

N-Pyrrolidine Functionalized C₆₀-Fullerenes/Epoxy Nanocomposites

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ABSTRACT: A series of functionalized C₆₀-fullerene/epoxy nanocomposites were prepared, and their respective ultimate tensile strengths were determined. The functionalization route of the fullerenes was performed using the Prato reaction, with modified amino acids, resulting in the formation of *N*-pyrrolidine rings across the [6,6] junctions. Characterization of the functionalized fullerenes was done using Laser Desorption Ionization Time-of-Flight (LDI-TOF) mass spectrometry. The mechanical properties of the nanocomposites were affected by the type of modified amino acid, the degree of functional

group attachment, and the consequent degree of dispersion into the epoxy matrix. A specially blended diglycidyl ether of bisphenol A (DGEBA) epoxy, having a low viscosity and high strain-to-failure was prepared by adding 1,4-butanediol diglycidyl ether to DGEBA. The lower viscosity blended epoxy allowed for easier mixing of the fullerenes. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1120–1126, 2010

Key words: composites; curing of polymers; dispersions; thermosets; stress

INTRODUCTION

Polymer-based nanocomposites consisting of carbonaceous materials have been the focus of research efforts in the design of lighter, tougher, and stronger materials for several years. Materials made from carbon fibers^{1,2} and carbon nanotubes (single-walled or multi-walled)^{3–7} continue to be an important research topic. The main issue with these materials is the degree of dispersion within the polymer matrices. Once the dispersion issue has been resolved, the next step is to optimize the mechanical properties of the nanocomposite by adjusting the nanomaterial. For instance, carbon nanotubes are a low-density material, so very little by mass is needed in the preparation of polymer composites. In fact, loading amounts in the wide range from 0.005 to 5% by mass have been prepared.^{8,9} In the case of nanotubes, an important factor lies in the dimensions of the tubes themselves. More often, they have individual lengths on the order of micrometers and radii on the order of nanometers. Nanotubes having micrometer lengths may have defect sites, kinks, and

branches of other tubes grown from them, which could be used as a means of breaking them up, by ultrasonication and chemical treatments. Conventional wisdom suggests that smaller particles, especially in the nanometer scale in all dimensions, could be more easily dispersed into polymer matrices.^{10,11}

Since their discovery more than 20 years ago,¹² there has been a tremendous amount of chemical and physical research on C₆₀-fullerenes.^{13–15} These carbon allotropes are chemically reactive, more specifically to addition and cycloaddition reactions.¹⁶ One of the simplest and elegant cycloaddition reactions in the well-known Prato reaction, which is a 1,3-dipolar cycloaddition of azomethine ylides, to a [6,6] junction on the fullerene.^{17–20} The end result is the formation of relatively thermally stable *N*-pyrrolidine rings, which form a class of compounds known as pyrrolidinofullerenes. The percent yield and simplicity of general reaction conditions of these classes of materials may be favorable, in some cases, for the production of gram-scale amounts, which can then be useful for the design of laboratory-scale polymer nanocomposites.

Other favorable attributes of C₆₀-fullerenes are the fact that the dimensions are on the nanometer scale in all three dimensions, and that they are completely soluble in a respectable range of nonpolar solvents. It is then no secret that the higher chemical reactivity, general solubility, and dimensions of fullerenes may make them more synthetically useful as a starting material for the preparation of carbonaceous-polymer composites than carbon nanotubes. There

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have been very few reports on composites prepared from C₆₀-fullerenes and epoxy, but there has been activity with other polymer matrices, such as polystyrene (PS),²¹ polyethylene (PE),²² polypropylene oxide (PPO) with PS-C₆₀,²³ and polymethylmethacrylate (PMMA).²⁴

In this report, functionalized C₆₀-fullerenes were used for the preparation of epoxy-based nanocomposites, consisting of diglycidyl ether of bisphenol A (DGEBA), 1,4-butanediol diglycidyl ether (Araldite RD-2)*, and meta-phenylenediamine (m-PDA, as curing agent). The types of modified amino acids used for the Prato reaction are sarcosine (*N*-methylglycine), *N*-ethylglycine, and a laboratory synthesized amino-based carboxylic acid.

After functionalizing the C₆₀-fullerenes, the nanocomposites were prepared based on a 5% mass fraction loading. Chemical characterization of the functionalized C₆₀-fullerenes was performed by Laser Desorption Time-of-Flight (LDI-TOF) spectrometry. The nanocomposites were then subjected to tensile stress measurements, but the strain data could not be obtained due to the lack of fiducial marking observations, due to the relative darkness of the samples, which impeded the transmission of focused light (*vide infra*).

EXPERIMENTAL

C₆₀-fullerene functionalization

For the C₆₀-functionalization with sarcosine and *N*-ethylglycine, in both cases, 500 mg of C₆₀-fullerenes (Aldrich; 99.5%)* was dissolved in 200 mL toluene, and then 4.0 g of paraformaldehyde and either 2.0 g of sarcosine or 2.0 g of *N*-ethylglycine were added. These purple-turned brown solutions were then subjected to reflux at 100°C overnight. The red-brown powders were recovered after toluene evaporation and silica gel column purification. The samples from the reaction with C₆₀ and sarcosine were labeled C₆₀-1, and from C₆₀ and *N*-ethylglycine as C₆₀-2.

The preparation of the C₆₀-fullerene containing the synthesized aminocarboxylic acid was accomplished after the aminocarboxylic acid was synthesized. We used a similar procedure for the synthesis of the aminocarboxylic acid.²⁵ The main differences were in the use of trifluoroacetic acid (TFA), for the removal of the Boc-protecting group (*tert*-butoxycarbonyl group), and the subsequent deprotonation of the ammonium ion into the free amine, by the use of ammonium hydroxide.

*Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

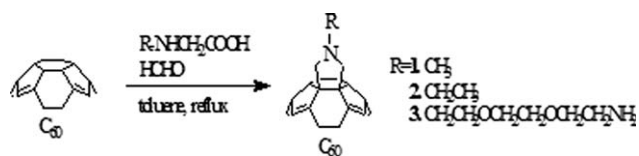


Figure 1 Reaction scheme for the functionalization of the C₆₀-fullerenes with the modified amino acids selected for this study. For C₆₀-3, two additional steps were needed for conversion into the free-amine form (see text).

Dissolution of 400 mg of C₆₀-fullerenes took place in 150 mL toluene, until a nearly homogeneous purple solution resulted. To this solution, 4.5 g paraformaldehyde and 3.3 g of the synthesized aminocarboxylic acid was added. The initial mixture was allowed to reflux at under 100°C overnight, although the purple solution soon took on a dark brown color after a few hours. The recovery of a red-brown powder was obtained after evaporation of the toluene and purification by silica gel column. The red-brown powder was dissolved in 100 mL tetrahydrofuran (THF), and then, 7 mL of TFA was added. The homogeneous brown solution was allowed to stir for 3 h. The TFA phase was removed by separatory funnel, into a 250 mL roundbottomed flask, then ammonium hydroxide was added (1 mL increments), until the pH reached between 9 to 10. Such high pH conditions resulted in the precipitation of a brown solid in a near colorless solution. The mixture was allowed to stir for 3 h, then filtered and washed with 25 mL of deionized water. The THF phase was evaporated, and also treated with 7 mL TFA, followed by similar precipitation conditions with ammonium hydroxide, filtered, and then washed. After precipitation by ammonium hydroxide, none of the brown solid was water soluble. The brown solid was subsequently washed with deionized water and dried in the oven at 60°C. Once the functionalized fullerenes were obtained, addition into the epoxy matrix was the same as all of the others. The product from this reaction scheme was labeled C₆₀-3. The reaction scheme for the attachment of all modified amino acids onto the [6,6] junction of the C₆₀-fullerenes, thus forming the relative stable five-membered *N*-pyrrolidine rings, are shown in Figure 1.

LDI-TOF mass spectrometry was used to determine the degree of substitution in the functionalized fullerenes and to obtain the average molecular mass of the recovered and purified products. A Bruker Daltonics (Billerica, MA) REFLEX II spectrometer in reflectron mode with delayed extraction at an extraction potential of 25 kV was employed. Positive ion mode data handling and analysis was performed using the Polymerix computer code (Sierra Analytics, Modesto, CA) in positive ion mode. Toluene was used to disperse the functionalized fullerenes onto the stainless steel target plates.

TABLE I
The Amounts (in mg) of Each Component Used During the Nanocomposites Preparation

Sample	Fullerene amount (mg)	DGEBA amount (mg)	RD-2 amount (mg)	m-PDA amount (mg)
C ₆₀ -neat	332	4200	1300	800
C ₆₀ -1	416	5400	1600	900
C ₆₀ -2	467	6000	1800	1100
C ₆₀ -3	150	1900	600	300

LDI-TOF analysis could not be performed for the ammonium hydroxide-precipitated brown solid, but was carried out on the brown solid before TFA workup. Although this material was labeled as C₆₀-3, for mass spectrometry purposes, the product still has the Boc-protecting group (*t*-butoxycarbonyl group) attached, due to the synthetic procedure. The workup of the final brown solid suggests that the free-amine ends further reacted with nearby fullerenes, thereby causing aggregation. This aggregation proved to be problematic during the epoxy blending step (*vide infra*).

We also determined the average molecular mass for untreated C₆₀-fullerenes, mainly to see how close we could get to the monoisotopic mass of 720 g/mol. This was necessary due to the 99.5% purity of the C₆₀-fullerenes.

Preparation of epoxy nanocomposites

Composites were prepared having a 5% mass fraction of either functionalized fullerenes or neat fullerenes. The actual amounts, along with the amounts of DGEBA, RD-2, and m-PDA are shown in Table I.

In each case, the fullerene-based powders were mixed into the DGEBA/RD-2 blends for 1 h (except for the C₆₀-neat, which did not disperse, so an additional 2 h were given), using a mechanical stirrer, then placed in a vacuum oven for degassing at 70°C for 2 h. Ultrasonication for the C₆₀-neat and C₆₀-3 may have been more successful, but consistency was priority in our mixing procedure. The m-PDA was melted at 70°C, and then added and mixed into the epoxy mixture. The mixtures were then loaded into silicone rubber molds.

The molds for the preparation of the dog-bone tensile test (DBTT) specimens were made with silicon rubber (General Electric Silicones, RTV664A/RTV664B) following a previously described procedure.²⁶ All molds were postcured at 150°C for 1 h, and rinsed with acetone before use.

The sample-filled molds were then placed into a preheated (60°C) programmable oven (Blue M, General Signal, model MP-256-1, GOP). A curing cycle of 3 h at 60°C followed by 2 h of post curing at 121°C was used.

Mechanical testing

Tensile tests were carried out on our automated tensile testing machine described elsewhere.²⁷ The instrument is equipped with a Fostec (150 W) illumination system and a digital camera that scans the gage length of the dog-bone specimen after each strain increment. Before testing, all samples were polished with emery paper of no. 800, no. 1200, and no. 2400, to remove stress concentration sites at the edges of the samples, and to get the average thickness and average width of each dog-bone section at around (1.55 mm ± 0.04 mm) by (4.05 mm ± 0.04 mm). To facilitate strain measurements, transverse fiducial marks (~ 10 mm apart) were applied to each end of the specimen gage length by a green color permanent pen. Strains at each step would have been calculated using the scanned images of each step. In this report, the only sample that had strain measurements was the neat epoxy. The expected standard uncertainty has been determined to be 1% of the values for the tensile strength measurements.

The specimen was loaded in the grips with a slight pretension (17N) and then loaded in tension by the sequential application of step-strains. During the test, 35 step-strains were scheduled and the total deformation was ~ 3.0 mm. Each step-strain was applied at a rate of 85 μm/s and the average deformation in the specimen during each step-strain was 85.7 μm. The delay time between the applications of successive step-strains was 10 min. In the absence of premature failure of the test specimens, the sample was unstressed and removed after the 35 strain-steps.

RESULTS AND DISCUSSION

The mass spectra of C₆₀-neat (Fig. 2) shows no pyrrolidine groups, C₆₀-1 (Fig. 3) and C₆₀-2 (Fig. 4)

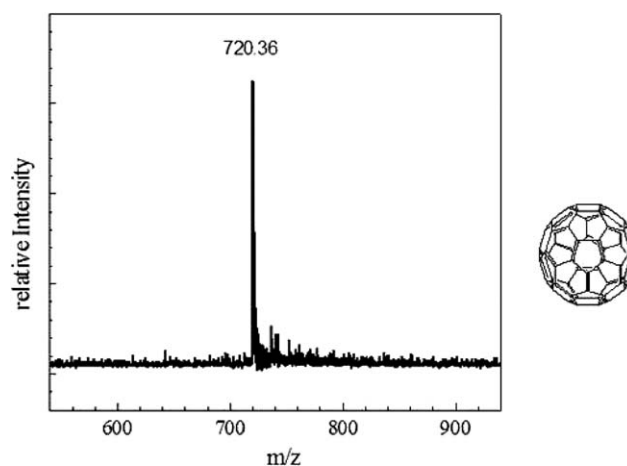


Figure 2 LDI-TOF mass spectrum of C₆₀-neat, producing a molecular mass of 720 g/mol.

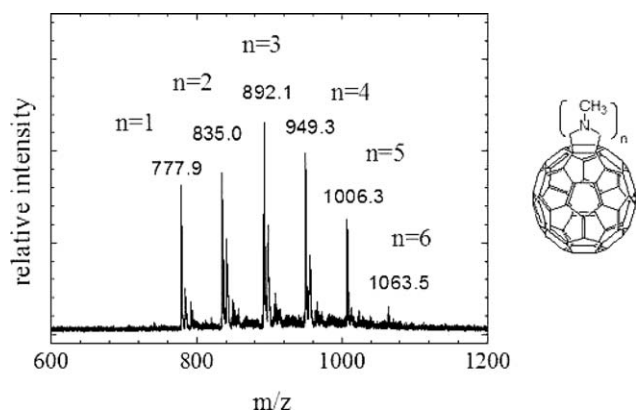


Figure 3 LDI-TOF mass spectrum of C₆₀-1, producing a number average molecular mass of 901 g/mol.

showed averages of three and four functional groups per fullerene molecule, respectively. Furthermore, Figures 3 and 4 show that upward of six and seven functional groups can be attached to the C₆₀-1 and C₆₀-2 substituted fullerenes, respectively. On the other hand, C₆₀-3 (Fig. 5) shows mainly one and a small amount of two pyrrolidine groups. To minimize fragmentation of the functional groups by the matrix, and to facilitate accurate determinations of the number average molecular mass of each treated fullerene, LDI-TOF analyses were performed. More recent work has shown that *trans, trans*-1,4-diphenyl-1,3-butadiene (DPB; CAS no. 886-65-7) is a viable matrix for such studies of functionalized C₆₀-fullerenes for producing abundant ions, without extensive functional group fragmentation.²⁸

The first observation is the extent of dispersion within the epoxy matrix. The C₆₀-neat and C₆₀-3 samples did not blend well. During the degassing step, it was noticed that the majority of the solids settled to the bottom, although the typically clear DGEBA/RD-2 blend did show some gray/brown color to it.

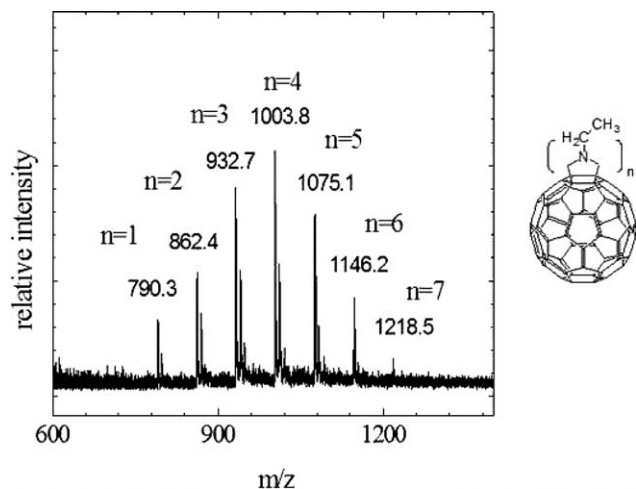


Figure 4 LDI-TOF mass spectrum of C₆₀-2, producing a number average molecular mass of 1012 g/mol.

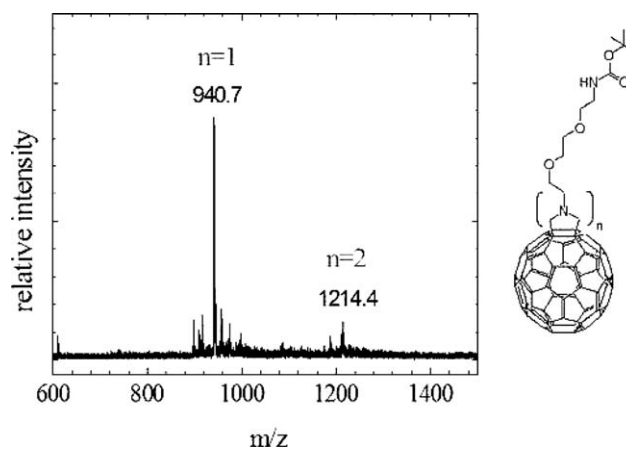


Figure 5 LDI-TOF mass spectrum of C₆₀-3, producing a number average molecular mass of 1062 g/mol. This mass spectrum was obtained for the functional groups with the Boc-protecting group still attached, due to the aggregation of the free-amine materials, and further complications due to ionic species. (see text).

During the workup of C₆₀-3, it was previously discussed that during deprotonation of ammonium to amine, precipitation occurred. It is not likely that the ammonium salt of C₆₀-3 would be considerably more soluble in water than the free amine, but previous reports on the general reactivity of amines to C₆₀-fullerenes have been noted.²⁹⁻³² The precipitation could very well be explained by the interactions between the free amine and the fullerene, resulting in particle aggregation (Fig. 6). This particle aggregation further inhibited dispersion into the DGEBA/RD-2 blend, resulting in particle settlement during the curing of the samples.

The C₆₀-1 and C₆₀-2 samples were so well dispersed in the DGEBA/RD-2, they could be considered relatively homogeneous, producing a reddish-brown solution. Upon curing, the brown color of m-PDA (a natural consequence of darkening) contributed in producing very dark-red dog-bone samples.

During the polishing step, the C₆₀-neat and C₆₀-3 dog bones were polished from the top, due to particle settlement, but it then became apparent that the untreated C₆₀-fullerenes did undergo a reaction within the curing epoxy. This was observed due to some polishing on the bottom of the dog bones producing reddish-brown residue. For the C₆₀-1 and C₆₀-2 samples, there was no concern about how to polish the samples, but we maintained consistency by always polishing from the top.

The mechanical testing focused on ultimate tensile strength. Important complementary data, such as strain-to-failure and modulus, could not be ascertained due to the difficulties in imaging the samples during testing. Our tensile testing instrument relies on a focused light source that transmits through the sample to a camera that obtains images during each

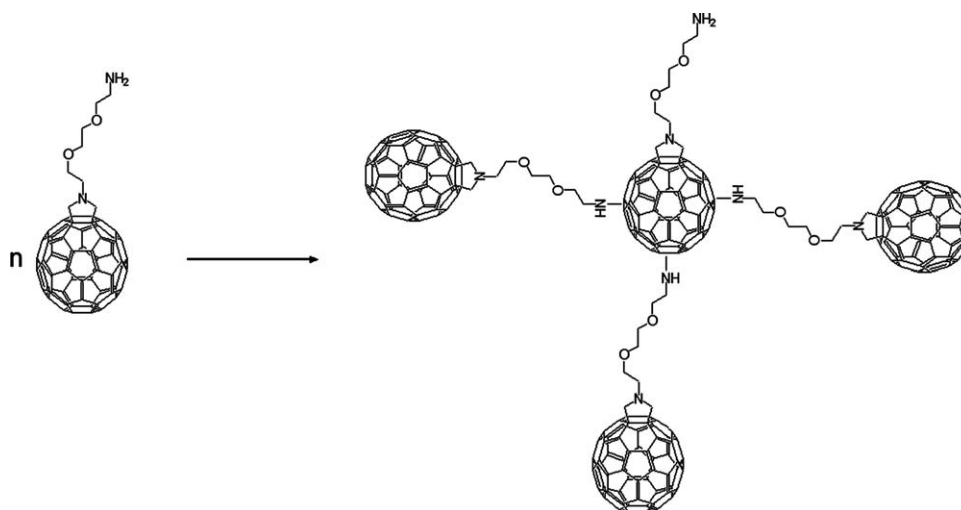


Figure 6 Simplified drawing showing the potential for the free-amine groups to react with other functionalized fullerenes, producing particle aggregation.

loading step. Of importance are the fiducial marks described earlier that are used to determine strain or percent elongation while the sample is undergoing stress. These samples were too dark for effective transmittance, so no images, and hence no strain data, could be gathered. In its place, stress versus displacement curves will be presented.

In each of the following figures, the curves appear to be undulating, but steadily increasing. The cause is due to applied stress, followed by relaxation during each loading step. Since these materials are viscoelastic, we would expect the material to begin relaxing, once the applied deformation is halted.^{33,34} The expected standard uncertainty has been calculated to be 1% of the values reported for the tensile strength measurements.

Figure 7 shows the stress versus displacement curve for the representative neat epoxy sample. Stress values exceeding 80 MPa were measured, with specimen breakage occurring just after 0.25 cm displacement. All of the C₆₀-fullerene samples will be compared to this one figure. Figure 7 also shows the stress versus displacement curve for the representative C₆₀-neat/epoxy sample. Stress values just below 60 MPa were measured, with specimen breakage occurring just before 0.12 cm displacement. This sample clearly does not have the tensile stress value of the neat epoxy and broke with fewer load steps.

Figure 8 shows the stress versus displacement curve for the representative C₆₀-1/ epoxy sample. Stress values just above 65 MPa were measured, with specimen breakage occurring just before 0.19

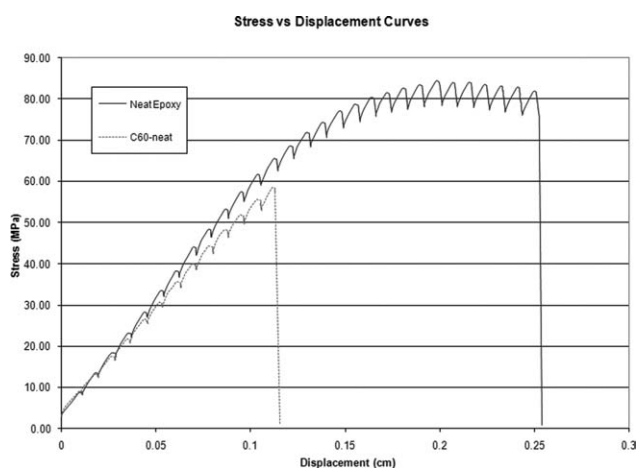


Figure 7 Stress versus Displacement curves for the representative neat epoxy and C₆₀-neat samples. Standard uncertainty $\pm 1\%$ for tensile stress values. Note: Slight positive prestress added to all samples to prevent slippage of dog-bone specimens in grips results in positive stress values before applied stress.

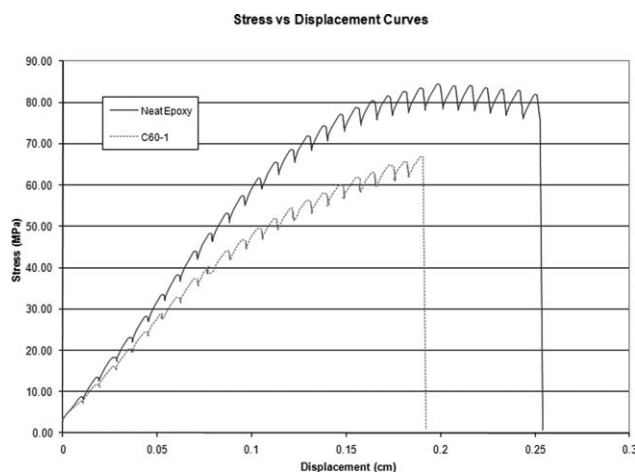


Figure 8 Stress versus Displacement curves for the representative neat epoxy and C₆₀-1 samples. Standard uncertainty $\pm 1\%$ for tensile stress values. Note: Slight positive prestress added to all samples to prevent slippage of dog-bone specimens in grips results in positive stress values before applied stress.

cm displacement. This sample has a higher tensile stress than the C₆₀-neat/epoxy and appears to be less brittle, but both its stress and displacement were below the neat epoxy.

Figure 9 shows the stress versus displacement curve for the representative C₆₀-2/ epoxy sample. Stress values just above 65 MPa were measured, with specimen breakage occurring at 0.16 cm displacement. This sample is similar to the C₆₀-1/epoxy sample, which makes sense, in terms of similar chemical composition.

Figure 10 shows the stress versus displacement curve for the representative C₆₀-3/epoxy sample. Stress values just around 55 MPa were measured, with specimen breakage occurring below 0.12 cm displacement. This sample shows similar behavior to the C₆₀-neat/epoxy sample. This is understandable, since it was these two samples which did not disperse well into the DGEBA/RD-2 blend.

Upon comparing each of the fullerene/epoxy samples against the neat epoxy, stress in the fullerene samples appears to be linearly increasing and then breaking abruptly. For the neat epoxy, the sample stress increased linearly, up to 80 MPa, and then leveled off before breakage. The neat epoxy samples that contain this matrix component generally show this trend. The leveling off near breakage is typical for these neat epoxies that generally have high strain-to-failure. To put it in another way, the fullerene/epoxy samples are much more brittle than the neat epoxy, and undergo catastrophic failure at lower loading steps.

What is of interest is that the untreated fullerenes produced higher tensile stress, with respect to C₆₀-3, even though both contained visible aggregates. The

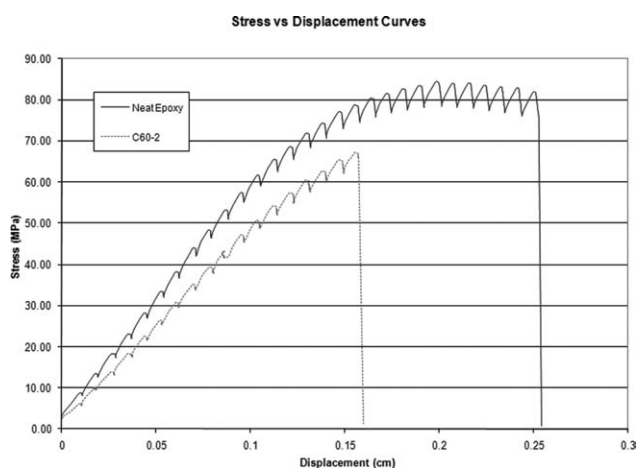


Figure 9 Stress versus Displacement curves for the representative neat epoxy and C₆₀-2 samples. Standard uncertainty $\pm 1\%$ for tensile stress values. Note: Slight positive prestress added to all samples to prevent slippage of dog-bone specimens in grips results in positive stress values before applied stress.

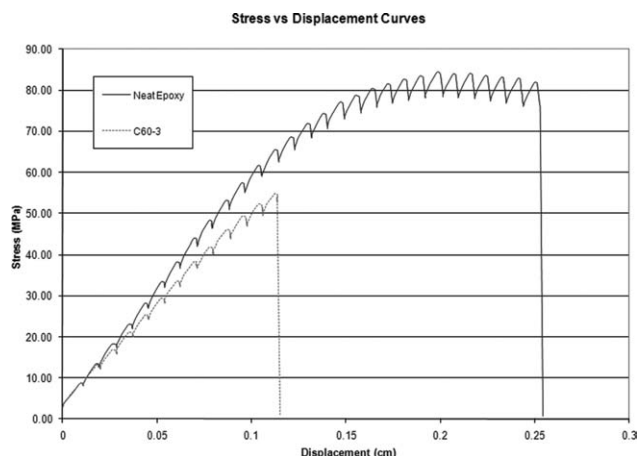


Figure 10 Stress versus Displacement curves for the representative neat epoxy and C₆₀-3 samples. Standard uncertainty $\pm 1\%$ for tensile stress values. Note: Slight positive prestress added to all samples to prevent slippage of dog-bone specimens in grips results in positive stress values before applied stress.

difference between C₆₀-neat and C₆₀-3 may be due to the degree of dispersion. It is also possible that the C₆₀-neat molecules have more favorable π - π interactions with the phenyl rings, of DGEBA and m-PDA. These π - π interactions would not be strong enough for complete dispersion of the untreated fullerenes, but the untreated fullerenes would have more conjugated six-member rings available for favorable interactions with the phenyl rings of DGEBA. Also untreated fullerenes, to a larger extent over C₆₀-3, may react with m-PDA, causing small amounts to be functionalized and better dispersed.

CONCLUSIONS

Epoxy-based nanocomposites consisting of functionalized C₆₀-fullerenes were prepared using a process known as the Prato reaction with modified amino acids. Dispersion was more successful with C₆₀-fullerenes treated with *N*-alkyl amino acids. For the well-dispersed functionalized fullerenes, slight improvements in the ultimate tensile strengths, relative to the C₆₀-neat epoxy, were noticed, whereas the low dispersed materials resulted in weaker samples. In all cases, displacement at breakage did not approach that of the neat epoxy, which may indicate that the C₆₀-fullerene/functionalized fullerenes produced a more rigid material.

Also of note, untreated C₆₀-fullerenes are reactive to the type of curing agent used in this study, with further evidence of the reactivity of C₆₀-fullerenes with other amine-based curing agents available in the literature.²⁶⁻²⁹ Also of importance in this study is the ability of a bonded *N*-pyrrolidone ring having a free-amine end group to further react with other

fullerenes, rendering a potentially well-dispersable material into insoluble aggregates, not only in water but in the epoxy system. This holds importance not only in the further study of different functionalized fullerenes and epoxy but also in the area of biological interests of the cytotoxicity of fullerenes/functional fullerenes, due to the difference in solubility behavior in cellular environments, which may depend on the functionalized fullerenes possessing electrical charge or maintaining charge neutrality.

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