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Influence of graphene oxide in polytriazoleimide nanocomposites

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Polytriazoleimide composites containing at least 1wt% graphene oxide nanoparticles exhibit substantially improved thermal, mechanical, flame retardancy, dielectric, and water-absorption properties.

Aromatic polyimides (PIs)—having a combination of exceptional mechanical, thermal, electrical, and optical properties, as well as chemical and solvent resistance—are one of the most important classes of high-performance polymers. They have therefore gained much attention in many applications, e.g., for use as insulating layers in semiconductor devices, microelectromechanical systems, or substrates for flexible printed circuits (particularly because of their relatively low dielectric constants).[1,2] Most aromatic PIs, however, are difficult to process—because they are insoluble in most organic solvents and because they do melt or soften below their decomposition temperatures—and their applications are thus restricted. Incorporating new functional groups to make PIs more tractable, and without decreasing their desirable properties, has thus become a major focus for PI modification.[3]

In recent years, ‘click’ chemistry (i.e., a class of biocompatible reactions used to join substrates with specific biomolecules) has received increasing interest in organic synthesis, supermolecular chemistry, and surface modification of materials. This is because of its high selectivity, high yields, tolerance to a wide range of functional groups, and high chemical stability. Specifically, the click reaction is a highly efficient organic reaction in which 1,3-dipolar cycloaddition occurs between azide and alkyne moieties in the presence of a copper catalyst.[3,4]

In our work,[5] we have thus exploited the click reaction to fabricate a number of nanocomposite films that contain graphene oxide (GO)—produced by the Hummers method[6]—within a polytriazoleimide (PTAI) matrix. In particular, we used the copper-catalyzed 1,3-dipolar cycloaddition of azides and alkynes (CuAAC) to synthesize a series of hetero-aromatic diamines (i.e., containing a 1,2,3-triazole ring). We then used a conventional two-step method[3,4] to mix these diamines with dianhydride, and to thus create our novel PIs (i.e., the PTAIs).

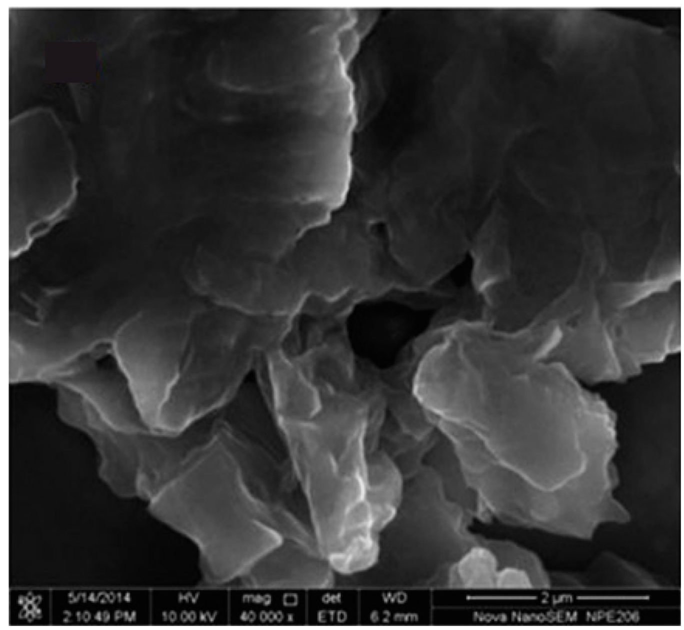

Figure 1. *Scanning electron microscope image of graphene oxide (GO) particles used in the polytriazoleimide (PTAI) nanocomposites.*[5]

In the first part of our study, we investigated PTAIs that contained either an aromatic or an alkyl spacer. We found that these polymers exhibited low dielectric constants, high thermal stabilities, as well as good flame retardancy and mechanical properties. In addition, these materials were readily soluble in highly polar solvents. Furthermore, the PTAIs that contained the aromatic spacer had better mechanical, thermal, and dielectric properties than those that contained the alkyl spacer.

We have also used the thermal imidization method[5] to examine the effect of the GO concentration (i.e., for 0.5, 1, 2, and 3wt% GO) on the PTAI hybrid system. Both our transmission electron microscopy and scanning electron microscopy (see, e.g., Figure 1) results reveal that

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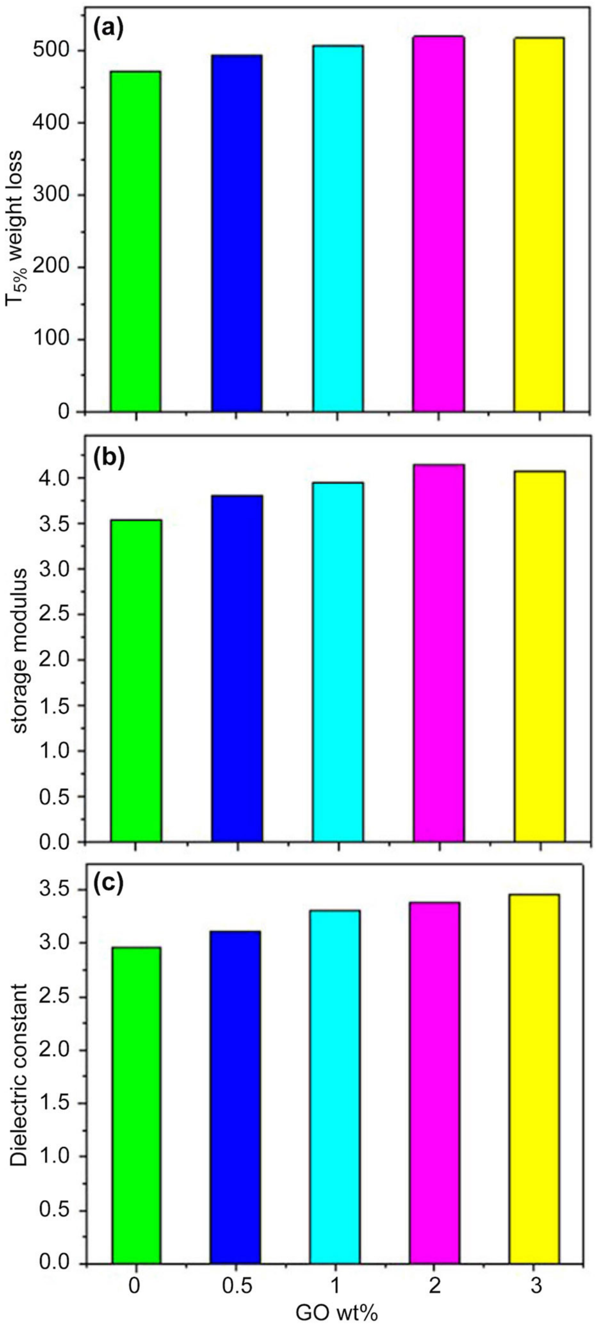

Figure 2. *Illustrating the (a) thermal properties, (b) results of a dynamic analysis, and (c) dielectric constants of the PTAI/GO nanocomposites. $T_{5\%}$: Temperature at which 5% mass loss occurs. wt%: Weight percent (i.e., concentration).*[5]

the GO is generally well dispersed (exfoliated) within the nanocomposites. In addition, we find that the nanocomposites have a high thermal stability—see Figure 2(a)—that increases with increasing GO content (from 473 to 518°C). We attribute the improvement in thermal properties to the good dispersion of the GO within the PTAI matrix, as well as to the strong interfacial adhesion and interlocking structure that exists between the GO and the matrix (arising from the wrinkled morphology of the GO particles).

We also observe that the char yield of the materials increases with GO content (55.1–58.1), which indicates that these PTAI/GO nanocomposites can be used for flame-retardancy applications (also suggested by their limiting oxygen index values). Likewise, our dynamic mechanical analysis results show that the glass transition temperature and storage modulus—see Figure 2(b)—of the nanocomposites also increase with GO content (255–263°C and 3.54–4.14GPa, respectively). Lastly, we observe that our samples have high dielectric constants—between 2.96 and 3.46: see Figure 2(c)—and low dielectric loss (0.38–0.09) at 1MHz. Our results (see Figure 2) also clearly show that a GO concentration of only 1wt% has a substantial influence on the thermal, mechanical, and dielectric properties of the nanocomposites, and that higher GO concentrations do not particularly improve the properties.

It is well known that the moisture-absorption properties of polymers are of great importance with regard to their practical use in microelectronics.[7] For instance, absorbed water in the polymer structure affects the performance and long-term stability of polymers. In our study we thus investigated the moisture-absorption properties of nanocomposites. For these tests we placed the PTAI/GO films in a water bath (at 25°C) for one week. We then removed the samples from the water and dried them with a tissue, before weighing them and calculating the percentage weight change of each specimen, i.e., according to the equation:

$$\text{Weight change (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weight (in grams) of the specimen before and after immersion in water, respectively. Our results were 0.76, 0.71, 0.69, 0.66, and 0.59% for the 0, 0.5, 1, 2, and 3wt% GO content samples, respectively. These values are lower than those of non-fluorinated polyetherimide films (e.g., Kapton®-H) because of the presence of water-proofing alkyl groups, ether linkage, and the hydrophobic nature of the GO in our films. Our results thus indicate that the PTAI/GO samples possess an outstanding moisture-uptake resistance property. Indeed, our low-moisture-absorption PIs are suitable for waveguide applications in optoelectronics.[5]

In summary, we used the popular click chemistry to produce novel nanocomposite films that consist of a polytriazoleimide matrix and

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graphene oxide nanoparticles. In particular, we investigated how the concentration of GO in the samples affected their characteristics. Our comprehensive characterization tests show that the incorporation of GO into the PTAI matrix improves the thermal, mechanical, flame-retardancy, and dielectric properties. We have also shown that the moisture-absorption properties of our samples are superior to commercially available polyetherimide films and are thus suitable for optoelectronics applications. In our future work we will investigate the effects of different alkyl carbon chain lengths, with different nanomaterials (e.g., carbon nanotubes, reduced graphene oxide, and functionalized graphene), on the properties of our PTAI nanocomposites.

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