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Fabrication and characterization of nano-particles-enhanced epoxy

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ABSTRACT

Epoxy has been widely used as adhesives in retrofitting structures with carbon fiber reinforced polymer (CFRP). In this study, different weight fractions of multi-walled carbon nanotubes (MWCNTs) and Silicon Carbide nanopowder (SiC) will be dispersed into epoxy to produce toughened adhesives that can effectively improve the CFRP/structure bonding performance. The preliminary experimental results indicate that adding 2 wt.% MWCNTs into Araldite-420 will increase its ultimate strength by 17% and its elastic modulus by 14%. On the other hand, Araldite-420's elastic modulus will increase by nearly 50% when 1.0 wt.% of SiC powder is added. Ultrasonic mixing may increase the elastic modulus of Sikadur-30 but reduce its strength and ductility regardless of the amount of nanoparticles dispersed. No significant effect of nano-particle infusion on the glass transition temperature of the epoxies was found. The mechanism of nanoparticles infusion effects on the mechanical properties of the epoxies is also examined using SEM.

1. Introduction

Carbon fibre reinforced polymer (CFRP) composites are very effective in retrofitting ageing structures. The success of retrofitting structures by using CFRP significantly depends on the performance of the CFRP/structure joint and the effectiveness of the adhesive used [1,2]. Due to its outstanding characteristics in good affinity to heterogeneous materials, chemical erosion resistance and on-the-spot processing capability, epoxy has been widely used as adhesives to join CFRP onto structural components in retrofitting structures. However, adhesive strength from conventional epoxy can be greatly affected by adverse environmental conditions such as high humidity, high temperature, saltwater. Therefore, the development of novel epoxy that provides outstanding bond performance under extreme environmental conditions will significantly promote the applications of retrofitting structures with CFRP in buildings, offshore, bridge, and so on.

From unique electronic properties and a thermal conductivity higher than diamond, to mechanical properties where the stiffness, strength and resilience exceeds any current material, nanoparticles offer tremendous opportunities for the development of fundamentally new material systems. In particular, the exceptional mechanical properties of carbon nanotubes (CNTs) and Silicon Carbide powder (SiC), combined with their low density, offer scope for the development of nanotube reinforced composite materials [3]. Research has shown that nanoparticles or CNTs infusion can bring superior thermal and mechanical properties to the epoxy matrix. With 1.5 wt.% loading of nanosized SiC fillers into epoxy, an average of 20–30% increase in mechanical properties has been observed as well as enhanced fatigue performance [4]. By adding 5 wt.% multi-walled carbon nanotubes (MWCNTs) in the epoxy adhesive, Hsiao et al. increased the average shear strength of the adhesion by 45.6% [5]. Zhu et al. observed a 30–70% increase in ultimate strength and modulus of the epoxy polymer material with the addition of only 1–4 wt.% of functionalized single-walled carbon nanotubes (SWCNTs) into the epoxy [6]. The nanotubes–reinforced epoxy composites also exhibited an increased failure strain, which suggests higher toughness.

The transition from micro to nanoscale leads to change in particles physical as well as chemical properties. These changes include increasing in the ratio of the surface area to volume. Therefore, nanoparticles infusion can increase the interactions between the particles and matrix, which will enhance the strength of the whole mixture. Strong interfacial bonding was found to be necessary conditions to obtain full advantage of the extraordinary properties of nanomaterials for the reinforcement of composites. Many methods were used to infuse nanoparticles inside polymers including ultra-sonication bath [7], probe sonicator [8], high shear mixing by ball milling [9], high speed stirrer [10], as well as combined methods in series or parallel.

On the other hand, all previously reported results for nanoparticles reinforced epoxy were usually associated with relatively small scale testing programs using special polymers. For the purpose of practical use, it will be more relevant if industry epoxies

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used for CFRP retrofitting structures are tested. Moreover, a comparison of results reported is often difficult, due to the usage of different epoxy matrices with different processing techniques and parameters as well as the choice of nanoparticles from various sources with again different types and qualities. Keeping most variables constant, it is the aim of this study to compare the influence of different percentages of nanoparticles on the mechanical properties and to appreciate the real potential of nanoparticles as structural modifiers of epoxy-based composites in CFRP retrofitting structures.

The remaining sections of the paper are arranged as follows. The procedure used to mix nanoparticles into epoxy is discussed in Section 2, which is followed by the results of the coupon testing and discussions. The conclusions are summarised in the last section.

2. Nanoparticles–epoxy mixing method

The most commonly used two-part epoxies to attach CFRP plates on steel are Araldite-420 and Sikadur-30. These epoxies have a good mechanical strength, durability, and are easy to apply on most building materials. To study the effect of the nano-sized type additives to the epoxy, MWCNTs (with diameter of 110–170 nm, length 5–9 μm and >90% purity , manufactured by Sigma–Aldrich Co.) or Silicon Carbide nanopowder (SiC) (particle size <100 nm Density 3.22 g/ml at 25 °C, both manufactured by Sigma–Aldrich Co.,) are added, in different weight percentage (0%, 1%, 2% and 3%), for each epoxy. The MWCNTs are de-agglomerated from each other by adding Ethanol (99% pure) in 1:10 concentration and are then left for curing for 48 h in a vacuum chamber. After that, the MWCNTs (or SiC) are dispersed in part-A, since this part is less reactive to ultrasound irradiation than part-B. After the nanoparticles are fully hand mixed with epoxy part-A inside the vacuumed chamber, it is safe to deal with the mixture in the open air.

Owing to its simplicity and efficiently mixing procedure, an ultrasonic probe mixer (VCX 500 from Sonics and Materials, Inc.) is used for the main dispersion of nanoparticles. At a 55% energy density, ultrasonic waves are applied for 30 s out of every 50 s for 50 min to prevent the energy dosage from increasing the mix temperature over the limit. In order to avoid rise in temperature during sonication, the temperature is monitored by the mixer temperature probe and controlled by submerging the mixing beaker in a mixture of ice and water, so that the mixture's temperature does not exceed 55 °C. At the end of mixing, the dispersion of nanoparticles seems homogeneous through colour and texture uniformity. For the purpose of comparison, epoxy samples are also prepared using fully hand mixing.

In the next step, Part-B of the epoxy will be added to the mixture at the recommended ratio and the mixing will be carried out by hand for about 4 min. Then the mixture will be poured into an engraved shaped Teflon mould, designed following ASTM: D 3039 [11], as shown in Fig. 1, and vibrated for 10 min by a vibration table to remove bubbles. Finally, a uniformly distributed load of 800 kg/m^2 will be applied over the epoxy for 24 h to ensure the surface uniformity of the coupons.

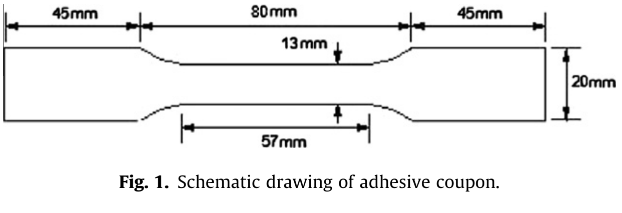

Fig. 1. Schematic drawing of adhesive coupon.

3. Experimental results and discussion

The coupons described in the above section are de-moulded and the extra epoxy grinded, then tested after 7 days from the casting. The samples are tested using an Instron testing machine at the rate of 2 mm/min at room temperature. Strain was measured using a strain gauge attached longitudinally to the two opposite sides of the sample. For each case, at least five coupons are tested and the average is taken.

3.1. MWCNTs-enhanced epoxy

The stress–strain curves of Araldite-420 coupons mixed with different amount of nano-additives using different mixing method are presented in Fig. 2, where AH stands for hand-mixed Araldite-420 without MWCNTs, AM machine mixed Araldite-420 without MWCNTs, and AC1, AC2 and AC3 machine mixed Araldite-420 with 1, 2 and 3 wt.% MWCNTs, respectively. As can be seen from the figure, adding MWCNTs to the Araldite-420 increases the strength from 26.7 MPa for hand mixing pure samples, and 26.4 MPa for sonicated pure samples, to 27.9 MPa for samples with 1 wt.% MWCNTs and 30.9 MPa for samples with 2 wt.% MWCNTs. With 3 wt.% MWCNTs, however, the strength of epoxy returns to 27.2 MPa. Moreover, adding MWCNT to Araldite-420 increases the stiffness as well. As can be seen from Fig. 2, the elastic modulus increases from 1.87 MPa for pure epoxy to 2.1 MPa for 1 wt.%, 2.13 MPa for 2 wt.% and 1.92 for 3 wt.% MWCNTs composites, respectively.

The stress–strain curves of Sikadur-30 mixed with different amount of MWCNTs using different mixing methods are given in Fig. 3, where SH stands for hand-mixed Sikadur-30 without MWCNTs, SM machine mixed Sikadur-30 without MWCNTs, and

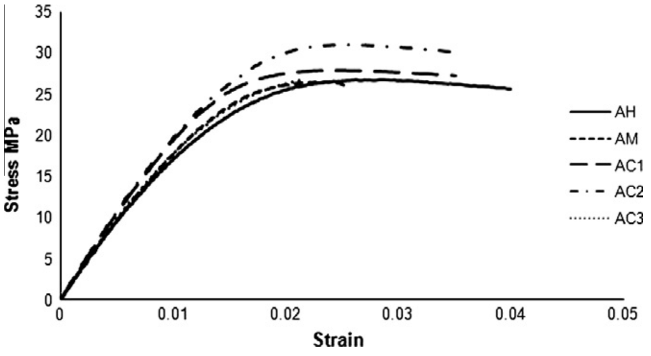

Fig. 2. Effect of MWCNTs infusion on the mechanical properties of Araldite-420.

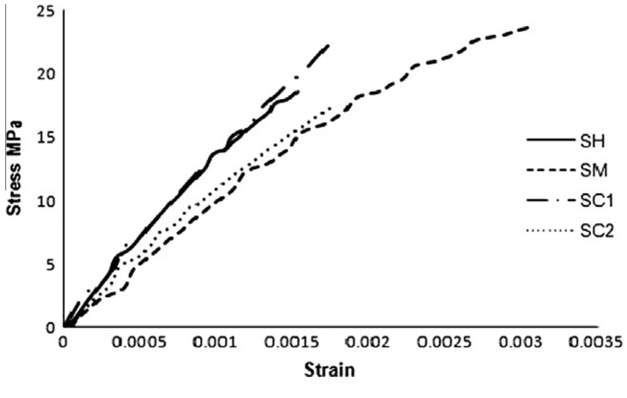

Fig. 3. Effect of MWCNTs infusion on the mechanical properties of Sikadur-30.

SC1 and SC2 machine mixed Sikadur-30 with 1 and 2 wt.% MWCNTs, respectively. As can be seen from Fig. 3, adding MWCNTs to Sikadur-30 will change the strength from 22.8 MPa in the sonicated pure sample to 23.5 MPa and 17.7 MPa for the 1 and 2 wt.% MWCNTs composites, respectively. Also, the modulus of elasticity changes from 9.29 MPa and 13.48 MPa for sonicated and hand mixed samples, respectively, to 12.37 MPa and 10.84 MPa for epoxy sonicated with 1 and 2 wt.% MWCNTs, respectively.

To understand the results presented in the previous section, it is necessary to study the behaviour of MWCNTs inside the epoxy. When the MWCNTs are infused into epoxy, due to their needle-like shape and high surface area, they tend to surround themselves by a thin layer of epoxy attached strongly to the outer wall of CNTs. These MWCNT–epoxy film components start to work as a reinforcing component and prevent nanotubes from agglomerate in the same time. These reinforcing particles reduce the crack width by bridging the gap between the two crack surfaces, and increase its width because the crack now needs to propagate longer distance around these items, which requires more energy to be absorbed. Also, when CNTs positioned between the resin molecules, they create an obstacle to the molecule sliding which increases the brittleness of the mixture [12].

Fig. 4 shows a single agglomeration of MWCNT inside Araldite-420 under SEM, where the strong thin epoxy film has no space to form and the agglomeration starts to form larger particle of MWCNTs that surrounded by a layer of epoxy. This layer, as can be seen in Fig. 5, is still attached strongly to the nanotube, but the CNTs themselves have a very weak connection between each other. The easy-to-break forces attach the nanotubes inside the agglomeration weaken reinforcing action and help to shorten the crack width through the nanotubes agglomeration.

With Sikadur-30, part-A has many filling materials, which have no pathway for chemical reaction when added into part-B. Therefore, the ultrasound irradiation enhances the homogeneity of the reaction mixture part-A of the epoxy resin and increases the homogeneity of the part-A particles, which helps part-B particles to create stronger bonds with it. Although, these bonds still have a nonreactive particles which create the same effect of adding MWCNTs to Araldite-420 and prevent the epoxy forming the strong film around the MWCNTs. Therefore, MWCNTs have a neglected effect on the strength, and even start to work as impurities which are poorly bonded to epoxy particles and lead to stress concentration at its tips. As a result, the strength of Araldite-420 is reduced by mixing with MWCNTs.

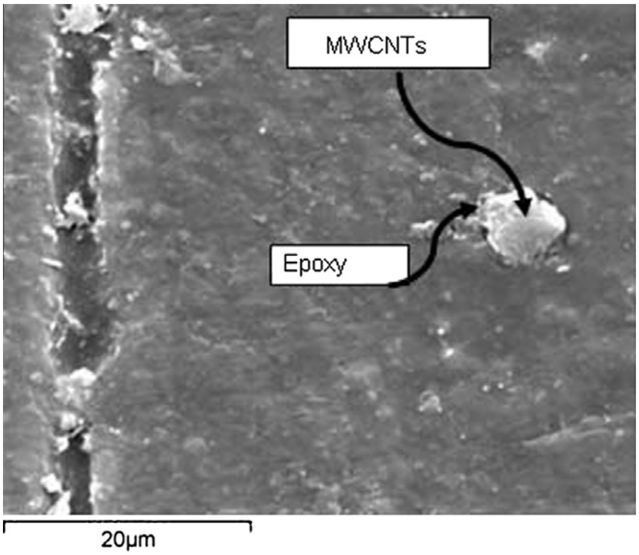

Fig. 4. Single agglomerations MWCNT inside Araldite-420 under SEM.

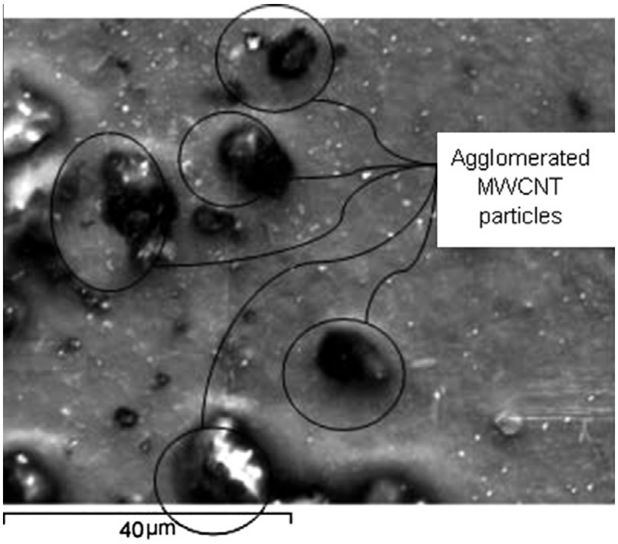

Fig. 5. Agglomerated 3% MWCNT inside Araldite-420 under SEM.

3.2. SiCs-enhanced epoxy

The stress–strain curves of Araldite-420 mixed with different amount of SiC using different mixing methods are given in Fig. 6, where SS1, SS2 and SS3 are machine mixed Sikadur-30 with 1, 2 and 3 wt.% SiC, respectively. SiC nanopowder has a small or even a negative effect on the strength compared with the hand mixed samples. An increment in strength, compared with neat epoxy samples (26.7 MPa for hand mix and 26.4 MPa for sonication), occurs when 1% of SiC added (27.9 MPa) and a decrement when 2 (23.5 MPa) and 3% (25.9 MPa) added.

The modulus of elasticity fallow the same pattern: a slight increase when 1% SiC added (1.92 MPa from1.87 MPa for the neat epoxy-hand mix and sonication mix), then a sharp decrease with 2% SiC (1.77 MPa) then a slight decrease with the 3% SiC (1.85 MPa).

To study the effect of the air bubbles that may created in the mixing process, Araldite-420 part-A, another coupon set prepared with vacuuming part-A in a vacuumed oven under a temperature of 55 °C for 2 h.

Fig. 7 compares the strength between the SiC–Araldite samples with and without vacuumed oven, where AMO, ASO1, ASO2 and ASO3 are machine mixed-vacummed Sikadur-30 with 0, 1, 2 and 3 wt.% SiC, respectively. Vacuuming increased the strength, from

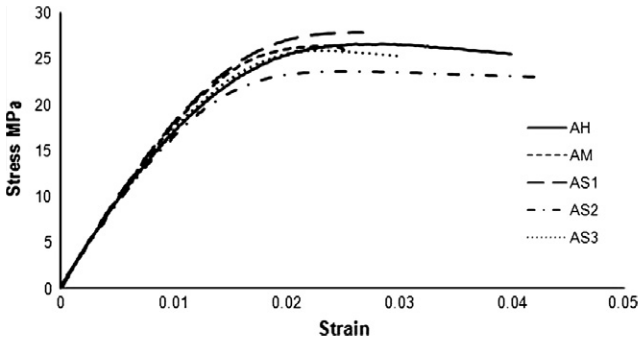

Fig. 6. Effect of SiCs infusion on the mechanical properties of Araldite-420.

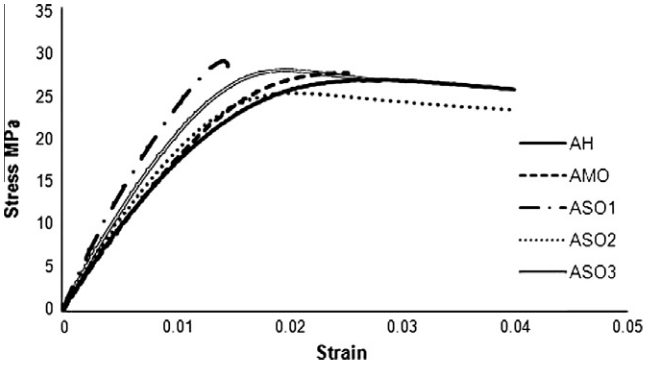

Fig. 7. Effect of SiCs infusion (with vacuuming) on the mechanical properties of Araldite-420.

27.9, 23.5 and 25.9 MPa for 1%, 2% and 3% SiC without vacuuming to 28.9, 24.3 and 27.7 MPa for 1%, 2% and 3% SiC vacuumed sample respectively.

SiC has a better effect on modulus of elasticity of Araldite-420, which increased to 2.75 MPa ,2.06 MPa and 2.27 MPa for vacuumed epoxy with 1%, 2% and 3% SiC respectively.

Fig. 8 compares the strength between the SiC–Sikadur-30 samples where SS1,SS2 and SS3 are machine mixed Sikadur-30 with 1, 2 and 3 wt.% SiC, respectively. Adding SiC–Sikadur-30 by 1 wt.% will increase the strength from 28.6 MPa and 22.8 MPa, for hand and sonicated neat epoxy, to 25.9 MPa. When SiC percentage increased, strength decrease to a level less than the hand mixing epoxy: 16.4 MPa and 17.4 MPa for 2% and 3% SiC wt.

The modulus increase from 9.29 MPa for the neat sonicated Sikadur-30 to 11.63, 10.56 and 11.39 MPa for 1%, 2% and 3% SiC respectively.

To understand the results presented in the previous section, it is necessary to study the behaviour of SiCs inside the epoxy. Due to the high irregular, surface area of the SiC, its particles can embedded inside the Araldite-420 bundles and create a thin, strong film around it. But if compared with nanotubes, the SiC has less effect on Araldite-420 strength.

The morphology of the SiC particles has a great influence: on nanotubes, its needle shape and circular cross section gives the optimum surface area which increase the amount of reinforcing particles. With SiC nano powder, its irregular shapes decrease the amount of reinforcing particles and when the amount increased , it start to work as stress concentrators and micro-crack initiators, reducing the strength of the composite.

If the number of particles increased, at a low strain level, the agglomerated particle increased the stiffness of the material, but at a high strain level, the stress concentration caused by the agglomerated particle initiate crack, which made the sample fail quickly [13].

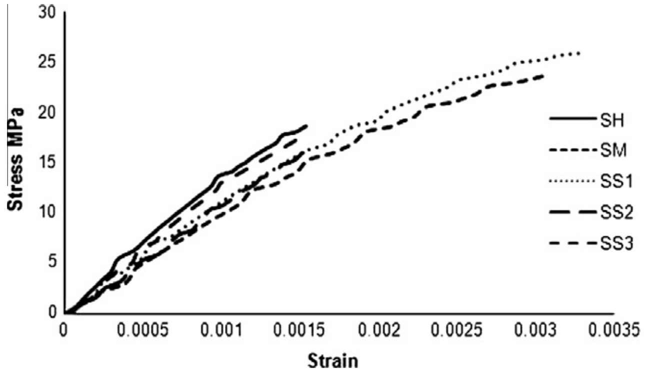

Fig. 8. Effect of SiCs infusion on the mechanical properties of Sikadur-30.

Increasing the modulus of elasticity is due to the irregular shape of the SiC, which prevent the epoxy bundles from slide on each other's. Therefore, the strain amount will decreased which increase the modulus of elasticity.

Table 1
Tg of nanoparticles enhanced epoxy for different epoxies and different nanomaterials.

Nanoparticles		Araldite 420	Sikadur 30
CNTs	0% Hand mixing	65	71
	1%	63	70
	2%	66	66
	3%	63	N/A
SiCs	0% Ultrasonic mix	68	70
	1%	63	69
	2%	64	67
	3%	65	69

3.3. Glass transition temperature tests

To find the effect of adding different nanomaterials to different epoxies on glass transition temperature, Tg, 2 samples containing 0, 1, 2 and 3 wt.% of MWCNTs or SiCs for each epoxy are tested using Rheometric Scientific INC. DMTA IV machine. The strain amplitude was set at 0.05% with 1 Hz frequency. The temperature was raised from 25 °C to 150 °C with a heating ramp rate 2 °C/minute. The output signals were analysed, and the rheological parameters were computed using established mathematical methods.

The glass transition is detected as a sudden and considerable change in the elastic modulus. All the samples showed a glassy state followed by the rubbery state. The recorded Tg's are summarised in Table 1. This small (and even negligible) effect is due to the fact that presence of nanoparticles in epoxy creates a strong molecular interaction between them and resin molecules, which hinder the interaction between resin and hardener molecules. This impedes the formation of the final cross-linked structure of the matrix during curing.

In our nanoparticles-epoxy samples, two competing processes occur: nanomaterials limit the mobility of epoxy resin macromolecules, which reduce the Tg, but simultaneously reduce the crosslinking density and loosen the interfacial layers because of the under cured binder in the material.

4. Conclusions

In this paper, the effects of MWCNTs and SiCs infusion on the mechanical properties of commercial construction epoxies, Araldite-420 and Sikadur-30 are investigated experimentally. The results show that probe sonication is not only an efficient method to infuse MWCNTs into the chosen epoxies, as can be seen directly from the SEM images, but also will increase the epoxy homogeneity. The optimum percentage of MWCNTs added to Araldite 420 is 2 wt.%. The increase in strength and elastic modulus of Sikadur-30 when adding MWCNTs and SiCs is due to the sonication process, and the effect of nanoparticles infusion is negligible. Sonicate 1% of SiC powder then vacuuming Araldite-part-A, gives the optimum increment for the elastic modulus of 2.75 MPa compared to 1.86 MPa for vacuumed, neat samples.

The result from this paper help designing a testing program of attaching CFRP laminate onto steel plate as reported in [14], which study the CFRP laminate behave when nanoparticles enhanced epoxy used to attach it onto steel plate. This technique (using nanoparticles enhanced epoxy) will increase the effectiveness of using CFRP laminate attached onto steel structures.

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