SC-15 Epoxy Reinforced with Magnetic Nanofillers under Uniform Magnetic Field – An Investigation of Anisotropic Physical Properties

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ABSTRACT

In this work, SC-15 epoxy is reinforced with magnetically-active nanofillers cured in a modest magnetic field. Several systems were prepared - a dilute system of various concentrations of Fe_2O_3 nanoparticles in SC-15 epoxy, a combination of Fe_2O_3 nanoparticles and chemically-functionalized single-walled carbon nanotubes (SWCNT(COOH)s) in SC-15 epoxy, and a dilute system of SWCNT(COOH)s decorated with Fe_3O_4 particles in SC-15 epoxy. The use of magnetic nanofillers allows for significant structural anisotropy in the nanocomposites with an application of only a modest curing field. Stress-strain analysis of the systems shows that the tensile strength and modulus are enhanced with the aligned nanofillers. Modulus of toughness and fracture strain of the samples with decorated nanotube inclusion are drastically enhanced after curing the systems in a modest magnetic field.

Keywords**:** polymer-based nanocomposite, magnetic alignment, sonochemical technique, solvent casting method, anisotropic properties.

1. INTRODUCTION

SC-15 epoxy is used for aerospace [1-3], submarine [4], armor [5] and many other military and industrial applications. It is well known that the mechanical and viscoelastic properties of epoxy polymers can be enhanced when reinforced with nanofillers [6, 7]. In this work magnetically active nanofillers and modest uniform magnetic field are used for the reinforcement. Because of the significant magnetic response of the nanofillers, it has been found that this is a low cost and relatively easy technique for imposing a strong magnetic anisotropy to the system without the need of a high field superconducting magnet. It is also found that this method is an effective way of enhancing the mechanical properties of epoxy.

In this project Fe_2O_3 nanoparticles are used as a basic nanofiller and nanocomposites are cured in a modest magnetic field of 10 kOe produced by electromagnet. Even this amount of field is enough for the Fe_2O_3 particles to align in chain-like structures along the field direction. Alignment of CNTs along a particular direction plays an important role in the enhancement of the properties of nanocomposites [8]. For this reason chemically functionalized carbon nanotubes (CNTs) are added in addition to the Fe_2O_3 nanoparticles as a second step of the project. In this case the particles alignment is used to orient the nanotubes. However, CNTs have low magnetic susceptibility therefore a sonochemical technique [9] is used as a third step of the project to decorate the outer surface of the CNTs with extremely magnetically active Fe_3O_4 nanoparticles. The induced anisotropy in physical properties of the nanocomposites is presented.

2. EXPERIMENTAL DETAILS

There are three types of nanofillers-loaded systems are prepared and analyzed. The first system consists of SC-15 epoxy mixed with 0.5–2 wt% Fe_2O_3 nanoparticles. These nanoparticles come from Sigma Aldrich Co. as a powder with a quoted particle diameters of < 50 nm and molecular weight of 159.69 g/mol. The second system consists of SC-15 epoxy with a combination of 1 wt% Fe_2O_3 nanoparticles and 0.2 wt% chemically functionalized single wall carbon nanotubes (SWCNT(COOH)s). The nanotubes are obtained from Cheap Tubes Inc. and have quoted outer diameter of 1–2 nm, a length of 0.5–2 lm, a purity > 90% by weight and a functional content 2.73% by weight. The third system consists of a SC-15 epoxy mixed with SWCNT(COOH)s. But this time the SWCNT(COOH)s are first decorated with Fe_3O_4 nanoparticles on the outer surface of the nanotubes by sonochemical technique.

Sonochemical technique consists of few steps: first, 50 mg of SWCNT(COOH), 250 mg of cetyl trimethyl ammonium bromide (CTAB) and 500 mg of 99.995% acetate are ultrasonically mixed in 50 mL of distilled water for 3 hours at 80°C. Next, mixture is centrifuged in distilled water for 30 minutes at 13,000 rpm three times and then again in ethanol at 13,000 rpm for 20 minutes. Finally, the resulting product is vacuum dried overnight at standard room conditions.

A solvent casting method is used for fabrication of epoxy-based nanocomposites [10]. The details of the preparation of the samples are described in previous paper [11].

High-resolution transmission electron microscope (HR-TEM) Jeol-JEM 2010 is used to observe particle sizes as well as distribution of the nanoparticles inside the epoxy-based nanocomposites for both RC and FC systems. For the system with decorated nanotubes, HR-TEM is also used to see how uniformly and strongly Fe_3O_4 nanoparticles attaché to the nanotubes.

Energy-filtered transmission electron microscope (EF-TEM) Zeiss Libra 120 is used for the structural characterization and for the images that highlight the presence of specific elements.

Magnetic measurements on the epoxy-based nanocomposites are performed by SQUID magnetometry (Quantum Design MPMS-5) at 300 K and applied magnetic fields $|H| < 2$ kOe. Measurements on the field cured samples are done both along the curing field (labeled ‘‘FC$\|$’’) as well as perpendicular to the curing field (labeled ‘‘FC$\perp$’’). For each sample, measured magnetic moments are normalized with respect to the nominal mass of the nanoparticles.

Tensile tests are performed on a Deben Tensile Tester. Due to small sample sizes test specimen is not standard. Sandpaper is used at both ends to prevent breaking and slipping of the sample inside of the gripping jaw. Load is applied parallel and perpendicular to the direction of the original curing field and three duplicate test samples of each type are examined. Force and displacement are recorded and converted to stress and strain, respectively.

3. RESULTS AND DISCUSSION

3.1 Transmission Electron Microscopy

To be able to observe the dispersion and arrangement of the particles after curing under magnetic field, EF-TEM is performed to get an image over several hundred nanometers within the sample as shown in Figure 1. The micrograph shows that the nanoparticles of the FC nanocomposite with 2 wt.% Fe_2O_3 concentration are dispersed evenly and aligned under external magnetic field in chains. The alignments of particles are indicated by the arrows. Thickness and length of the chains is approximately 20 nm and 100 nm respectively. The chains are well separated from each other. Nanoparticles have a spherical shape and a roughly 20 nm diameter.

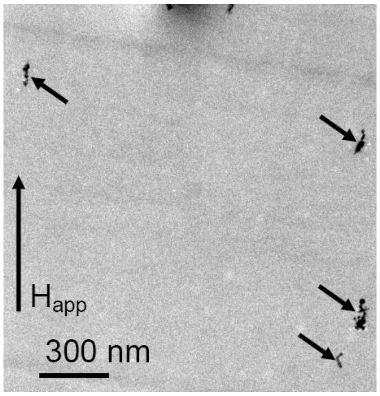

Figure 1: EF-TEM image of the FC nanocomposite of Fe_2O_3 in SC-15 epoxy.

HR-TEM images of $SWCNT(COOH)/Fe_3O_4$ powder are taken in order to understand the dispersion of Fe_3O_4 nanoparticles on outer surface of the SWCNT(COOH)s. Figure 2a shows the HR-TEM image of as-received SWCNT(COOH)s. Figure 2b illustrates SWCNT(COOH)s decorated with Fe_3O_4 nanoparticles. The roughness of the Fe_3O_4 coating contributes to sufficient interface interaction between the COOH group and the SC-15 epoxy matrix for the enhancement of mechanical properties. Figure 2c presents a high-magnification image of $SWCNT(COOH)/Fe_3O_4$ powder to estimate the size of Fe_3O_4 nanoparticles. Particles have a spherical shape, a roughly 20 nm diameter and are firmly attached to the surface of SWCNT(COOH).

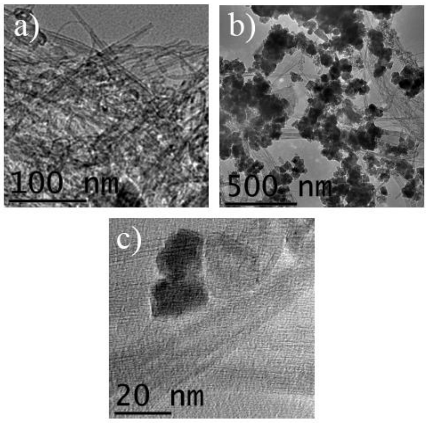

Figure 2: HR-TEM images of (a) as-received SWCNT(COOH)s, (b) as prepared SWCNT(COOH)s decorated with Fe_3O_4 and (c) HR-TEM of the Fe_3O_4 nanoparticles decorated on a SWCNT(COOH).

An EF-TEM image of FC nanocomposite with 0.5 wt.% $SWCNT(COOH)/Fe_3O_4$ concentration is illustrated in Figure 3. Small arrows indicate alignment of the nanotubes under external magnetic field $\mathbf{H}_{\mathbf{app}}$

inside the epoxy matrix. Nanoparticles are still firmly attached to the nanotubes after sonication and curing under magnetic field.

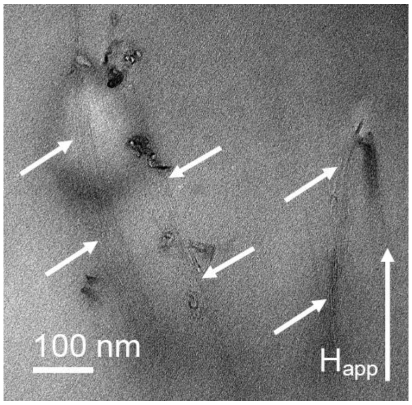

Figure 3: EF-TEM image of FC sample with SWCNT(COOH)s decorated with Fe_3O_4.

3.2 Magnetic Analysis

The effect of field orientation on the sample with 1 wt% Fe_2O_3 nanoparticles in SC-15 epoxy is illustrated in Figure 4. Three orientations are considered — RC, FC⊥ and FC||. It is clear from Figure 4 that the low-field magnetic susceptibility for FC|| is much higher than that of the RC or FC⊥.

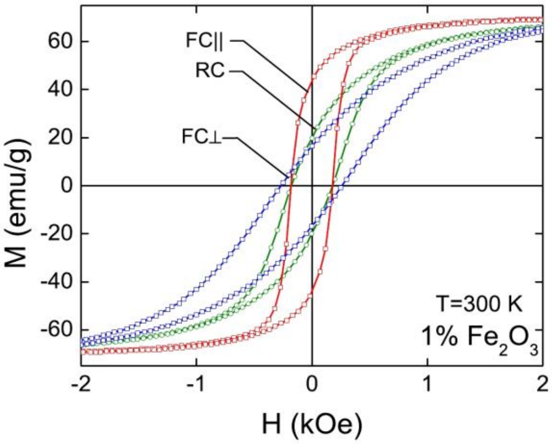

Figure 4: Magnetization curves at various orientations with respect to the sample curing magnetic field in the system with 1 wt.% Fe_2O_3. These are put in perspective by the system that had no field curing.

This implies that there is an easy magnetic axis in the direction of the curing magnetic field in the case of FC sample. The same results are observed for 0.5 and 2 wt.% Fe_2O_3 nanoparticles. Appearance of an easy magnetic axis is due to the magnetic dipole-dipole attraction between the nanoparticles in the presence of the magnetic field. As a result of such interaction, the particles rotate and organize in chains along the magnetic field (flocculation). Another reason for this flocculation process during field curing is the reduction of magnetostatic energy.

Figure 5 compares the three cases of RC, FC⊥ and FC|| for a combination of 1 wt.% Fe_2O_3 and 0.2 wt.% of SWCNT(COOH)s in SC-15 epoxy at room temperature. There is again a clear difference between the low-field magnetic susceptibility of FC|| and RC/FC⊥. The high initial susceptibility of FC|| means that the presence of SWCNT(COOH) does not impede the flocculation of magnetic nanoparticles. The same result is observed for the sample with 0.5 wt.% SWCNT(COOH)/Fe_3O_4 powder in SC-15 epoxy. As in the second type of the systems, SWCNT(COOH)s do not impede the mobility of Fe_3O_4 nanoparticles. By decorating SWCNT(COOH)s with Fe_3O_4 nanoparticles, the interaction between the applied curing field and induced moments of nanotubes is allowed. The result is in the alignment of nanofillers along the direction of the curing field.

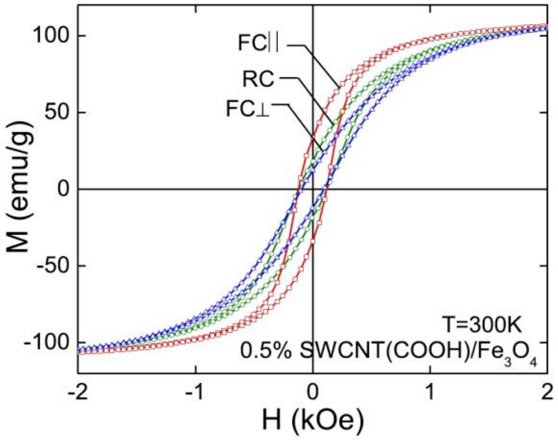

Figure 5: Magnetization curves at various orientations with respect to the sample curing magnetic field in the system with 0.5 wt.% SWCNT(COOH)/Fe_3O_4. These are put in perspective by the system that had no field curing.

3.3 Mechanical Analysis

Typical tensile stress–strain diagram for the system with 2 wt% of Fe_2O_3 nanoparticles in SC-15 epoxy is shown in Figure 6. The tensile strength is increased in all samples and orientations with respect to the neat SC-15 epoxy. There is a particular enhancement for the case where load is applied along the curing field. It can be explained as a case where the nanoparticle chains act as a ‘‘backbone’’ structure that pins the curing epoxy. This backbone is more effective as particle concentration increases to form more substantial chains.

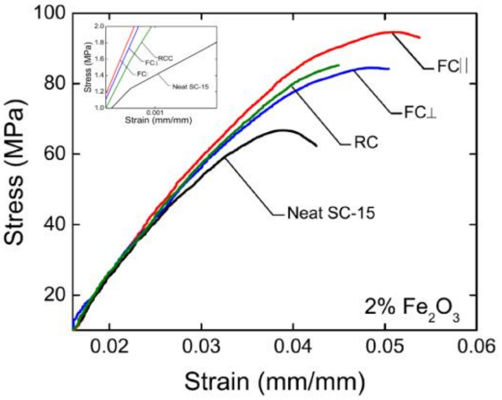

Figure 6: Tensile stress-strain response of the system with 2 wt.% Fe_2O_3.

In case of the system with 1 wt.% of Fe_2O_3 nanoparticles and 0.2 wt.% SWCNT(COOH) while the tensile strength and modulus are not changed significantly with respect to the systems with particles alone, the modulus of toughness is drastically enhanced. This enhancement is most pronounced when load is applied along the curing field direction. The toughness of the sample with 1 wt.% Fe_2O_3 and 0.2 wt.% SWCNT(COOH) (4.8 MJ/m^3) is increased by a factor of 4 over the toughness of neat epoxy (1.3 MJ/m^3). When particles and nanotubes are aligned, they share load according to their modulii. This gives the FC|| samples more strength. Since modulus is governed by the rule of mixture at the microscopic scale, a sufficient load transfers from polymer to the nanotubes and the modulus of the nanocomposite is increased.

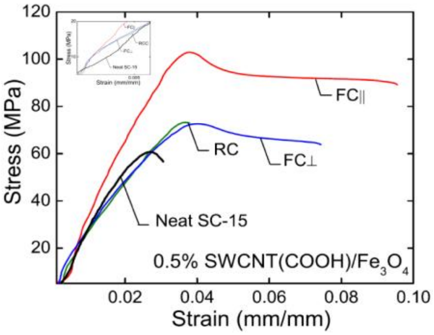

Figure 7: Tensile stress-strain response of the system with 0.5 wt.% SWCNT(COOH)/Fe_3O_4 powder in SC-15 epoxy.

Figure 7 illustrates tensile stress-strain diagram for the 0.5 wt.% SWCNT(COOH)/Fe_3O_4 powder in SC-15 epoxy. It is well known that carbon nanotubes have higher strength and modulus parallel to the tube axis [12, 13].

When they are oriented along some direction, they enhance mechanical properties of an epoxy in that particular direction – even more than just regular reinforcement of the epoxy with carbon nanotubes. That is why the maximum enhancements in tensile strength and modulus are observed in FC|| samples. The modulus of toughness, modulus or resilience and failure strain are drastically enhanced after curing the system under a magnetic field.

4. CONCLUSION

The achievement of this work is that the nanoparticles such as Fe_2O_3 and Fe_3O_4 allow for structural anisotropy in composites with an applied curing field of just 10 kOe. Magnetic anisotropy that is shown by DC magnetic measurements leads to a structural anisotropy in the systems cured under magnetic field. The tensile strength and modulus, modulus of toughness, modulus of resilience and failure strain are significantly enhanced. This demonstrates that by loading magnetic nanofillers into epoxies, in conjunction with modest magnetic field, mechanical properties of these epoxies can be significantly improved.

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