STOICHIOMETRY AND MECHANICAL PROPERTIES OF A HIGH PERFORMANCE EPOXY RESIN AND ITS SWCNT MODIFIED NANOCOMPOSITES

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Abstract
The effect of stoichiometric and off-stoichiometric ratios on various mechanical and thermal properties such as fracture toughness, tensile and dynamic mechanical response of an epoxy resin and its single walled carbon nanotube (SWCNT)-modified nanocomposites is evaluated. The pattern in property change with reaction stoichiometry for nanocomposites reinforced with pristine and reduced SWCNT was considerably different from the neat epoxy. A resin-to-hardener molar ratio of 1:0.8 offers the best overall properties for the neat epoxy while a 1:1 molar ratio considerably outperforms the other ratios examined for the nanocomposites. This composition at 0.2 wt% SWCNT loading provides the highest overall mechanical properties by improving fracture toughness, ultimate tensile strength and ultimate tensile strain of the epoxy resin by 40%, 34%, 54%, respectively.

1 Introduction

Carbon nanotubes (CNT) have shown great promise to improve mechanical, thermal and electrical properties of polymers [1]. Epoxies have particularly attracted attention due to their wide range of applications as coatings, adhesives and matrices in fiber reinforced composites. Epoxy resins have several unique characteristics such as good mechanical properties, strong chemical and wear resistance, strong bonding and relatively low cost; however, they typically suffer from brittle failure. Experimental studies on the influence of CNT on epoxy toughening have suggested a marginal improvement [2] far below theoretical predictions based on mechanisms such as fiber bridging. As a result, there are opportunities for further improvement of fracture toughness in epoxy resin upon addressing issues with experimental practices and formulations. The integration of epoxy resins and CNT can also modify the epoxy molecular network formation and cure behavior [3]. While it has been suggested that the increase in fracture toughness of epoxy resins and decrease of glass transition temperatures upon the addition of CNT could be mainly due to changes in the crosslink density of epoxy resins [4,5], no study has yet been performed to demonstrate this hypothesis. This work focuses on the role of the resin/hardener system stoichiometry on the mechanical

and thermal properties of a high temperature epoxy modified with single-walled carbon nanotubes (SWCNT). A high-performance aerospace-grade epoxy resin was used for this study. This epoxy has a remarkable glass transition temperature of ~270°C but a medium-to-low fracture toughness (~1 $MPa.m^{0.5}$). Composites containing pristine unfunctionalized SWCNT (u-SWCNT) and reduced SWCNT (r-SWCNT) have been prepared at three different weight ratios of resin-to-hardener. The effects of the stoichiometry on the mechanical and thermal properties of the neat and SWCNT-modified resin were evaluated.

2 Materials and testing methods

2.1 Materials

A commercial tridentate epoxy resin used in the aerospace industry, triglycidyl p-aminophenol (TGAP-trade name: Araldite MY0510), was used as the polymeric matrix precursor. Aradur HT 976, 4,4'-diaminodiphenylsulfone (DDS), was chosen as the curing agent. SWCNT were synthesized using a two-laser method as reported previously [6].

2.1.1 Reduction and integration of SWCNT into the epoxy resin

The procedure to reduce (negatively charge) the SWCNT by electron transfer from alkali-naphthalene salts and integration into the epoxy monomer TGAP has been previously described [7]. Reduced-SWCNT/TGAP and unfunctionalized-SWCNT/TGAP samples at two different loadings of 0.1 and 0.3 wt% were prepared. The curing agent DDS was then added at three different weight ratios (100:49, 100:60 and 100:67), which corresponds to 1:0.8, 1:1 and 1:1.1 epoxide:amine hydrogen molar ratios, respectively, considering an epoxy equivalent weight of 102 g eq^{-1}. The cure protocol has been previously described [7]. Table 1 summarizes the nomenclature, type of SWCNT and loading as well as the stoichiometry of materials studied in this work. The final loadings of SWCNT in the nanocomposites are given in parentheses in Table 1. These differences in loading have an impact on making direct sample-to-sample comparisons, however, using the same master-batch for making different nanocomposites has the important advantage of reducing the potential batch-to-batch variability involved with CNT-resin integration. To differentiate the effects of loading and stoichiometry, SWCNT/TGAP mixtures at two different loadings of 0.1 and 0.3 wt% SWCNT were used to prepare the nanocomposites.

Batch names	**SWCNT functionalization****	**SWCNT content (wt%)***	**Resin to hardener wt ratio**
MY100:49	ð	ð	100:49
MY100:60	ð	ð	100:60
MY100:67	ð	ð	100:67
0.1r-SW100:49	r-SWCNT	0.1 (0.067)	100:49
0.1r-SW100:60	r-SWCNT	0.1 (0.063)	100:60
0.1r-SW100:67	r-SWCNT	0.1 (0.060)	100:67
0.3r-SW100:49	r-SWCNT	0.3 (0.201)	100:49
0.3r-SW100:60	r-SWCNT	0.3 (0.188)	100:60
0.3r-SW100:67	r-SWCNT	0.3 (0.180)	100:67
0.3u-SW100:49	u-SWCNT	0.3 (0.201)	100:49
0.3u-SW100:60	u-SWCNT	0.3 (0.188)	100:60
0.3u-SW100:67	u-SWCNT	0.3 (0.180)	100:67

*The numbers in the parenthesis are the contents after adding the hardener.

**r-SWCNT and u-SWCNT stand for reduced and unfunctionalized SWCNT, respectively.

Table 1. Material nomenclature, type and loading of SWCNT and mix ratios of epoxy resins and nanocomposites.

2.2 Testing methods

Fracture toughness samples were prepared according to the standard test method for measurement of fracture toughness of polymer materials, ASTM D 5045 ï 91 [8]. A single Edge Notch Bending (SENB) test was used and the dimensions of the samples were chosen as 20 × 4 × 2 mm in order to minimize the use of material. The notch depth was 2 mm with a span of 16 mm. A 100 lb Fullam tensile fixture was used to perform the tests under an optical microscope (Olympus BX-51M).

Dynamic mechanical analysis (DMA) was performed using a Q800-TA Instruments dynamic mechanical analyzer using a 3-point bending fixture. For each material, 3 coupons (length: 60 mm; width: 5-6 mm; thickness: 3.5-4 mm) were tested under force control. The test was performed at 1 Hz using an oscillatory displacement with a magnitude of 15 εm while temperature was swept from room temperature to 300°C at a ramp rate of 3°C/min.

Tensile tests were performed on an MTS 858 Table Top Servohydraulic test frame equipped with hydraulic grips. Each dog-bone coupon was placed in the grips and tested in displacement control at a loading rate of 1.27 mm/min to failure. The maximum tensile strain (ε_{max}) and ultimate tensile stress (*UTS*) have been extracted from the curve immediately before failure. Youngôs modulus (*E*) was obtained from the slope of the linear fit of the initial linear section of the curve (up to 0.5 % strain). Finally, the toughness (*G*) was estimated by calculating the area under the curve. For each batch, 5 to 6 coupons were tested and the average value was reported.

Differential scanning calorimetery (DSC) was performed with a Modulated Differential Scanning Calorimeter (MDSC) Q100 from TA Instruments. Dynamic tests were performed with a heating rate of 3°C/min from room temperature to 300°C to measure the total heat of reaction released during the cure.

3 Results and discussion

3.1 Fracture toughness results

Figure 1 summarizes the fracture toughness (K_{IC}) of epoxy and nano-modified resins with different stoichiometries. The 100:49 mixing ratio is the ratio recommended by the resin manufacturer which corresponds to a 1:0.8 resin-to-hardener molar ratio. A slight excess of epoxy is commonly used in commercial practice where it has been found that a higher degree of conversion and a higher crosslink density can be obtained. Similar to previous reports for a tetrafunctional epoxy [9], the K_{IC} values of the unmodified resin increased with the added amount of the curing agent. Those studies concluded that at higher DDS contents, most of the network structure is developed through the reaction of primary amine and epoxide groups, leaving un-reacted -NH groups with a larger molecular weight (M_c) between crosslinks. In general, decreasing the crosslink density causes the toughness to increase because of the formation of a looser, more mobile network. However, this will have a negative effect on other important mechanical properties like modulus and glass transition temperatures, as will be discussed later.

For r-SWCNT nanocomposites, two important observations were made. First, it was found that the addition of r-SWCNT, for all the resin/hardener stoichiometries, resulted in a considerable reduction of the K_{IC} variation, demonstrating that r-SWCNT nanocomposites show more predictable fracture behavior (more ductile) as compared to the neat resin materials. This variation reduction also scales with the addition of r-SWCNT. Second, it was found that the trend between K_{IC} and mixing ratio was totally different than the one observed for the neat resin. For 100:49 and 100:60 ratios, the K_{IC} increased by the addition of r-SWCNT (similar to the epoxy). However, for the 100:67 ratio, a reverse effect was obtained. The highest K_{IC} was obtained for the 0.3r-SWCNT nanocomposite with the 100:60 ratio in which a 37% increase in K_{IC} was recorded versus the 100:60 neat resin. Note that the final content of SWCNT in the epoxy resin is slightly different for each ratio (see Table 1). In order to rule out the possibility that different SWCNT loadings were responsible for the observed trend, another nano-modified resin with a lower r-SWCNT loading was also evaluated at each mixing ratio. As can be seen, the trend remains unchanged as the nanocomposite samples containing 0.1 wt% r-SWCNT offered K_{IC} values between the neat epoxy and the nanocomposites with 0.3wt% r-SWCNT. This demonstrates that the observed trend is not due to changes in SWCNT loading but rather that there is an optimal composition of the epoxy network, different from the neat resin, at which the toughening effect of r-SWCNT is more significant.

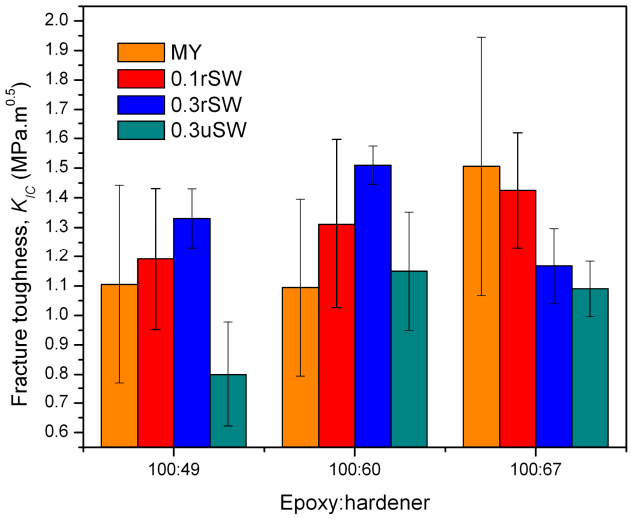

Figure 1. Effect of stoichiometry on K_{IC} values of the neat epoxy, functionalized and unfunctionalized nano-modified resins.

In nanocomposites containing u-SWCNT, for all mixing ratios a reduction or no change of K_{IC} was observed as compared to the neat resins. In a previous paper, we demonstrated that the effectiveness of r-SWCNT for K_{IC} improvement is due to the formation of a softer, less cross-linked structure at the SWCNT/matrix interface, created by a reaction between r-SWCNT and epoxide groups [7]. The results obtained for nanocomposites prepared at different mixing ratios indicate that the formation and structure of this softer interface depend on the stoichiometry of the epoxy resin.

3.2 Dynamic mechanical analysis results

Figure 2 summarizes the average values of room temperature storage modulus (E') and glass transition temperature (T_g) of all tested specimens with error bars calculated as 1 standard

deviation from the mean. The T_g was determined from the peak of the tan(ŭ) curve. For the unmodified epoxy resin materials, the T_g decreases with the addition of more hardener. Similarly, a slightly lower E' was obtained at the higher hardener ratio (100:67). As explained in Section 2.1, the reduction of the crosslink density may be responsible for such trends. In agreement with the fracture toughness results, the addition of increasing amounts of hardener to r-SWCNT/TGAP mixtures considerably changed the trend observed for the neat epoxy. A significant reduction of T_g was obtained for 100:49 and 100:67 ratios as compared to their corresponding neat samples. However, for the ratio of 100:60, T_g is only slightly reduced (about 4°C) as compared to the neat resin. A similar trend was also observed for E'. DMA tests were also performed on one u-SWCNT nanocomposite with 100:60 resin-to-hardener ratio, which corresponds to the composition of the r-SWCNT nanocomposite with the best properties. For this specific composition the incorporation of u-SWCNT, unlike r-SWCNT, resulted in a slight improvement of storage modulus. This is expected as the formation of a soft interface in the case of r-SWCNT nanocomposites [7] reduced the effectiveness of stiff SWCNT for modulus improvement. Unfunctionalized SWCNT, on the other hand, negatively affect the fracture toughness of the resin, a property that is more important for most structural applications in composites and adhesives.

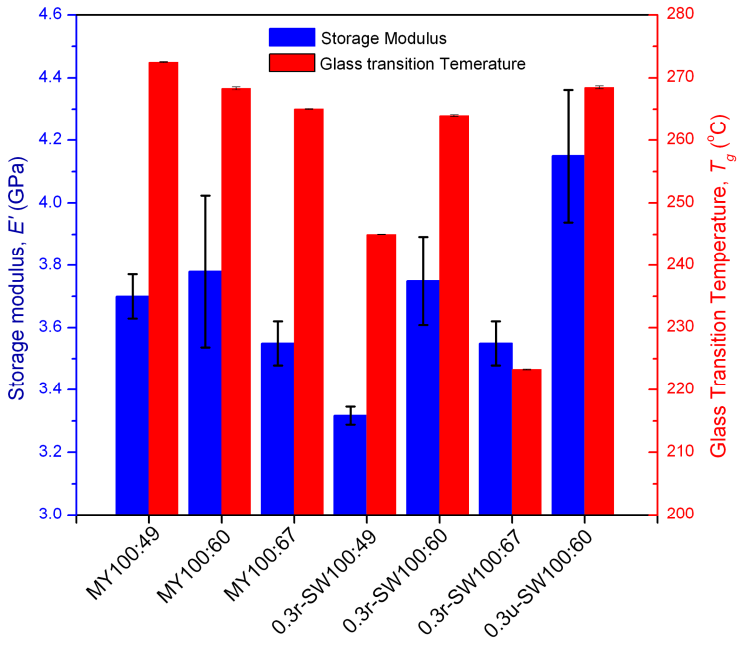

Figure 2. Room temperature storage modulus and glass transition temperature of different tested materials.

3.3 Tensile Testing

Representative tensile stress-strain curves of different materials are shown in Figure 3. Table 2 summarizes the tensile properties of the baseline and nano-modified resins. For the neat resin, except Youngôs modulus, other mechanical properties drop significantly upon the addition of increasing amounts of hardener. As it was shown in Figure 1, the highest fracture toughness values were obtained for the highest content of DDS (100:67); however, as expected, this resin composition results in the worst tensile results.

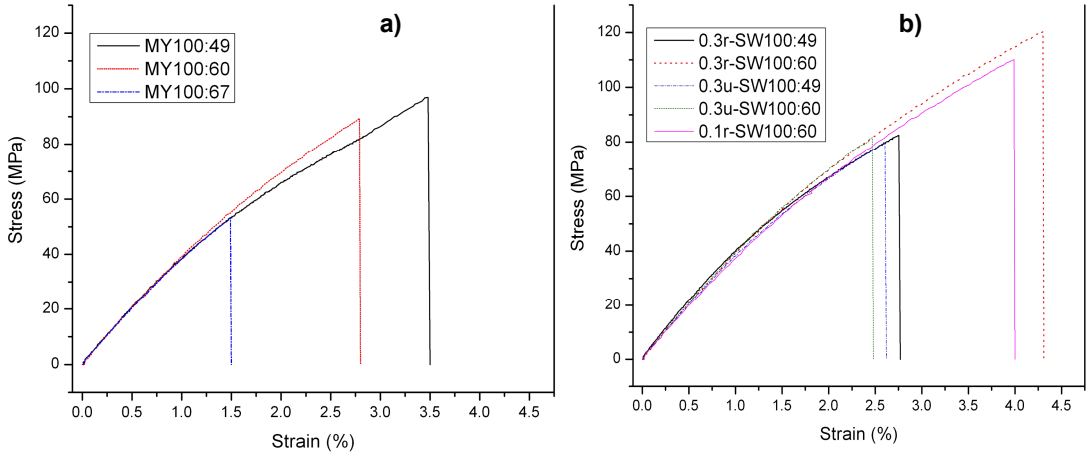

Figure 3. Representative stress-strain curves for tested specimens of a) neat epoxy resin and b) nanocomposites.

Sample	Tensile modulus, *E* (GPa)	Ultimate tensile strength, *UTS* (MPa)	Ultimate tensile strain, ε_{max} (%)	Tensile toughness, *G* (MPa)
MY100:49	4.0±0.2	92±9	3.2±0.5	1.7±0.4
MY100:60	4.3±0.3	88±14	2.7±0.7	1.3±0.5
MY100:67	4.3±0.3	48±21	1.3±0.7	0.4±0.3
0.3u-SW100:49	4.4±0.5	70±25	2.0±0.9	0.9±0.6
0.3u-SW100:60	4.3±0.1	86±5	2.6±0.1	1.3±0.1
0.3r-SW100:49	4.1±0.5	81±8	2.7±0.4	1.3±0.5
0.3r-SW100:60	4.1±0.1	118±2	4.2±0.2	2.8±0.2
0.1r-SW100:60	4.3±0.3	111±15	3.8±0.7	2.5±0.8

Table 2. Tensile properties of the neat epoxy resins and their nanocomposites.

The resin-to-hardener ratio of 100:67 was not considered for nanocomposites samples, as fracture toughness and DMA results showed an unfavorable trend. The 0.3r-SW100:49 sample exhibits better properties than the 0.3u-SW100:49 sample but lower than the corresponding neat resin (MY100:49). The nanocomposite 0.3r-SW100:60 offers the best mechanical properties in comparison with all other batches including all baseline samples with different hardener ratios. Similar to fracture toughness and DMA results, the optimized stoichiometry for the neat resin and nanocomposites with r-SWCNT was different. In order to confirm that the improvement reported for 0.3r-SW100:60 (with 0.19 wt% SWCNT) is not simply because of a small difference in SWCNT loading as compared to the 0.3r-SW100:49 (with 0.20 wt% SWCNT), the 0.1r-SW100:60 sample (containing 0.06 wt% SWCNT) was also tested. It was found that the improvement reported for this specific ratio (100:60) was also found for the batch with lower content of r-SWCNT. For the 0.1r-SW100:60 the improvement is slightly lower than that of 0.3r-SW100:60. For u-SWCNT nanocomposites, a slight improvement in Youngôs modulus was found for 0.3u-SW100:49 samples, in agreement with DMA results. However, other properties were significantly affected, most notably the maximum strain at failure. Unlike the neat resin, the addition of more hardener (100:60) to u-SWCNT/TGAP mixtures resulted in improvement of all properties, except modulus. No improvements in properties of 0.3u-SW100:60 were reported as compared to its baseline (MY100:60).

3.4 DSC results

Further investigation of these nanocomposites was undertaken by DSC. Several publications suggest that the addition of CNT, either MWCNT or SWCNT, whether functionalized or unfunctionalized, can decrease the overall degree of cure as a result of CNT interference with the epoxy network formation [3,10]. However, the CNT influence on properties such as the total heat of reaction and its correlation with mechanical properties (mainly DMA and tensile properties) has been explored only in a limited number of studies. DSC tests were performed on the neat epoxy resin, unfunctionalized and functionalized CNT composites at the three different resin/hardener weight ratios previously evaluated. Table 3 summarizes the heat of reaction of the fully cured samples with different DDS content obtained with the dynamic tests. For the neat resin an increase in hardener content resulted in a decrease of the heat of reaction with the highest value obtained for the 100:49 ratio, in agreement with the manufacturer recommendations and previous mechanical (tensile and fracture toughness) and DMA results. As an illustration, the total heat of reaction was comparable for both MY100:49 and MY100:60, resulting in comparable fracture toughness (Figure 1). For MY100:67, however, a considerable drop in the total heat of reaction translated into an increase in fracture toughness. A similar argument is also valid for tensile and DMA results.

Samples	Total heat of reaction (J/g)
MY100:49	604.7±23.9
MY100:60	593.1±39.0
MY100:67	554.1±23.8
0.3u-SW100:49	693.9±3.0
0.3u-SW100:60	623.3±2.4
0.3u-SW100:67	592.9±17.7
0.3r-SW100:49	672.6±2.3
0.3r-SW100:60	644.3±0.1
0.3r-SW100:67	634.3±17.8

Table 3. DSC dynamic results.

For all nanocomposites examined in this work an increase in the total heat of reaction was observed with the introduction of SWCNT. Also, a higher total heat of reaction was generally measured for the r-SWCNT nanocomposites compare to u-SWCNT ones. Hence the introduction of unfunctionalized SWCNT and, to a greater extent, r-SWCNT favors the conversion reaction of the epoxy. This result is different from other studies in which SWCNT were shown to hinder the network formation in a DGEBA bifunctional system [10]. Although the total heat of reaction for 0.3r-SW100:67 is smaller than the other two r-SWCNT nanocomposites, there is a significant drop in fracture toughness. This clearly demonstrates that the increase in fracture toughness of the resin upon the addition of SWCNT cannot be solely explained by the reduction of crosslink density. In fact, SWCNT contributes to the improvement in fracture toughness through different mechanisms such as crazing or bridging. The formation of a softer interface as reported previously for the 0.3r-SW100:60 material also plays an important role on the mechanical and thermal properties.

4 Conclusions

The effect of three different stoichiometries on mechanical and thermal properties of an aerospace-grade epoxy resin (Araldite MY0510) and its SWCNT-modified nanocomposites was evaluated. For the neat resin, the sample with 1:1.1 (resin/hardener) molar ratio shows the highest fracture toughness. However, the standard deviation for this sample is considerably higher than for all of the other samples, suggesting that the fracture toughness is more unpredictable for this material. Additionally, this sample possesses the lowest T_g, by about 8°C, among the studied molar ratios. On the other hand the sample with 1:0.8 molar ratio provides considerably better tensile properties and higher T_g than the epoxy resin with 1:1 and 1:1.1 molar ratio. For the neat epoxy resin, the molar ratio with the lower DDS content (1:0.8) provides the best overall properties in accordance with the optimal recommended ratio by the resin manufacturer. In contrast to this observation, the pattern in property change versus resin/hardener ratio was considerably different for nanocomposites reinforced with u-SWCNT and r-SWCNT. A comparison among functionalized nanocomposites suggests that a 1:1 molar ratio considerably outperforms the other two ratios examined in this work (1:0.8 and 1:1.1) by offering higher mechanical properties (K_{IC}, G, UTS and ε_{max}) and T_g. In comparison to all examined samples, including the neat epoxy resin, this nanocomposite offers the best performance by increasing G, K_{IC}, UTS and ε_{max} by 118%, 40%, 34%, 54% with respect to the neat resin with the same molar ratio (1:1) and by 67%, 36%, 28%, and 30% with respect to the neat resin with the optimal ratio (1:0.8). Improvement in ductility is observed without considerably affecting E, E_N and T_g. It is found by DSC tests that the presence of SWCNT can considerably modify the curing behavior of the resin. The introduction of unfunctionalized SWCNT and, to a greater extent, r-SWCNT favors rather than hinder the conversion reaction of the epoxy. This requires the re-optimization of the system stoichiometry for particular applications or properties.

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