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Liquid-crystal-functionalized carbon nanotubes improve nanocomposite properties

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The addition of carbon nanotubes, functionalized with 4′-allyloxy-biphenyl-4-ol, to silicone resin improves the mechanical and thermal properties of the resultant nanocomposites.

Carbon nanotubes (CNTs) have been shown to effectively improve the thermal, mechanical, and electrical properties of polymer materials.[1–3] As a result of these features, polymer/CNT nanocomposites find application in a wide range of scientific and industrial applications. Indeed, recent studies have shown that these nanocomposites can be implemented in devices for biomedical diagnostics.

However, many studies of polymer/CNT nanocomposites reveal segregation and non-uniform mixing behavior. These issues often cause serious concerns regarding the reproducibility of the electrical, mechanical, and thermal behaviors of the resulting composites.[4] To take full advantage of the remarkable geometric structure of CNTs for a variety of applications, particularly for their integration in polymer composites, CNTs can be functionalized with complementary molecules to improve the dispersion and compatibility of CNTs within the polymer matrix.[5,6]

We synthesized and characterized a liquid crystal molecule—4′-allyloxy-biphenyl-4-ol (AOBPO)[7]—and used this molecule to functionalize CNTs via physical and chemical means. We then mixed the resulting CNTs with a silicone resin to create nanocomposites, which we investigated in order to determine the effect of this functionalization on the mechanical properties of the samples. The specific structure and crystallinity of AOBPO make it compatible with silicone resin and enable its homogeneous dispersion in polymer matrices.

To synthesize the AOBPO, we added 10.1g of potassium hydroxide, 6.7g of 4,4′-dihydroxybiphenyl, and moderate concentrations of H_2O and ethanol into a 250mL three-necked flask equipped with a dropping funnel and a reflux condenser. We slowly heated this mixture to 80°C and then added 15.5mL of allyl bromide via the dropping funnel. The reaction mixture was refluxed for 24 hours at 80°C. We then filtered

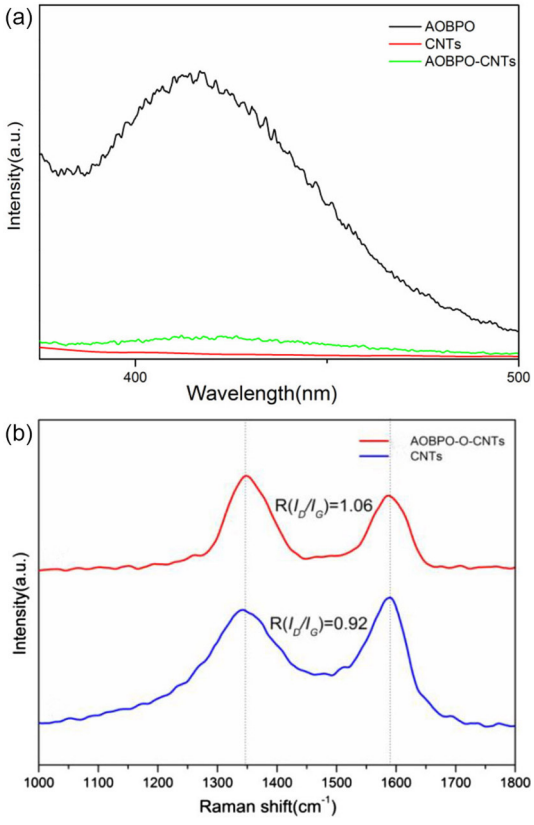

Figure 1. *(a) Room-temperature photoluminescent emission spectra, obtained using an excitation wavelength of 325nm, and (b) Raman spectra of carbon nanotubes (CNTs). AOBPO-CNTs and AOBPO-O-CNTs: CNTs that have undergone functionalization with a liquid crystal molecule (4′-allyloxy-biphenyl-4-ol, AOBPO) via physical and chemical means, respectively. R(I_D/I_G): Band-intensity ratio of the two first-order bands.*

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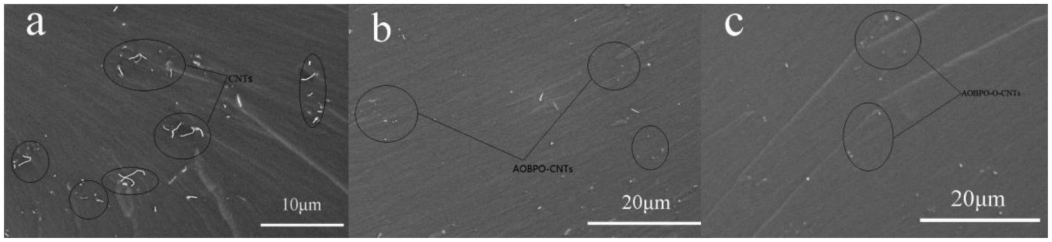

Figure 2. *Scanning electron micrographs of (a) pristine CNTs, (b) AOBPO-CNTs, and (c) AOBPO-O-CNTs dispersed in silicone resin.*

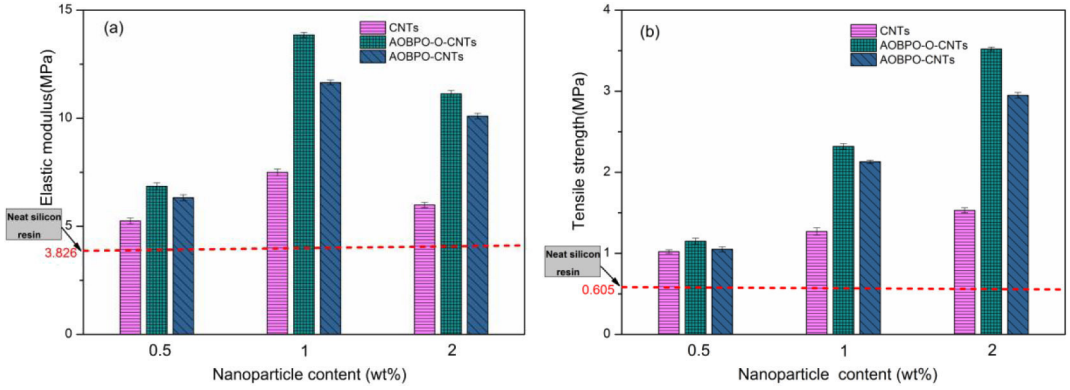

Figure 3. *(a) Elastic modulus and (b) tensile strength of neat silicone resin and nanocomposites of silicone resin and CNTs, AOBPO-O-CNTs, and AOBPO-CNTs.*

and recrystallized the precipitated product twice over ethanol and used the resulting AOBPO molecules to both physically and chemically functionalize the CNTs. To achieve physical functionalization, we dissolved 0.04g of AOBPO in 10mL of ethyl alcohol and added 0.3g of CNTs. The resulting mixture was sonicated in an ultrasonic bath for 30 minutes and then filtered and washed with distilled water. We then dried the final products in a vacuum at 80°C for 24 hours to create CNTs physically functionalized with AOBPO (AOBPO-CNTs). To chemically functionalize CNTs, we dispersed 0.3g of oxidated CNTs (O-CNTs) in 50mL of ethyl alcohol and sonicated the resulting mixture in an ultrasonic bath for 30 minutes. We then added 0.04g of AOBPO to the solution and poured the mixture into a 100mL three-necked flask. The flask, equipped with a reflux condenser and a magnetic stir bar, was kept at 80°C and vigorously mixed for 12 hours. The resulting product was filtered and washed with distilled water and then dried in a vacuum at 80°C for 12 hours to create AOBPO chemically functionalized CNTs (AOBPO-O-CNTs).

We then characterized CNTs, AOBPO-CNTs, and AOBPO-O-CNTs using Fourier transform IR spectroscopy, thermogravimetric analysis, fluorescent spectroscopy, and Raman spectroscopy. The results show drastic quenching of the AOBPO fluorescence in both functionalized CNT types, suggesting that the biphenyl anchoring unit of liquid-crystalline AOBPO strongly interacts with the surface of CNTs via π-π interactions: see Figure 1(a). The increased band-intensity ratio of the functionalized CNTs—see Figure 1(b)—reflects the relative degree of functionalization versus defects in the CNTs, and indicates that covalent functionalization has taken place in the AOBPO-O-CNT nanocomposites.

We mixed the two functionalized CNTs with silicone resin to fabricate silicone resin nanocomposites. For comparison, we also fabricated nanocomposites with neat CNTs. Scanning electron microscopy images (see Figure 2) indicate that the dispersion and compatibility of CNTs in silicone resin were improved effectively after both physical and chemical functionalization with AOBPO.

Our experimental investigations determined that nanocomposites reinforced with AOBPO-O-CNTs had a higher elastic modulus and tensile strength than those with AOBPO-CNTs. With an AOBPO-O-CNT mass fraction of 1%, the elastic modulus of the silicone resin nanocomposites increased by 262% over that of neat silicone resin, and with a mass fraction of 2%, tensile strength increased by 482%: see Figure 3. In comparison, the enhancements to tensile strength that occurred as

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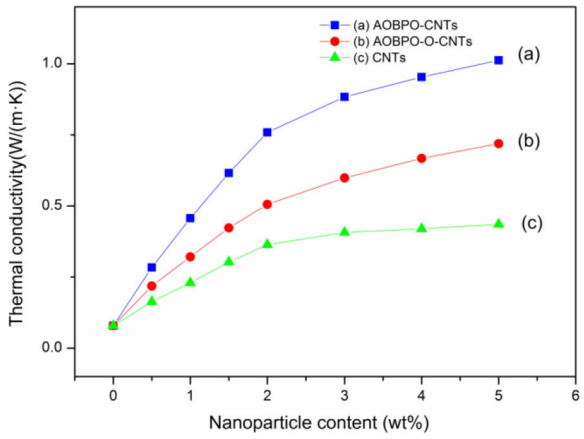

Figure 4. *Thermal conductivities of silicone resin nanocomposites filled with CNTs, AOBPO-CNTs, and AOBPO-O-CNTs of different mass fractions (from 0 to 5wt%) at 25°C.*

a result of the addition of AOBPO-CNTs were lower, but still showed significant increases over neat CNTs.

The nanocomposites reinforced with AOBPO-CNTs, however, provided higher thermal conductivity than those fabricated with AOBPO-O-CNTs (see Figure 4). The thermal conductivity of the resin filled with the AOBPO-CNTs was increased to 1.176W/(m·K) at a mass fraction of 5%, which constitutes an enhancement of more than 14 times that of neat silicone resin.

In summary, we used a liquid crystalline molecule (AOBPO) to functionalize CNTs via both physical and chemical means. The results of our mechanical and thermal measurements indicate that silicone resin nanocomposites filled with AOBPO-O-CNTs or AOBPO-CNTs greatly increase both the thermal conductivity and mechanical performance compared with those fabricated using neat silicone resin. In the next stage of our work, we will investigate the interaction mechanism between liquid crystal molecules and CNTs to develop high-performance CNT nanocomposites.

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