

DEFECT SITE FUNCTIONALIZATION: AN APPROACH FOR PROMOTING ADHESION IN CARBON NANOPARTICLE/EPOXY NANOCOMPOSITES

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Introduction

Adhesion has often been altered in polymer nanocomposites composed of nanotubes by treating the nanotubes with acid solutions that completely disrupts the nanotubes' π - π bonding structure, thereby greatly reducing their electrical conductivity and possibly their mechanical strength. It has recently been demonstrated that specific sites on C₆₀-fullerenes and the defect sites on carbon nanotubes can be selectively functionalized, without significantly altering the π - π bonding structure of the carbon nanotubes. Although this approach will only generate a fraction of the possible adhesion sites, Holmes *et al.* in 2003 demonstrated that 80 % of the maximum adhesion at the fiber matrix interface in conventional composites can be obtained by having only 33 % of the fiber surface containing groups capable of promoting covalent bonding [1].

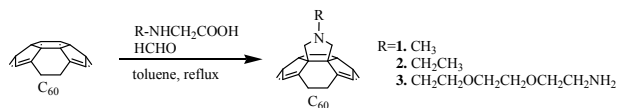
This research seeks to expand on the Holmes *et al.* research results by quantifying the impact that a site-specific functionalization approach has on the mechanical performance of nanocomposites composed of carbon nanoparticles embedded in epoxy resins, as the adhesion strength at the nanoparticle-matrix interface is altered. Recent research by Kinloch *et al.* indicates an increase in fracture energy due to debonding of the nanoparticles and subsequent plastic void growth for anhydride cured epoxy nanocomposites composed of well dispersed silica nanoparticles [2,3].

In this study, C₆₀-fullerenes were functionalized with *N*-methylpyrrolidine, *N*-ethylpyrrolidine and an amine-functionalized pyrrolidine derivative with ethylene oxide spacers for the preparation of C₆₀-epoxy nanocomposites through a process known as 1,3 dipolar cycloaddition. The amine-functionalized derivatives can form covalent bonds with the epoxy molecules, which should enhance the adhesion between the functionalized fullerenes and the epoxy matrix. **Scheme 1** shows the C₆₀-nanocomposites we have made for this study.

The specific epoxy matrix consist of diglycidyl ether of bisphenol A (DGEBA) as the bulk epoxy with a small amount of 1,4-butanediol diglycidyl ether (DGBD) added in order to decrease the viscosity of the matrix, enabling easier dispersion of the functionalized fullerenes.

Experimental

C₆₀ derivatives were synthesized by the decarboxylation of immonium salts derived from condensation of α -amino acids with aldehydes [4,5]. For product **1** shown in **Scheme 1**, a mixture of C₆₀, *N*-methylglycine, and paraformaldehyde was heated in 75 mL of toluene for 2 h. The resulting brown solution was washed with water (2 x 50 mL), and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, eluant toluene, triethylamine). For product **2**, the same procedure was applied using *N*-ethylglycine instead of *N*-methylglycine.



Scheme 1. C₆₀ derivatives

For the synthesis of product **3**, we followed ref 6. At first, we synthesized the Boc-monoprotected diamine, and then the free amine side was reacted with benzyl bromoacetate and followed by hydrogenation for conversion to an α -amino acid. The resulting Boc⁺-monoprotected amino acid was reacted with C₆₀ using the same process of product **2**, and then the Boc-protecting group was removed using trifluoroacetic acid (TFA). All reagents were used as received.

Laser Desorption/Ionization Time-of-Flight (LDI-TOF) mass spectrometry was used to examine the derivatives and to determine the degree of substitution in the product and the average molecular mass. Toluene was used to disperse the functionalized fullerenes onto the stainless steel target plates. The mass spectrometer was used in

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⁺ Abbreviation: Boc, (*tert*-butoxy)carbonyl.

reflectron mode with delayed extraction at an extraction potential of 25 kV. The positive ion mode was used.

The testing of the C₆₀-epoxy nanocomposites consisted of a 5 mole fraction (%) loading of the functionalized fullerenes into an epoxy matrix consisting of a blend of diglycidyl ethers (77 % DGEBA and 23 % DGEBD), followed by curing with meta-phenylenediamine (m-PDA). Mechanical properties such as tensile strength, modulus, and hardness were subsequently measured.

Results and Discussion

Figure 1, and **Figure 2**, show the mass spectra of *N*-methylpyrrolidine and *N*-ethylpyrrolidine derivatives of C₆₀ after column separation. Both figures show up to 6 or 7 pyrrolidine rings on the fullerenes using our procedure, although Prato and Maggini *et al.* reported that up to 9 pyrrolidine rings can be introduced [7]. The average molecular masses using the first peak series were calculated and appear in **Table 1**.

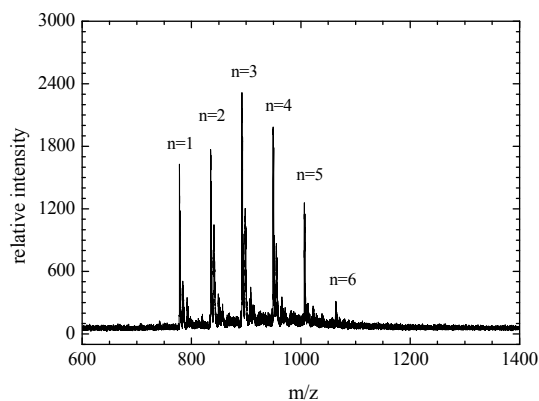


Figure 1. LDI-TOF mass spectrum of the *N*-methylpyrrolidine derivatives of C₆₀.

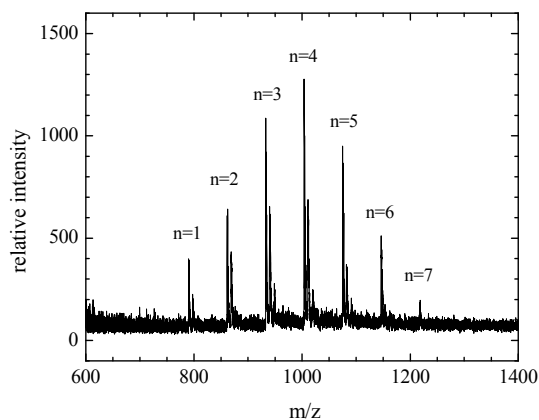


Figure 2. LDI-TOF mass spectrum of the *N*-ethylpyrrolidine derivatives of C₆₀.

Table 2 shows the tensile strengths of the neat epoxy and the functionalized fullerene-epoxy nanocomposites by applying step loading. The tensile strengths of the nanocomposites are comparable to the neat epoxy, signifying good adhesion between the functionalized fullerenes and the epoxy matrix.

Table 1. The average molecular mass of *N*-methylpyrrolidine, and *N*-ethylpyrrolidine functionalized C₆₀.

Sample	Mn (u)	Mw (u)
C ₆₀ -R1	901	908
C ₆₀ -R2	1012	1035

Table 2. Tensile strength tests for the functionalized fullerene-epoxy samples, including the neat epoxy as reference.

C ₆₀ -epoxy Sample	Tensile Strength (MPa)
Neat Epoxy	76.3
C ₆₀ -R1	79.3
C ₆₀ -R2	75.0
C ₆₀ -R3	-

- C₆₀-R3 was not measured yet.

Conclusions

C₆₀-fullerenes were functionalized through the process of 1,3 dipolar cycloaddition of azomethine ylides producing up to six or seven adducts on the fullerenes. The functionalized fullerenes were used to produce nanocomposites with a specific epoxy matrix. Mechanical properties of the functionalized fullerene-epoxy nanocomposites were characterized in this study. Preliminary results showed that the tensile properties of the functionalized fullerene-epoxy samples closely matched those of the neat epoxy.

References

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