

Tensile Response of SiC-Nanoparticles Reinforced Epoxy Composites at Room and Elevated Temperatures

René M. Rodgers *, Hassan Mahfuz**, Vijay K. Rangari, Shaik Jeelani***, and Leif Carlsson** [René M. Rodgers]: Renee_M_Rodgers@raytheon.com
*Raytheon Missile Systems, **Florida Atlantic University, ***Tuskegee University

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Abstract

This study investigated the effect of elevated temperature on the tensile response of SiC-nanoparticles reinforced epoxy composites. The optimal filler concentration for improved mechanical properties of SC-15 epoxy resin was determined in a related study earlier. A concentration of 1 wt% β -SiC nanoparticles was used to prepare test specimens for elevated temperature analysis. In this investigation ultrasonic mixing was utilized to disperse SiC nanoparticles into SC-15 epoxy.

Results showed that while the improvements in tensile modulus and strength were modest by the addition of SiC nanoparticles, the fracture strain increased by more than 50%. Details of the tensile response of the nanocomposite are described in the paper.

1 Introduction

Epoxy resin has been of significant importance to the engineering community for many years. Components made of epoxy based materials have provided outstanding mechanical, thermal, and electrical properties, and ease of processing [1]. Using an additional phase (e.g. inorganic fillers) to strengthen the properties of epoxy resins has become a common practice [2]. The use of these fillers has been proven to improve the material properties of epoxy resins. Building on the fact that micro scale fillers have successfully been synthesized with epoxy resin [3-6], nano-scaled fillers are now being considered to produce high performance composite structures with further enhanced properties.

2 Experimental

2.1 Material and specimen preparation

The materials used for this study are a commercially available SC-15 epoxy obtained from Applied Poleramic. It is a low viscosity two-phased toughened Diglycidylether of Bisphenol -A (DGEBA) epoxy resin system with a cycloaliphatic amine curing agent. Spherical β -Silicon carbide (β -SiC) nanoparticles, approximately 30 nm in diameter are used as fillers. These nanoparticles were procured from MTI Corporation. The dispersion of nanoparticles into part-A of SC-15 was carried out with a high intensity ultrasonic liquid processor, Sonics Vibra Cell. The loading of nanoparticles was 1 wt%.

Since epoxy coupons are much easier to cast on metallic molds, rather than machining them from panels, molds were developed for casting test specimens. Aluminum molds were designed based on Type II specimen dimensions per the ASTM 638-03 [7]. These dimensions were: overall length (LO) = 216 mm, gage length (G) = 50 mm, overall width (WO) = 19mm, and a width in the gage section (w) = 6mm.

Prior to filling the molds the two sides were fitted together and secured with screws. A plastic tube with a tip was carefully filled with the resin mixture making sure that no air bubbles were introduced during the pouring. Resin was injected into the molds using a pneumatic pump equipped with a foot press. The tip of the plastic tube was cut off and the end was placed in the injection hole for the first specimen. Pressure was applied to the foot press of the pumping device and the resin was injected to fill the mold cavity. The resin was injected slowly until it came out of the spew hole at the other end. The injection tube was removed and the inlet hole was immediately plugged with a rubber stopper. This process was repeated for each of the five specimens.

2.2 Test Procedure

Tensile tests were performed on nanocomposites samples in a universal mechanical testing machine. The tests were conducted at room and elevated temperatures according to ASTM D638-03 [7]. The tensile tests were performed using a MTS servo-hydraulic testing machine fitted with a 29 kN load cell. Axial strain was measured using an Epsilon 50 mm gage length strain extensometer. The tension tests were conducted at a constant test speed of 1.27 mm/min. Five replicate specimens were used.

Tensile test data for load and extension was recorded by The Test Ware software. The tensile modulus was reduced based on the initial linear portion of the load-deflection curve,

$$E = \frac{\Delta \sigma}{\Delta \epsilon}$$

Tensile strength was calculated by dividing the maximum load by the original cross-sectional area of the gage section.

3 Thermal Analysis

As stated, an earlier study investigated the effect of elevated temperature on the tensile response of SiC-nanoparticles reinforced epoxy composites. This study included thermal analysis of nanocomposites made with varying concentrations of SiC.

Modulated Differential Scanning Calorimetry (MDSC) (TA Instruments) was performed on 4 different SiC wt.% nanoparticle loading samples to determine the effect on glass transition temperature of the SC-15 epoxy resin. These experiments were carried out under nitrogen gas atmosphere, and the sample sizes were ~ 10-25 mg. MDSC were run at a modulation of ± 1°C every 60 seconds at a ramp rate of 3°C/min to 200°C. The real time characteristic curves were generated by Universal Analysis 2000-TA Instruments data acquisition system. MDSC analyses were used to measure the changes in heat flow associated with the material glass transition, [8] and glass transition temperature, T_g , for various concentrations of SiC nanoparticles.

The DSC curves shown in Figure 1 illustrate the typical heat flow versus temperature curves generated for neat epoxy and SiC / SC-15 epoxy composites. The broad endothermic peak detected in Figure 1(A) at 73°C is assigned to the T_g of the neat epoxy resin system. T_g s measured for the various nanocomposites (.5, 1.0, 1.5 wt.% SiC) are

80, 85, and 65°C, respectively. Hence, T_g has increased by 12°C by addition of 1 wt. % SiC system. This increase in T_g is attributed to the increased cross linking of epoxy resin in the presence of SiC nanoparticles. Usually T_g increases with increasing cross-linking density of epoxy resins because of the restriction in molecular mobility imposed by cross-linking [9,10]. This effect can be understood in terms of decreasing free volume [11]. The T_g of 1.5 wt.% SiC system, however, decreased by 8°C. The reason for this decrease in T_g could be the agglomeration of SiC nanoparticles where the particle to particle interactions are greater than the particle to polymer interactions that are seen in the case of epoxy with 1 wt.% SiC. Data is given in Table 1.

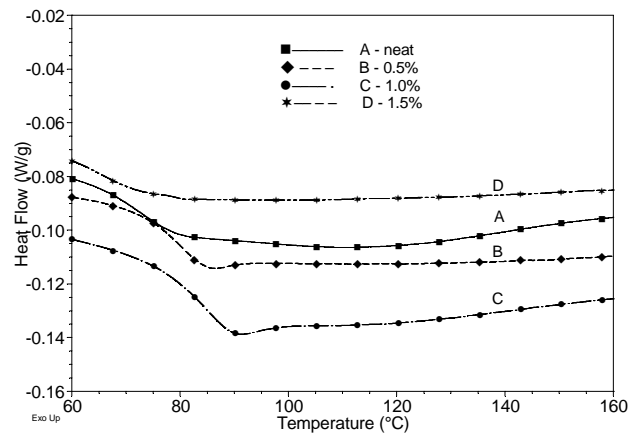


Fig. 1. Modulated DSC Curves – Varying SiC Nanoparticle Concentration (in wt.%)

Table 1 Effects of SiC Nanoparticles on Glass Transition Glass Transition Temperatures of SC-15 Epoxy

SiC Nanoparticle Concentration (wt.%)	DSC T_g (°C)	Change (°C)
0	73	----
0.5	80	7
1.0	85	12
1.5	65	-8

4 Results and Discussion

4.1 Room temperature testing

Representative stress-strain curves for the specimens tested at room temperature are shown in Figure 2. The results show that the modulus is very similar for the neat and nanoreinforced epoxy. The failure strain, however, is greatly increased by the addition of SiC nanoparticles. The neat epoxy specimens fail at a strain of about 3% while those with 1.0 wt. % SiC nanoparticles failed at a strain of approximately 4.9 %.

The average tensile modulus and strength are reported along with the standard deviation in Table 5. The tensile modulus was relatively unchanged, actually showing an insignificant (0.75%) decrease, by the addition of SiC nanoparticles. The tensile strength is 17% higher for the nano-modified resin. A study conducted by Mahfuz et al.[6] reported very similar strength improvements from the addition of carbon nanoparticles/whiskers into polyethylene.

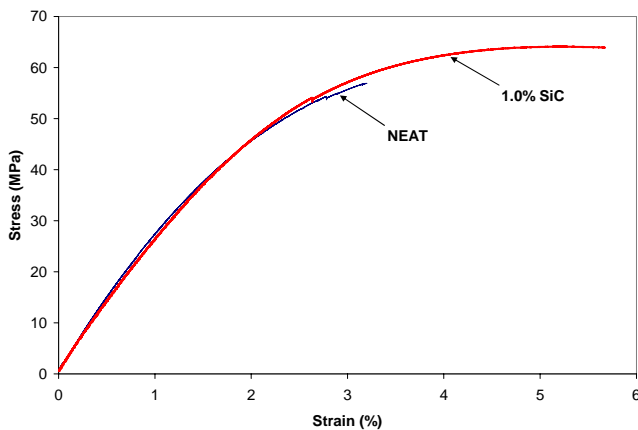


Fig. 2. Representative stress strain curve for room temperature (RT) tensile tests of neat epoxy and SiC/epoxy.

Since nanoparticles are small, there will be a prolific growth of interface between the particle and the polymer. These interface zones may be visualized as defects whose concentration will be very large in the nanocomposites. Any micro cracks developed in the epoxy at their very nascent stage during loading will get deflected and eventually dissipated into these interface zones attributing a crack-blunting feature to the nanocomposites.

The improvements seen in tensile strength may be attributable to the conformation of the long chain molecules due to the presence of SiC nanoparticles.

These chains of molecules and their backbones are held together by covalent bonds. Single-crystal SiC molecule is formed in a horizontal lattice with alternating hexagonal planes of silicon and carbon atoms. Each silicon atom bonds to four nearest-neighbor carbon atoms and each carbon atom bonds to four nearest silicon atoms. Atoms in the 2nd silicon plane are offset with respect to atoms in the 1st silicon plane. This produces a permanent dipole moment in a SiC molecule. Covalent bonds are further enhanced by presence of such dipole moments. In addition, thermal oxidation of SiC during manufacturing produces layer of SiO₂ on the surface of nanoparticles. This layer in presence of moisture and OH-groups present in the matrix will tend to form a different covalent bond known as Si-O-Si (Siloxane) bond. From mechanical point of view, the addition of fillers to the polymer lead to improved properties by inhibiting the motion of the polymer chains. This phenomenon serves to arrest the propagation, and growth of cracks which lead to material failure [6,12].

It is also noticed in Figure 2 that the nanophased SC-15 failed during tension in a manner typical for a semicrystalline polymer. While epoxy in essence is amorphous, the semicrystalline nature must have been promoted by nanoparticle infusion. Initially, stress increased in a linear fashion to about 50% of the peak and then shifted to a nonlinear mode until it reached the peak. At this stage the elongation is about 1.5%. It is known that deformation in this elastic region involves linear viscoelastic shear flow of the polymer molecules. After reaching about 4% strain, the specimen elongates in an almost uncontrolled fashion. This stage is characterized by plastic flow of polymer molecules accompanied by pulling out of polymer chains from the un-deformed crystals. Finally, polymer chains rupture and failure takes place at about 6% elongation.

Gain in strength can also be attributed to the chemical changes that are taking place in the matrix due to SiC nanoparticle infusion. The physical interaction between SiC and the polymer is considerably intense, which enhances the thermal and crystalline behavior of the polymer as indicated earlier. The improvement in matrix properties gets translated into the properties of the nanocomposites.

Figure 3 shows an optical image of tensile test specimens post testing. We observe two distinct phenomena in the SEM images of the fracture surfaces shown in Figure 4. The SEM images show failure modes that are typical with plastic or metallic

samples. In the neat epoxy, Figure 4(A), failure initiated in the upper left corner. However, in case of nanophased sample, the failure is not necessarily initiated at the edge. In this particular case, we see that failure cracks have initiated at the upper surface of the sample where there was an agglomeration of particles, Figure 4(B). The presence of such a large agglomerate produced a weaker area or defect in the specimen, this defect site can be considered as a stress concentration point where failure initiated. It is seen in Figure 4(B), that numerous cracks have propagated in a radial manner across the thickness of the specimen and caused the final failure of the coupon.



Fig. 3 Optical Images of Specimens Post Tensile Testing: Above, SC-15 Neat and Below, 1.0 wt.% SiC/SC-15

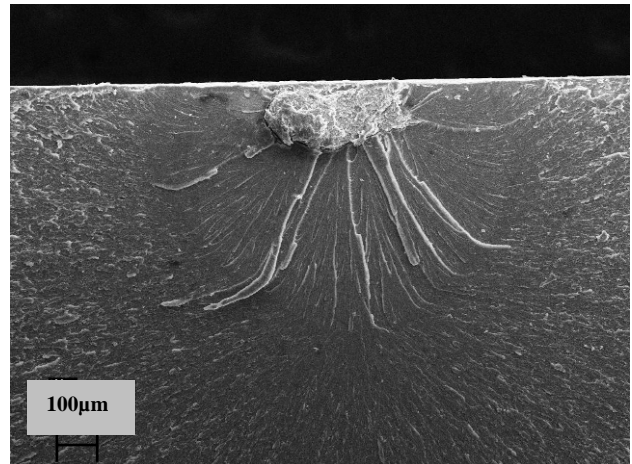
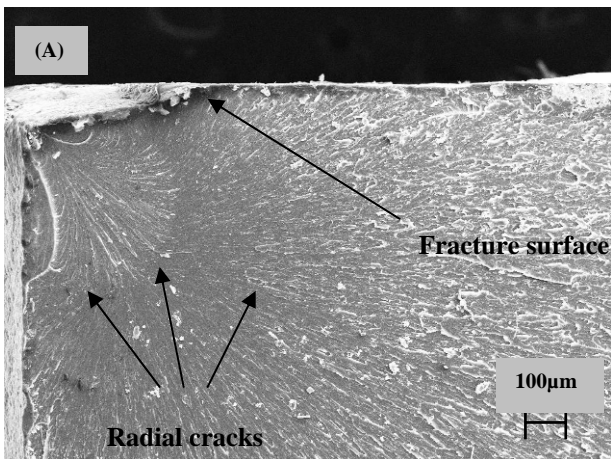


Fig. 4. SEM Images of Tensile Fracture Surfaces: (A) Neat SC-15 and (B) 1.0wt.%SiC/SC-15

4.2 Elevated temperature testing

It is commonly accepted that the properties of polymers experience a dramatic change at the material glass transition temperature [13]. In the regime above the glass transition temperature there is a linear variation with temperature of the free volume. Physical properties such as heat capacity and refraction index also change abruptly at the glass temperature. A glassy polymer will experience dramatic losses of its stiffness and strength, and will have a tendency to flow. At the glass transition, the polymer segments, which have been effectively frozen in position in the polymer glass, become free to rotate and translate. It may be reasonable to assume that movements of polymer segments will be restricted or affected by the reinforcing SiC nanoparticles. Previous studies on filled polymers provide evidence for elevation of T_g due the addition of reinforcing fillers [2,12,14]. The addition of these fillers to a polymer acts a barrier to movement of polymer segments, effectively inhibiting flow and elevating T_g . This prompted us to conduct mechanical tests at elevated temperatures close to the T_g to determine any changes in the mechanical properties due to the particle reinforcement.

The tensile tests were again performed on the MTS servo-hydraulic testing machine arranged with an air circulation oven that enclosed the testing set-up. The oven was equipped with a Barber-Coleman programmable temperature controller.

Two, namely, neat SC-15 and SiC / SC-15, were tested under tensile loading conditions

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according to ASTM D638-03[7]. Five replicate test specimens were prepared.

Representative stress-strain curves for the materials are given in Figure 5. The figure illustrates the practical enhancements provided to the SC-15 resin by the addition of just 1wt.% SiC. The tensile strength of the nanocomposites is observed to be higher than the neat resin at all temperatures considered. This enhancement is more pronounced at higher temperatures. The corresponding test data is presented in Table 2.

A 10% increase in tensile strength and modulus is seen at 70°C. Figure 6 shows that nanocomposites exhibit a linear reduction in strength as a function of increasing temperature, until 55°C is passed and then both materials show a sharp decrease in strength. The addition of the SiC nanoparticles is credited for retarding the degradation of the strength and stiffness.

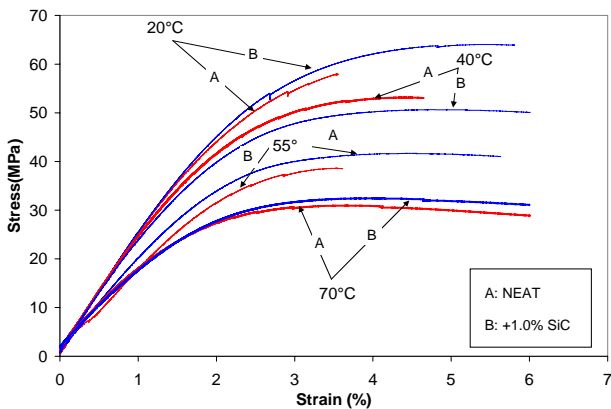


Fig. 5. Representative Tensile Stress vs. Strain Curves: Room and Elevated Temperature Response

Table 2 Tensile Modulus and Strength Data for SiC/SC-15 Epoxy Nanocomposites: Elevated Temperature Tests

SiC [wt.%]	Test Temp [°C]	Tensile Modulus, [GPa]	Change [%] in Modulus	Tensile Strength [MPa]	Change [%] in Strength
0	20	2.66 ± 0.12	---	54.1 ± 7.81	---
1.0	20	2.64 ± 0.7	4	63.3 ± 1.0	15
0	40	2.40 ± 0.9	---	50.0 ± 3.7	---
1.0	40	2.5 ± 0.5	4	50.1 ± 0.9	0.2
0	55	1.91 ± 0.2	---	38.4 ± 1.6	---
1.0	55	2.1 ± 0.2	9	39.9 ± 4.4	4
0	70	1.69 ± 0.1	---	28.1 ± 2.4	---
1.0	70	1.87 ± 0.2	9	31.3 ± 2.4	10

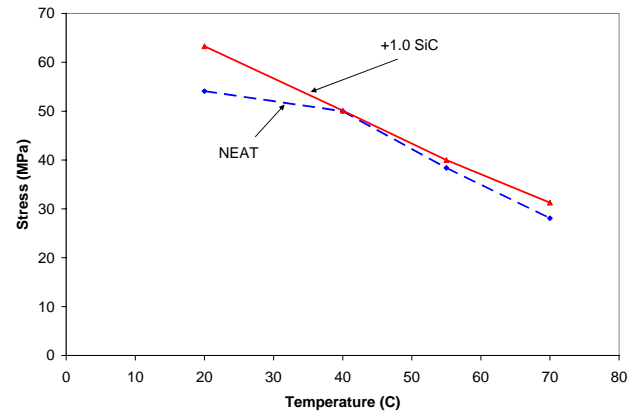
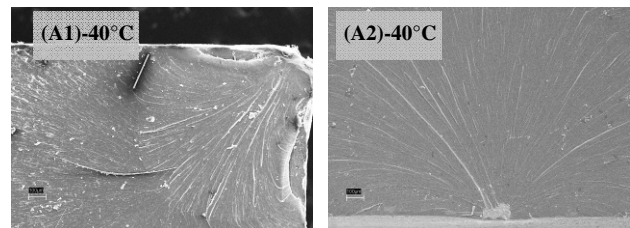


Fig. 6. Tensile Strength of SiC/ SC-15 Nanocomposites as a Function of Temperature

4.3 Scanning electron microscopy

To further examine the failure mechanism, the post-fractured specimens were examined in a scanning electron microscope (SEM). Figure 7 shows that the failure mode of the neat and nano-modified test specimens transitioned from a brittle fracture to a more ductile failure. The specimens tested at elevated temperatures exhibit surfaces that have been pulled before a catastrophic failure occurs. Figure 7 (C1) and (C2) show the fracture surfaces of the neat and SiC/SC-15 specimens (respectively) tested at 70°C. In these images large areas of missing material can be seen where sections pulled completely away from the specimen. At 40°C, Figure 7(A1) and (A2) show that epoxies experienced more brittle failures. In these images very clean breaks produced the smooth surfaces shown in the figure. The images shown for the specimens tested at 55°C, Figure 7(B1) and (B2), indicate the beginnings of a failure mode transition. Both smooth and pulled areas were seen in these specimens, similar to those seen in the specimens tested at 40°C and 70°C.



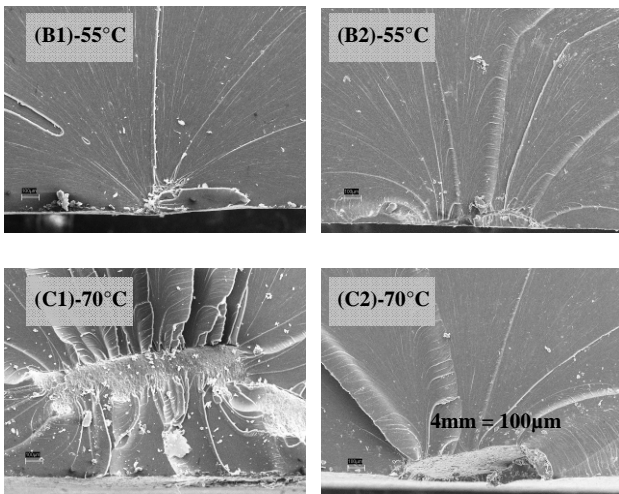


Fig.7. SEM Micrographs Showing Effects of Increasing Temperature on Tensile Fracture Surfaces: Neat SC-15 epoxy, (A1, B1, and C1) and 1.0 wt.% SiC/SC-15 (A2, B2, and C2) (Scale: 4mm = 100µm)

5 Summary

The investigation is summarized as follows:

SC-15 Epoxy witnessed a 12°C increase in glass transition with the addition of 1.0 wt% SiC nanoparticles

SiC nanoparticles reinforcement provided modest increase in modulus and strength at RT. But average increase in fracture strain was about 56%.

At elevated temperature, tensile tests showed similar trends in modulus and strength. This was maintained up to about 40-55°C, but as the test temperature approached closer to T_g , SiC nanocomposites exhibited lower strength than the neat resin.

A threshold temperature level within 40-50°C range was identified at which a distinct shift in the rate of degradation in strength of the nanocomposite was noted.

6 Acknowledgement

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