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

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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^{o}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^{o}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

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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.

Keywords: Epoxy resin; particulate fillers; in-service elevated temperature; mechanical properties; microstructure; prediction model.

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^{o}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 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 to 480 hours 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 Bărbuţă 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.

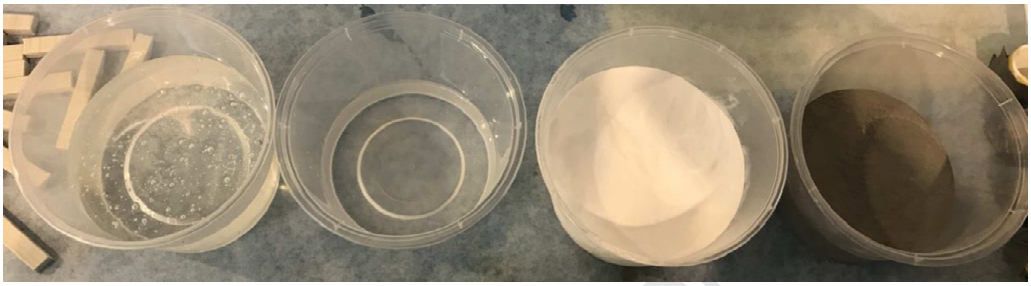
In this study, experimental investigations were conducted to determine the effect of in-service temperatures on the durability of particulate-filled epoxy based resin containing FA and FR fillers. It focuses on understanding the effect of in-service elevated temperature on physical, mechanical, and physico-chemical 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

Figure 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/cm^3 were used to mix with 32 g of Part-B with density of 1.182 g/cm^3 to maintain the mixing ratio. Two different fillers including FR (hydrated alumina powder) with a density of 2.411 g/cm^3 and FA with a density of 2.006 g/cm^3, 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

121 powder and fly ash have been used together [33, 34]. The FR used was non-toxic and had low
122 abrasiveness, chemical inertness, acid resistance, smoke suppression and electric arc
123 resistance, and was supplied by Huber Engineered Materials (HEM), while Cement Australia
124 Pty Ltd supplied FA. The fillers were round with a diameter of 0.1 to 30 µm for FA and 75 to
125 95 µm for FR [14].



126

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

128 **2.2.Mixture proportions**

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

139 **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

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 *Tg.* 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		5	5	5	5

(SEM)				
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×10 mm×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 [16]. In order to achieve the required test temperature, Instron 3119 environmental chamber mounted on a 100kN 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.

3.4.1 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.

3.4.2 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 400–4000cm-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

Figure 2 shows the hardened densities of all epoxy mixes. It can be 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 F40because 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 **(Figure 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.

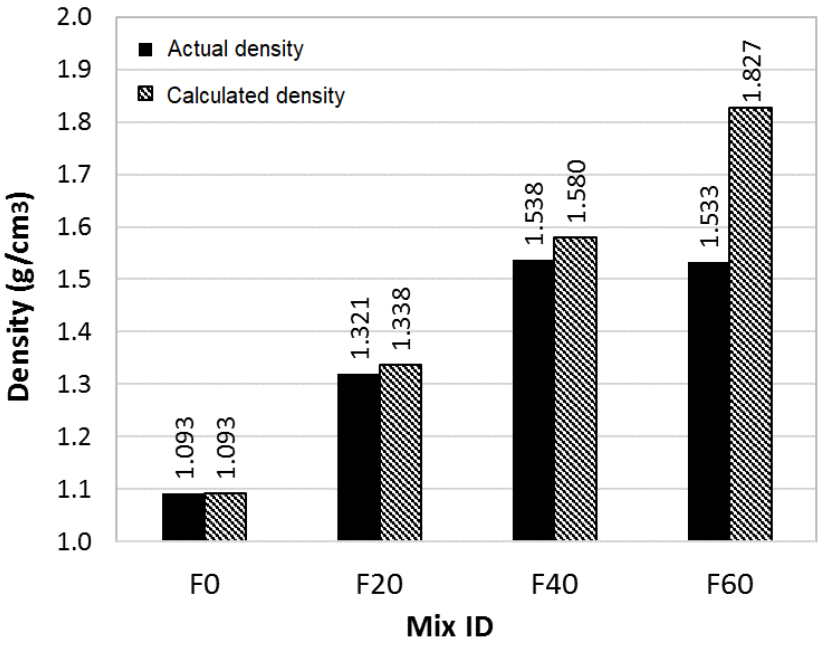
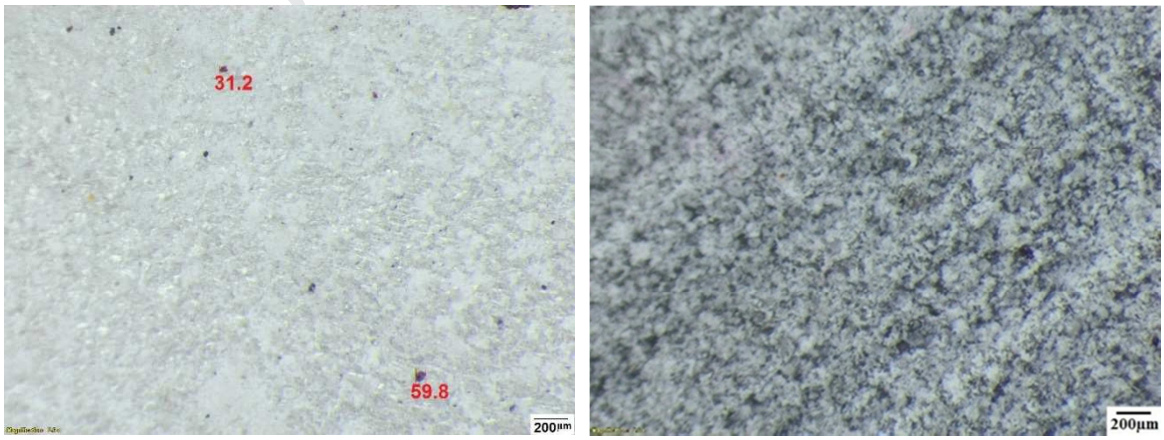


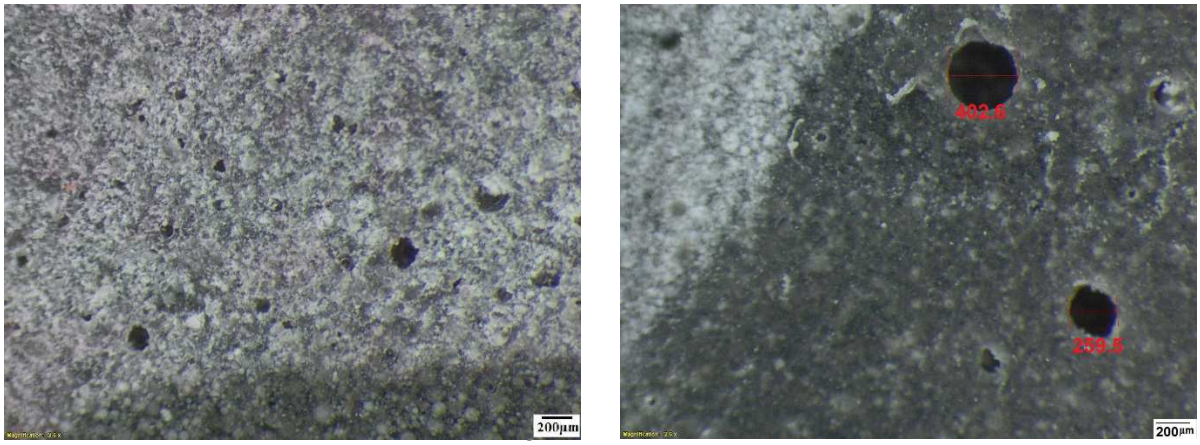
Figure 2: Density of different epoxy mixes

The variations in density of the particulate-filled resin can be explained by the measured porosity of the mix. **Figure 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 **Figure 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. **Figure 4** also shows the porosity of the surfaces of samples without fillers tested at 60^{o}C and 80^{o}C. Compared to **Figure 3a** which showed the porosity of the F0 at room temperature, it is obvious from **Figure 4a** that by increasing the temperature to 60^{o}C, the volume and size of the pores reduced. The size of the pores of F0 further reduced at 80^{o}C as shown in **Figure 4b** (from 60 µm at room temperature to 18µm at 80^{o}C). The trend was similar for F60 as can be seen in **Figure 5**, wherein the increase of temperature showed a significant decrease on the volume and size of the pores compared to that at room temperature **(Figure 3d)** (from 402µm at room temperature to 73µm at 80^{o}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.

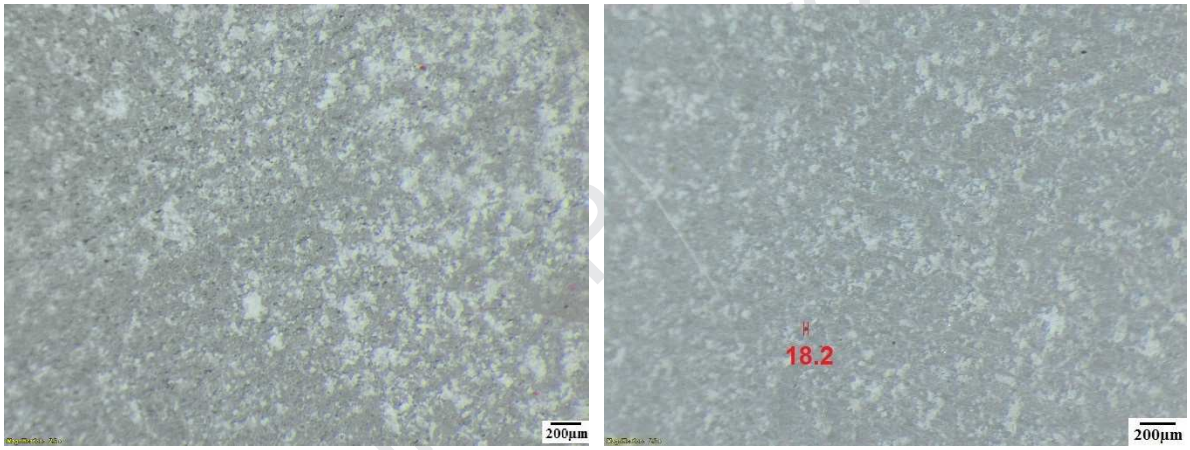


(a) F0 (b) F20



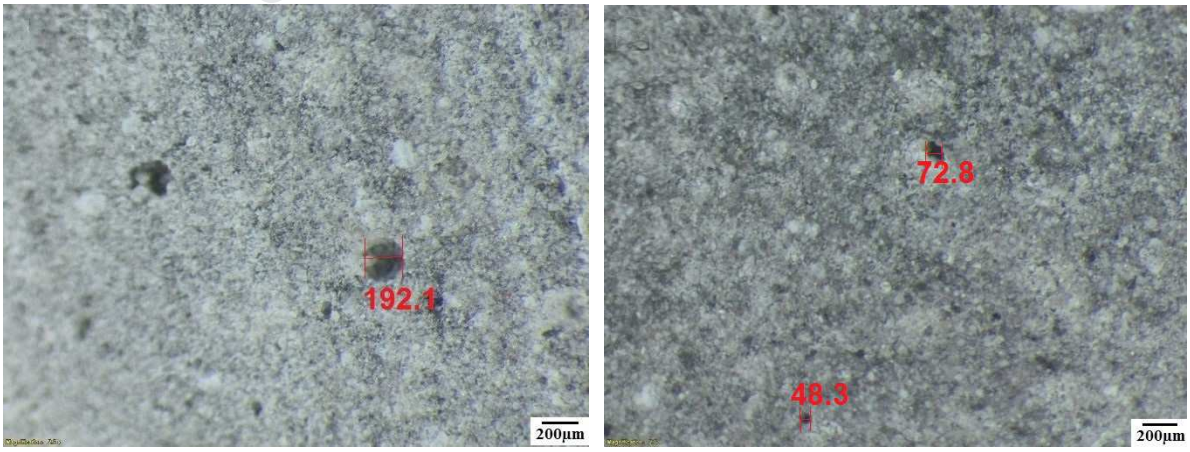
(c) F40 (d) F60

Figure 3: Porosity of epoxy based resin with different amount of fillers



(a) 60°C (b) 80°C

Figure 4: Porosity of F0 at elevated temperature



(a) 60°C (b) 80°C

Figure 5: Porosity of F60 at elevated temperature

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

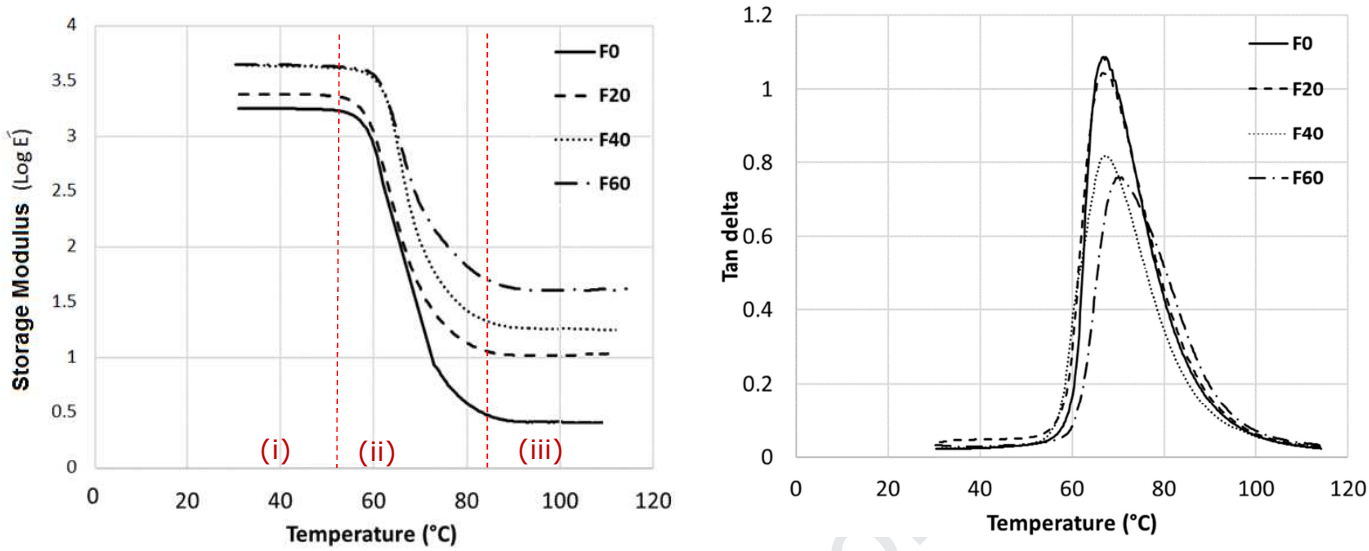
The effect of percentage of fillers and temperature on thermo-mechanical properties of the particulate filled epoxy resins was evaluated using the Dynamic Mechanical Analysis (DMA). In addition, the Simultaneous Thermal Analysis (SDT) was conducted to measure weight loss at elevated temperatures to characterise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

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

where T is the temperature (K) and R is the gas constant. As shown in **Figure 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.



(a) Storage Modulus (b) Tan delta

Figure 6. Variations in dynamic mechanical properties with temperature

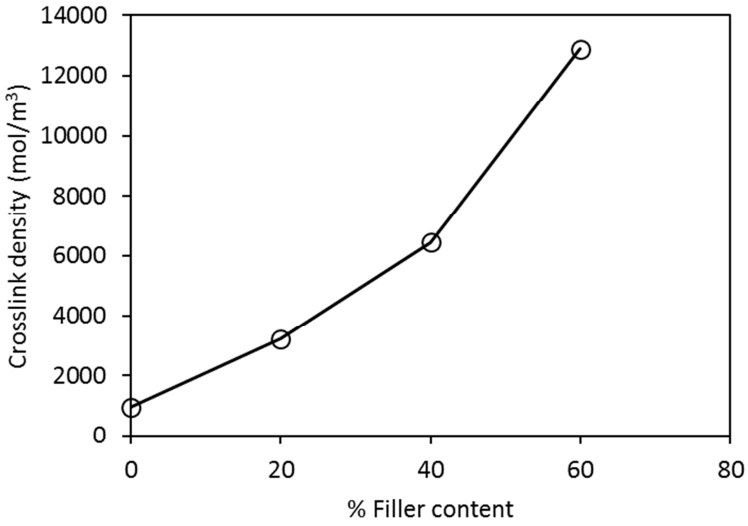


Figure 7. Crosslinking density of particulate filled epoxy polymer

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 usuallyapplied . Volatile degradation species that are 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 **Figure 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.

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

354

355 **4.3 Effect of percentage fillers and temperature on mechanical properties**

356 The mechanical properties of the epoxy-based polymer with different percentages of fillers
357 and at elevated temperature were assessed under compression and split tensile testing. **Table**
358 **4** summarises the results of the mechanical tests. In order to have a fair comparison of strength
359 among the mixes with different densities, the specific strength also has been provided. The values
360 listed within parentheses are the standard deviation of the test results.

361 **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	strength	Specific strength	strength	Specific strength	strength	Specific strength	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

362

363 **Figure 8** shows the typical failure mode of particulate-filled epoxy resin in compression at
364 elevated temperature. As shown in **Figure 8**, despite the creation of micro cracks, which were
365 not easy to see with the naked eye, specimens F0 and F20 were deformed without crushing
366 even after reaching their ultimate strengths **(Figure 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 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 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.

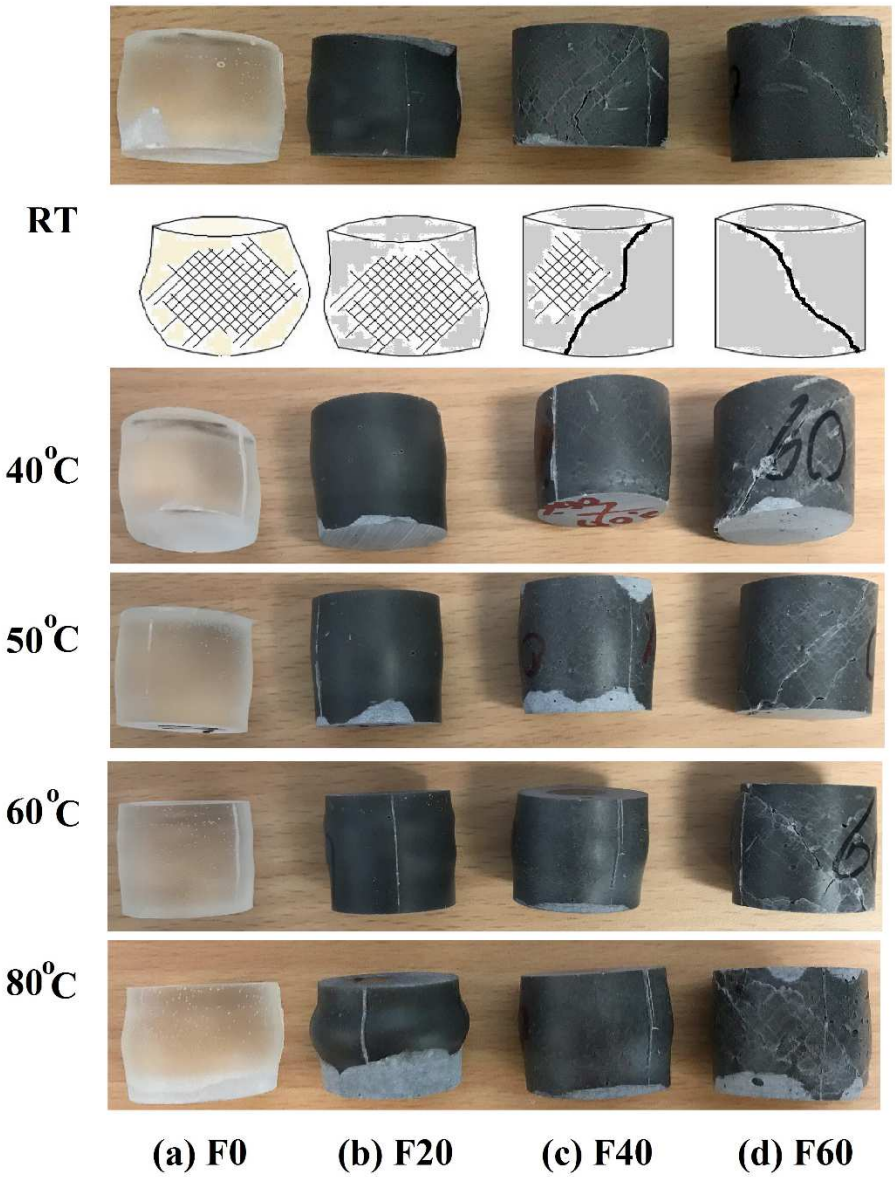
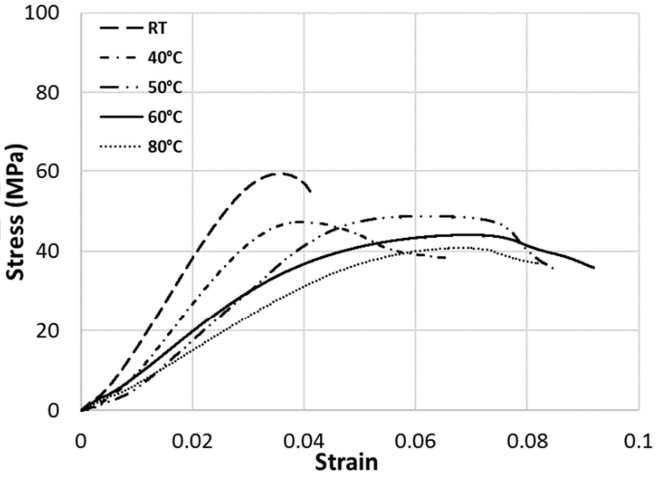


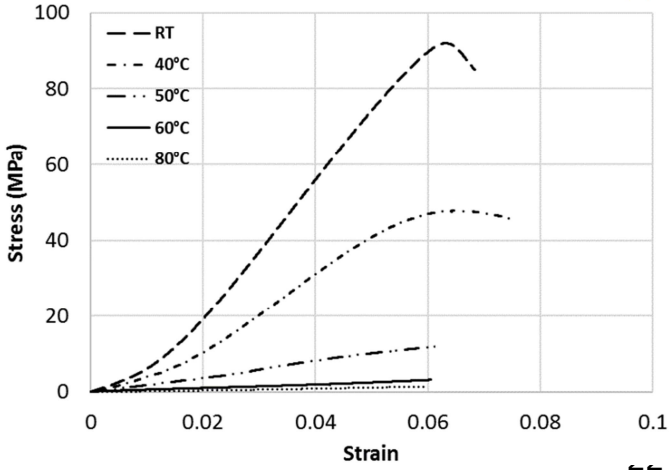
Figure 8: Failure modes of particulate-filled resin under compression at different temperatures

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 **Figure 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 **(Figure 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 **(Figure 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.

Figure 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 **Figure 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 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 **Figure 8**.





(a)

Figure 9: Compressive stress and strain behaviour at in-service elevated temperature

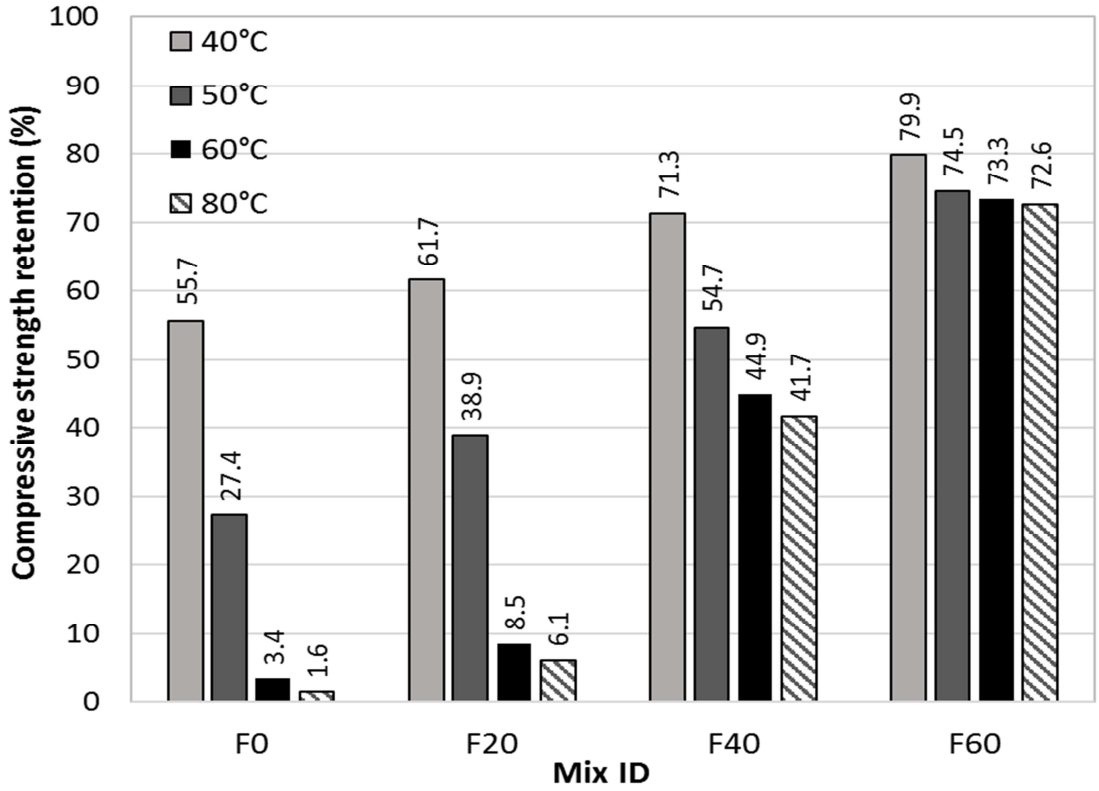
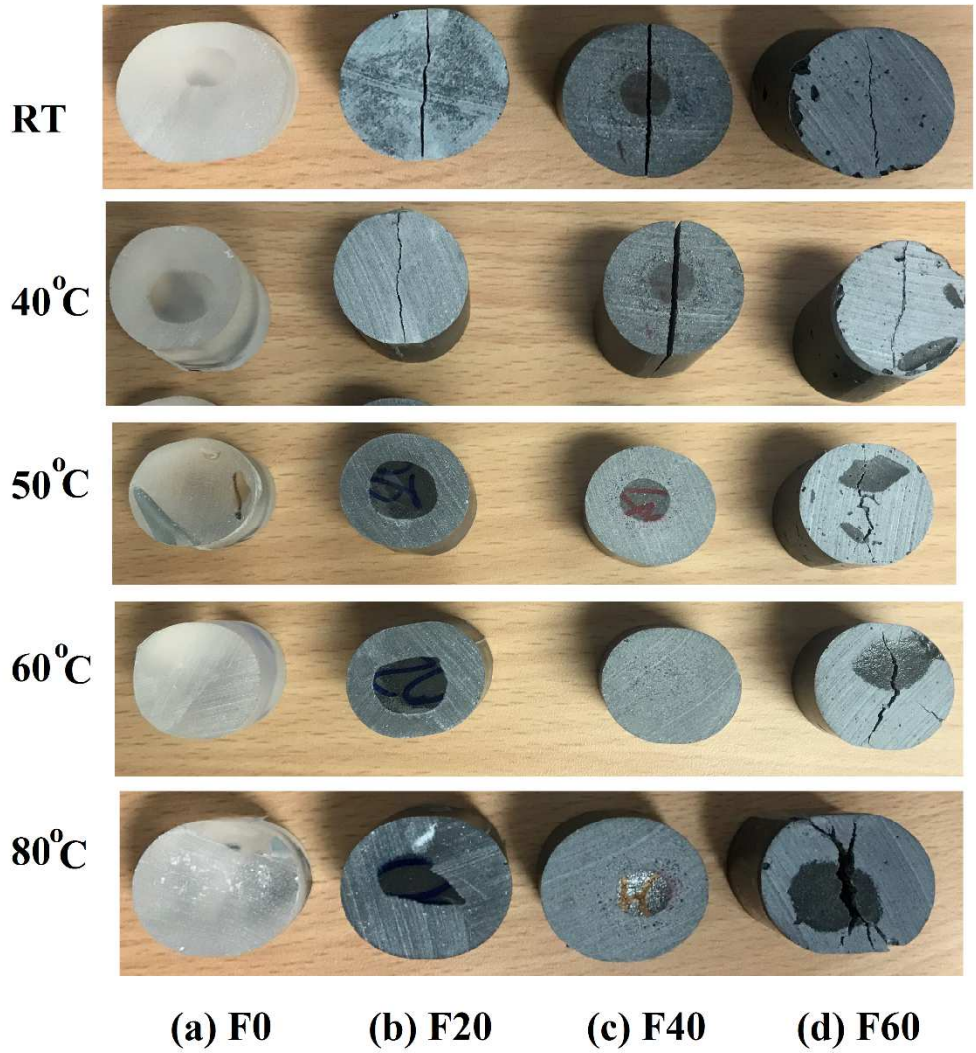


Figure 10: Compressive strength retention at in-service elevated temperature

Figure 11 shows the failure mode of various mixes after a splitting tensile test at room temperature and at the maximum temperature of 80 ºC. As can be seen in **Figure 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 ºC, 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

464 temperature of 80 ºC. The resin transfers stress however, as the temperature increased, caused
465 the resin to become malleable and soft, thus, better interlocking between resin and fillers was
466 achieved.

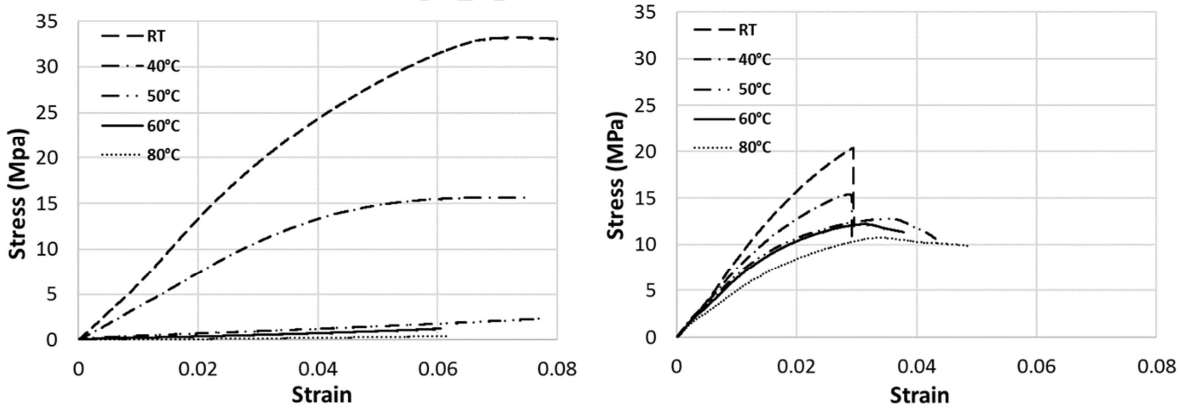


467

468 **Figure 11:** Failure modes of particulate-filled resin under tension at different temperatures

469 From **Figure 12,** stress-strain graphs show that at lower temperatures, F60 was completely
470 brittle, while F0 was ductile. Moreover, split tensile results at **Table 4** show the reduction of
471 strength with increasing filler volumes at room temperature due to gradual increases in the
472 amount of higher stiffness filler materials. This result is in agreement with the trend reported
473 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 80ºC, 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 ºC and 80 ºC. 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 tensile retention results given in **Figure 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 60ºC and 80ºC,. Resin-rich samples (F0 and F20) significantly lost their strength particularly after 60ºC. F0 experienced a significant reduction of 97% and 98% respectively in its strength at 60 ºC and 80ºC,.



(a) F0 (b) F60

Figure 12: Tensile stress and strain behaviour at in-service elevated temperature

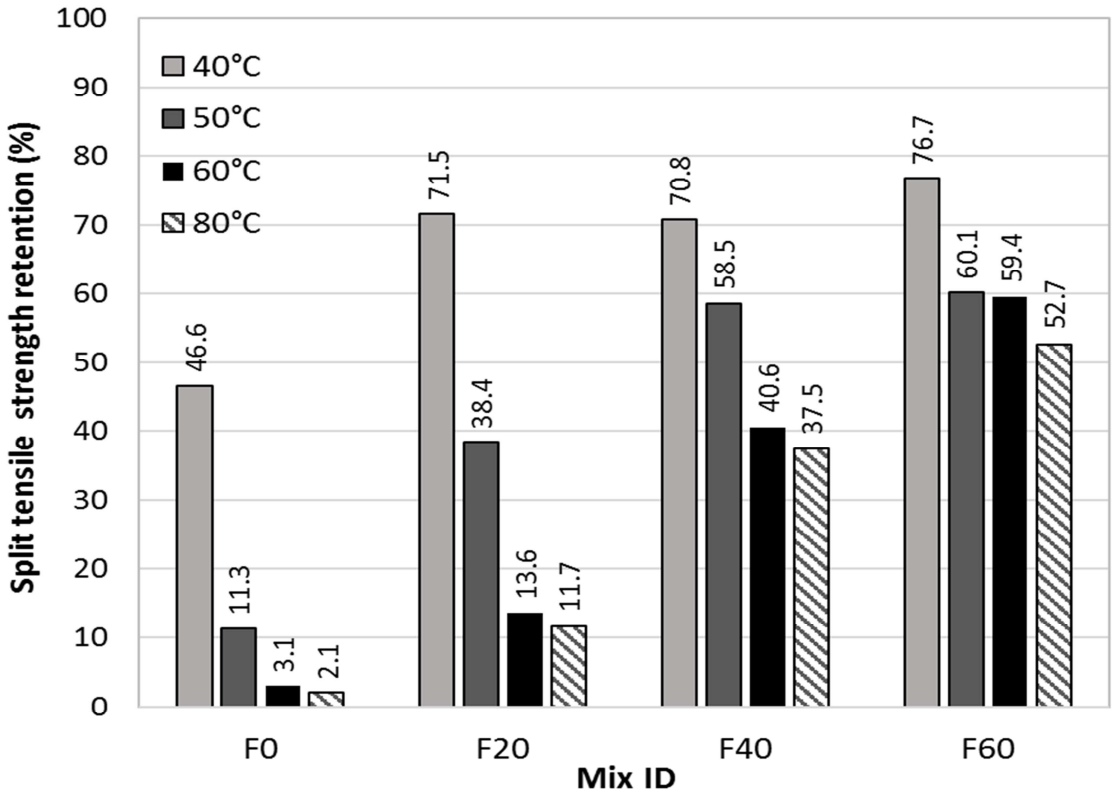


Figure 13: Tensile strength retention at in-service elevated temperature

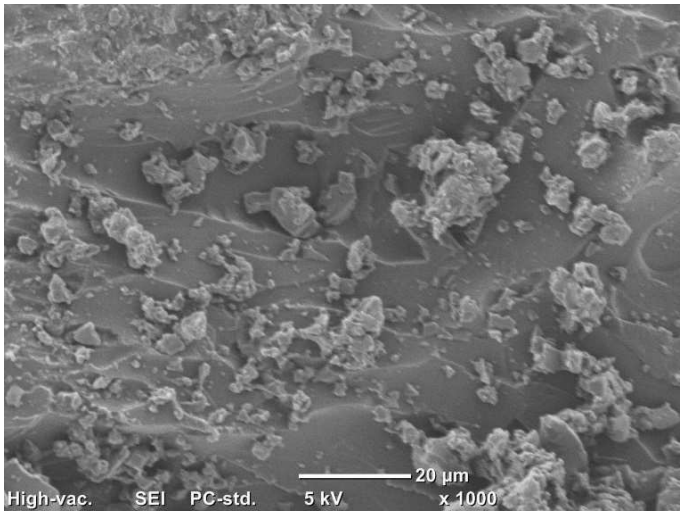
4.5 Microstructure of particulate-filled epoxy resin at elevated temperature

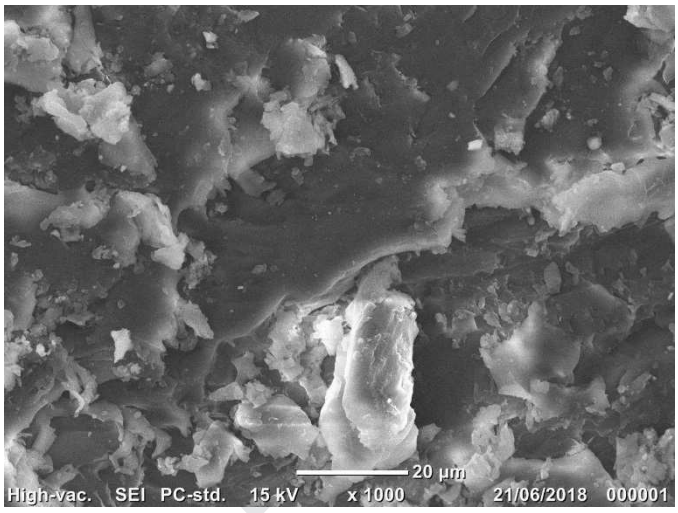
When materials are combined, their properties are governed not only by the characteristics of individual components, but also by the interface between them [48]. Moreover, the mechanical characteristics of a particulate filled polymer depend on the type of distribution of particles, which can be characterized 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 (**Figure 14**). Specimen F60 was chosen since it exhibited the highest property retention at 80^{o}C. The FTIR of specimen F0 was also analyzed and presented for comparison. As can be seen in **Figures 14a and 14c**, 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

505 interfacial bond between different fillers and the resin through the matrix due to pores and
506 voids in the matrix **(Figure 14c).** This subsequently decreased the mechanical performance of
507 the polymer matrix at room temperature. Ahmad et al. [50] pointed out that the presence of
508 fused silica resulted in inhomogeneous distribution and weakened the interaction between the
509 matrix and the filler due to the defect in the matrix caused by the voids between the particles,
510 and led to undesirable material properties.

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

523

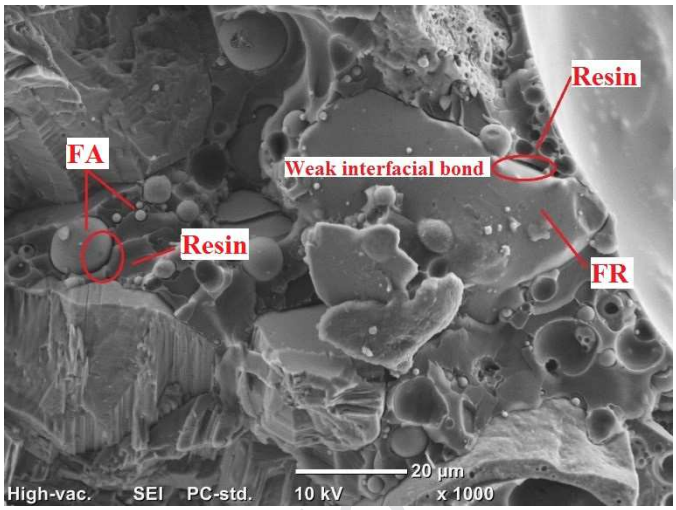


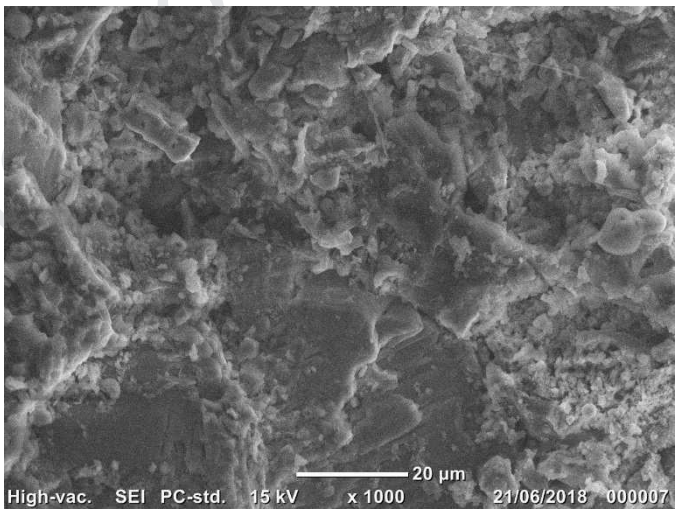


524 7

525 (a)F0 at room temperature (b) F0 at 80°C

526





527

528 (c) F60 at room temperature (d) F60 at 80°C

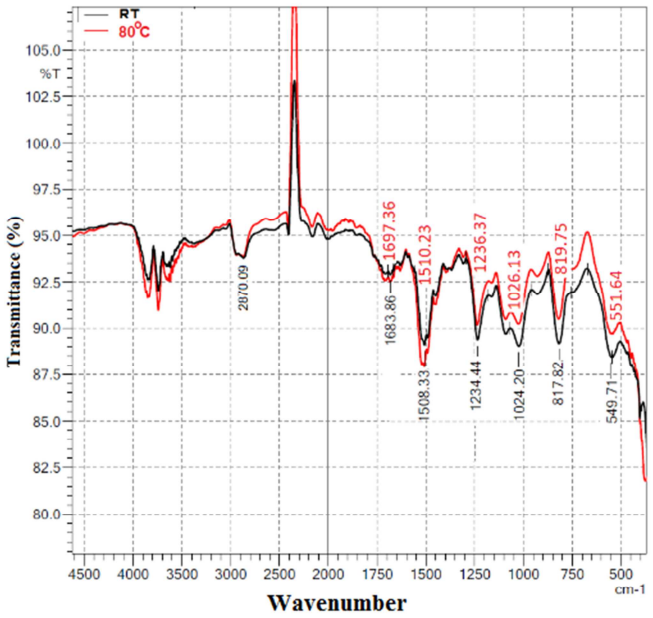
529 **Figure 14**: SEM micrographs of particulate filled epoxy resins

530 **4.6 FTIR results of particulate filled resin subjected to elevated temperature**

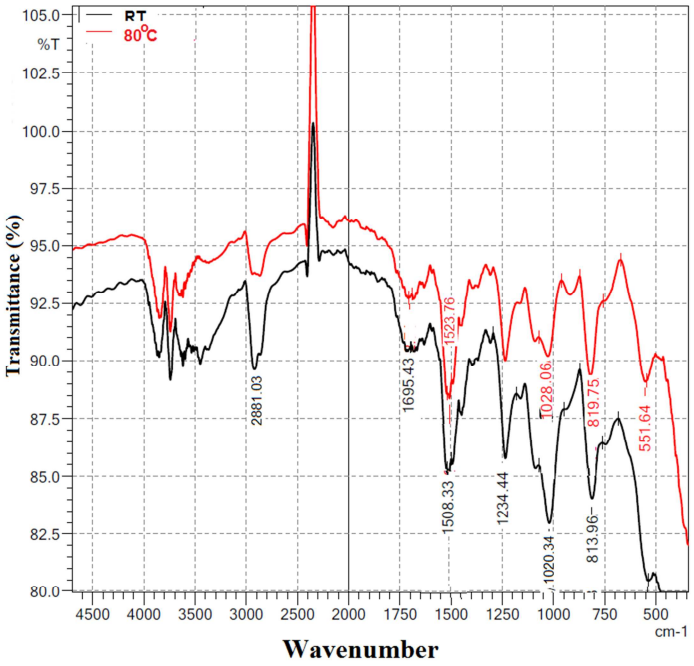
531 FTIR spectra was performed after the mechanical tests to determine functional groups
532 presented in the particulate filled epoxy base resin. The mixing of epoxy resin produced
533 carboxylic and carbonyl acid by-products due to the reaction of the curing agent and epoxy
534 resin [51]. The solid particulate-filled epoxy resin composite was formed through the ring
535 opening polymerisation reaction in the presence of DGEBA, amine-based hardener and fillers
536 (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 **Figure 15**. C-H and C-O were found to be major phases for all specimens. The band observed at ~3800 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 (~817 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 **(Figures 15c and 15d)**. This was due to the decrease in the amount of resin by increasing the percentages of fillers. As shown in **Figure 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 5 to 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. **(Figure 14).** These results showed that the sensitivity of epoxy resin against in-service temperature can be sufficiently reduced by the inclusion of fillers. This

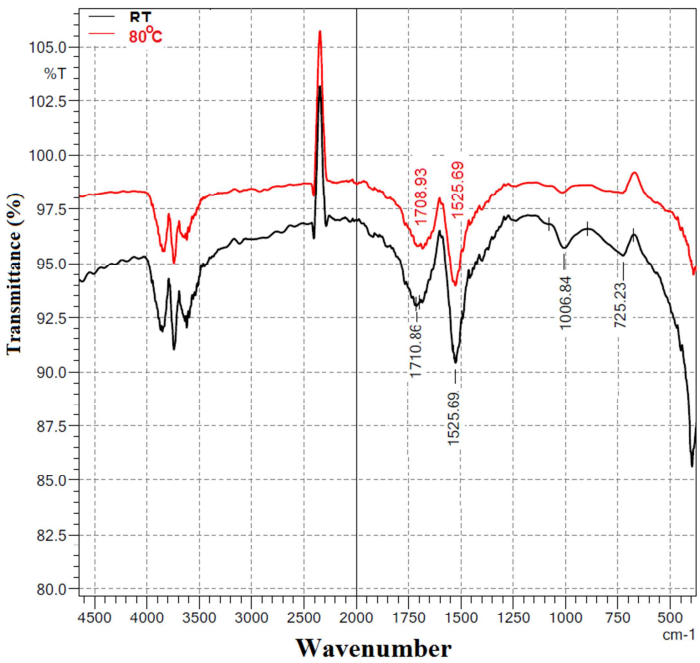
562 further indicates that the particulate filled epoxy resin will exhibit better engineering
563 properties against in-service elevated temperature, as the fillers provide protection against
564 thermal conditioning increasing their durability and suitability in civil engineering
565 applications.



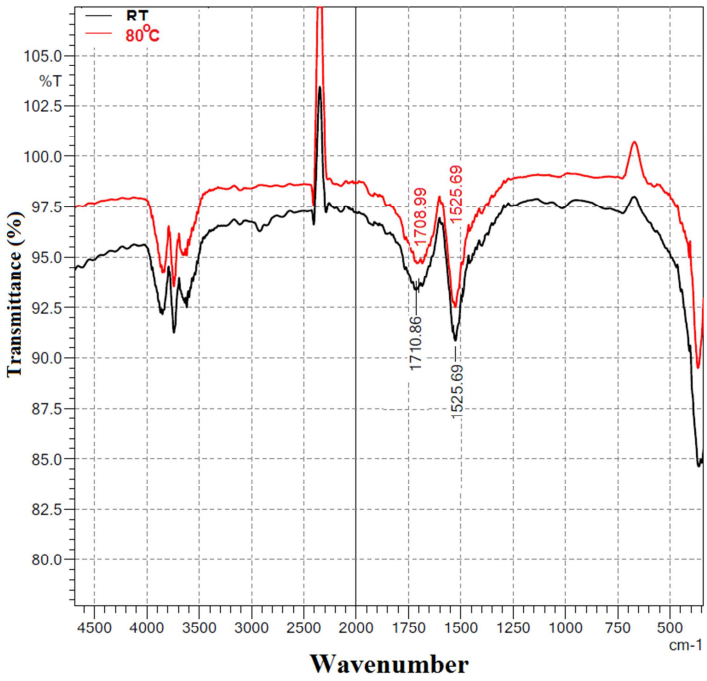
(a) F0



(b) F20



(c) F40



(d) F60

Figure 15. FTIR graphs at room temperature and at 80^{o}C

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 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.

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

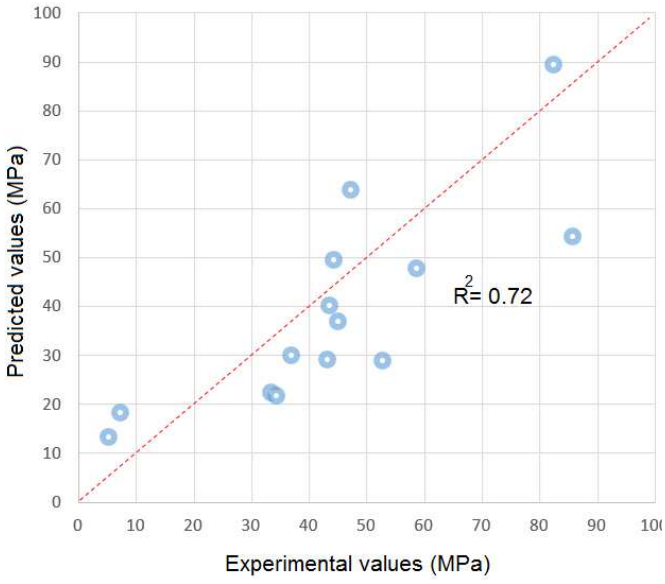
where X_1 is percentage amount of fillers, X_2 is the level of in-service elevated temperature, and K_1, K_2, K_3 are regression parameters.

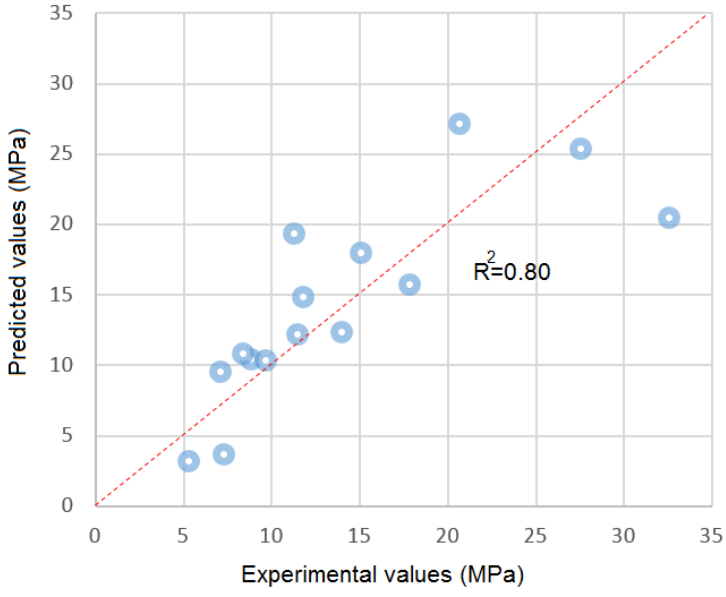
The regression equations to predict the compressive strength (Y_{Comp}) and the splitting tensile strength ($Y_{Split\_tensile}$) are presented in **Table 5**. The regression parameters of the different

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 **Figure 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.

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× (Filler content) $^{0.719}$× (Temp) $^{-1.1379}$	0.72
$Y_{Split\_tensile}$= 183.088× (Filler content) $^{0.413}$× (Temp) $^{-1.090}$	0.80





(a)

(b)

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

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 **Figure 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 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.

$$Y_{Split\_tensile} = 0.3069(Y_{Comp}) + 0.2746 \quad (2)$$

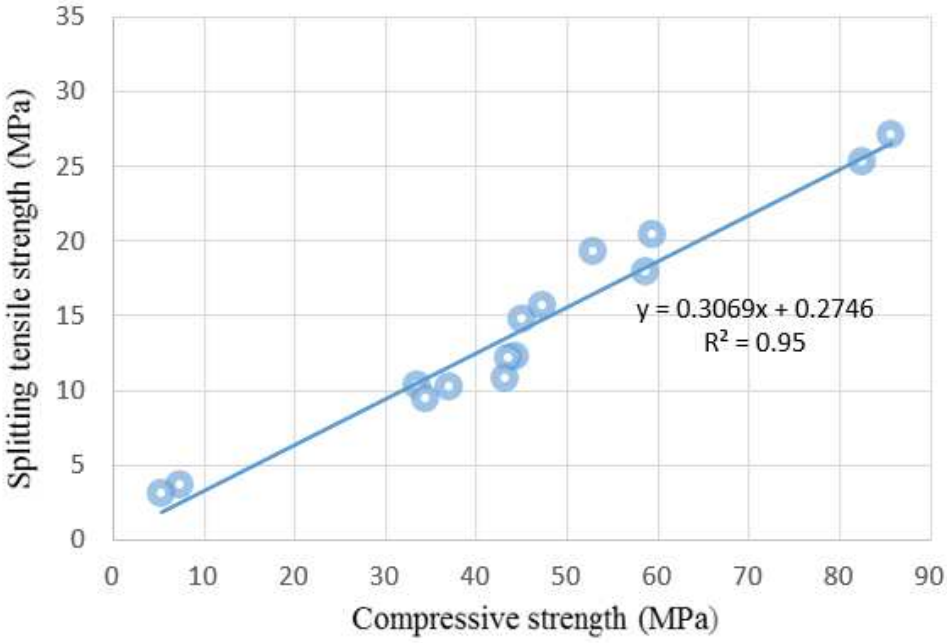


Figure 17. Relationship between the compressive strength and splitting tensile strength

5 Conclusions

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 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 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 Tg 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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Highlights

- Degradation and stability of particulate-filled epoxy polymers at elevated temperature.
- High strength retention of epoxy due to the high thermal stability of fillers.
- Fillers make epoxy resin with a dense microstructure at elevated temperature.
- FTIR analysis revealed no chemical changes in the epoxy at elevated temperature.
- Strong correlation between predicted values and experimental results