 °C to 88 °C. On the other hand, HG conditioning increased the T_g to around 78 °C to 84 °C. It is possible that HG at 60 °C allowed more pseudo cross-linking from hydrogen bonding of water molecules to the epoxy network to occur in HG samples than the control samples. Moreover, the additional cross-linking that occurred in 60 °C samples can be due to the increased mobility of the materials near the T_g . Similar observations was reported by Blackburn et al.[41]. Similarly, UV exposure for up to 2000 hrs further increased the T_g of HG-conditioned samples to 80 °C to 93 °C. This increase in T_g in the inner part of the samples could be due to post curing effect on the samples as a result of the higher temperature (60 °C) during exposure to HG, UV, and HG + UV exposure. The implication is that the exposure to elevated temperature and UV enhanced the curing reaction of the polymer mixes, leading to an increase in cross-link density, as suggested by Marouani et al. [42]. It is well known that T_g can be used as a reliable indication of the cross-link density in epoxy resins [43]. This result is supported by the considerable increase in T_g in the control specimens post-cured for 24 h at 60 °C, whereas the T_g increased from 57 °C to 81 °C for F0 and from 61 °C to 84 °C for F60. This result further indicates that epoxy resin with particulate fillers can retain most of its storage modulus after UV exposure and HG conditioning. The storage modulus can be an indication of the polymer's ability to store deformation energy, which can be related to the degree of cross-linking of the polymers.

As can be seen in Table 2, while there is the T_g on the surface and inner parts of control samples does not show any significant difference, the T_g on the outer surface is lower than in the inner portion of the samples, suggesting the harmful effect of exposure

Table 2 Mechanical and thermomechanical properties of particulate-filled epoxy polymers.

MIX ID	Control			Conditioned					
				HG		UV		HG + UV	
	Control	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner
	Control			Post cured @60 °C					
Glass transition temperature (T_g) (°C)									
F0	57.9	58.2	81.3	73.9	78.5	68.9	82.67	66.7	79.6
F20	59.5	59.6	82.4	75.9	78.9	72.0	85.92	70.8	87.9
F40	60.5	60.2	82.7	78.3	80.9	73.1	86.13	77.2	92.9
F60	61.4	61.6	84.5	81.2	83.7	74.2	87.74	79.1	92.4
Flexural strength (MPa)									
F0	98.9 (3.2)		103.6 (2.8)		101.1(3.4)		59.4 (2.8)		52.2 (2.9)
F20	47.8 (2.1)		52.5 (2.4)		48.2 (1.6)		32.8 (0.9)		30.6 (1.7)
F40	26.1 (1.5)		42.7 (1.8)		39.9 (0.8)		47.2 (1.3)		46.2 (1.5)
F60	13.6 (1.6)		33.4 (1.4)		29.9 (1.1)		41.1 (0.7)		38.5 (3.8)

to hydrothermal and UV environments. The T_g measured at this location was 4 °C, 13 °C, and 15 °C lower than in the inner part with HG, UV, or HG + UV conditioning, respectively. Water uptake by polymers is known to cause plasticization in the short term and saponification, hydrolysis, and chain scission over the long term through attack of the network linkages. These processes might have resulted in the decrease in T_g [44]. Moreover, the higher decrease in T_g on the surface for specimens with UV or HG + UV exposure compared to those with HG conditioning is due to the ultraviolet rays breaking the epoxy bonds to form free radicals. These free radicals react with oxygen, producing carbonyl groups in the main chain, resulting in oxidation [10]. Notably, the lowest T_g on the exposed surface of UV-conditioned samples was measured on F0 (68.9 °C). The inner surface of the specimen had a T_g of 82.6 °C. The T_g value decreased even more with HG + UV conditioning. In contrast, the T_g measured on the exposed surface of F40 and F60 after 2000 hrs of UV was at least 73 °C, which is almost same as for samples exposed to HG + UV conditioning. This is consistent with the results for affected depth in the preceding section, in which HG conditioning had more impact on increasing the affected depth at low filler concentrations, while this effect was marginal for F40 and F60. This result further shows that the particulate fillers helped reduce the surface degradation of epoxy polymers by helping to block the penetration of UV radiation.

3.2.2. Effects on flexural strength

The flexural strength of the unconditioned samples decreased from 97 MPa to 13 MPa as the filler percentage increased. This could be expected given the decrease in resin content, which provides the strength for the epoxy matrix. Similarly, the behavior of the particulate-filled epoxy polymer coating changed from

relatively flexible to rigid as the filler volume increased. The first column in Fig. 5 shows that the unconditioned F0 samples deformed significantly under flexural load with only microcracks in mid-span at the bottom of the specimen. On the other hand, samples including fillers (F20, F40 and F60) failed with a large vertical flexural crack at the mid-span. The first and second columns in Fig. 5 show similar failure modes for the F0 control and HG conditioned samples, with increased microcracks at the bottom of the HG conditioned specimens. These microcracks were due to the effect of moisture absorbed by the samples. Fig. 6a also shows that the stress strain behaviour of unconditioned and HG-conditioned F0 samples were almost similar and they exhibited a non-linear stress-strain behavior before failure. In the samples containing filler, the failure mode changed from relatively rigid to more flexible, with microcracks forming prior to a large vertical flexural crack after HG conditioning. The stress-strain behavior of conditioned samples could be due to HG conditioning at temperature of 60 °C as the samples are absorbing moisture, resulting in more non-linear behavior [26]. As Fig. 6c shows, F40 and F60 experienced a significant increase in flexural strength after HG conditioning, while the resin-rich samples (F0 and F20) maintained about the same level of flexural strength after 2000 hrs. This could be due to uniform dispersion of fillers and better interlocking between resin and fillers in the conditioned particulate-filled epoxy polymers at 60 °C, leading to higher strength. This is supported by the flexural results of samples post-cured at 40 °C or 60 °C for 24 h (as shown in Table 2), which evidenced higher flexural strength, probably caused by the increase in cross-link density of the particulate-filled epoxy polymers.

The UV column in Fig. 5 shows that the F0 samples exposed to UV for 2000 hrs failed because of a flexural crack at mid-span, and

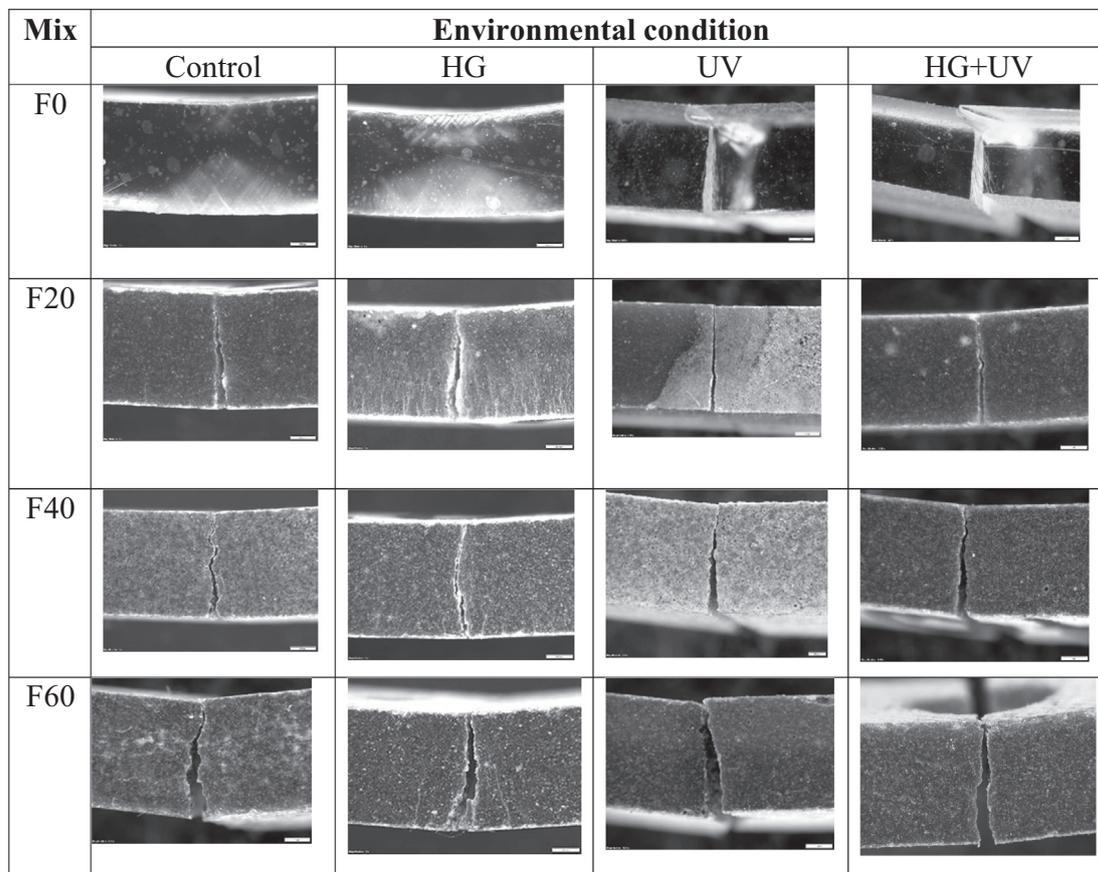


Fig. 5. Failures of different mix samples observed after flexural testing.

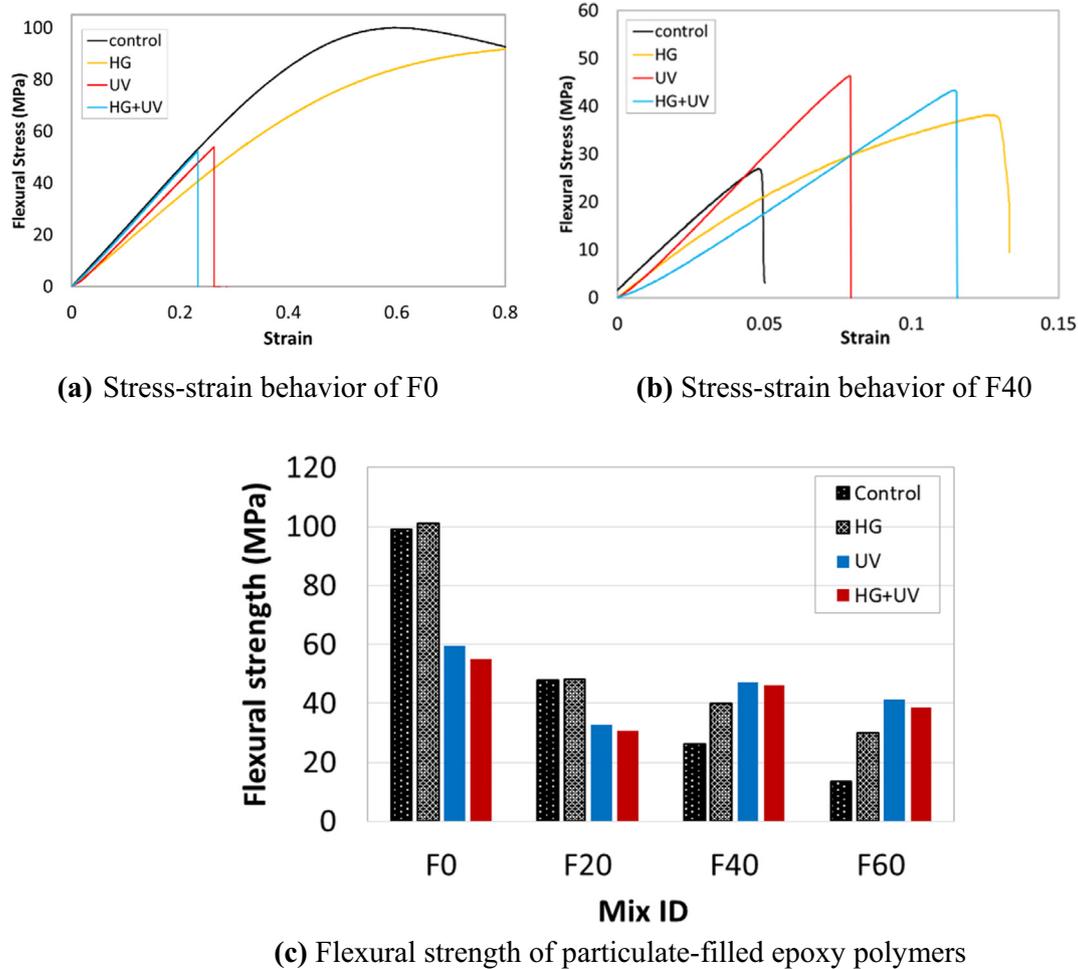


Fig. 6. Flexural behavior of control and conditioned particulate-filled epoxy polymers.

specimens F20, F40, and F60 failed with a large vertical flexural crack at the mid-span. Fig. 6a and 6b show that the UV-exposed specimens were more brittle than the control and HG-conditioned specimens. This brittle behavior can be attributed to the microcracks in the surface of the specimens which might be caused by photooxidation during UV exposure and loss of moisture. The exposure to solar UV radiation at 60 °C led to post-curing of the inner part of the samples which increased the flexural strength of F40 by almost 90% and that of F60 by almost 300% compared to control samples, and approximately 10% and 25% compared to the samples post-cured at 60 °C (from 26 MPa to around 47 MPa as shown in Fig. 6). In contrast, the flexural strength of F0 decreased by 55%. These changes could be due to the transparent nature of neat epoxy resin, letting UV affect its structure significantly causing the highest level of surface degradation, which is critical for materials subjected to the flexural test as the topmost and bottommost layers are subjected to the highest levels of flexural stress [30]. On the other hand, the penetration of UV through the very thin surface of F40 and F60 significantly increased the flexural strength of the specimens with high filler content. This can be also attributed to the oxidative degradation just occurring within the region close to the exposed surfaces. The increase of filler with the dark grey colour can increase the rate of absorption of UV radiation. This implies that the fillers will absorb UV radiation at the surface level and it will reduce the affected depth (in agreement with result of affected depth in Fig. 3). This reduction can be due to the degraded surface of the

samples with a high amount of fillers could act as a protective coating impeding the penetration of UV radiation and resulting in retaining the flexural strength, while the heat caused by the UV exposure resulted in post curing of the inner portion of the samples. This result can be supported by the post-cured samples at temperature of 60 °C in Table 2, where the flexural strength significantly increased after post curing, particularly in filler dominant samples (F40 and F60). This could be also due to higher T_g of F40 and F60 compared to F0 and their higher storage modulus and consequently higher increase in crosslink density of these mixes as was suggested by Khotbehsara et al. [25]. On the other hand, the significant reduction in flexural strength for resin-rich samples, particularly F0, can be related to the highest level of surface degradation, which is critical for materials subject to flexural testing, as the exposed surface is subject to the highest level of flexural stress.

Column 4 in Fig. 5 indicates that the failure behavior of HG + UV conditioning was similar to UV conditioning: all the samples failed with a large vertical mid-span crack. Moreover, the flexural strength decreased in all mixes exposed to HG + UV conditioning compared to UV conditioning alone (Fig. 6c). This decrease could be due to the surface microcracks resulting from UV exposure, which extracted moisture and made the samples brittle. It is worth mentioning that the flexural strength of samples F40 and F60 with HG + UV conditioning was higher than that of their control and HG-conditioned counterparts. The degraded surface of the specimens with a high filler content acted as a protective coating, impeding the penetration of UV radiation and preserving flexural strength.

These results are supported by the results for weight loss and UV affected depth in Fig. 4, the affected depth decreasing as the filler percentage increased.

4. Microstructure

The microstructure of surface of F0, F20, F40 and F60 samples was observed under SEM (see Fig. 7). As show in Fig. 7, control samples F0 and F20 exhibited a denser microstructure with smaller pore sizes than its F40 and F60 counterpart, which had larger pores and a weak interfacial bond between the resin and fillers due to voids and pores in the matrix. Khotbehsara et al. [25] suggested that such voids and pores could reduce the flexural properties of highly filled polymer coatings compared to neat epoxy. Comparison of the un-conditioned and HG-conditioned F0 samples shows that the unconditioned samples had a more compact but relatively rougher surface because more pores were created at the surface when water molecules penetrated the mix. Columns 3 and 4 show that the exposure to UV and HG + UV conditioning caused surface microcracks (indicated by arrows) in the polymer coating. This result agrees with the flexural tests, in which the specimens exposed to UV and HG + UV exhibited significant brittleness and reduced strength due to a loss of moisture. Close inspection

revealed that the exposure of F40 and F60 to HG, UV, and HG + UV conditioning improved the interlock between the resin and fillers (indicated in red circles) compared to the control specimens (Column 1), despite the creation of microcracks after UV exposure. The first column in Fig. 7 shows that the surface of the unconditioned F40 and F60 sample had a two-phase morphology of isolated spherical particles (FA and FR) and a rigid continuous phase (resin). The dense microstructure after 2000 hrs of UV exposure and HG conditioning could be due to a post-curing effect of UV and HG conditioning at 60 °C; this is also shown by the increase in *T_g* of the conditioned samples. The high temperature during conditioning increased the mobility of the epoxy resin and created a better interlock with fillers, which confirms the mechanism of HG-conditioned samples having higher flexural strength than their control counterparts.

5. Quantifying the influence of exposure condition and filler content with ANOVA

Analysis of variance (ANOVA) was used to determine the influence of the exposure conditions and filler content on the flexural strength of the particulate-filled epoxy polymers with SPSS statistical analysis software [45–48]. Separate analyses were run for

Mix	Environmental condition			
	Control	HG	UV	HG+UV
F0				
F20				
F40				
F60				

Fig. 7. SEM micrographs of epoxy polymers.

Table 3
Pairwise comparisons and determination of the level of influence with SPSS.

Multiple Comparisons		Mean Difference				Significance (p-value)			
		0	20	40	60	0	20	40	60
% filler									
Control	HG	-0.81	-1.65	-13.32*	-16.24*	0.992	0.894	0.003	0.000
Control	UV	39.57*	15.06*	-21.06*	-27.53*	0.000	0.001	0.000	0.000
Control	HG + UV	43.78*	17.19*	-20.04*	-24.90*	0.000	0.000	0.000	0.000
HG	UV	40.38*	16.71*	-7.74*	-11.29*	0.000	0.001	0.043	0.001
HG	HG + UV	44.59*	18.85*	-6.73	-8.66*	0.000	0.000	0.077	0.003
UV	HG + UV	4.21	2.14	1.02	2.63	0.429	0.747	0.956	0.225

*The mean difference is significant at 0.05.

each filler content (0%, 20%, 40%, and 60%) and exposure condition (unconditioned control and HG, UV, or HG + UV conditioning). Table 3 provides the results of the one-way ANOVA (multiple comparisons in accordance with Tukey's post-hoc analysis).

Table 3 presents the multiple comparisons and evaluates the level of influence based on flexural strength. The mean difference or a p-value below 0.05 marked with an asterisk indicates a statistically significant difference in pairwise comparisons. The mean difference is the difference in mean value between the two environments. The HG conditioning positively affected flexural strength when the filler content was 40% or 60%, as demonstrated by p-values of 0.003 and 0.000 for samples F40 and F60, respectively (which are below 0.05). On the other hand, regardless of filler content, the UV and HG + UV conditioning significantly affected the flexural properties. Although the environmental conditions negatively (+ve mean difference) impacted the flexural properties at filler contents of 0% and 20%, it has a positive impact (-ve mean difference) at filler contents of 40% or 60%. The mean differences were -21.06 and -27.53 after UV exposure, and -20.04 and -24.90 after UV + HG for F40 and F60, respectively. This result also indicates that the average strength of the conditioned samples at UV were 21.06 MPa and 27.53 MPa higher than that of the controlled sample. On the other hand, the average strength of the conditioned samples at UV + HG were 20.04 MPa and 24.90 MPa higher in F40 and F60, respectively. The highest mean differences (compared to the control samples) were obtained for the combined effect of HG and UV conditioning for resin-rich mixes (up to 20% filler content), indicating the highest decrease of flexural strength. An interesting observation is that the combined effect of HG and UV conditioning is not statistically the sum of their individual effects in any of the mixes. Fig. 6c shows that F0 and F20 samples had similar behavior but differed from F40 and F60. After HG conditioning, the resin-rich samples retained their flexural strength, while UV exposure dramatically decreased it. On the other hand, filler-rich samples experienced a significant increase of flexural strength after HG conditioning or UV exposure. This trend decreased slightly when the samples were subjected to the synergistic effect of HG and UV conditioning, nevertheless, their flexural strength was much higher than that of the control samples. The high flexural strength might be due to the fillers have properties that resist UV and absorb heat that preserve flexural strength at high levels of filler content. This can be further explained by the fact that the impact is considered statistically significant at a p-value of less than 0.05.

6. Conclusion

This research assessed the physical, mechanical, thermomechanical, and microstructural characteristics of epoxy-based polymer coatings with different percentages of fly-ash and fire-retardant fillers. The coatings were exposed to hygrothermal (HG), solar UV radiation (UV), and combined hygrothermal and

UV (HG + UV) environments. The following conclusions can be drawn from this study.

- The resin-rich polymer coatings (F0 and F20) evidenced noticeable yellowing when exposed to UV or UV + HG conditioning, while fading was barely noticeable with the filler-rich coatings (F40 and F60). This is due to the dark pigments provided by the fly ash, which made the matrix less transparent.
- The depth of the degraded surface of the polymer coating exposed to hygrothermal conditioning, UV radiation, or a combination of the two decreased with the addition of fillers, which provided a protective layer against exposure to severe environmental conditions. The rate of degradation for polymer coatings with fillers was three times slower than the resin-rich coatings.
- The glass transition temperature at the exposed surface was lower than the inner portion of the polymer coating, suggesting the damaging effect of hygrothermal and solar UV radiation. The T_g measured in the surface was at least 5 °C lower than the inner part of the polymer coating HG conditioning and up to 13 °C lower when exposed simultaneously to both UV and HG conditioning.
- Environmental conditioning had different effects on the failure behavior of the coatings. Hygrothermal conditioning had no significant effect on the coatings, which failed in a similar way to the unconditioned specimens. Exposure to UV radiation or combined HG and UV conditioning rendered the coatings brittle. The coatings eventually failed with a large vertical mid-span crack.
- The flexural properties of resin-rich polymer coatings (F0 and F20) were unaffected by hygrothermal conditioning but were significantly reduced when exposed to UV or HG + UV conditioning. In contrast, exposure to different environments improved the flexural properties of the coatings with fillers due to the post-curing effect, resulting in better interfacial strength between the matrix and fillers. The dark color of the fillers acted as protective layers minimizing UV penetration, which affected only the very thin surface of the coatings.
- SEM images show that the exposure of particulate-filled epoxy polymer to HG conditioning improved the interlock between the fillers and the resin, while UV exposure caused surface microcracking. These microcracks became wider with HG + UV conditioning than with UV exposure, due to more moisture being expelled from the coatings.
- ANOVA analysis shows that HG conditioning increased the flexural strength of the coatings with at least 40% filler content but did not statistically affect the flexural strength of resin-rich samples (F0 and F20). On the other hand, UV and UV + HG environmental conditions negatively impacted the flexural properties of epoxy-based polymer coating with up to 20% filler but enhanced the flexural strength when the filler content was above 40%.

The findings herein provide a good representation and comparison of the long-term properties and durability performance of particulate-filled epoxy polymer structural coatings in different harsh environments. It is interesting that not all environmental conditions are detrimental to the properties of particulate-filled epoxy, indicating the suitability of this material as a protective coating for fiber composites and other construction and building materials. Further studies are, however, needed, such as increasing the exposure time beyond 2000 hrs to clearly assess the long-term properties and durability of novel polymer-based coating materials, and to evaluate their suitability in civil-engineering applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Chapter 7

Conclusion

Epoxy-based polymers are currently applied as protective coatings to minimise the environmental effects on the properties of fibre composites and other construction materials. Recently, different particulate fillers were introduced to reduce the cost of epoxy-based polymers. While the optimum amount of fillers was found to enhance the short-term properties of epoxy-based polymers, their effect on the long-term properties is still unknown. This study focused on understanding the single and synergistic effects of different weathering conditions such as high moisture, elevated in-service temperature and solar ultraviolet (UV) radiation on the long-term performance and durability of the particulate-filled epoxy-based polymer coating with hydrated alumina powder and fly ash as fillers. Extensive experimental investigations were implemented to systematically evaluate the effects of these harsh environmental conditions on the physical, mechanical and microstructure behaviour of epoxy based polymer coating. The major findings from this work are presented in the succeeding sections.

7.1. State-of-the-art review on the durability of epoxy-based polymer

The applications of epoxy-based polymers in civil engineering are now increasing. In this application, epoxy based polymers are exposed to different environmental conditions which affects their long-term durability properties. Although a number of studies have focused on the effects of harsh environments on the properties of polymeric materials, most of them have evaluated the materials resistance exposed to one weathering condition. In service, particulate-filled epoxy-based polymer coating

through their outdoor applications are generally exposed to different types of environment. The major findings from this study can be drawn as follows:

- Epoxy-based polymers have sparked a growing interest in civil engineering owing to their mechanical strength and great resistance to chemical aggression. These materials are now extensively used as protective coatings, wherein they are exposed to high moisture, in-service temperature and solar ultraviolet (UV) radiation.
- The ingress of moisture can weaken polymeric materials as they react with the polymer matrix or impose internal stress, which can reduce overall mechanical properties. When moisture penetrates the resin it can weaken the Van der Waals force between polymer chains, which can lead to a significant decrease in bond strength.
- The application of epoxy resin is limited by their inherent flammability. When the polymers exposed to high temperature the matrix will soften, and this can cause distortion, buckling and failure of load-bearing structures. Fire retardant fillers like ATH, MH, and, to a lesser extent, hydromagnesite/huntite mixtures are used in resin. The heat capacity of these fillers and, in particular, the strong endotherm can strongly influence the input of heat required for polymer decomposition and release of combustible volatiles. At sufficiently high filler levels, hydrated fillers can also reduce the mass burning rate by inhibiting the rates of heat transfer from the flame to the underlying matrix.
- Combined moisture and temperature (hygrothermal) may result in additional weight gain and faster diffusion of water of polymeric materials. Prolonged hygrothermal ageing can lead to irreversible damages of the resin such as

oxidation, microcavity growth, cracking and debonding, and polymer network relaxation.

- The photo-oxidative reaction caused by exposure to solar UV radiations reduces the molecular weight, breaks the polymeric chains and makes the polymer more brittle. Solar UV radiation also effects on the physical and mechanical properties of epoxy polymers.
- The addition of filler materials such as fly ash (FA), fire retardant (FR) fillers, hollow microsphere (HM), and silica can improve certain physical and mechanical properties and at the same time, reduce the cost of epoxy-based polymer matrix and provide environmental benefits. Particulate fillers also increase the heat resistance of polymers.

From the review of related literature, the addition of optimal amount of fillers can enhance the physical and mechanical properties of epoxy polymers. As a coating material, epoxy polymers are exposed to harsh environmental conditions. Thus, a detail understanding of the long-term durability properties of epoxy-based polymer coating with fillers is important and requires systematic investigation.

7.2. Effect of elevated in-service elevated temperature

The effect of in service elevated temperature (room, 40, 50, 60 and 80°C) on the physical, mechanical and microstructure of particulate-filled epoxy polymers with FA and FR was investigated. The density, porosity DMA, TGA/DSC, compressive strength, split tensile strength, SEM and FTIR were conducted. The major findings of this study can be drawn as follows:

- Density of polymer mixes increased with the addition of fillers, as FA and FR fillers had higher density than neat epoxy. The size and number of pores of the

particulate-filled epoxy-based polymer resin decreased with increasing temperature due to softening of the epoxy resin.

- The increase in the filler improved the matrices thermal properties and help retained the mechanical properties at in-service elevated temperature due to the high thermal stability of particulate fillers. A retention of compressive and tensile strengths by up to 72% and 52%, respectively for F60 at 80°C.
- The addition of particulate fillers led to formation of dense microstructures of epoxy polymers at high temperatures. This resulted in higher compressive and split tensile strength retention in epoxy with fillers under elevated temperature.
- The FTIR revealed a restrictive stretching with the addition of fillers up to 60%. All of the functional group had the same peak values , which shows the in-service temperature, did not lead to significant changes in the spectra of epoxy-base polymers.
- The developed simplified prediction equation based on power function predicted reliably the mechanical properties of the epoxy resin system with different percentages of particulate fillers at in-service elevated temperatures. Comparison between the predicted values and experimental results showed a strong correlation and the coefficient of correlation is at least 0.72.

The results from this study showed that the sensitivity of epoxy resin against in-service temperatures can be significantly improved by the inclusion of particulate fillers. Along with elevated in-service temperature, hygrothermal environment is identified as another factor that can affect the long-term behaviour of epoxy polymer matrix.

7.3. Effect of combined high moisture and in-service elevated temperature

The effect of combined moisture and elevated temperature (hygrothermal conditioning) on the durability and long-term performance of particulate filled epoxy resin was investigated. Samples with different filler content were exposed to 1000, 2000 and 3000 h at a temperature of up to 60°C and a relative humidity of 98%. The physical, mechanical, thermo-mechanical and microstructural properties of the epoxy-based polymer coating was then evaluated. The following conclusions can be drawn out of this study:

- The addition of particulate fillers reduced the water uptake of epoxy resin at high temperatures after hygrothermal conditioning. The smaller weight gain at higher temperatures can be related to higher crosslinking density between the epoxy matrix and fillers resulting in less free volume.
- Hygrothermal conditioning promoted the post-curing and increased the glass transition temperature (T_g) of the particulate filled epoxy-based polymers. At least a 5°C increase in T_g was measured with the introduction of 60% fly-ash and fire retardant fillers.
- Hygrothermal conditioning changed the failure behaviour of particulate filled epoxy resin from brittle to semi-ductile in both compression and splitting tensile. Moreover, less than 10% reduction in compressive and tensile strength was observed due to the post-curing of the resin at the initial stage of the hygrothermal conditioning. The flexural strength was significantly improved at the early stage of hygrothermal conditioning and increased the flexibility of the polymers due to the better interlocking between resin and fillers.
- SEM revealed an increased density of epoxy resin with the addition of particulate fillers. Hygrothermal conditioning also had some minor effects of the chemical composition of particulate filled epoxy. FTIR analysis showed the

presence of C–H and C–O in major phases for all specimens, with restrictive stretching in the epoxy polymers due to the addition of particulate fillers.

- Based on the Arrhenius model, the particulate filled epoxy polymers are expected to retain more than 70% of their mechanical properties after 100 years of service in the Australian summer environment.

The results of this study highlighted the beneficial effects of adding particulate fillers in improving the long-term properties of epoxy-based polymers exposed to moisture and elevated temperature. An understanding of the performance of this coating material when exposed to the photochemical reactions from solar UV radiation is also necessary and is investigated next.

7.4. Effects of solar ultraviolet (UV) radiation

The effect of the photochemical reactions from solar ultraviolet (UV) on the durability of particulate-filled epoxy resin coating was investigated. Epoxy-based resin systems containing up to 60% by volume of fire retardant and fly-ash were exposed under 1000 and 2000 h of UV at a temperature of 60°C using a Xenon arc lamp. This exposure condition produces an output that could easily equate to approximately 5 years of UV exposure in the Australian environment. The physical, mechanical, thermo-mechanical and microstructural properties of these coating systems were evaluated. Based on the results of this study, the following conclusions can be drawn.

- The addition of hydrated alumina powder and fly ash significantly improved the UV resisting properties of epoxy resin. Adding up to 60% by volume of these fillers affected only 0.5 mm of the surface of the coating after 2000 h UV exposure, which is 5 times less than that of the neat epoxy resin. The presence

of particulate fillers also reduced the discolouration compared to the neat epoxy resin where the surface became yellowish in colour.

- Exposure to UV changed the failure behaviour of the particulate filled epoxy polymers from ductile to brittle. This also decreased the flexural strength of neat epoxy resin by almost 40% but increased the strength of highly filled epoxy resin mix by 300%.
- The fillers minimised the UV effect on the T_g of epoxy based polymer coating. The reduction of T_g at the exposed surface of the coating with fillers is only 3°C lower than the inner part but up to 15°C lower for resin rich epoxy polymers.
- The particulate fillers reduced the surface degradation of polymer coating by blocking the penetration of UV radiation. SEM images showed the creation of micro-cracks in neat resin but an improved interlocking between the fillers and epoxy resin and a dense microstructure in particulate filled epoxy resin after exposure to 2000 h of UV radiation.
- UV affected only the thin surface of the epoxy-based polymer coating with fillers and there were no signs of chemical changes beyond the affected depth. FTIR analysis showed stronger carbon-hydrogen and carbon-oxygen bonds for particulate filled resin than neat epoxy resin after exposure to UV radiation.
- A thickness of at least 6 mm of epoxy-based coating with 60% by volume particulate fillers is required to provide protection from UV radiation for 50 years. This thickness is only 20% of the required thickness if neat epoxy resin is used as a coating material in outdoor applications.
- The significant reduction of required thickness for filled coating system is due to the particulate fillers blocking the penetration of UV radiation and reducing the surface degradation of the polymer coating.

In actual environment, moisture, elevated temperature and solar UV radiation are acting at the same time and affecting the properties of epoxy-based polymer coatings. The synergistic effects of these environmental conditions are investigated.

7.5. Synergistic effects of temperature, moisture and UV radiation

The synergistic effects of UV solar radiation, moisture and in-service temperature on the thermal, mechanical and physical properties and microstructure of particulate-filled epoxy-based polymer coating were investigated in terms of physical properties including discoloration, affected depth and weight loss, thermo-mechanical and flexural properties, microstructure via SEM observations, and also the functional groups using FTIR. The following conclusions can be drawn out of this study:

- Neat epoxy resin showed yellowing on the surface after hygrothermal and UV exposure but the presence of fillers minimised fading and weight loss. The latter was due to the black pigments provided by the fly ash which made the matrix less transparent.
- The rate of surface degradation for polymer coating with fillers is three times slower than those with resin rich coating systems. Exposure to hygrothermal conditioning, UV radiation and a combination of the two affects the exposed surface of filled epoxy resin at a rate of around 0.0004 mm/hr while the rate of surface degradation for neat resin is 0.0014 mm/hr.
- The glass transition temperature at the exposed surface was lower than the inner portion of the polymer coating, suggesting the damaging effect of hygrothermal and solar UV radiation. The measured T_g in the surface was at least 5°C lower than the inner part of the polymer coating when conditioned in

HG, and up to 13°C lower when exposed simultaneously to both UV and HG environments.

- Environmental conditioning had different effects on the failure behaviour of polymer coating. Hygrothermal conditioning had no significant effect on polymer coating and failed in a similar way to unconditioned specimens while exposure to UV and combined HG and UV made the polymer coating brittle. The polymer coating eventually failed, with a large vertical crack at the midspan of the samples. This brittle behaviour can be attributed to the micro-cracks in the surface of the specimens caused by the photo-oxidation during UV exposure and loss of moisture
- Exposure to different environments improved the flexural properties of polymer coating with fillers due to the post curing effect, resulting in better interfacial strength between the matrix and the fillers. In contrast, the flexural properties of resin rich polymer coating were not affected by the hygrothermal conditioning but were significantly reduced when exposed to UV and combined hygrothermal conditioning and UV.
- SEM images showed that the exposure of particulate filled epoxy polymer to hygrothermal conditioning improved the interlocking between the fillers and the resin. The post curing of the matrix also helped to retain the flexural strength. On the other hand, exposure to UV and combined hygrothermal conditioning and UV caused micro-cracking on the surface due to the expulsion of moisture in the polymer coating.
- All of the functional groups of epoxy-based polymer coating exposed to different environments had the same peak values except for some shifting of

bands and fluctuations in intensity, indicating that there is no or very minimal change in the functional groups of the particulate filled polymer coating.

- ANOVA analysis showed that hygrothermal conditioning increased the flexural strength of polymer coating with at least 40% of fillers but did not statistically affect the flexural strength of resin-rich samples. On the other hand, exposure to UV and combination of UV and hygrothermal conditioning negatively impacted the flexural properties of epoxy-based polymer coating with up to 20% filler but enhanced the flexural strength when the filler content was above 40%.

From the results of this study, it was found that not all environmental conditions are detrimental to the properties of particulate filled epoxy, indicating the suitability of this material as a protective coating to fibre composite and other construction and building materials. However, a longer exposure time to these environmental conditions will help verify this finding. Other opportunities and future research on the further understanding on the synergistic effects of different environmental conditions on durability and long-term performance of particulate filled epoxy-based polymer coating are recommended in the next section.

7.6 New opportunities and future research

The effectiveness of the inclusion of fillers in improvements in durability of particulate filled epoxy resin as presented in this thesis demonstrates the potential to extensively investigate the behaviour of this coating material to provide a durable and reliable protecting for fibre composite and other construction and building materials. Based on the outcome of this research, opportunities and new research areas can be explored to further understand how the environmental parameters affect the durability of the

structures coated by this material. A well-defined understanding of this issue will enable the clear evaluation of the long-term properties and durability of novel polymer-based coating materials, and to evaluate their suitability in civil engineering applications as follows:

- The effect of hygrothermal conditioning and UV exposure on the durability of particulate filled epoxy-based polymers was evaluated at a maximum duration of 2000 hrs. New research areas can be explored to further understand how exposure time beyond 2000 hrs affects the durability of this material to clearly evaluate the long-term properties and durability of this novel polymer-based coating materials, and to evaluate their suitability as coating materials in civil infrastructure, which are typically designed to have a 100-year service life. Moreover, in this study due to time limitation of PhD program and accessing to one environmental chamber the experimental work was conducted on the samples conditioned to hygrothermal environment where the effect of wet and drying was not evaluated. Further studies can be conducted on the effect of various cycling including wet and dried cycling.
- In this study, the synergistic effects of hygrothermal conditioning and UV on the long-term performance of particulate filled epoxy polymers were evaluated by first conditioning the samples in an environmental chamber then exposing them to UV. New research can be conducted using equipment where the particulate filled epoxy polymers can be exposed simultaneously to these different weathering conditions.
- The contribution of epoxy polymer coating in long-term behaviour of civil structures was demonstrated. In this study, the durability of epoxy polymer coating when exposed to elevated service temperature, hygrothermal conditioning and UV exposure was investigated. Further research can be conducted in evaluating the

durability of a composite structure coated with the novel particulate filled epoxy resin for better understanding their overall long-term performance.

- New predictive models were developed to evaluate the long-term properties of epoxy-based polymers when subjected to individual environmental conditions. New predictive models that can accurately predict the long-term behaviour of the particulate filled epoxy polymer considering the synergistic effects of environmental conditions should be developed.
- This thesis focused on the long-term durability and thermal behaviour of the particulate filled epoxy polymers, in addition to their microstructure after exposure to high moisture, in-service elevated temperatures, UV, and a combination of these (temperature up to 80°C). Further study on temperature beyond 80°C or the fire resistance properties of polymer coating after exposure to these different environments should be examined to investigate their behaviour, particularly in relation to fire, which is considered to be a serious challenge faced by composite materials.
- In this study, the synergistic effects of hygrothermal conditioning and UV on the long-term performance of particulate filled epoxy polymers were evaluated following the industry procedure in manufacturing composite railway sleepers wherein no post-curing is preferred to minimise cost of production. Further study on post-cured samples can be conducted
- This thesis focused on using FR and FR as fillers to improve the durability of particulate filled epoxy resin. Using fillers with different particle sizes or shapes can be investigated to find out whether fillers that are in the shape of platelets would prove more effective than the spherical fillers used in this study. Moreover,

experimental work on the effect of conditioning on each filler separately can be conducted.

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Appendix A: Posters

A.1 Long term behavior of epoxy-based polymer matrix with fillers



**Centre for
Future Materials**

Researcher: Mojdeh Mehrinejad Khotbehsara
✉ Mojdeh.Mehrinejad@usq.edu.au

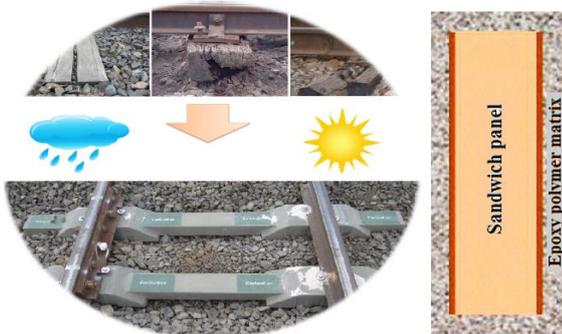
Long-term behaviour of epoxy-based polymer matrix with fillers

Supervisor: Prof Allan Manalo
Co-Supervisor: Prof Thiru Aravinthan



Introduction

- Epoxy-based polymers are now widely used in different civil applications like bonding and coating materials for structural elements, and infill for structural repair systems.
- Composite railway sleepers coated with epoxy polymer resin has been developed and trialled in actual railway.
- Epoxy polymer as a coating material are subjected to the weathering effects of moisture, heat, ultraviolet radiation (UV), and synergistic effects of these environments.



Study 2 – Hygrothermal conditions

Assessment of the physical, mechanical, thermal and microstructural properties of polymer-filled epoxy based resin and composites coated by epoxy matrix exposed to elevated temperature and moisture

- Hygrothermal environments: (RT, 40°C and 60°C at 98% RH)
- Fillers (0%; 20%; 40%; 60%)
- Duration: (1000, 2000 and 3000 hrs)



Study 3– UV

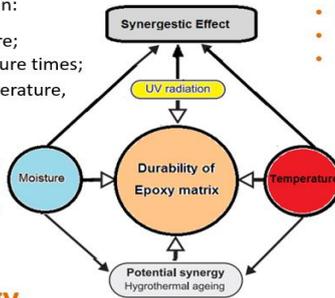
Investigation of the mechanical (compressive, split tensile and flexural strength), thermal (DMA and DSC), microstructural and chemical (SEM and FTIR) properties of epoxy based polymer matrix exposed to UV and moisture.

- Hygrothermal and UV chamber
- Fillers (0%; 20%; 40%; 60%)



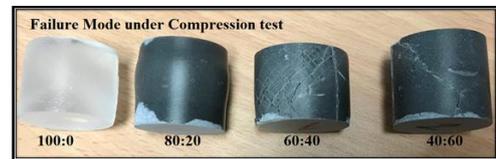
Research Objectives

- Investigate the physical, mechanical and microstructural properties of polymer-filled epoxy based resin:
 - exposed to elevated temperature;
 - at different hygrothermal exposure times;
 - under synergistic effect of temperature, moisture and UV.
- Predict the long-term properties of polymer-filled epoxy based resin when subjected to different environmental conditions.



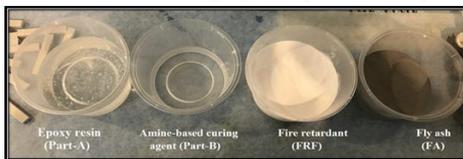
Research Result

- Effect of elevated in-service temperature**
- 40:60 epoxy resin/filler → The least affected by elevated temperature
- 60°C (100:0 and 80:20 epoxy resin/filler) → Dramatic drop in strength

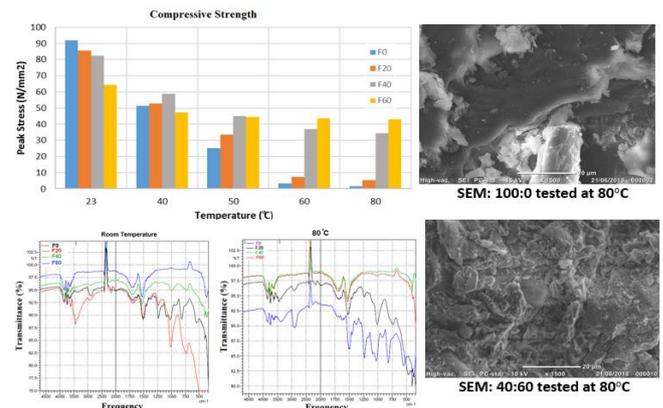


Research Methodology

- Study 1 – Effect of temperature**
- Physical property (density and porosity)
- Mechanical property (compressive and split tensile strength)
- Thermo-mechanical property (DMA and DSC)
- Microstructure and chemical properties (SEM and FTIR)



- Temperature (°C): RT, 40, 50, 60, 80
- Percentage of fillers % (0, 20, 40, 60)



FTIR analysis of epoxy resin with fillers at room and 80°C

On-going Works

- Durability and long-term investigation of epoxy coating and epoxy-coated composites: under moisture in different temperatures and exposure times, and under UV radiation
- Prediction of the long-term behaviour of polymer-filled epoxy based resin and epoxy bonded sandwich panels

A2. Long-term performance of particulate filled epoxy coating under hygrothermanl conditions

Long-term performance of particulate-filled epoxy coating under hygrothermal conditions

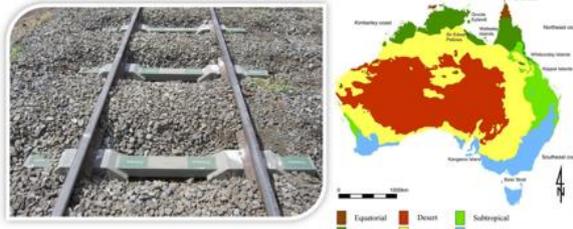
Researcher: Mojdeh Mehrinejad Khotbehsara
 ✉Mojdeh.Mehrinejad@usq.edu.au

Supervisor: Prof Allan Manalo
 Co-Supervisor: Prof Thiru Aravinthan



Introduction

- Epoxy-based polymers are widely used in civil applications including bonding and coating materials for structural elements and infill for structural repair systems.
- Epoxy polymer as a coating material is subjected to the weathering effects of moisture, in-service temperature and the synergistic effects of these environmental factors.



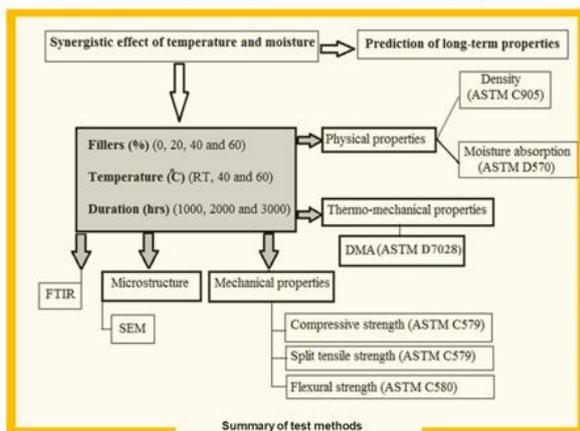
Composite railway sleepers coated with epoxy polymer resin trialled in an Australian railway track

Research Objectives

Investigate the physical, mechanical and microstructural properties of particulate-filled epoxy based resin under the combined effect of moisture and elevated temperature.

Predict the long-term properties of particulate-filled epoxy based resin when subjected to hygrothermal conditions.

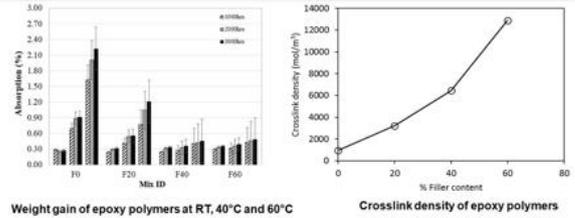
Research Methodology



Research Result

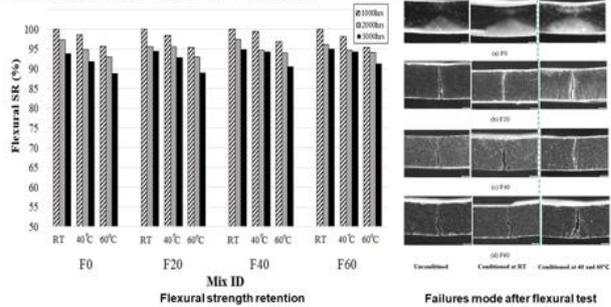
Effect on physical properties

Particulate fillers reduced the water uptake of epoxy resin at high temperatures due to increase in crosslink density.



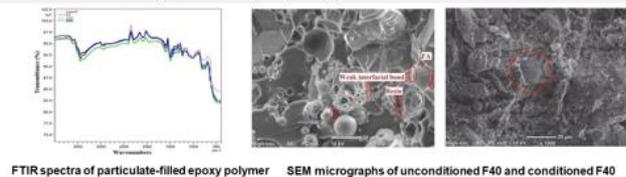
Effect on mechanical properties

- Failure mode of particulate-filled samples changed from relatively rigid to more flexible.
- Up to 70% flexural strength retention.



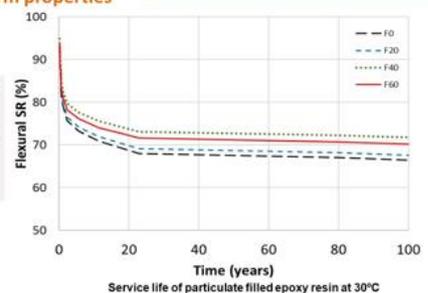
Effect on microstructure

- Fillers make the mix with a dense microstructure at hygrothermal conditions.
- No chemical changes in the epoxy at hygrothermal conditions.



Prediction of long-term properties

Particulate filled epoxy polymers will retain almost 70% of the flexural strength after 100 years.



Conclusion

- Hygrothermal conditioning promoted the post-curing and increased the T_g .
- Hygrothermal environment improved the interlocking between the fillers and resin and increased the density of the section mode.
- Particulate filled epoxy polymers can retain more than 70% of the mechanical properties after 100 years of service.
- Particulate filled resin is a suitable coating material for civil infrastructure to protect it from the adverse effects of moisture and elevated temperature.

Appendix B: Conference papers

B1. ACCM-11 (2018)-Australia

ORAL PRESENTATION

CIVIL AND INFRASTRUCTURE APPLICATIONS

EFFECT OF ELEVATED TEMPERATURE ON THE PROPERTIES OF EPOXY-BASED POLYMER COATING

Mojdeh Mehrinejad Khotbehsara¹, Allan Manalo¹, Thiru Aravinthan¹ and Kate T. Q. Nguyen²

¹ University of Southern Queensland, School of Civil Engineering and Surveying, Centre for Future Materials, Toowoomba, Queensland 4350, Australia (Corresponding author: Mojdeh.Mehrinejad@usq.edu.au)

²The University of Melbourne, Department of Infrastructure Engineering, Victoria 3010, Australia

Keywords: Epoxy resin matrix; Composite; Temperature; Filler

ABSTRACT:

Epoxy-based polymer resins are being used as coating for civil composites like railway sleepers. In this application, the composite sleeper is exposed to harsh environmental conditions, including elevated temperature, particularly in the summer season. As the epoxy based polymer resin coats the sleepers, this material is the one directly exposed to elevated temperature. However, its properties when subjected to this type of in-service environment is not yet been properly understood. This study investigated the effect of a range of in-service temperature (ranging from 23°C to 80°C) on the compression and tensile properties of epoxy resin with various percentages of lightweight filler materials (0%, 20%, 40% and 60%). The results showed that both the compressive and tensile strength properties of epoxy-based fillers decreased with increasing in-service temperature. However, the addition of lightweight fillers helped in retaining the mechanical properties of epoxy-based resin at high level of temperatures. The epoxy-based resin with 40% fillers was the least affected by the increase in temperature.

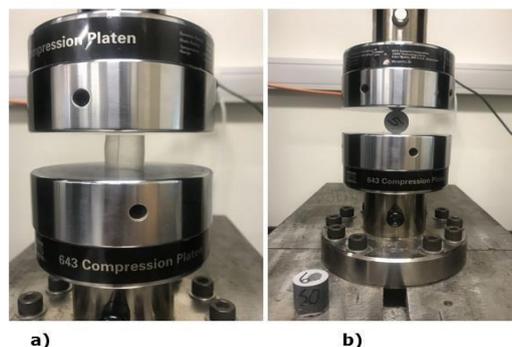


Figure 1: a) Compressive Strength and b) Split Tensile of solid polymer matrices

Temperature resistance of epoxy-based polymer coating with fly ash and fire retardant fillers for composite materials

Mojdeh Mehrinejad Khotbehsara^{1*}, Allan Manalo¹, Thiru Aravinthan¹

¹Centre for Future Materials (CFM), School of Civil Engineering and Surveying,
University of Southern Queensland, Toowoomba, Australia

* Corresponding author (Mojdeh.Mehrinejad@usq.edu.au)

Keywords: Epoxy resin, Filler, Mechanical properties, Microstructure

Abstract

Epoxy-based polymer resins are being used as coating for composite materials and structures like railway sleepers. In this application, the epoxy-based polymer coatings are exposed and subjected to different environmental conditions including in-service elevated temperature. However, understanding on the properties of epoxy-based polymer resins with fly ash and fire retardant fillers when subjected to this type of in-service environment is still limited. This study evaluates the effect of in-service elevated temperature (ranging from room temperature to 80°C) on the properties and microstructure of particulate-filled epoxy based resin containing up to 60% by volume of fire retardant and fly ash fillers. An improvement in mechanical properties retention at in-service elevated temperature was achieved by increasing the percentages of fillers. Moreover, thermo-dynamical analysis showed an increase in the glass transition temperature with inclusion of fillers. Scanning electron microscopy images showed the formation of dense microstructure for particulate-filled epoxy based resin at elevated temperature. This indicates that the particulate filled epoxy-based polymer coating exhibits better engineering properties against in-service elevated temperature thereby increasing the durability of the coated composite materials.