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Dielectric Properties of Graphite Nanocomposites

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Polymer nanocomposites are an emerging class of multifunctional materials that have not been optimized for their functional potential. In this study, the dielectric properties of graphite polymer nanocomposites were evaluated. The objective was to develop for composite applications, an alternative cost-effective nanoscale carbon material with properties comparable to those of carbon nanotubes. J. VINYL ADDIT. TECHNOL., 12:127-130, 2006. © 2006 Society of Plastics Engineers

INTRODUCTION

Instead of trying to discover much-lower-cost processes for carbon nanotubes (CNT), the research in our laboratory makes use of a mass production processing technology and formulates a distinct and cost-effective breed of nanoscale reinforcements. These nanomaterials can be made available at much lower cost and are tailorable for functional requirements. A graphene nanoplatelet is composed of naturally occurring one or several layers of graphene plane (basal plane). In a graphene plane, carbon atoms occupy a 2-D hexagonal lattice. These carbon atoms are bonded together through strong covalent bonds lying on this plane. In the *c*-axis direction, several graphene planes may be weakly bonded together through van der Waals forces (see Fig. 1). The graphene nanoplatelet can be well dispersed and exfoliated in thermosetting and thermoplastic polymers. Although graphene nanoplatelet and CNT are geometrically different in architecture, some preliminary calculations have indicated very similar mechanical properties (in-plane stiffness and strength) and thermal and electrical conductivities.

It is attractive to take advantage of the functional properties of cost-effective graphene nanoplatelet imparted into polymer matrices for composite applications. The weak van der Waals forces between the graphene interlayers also provide some attractive routes for ductility enhancement and toughening behavior.

Recent studies on cost-effective polymer nanocomposites have focused on the development of smectite clay systems. Since there are no reactive ion groups on the graphite layers, it is difficult to prepare the polymer/graphite nanocomposites via ion exchange reactions in order to intercalate the monomers into the graphite sublayers. The expanded graphite (EG), however, contains abundant multipores ranging in size from 2 nm to 10 μm . Average size of the pores is about 2 μm . In graphite-based nanocomposites, the monomer was first introduced into the pores of the EG to be followed by polymerization. The graphite maintains the layered structure similar to that of natural flake graphite but with larger layer spacing [1–4]. It was reported that markedly lower volume fractions of EG were able to reach the percolation threshold for electrical conductivity in nylon 6, PS, and PMMA nanocomposites by in situ polymerization of polymer matrices [5–8].

Enhancement in strength and stiffness for nanoscale reinforcement is well documented in the literature [9, 10]. Mechanical properties can be improved with proper surface functionalization to promote interaction between the filler and polymer molecules. Barrier properties in the nanocomposites derived from layered silicates, intercalated or exfoliated likewise, were investigated in recent years [11–14]. However, nanoclay-reinforced polymers do not possess electrical conductivity and dielectric properties as good as those of functional composites such as carbon black- [15, 16], metallic powder- [17–19], polyaniline- [20], and graphite- [21] containing polymers. A nanocomposite that contains a minimal filler concentration for reduced costs and weight is lacking. In our research group, we aim to establish

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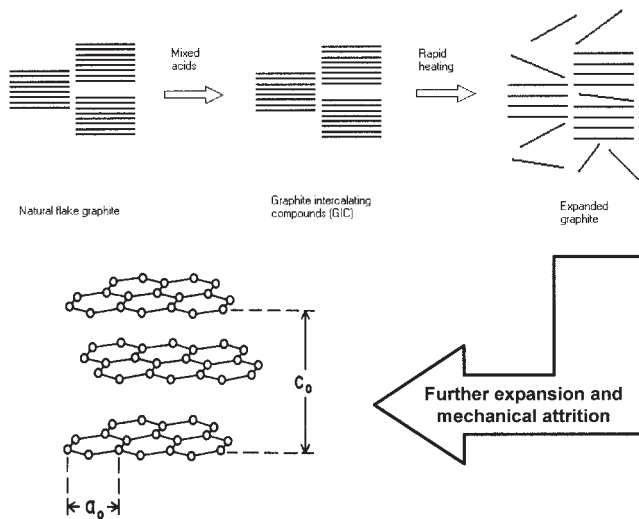


FIG. 1. A schematic showing the formation of EG from natural flake graphite.

a paradigm such that cost-effective polymer nanocomposites can be produced for functional and high toughness applications. The concept is illustrated in Fig. 2. In this article, we focus on some preliminary results for dielectric properties of graphene-nanoplatelet-containing polymers.

EXPERIMENTAL

Acid-treated graphite (GRAFGuard® from Graftech Inc.) was dried in a vacuum oven. Some preliminary studies were conducted on the natural flake graphite supplied by Beishu Graphite Co. in China. The graphite flakes were mixed and saturated with acids consisting of concentrated sulfuric acid and concentrated nitric acid, in order to form the graphite-intercalated compound (GIC). Nitric acid serves as an oxidizer and sulfuric acid is an intercalant. The intercalant could be a solution of sulfuric acid or sulfuric acid and phosphoric acid, and an oxidizing agent. The heat

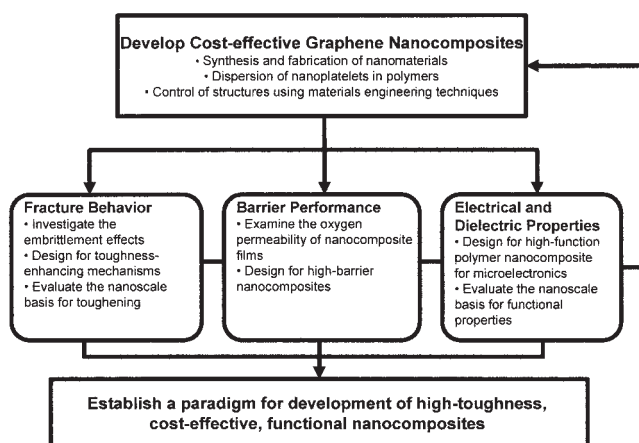


FIG. 2. Design for high function, high toughness, and cost-effective polymer nanocomposites.

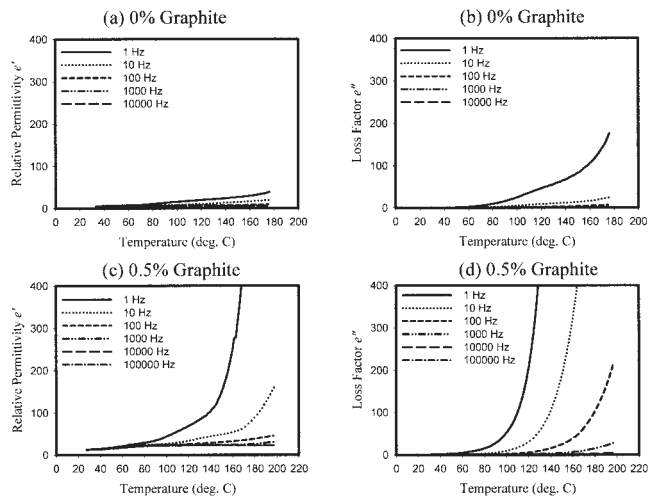


FIG. 3. Relative permittivity and loss factor of the graphite-nanoplatelet-reinforced polymer coatings as a function of temperature.

treatment temperature and time could be varied to generate, by design, various graphene nanoplatelet materials with a wide range of nanoplatelet thickness, width, and length values. The mixture was carefully washed and filtered with deionized water until the pH level of the solution reached 6. After being dried in an oven, the GIC was rapidly expanded in a muffle furnace to form EG. The schematic illustrating the preparation of EG from natural flake graphite is shown in Fig. 1. Ball milling is a mass production process which allows graphene nanoplatelets to be produced in large quantities. The EG was pulverized by using a planetary ball mill at high rotational speeds. The processing ease and the wide property ranges render graphene nanoplatelets ideal for nanomaterials formulation. The structures were examined under a transmission electron microscope (TEM).

In this study, UV-curable urethane acrylate was prepared by using a Dymax light source with a 200 EC silver lamp (UV-A, 365 nm). The coating ($\sim 40 \mu\text{m}$) mixed with the EG was mounted on an aluminum panel and exposed to the UV source. The intensity was 35 mW/cm^2 . Dielectric experiments were conducted with a TA Instrument DEA 2970 Dielectric Analyzer in Ceramic Parallel Plate mode. The sample dimensions were $25 \times 25 \times 0.5 \text{ mm}^3$. Testing temperature ranged from room temperature to 150°C . Nitrogen gas was used to provide an inert environment at a flow rate of 500 mL/min . The ramping rate was 3°C/min with multi frequencies of 1, 10, 100, 1000, 10,000 and 100,000 Hz. Particle size was analyzed by a Nicomp Particle Analyzer.

RESULTS AND DISCUSSION

Dielectric Properties of Graphene Nanocomposites

Figure 3 shows the relative permittivity and loss factor as a function of temperature for the graphite-nanoplatelet-re-

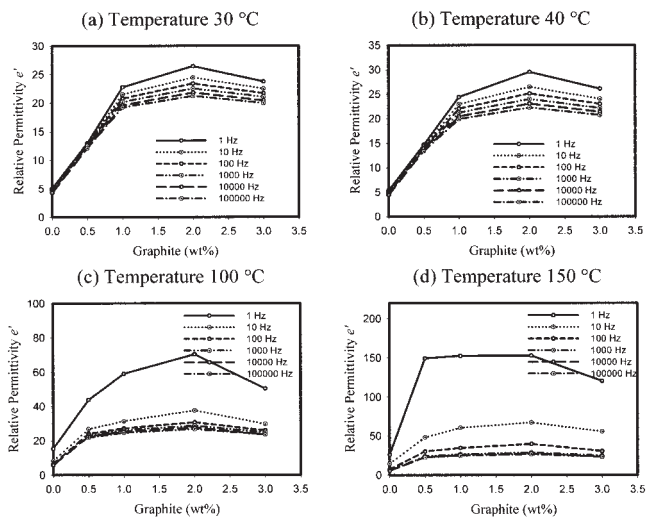


FIG. 4. Dielectric properties of graphite-nanoplatelet-containing acrylate nanocomposites as a function of filler content.

inforced acrylate coatings. Figures 3a and 3b show the reference samples with 0 wt% graphite. As expected, the permittivity increases as temperature increases and decreases when the frequency increases. What is noteworthy, however, is the jump in permittivity upon slight introduction of 0.5 wt% of graphite (Figs. 3c and 3d). Figure 4 compares the relative permittivity of highly expanded EG samples in thermosetting acrylate under different temperature conditions. Note that in Fig. 4a, the relative permittivity increases four- to five-fold between 0 and 1 wt% of graphite. At higher graphite content, the permittivity slowly levels off and reduces after 2 wt% graphite is added. Such an increase was considered dramatic. It shows the effectiveness of graphene nanoplatelet in altering the dipole moments and thus the charge-storing capacity of the polymers. As anticipated, at a lower frequency, the change in relative permittivity is higher, whereas at higher frequencies, the variation is more constrained. The increase in relative permittivity vs. graphite content is more pronounced at higher temperatures (Figs. 4b–4d). Note that the scales of the *Y*-axes have to be varied in order to provide sufficient contrast for comparison among different frequencies. The differentiation between the low frequency permittivity and the high frequency permittivity is most drastic at a high temperature of 150°C.

Morphology

Figure 5 shows the distribution of platelet size following the ball milling process. It is noted that a bimodal distribution occurs. This result is attributed to two contributing factors: (1) there are two dimensions (edge thickness and platelet width) being targeted in the analyzer and (2) the distribution of submicron-sized particles in addition to nanoscale particles. It is clear that the edge thickness dimension is in the range of 100 nm, while the platelet width is over 400 nm. The size distribution is generally consistent

Milled Natural Graphite

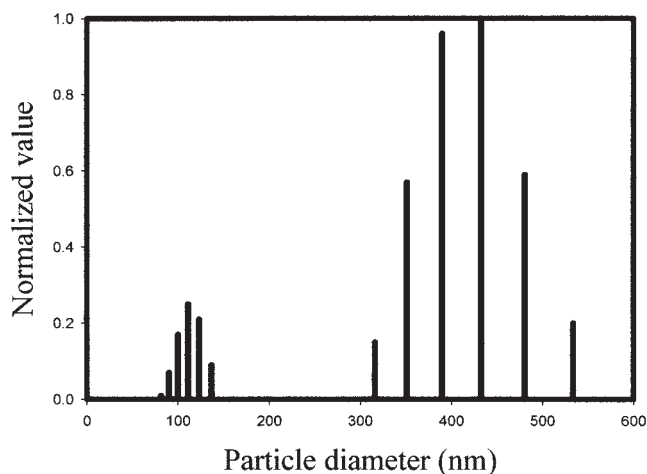


FIG. 5. Bimodal distribution of micron-sized and nano-sized dimensions of nanoplatelets.

with the platelet shape. Figure 6 shows a TEM photograph displaying the ball-milled graphite in a polymer coating. The dispersion at this stage is not optimized. As a result, the TEM micrograph shows aggregates of platelets in a thin polymer section. Nevertheless, the nanoscale features of graphite nanoplatelets are clearly evident in Fig. 6. The optimization in the dispersion will be conducted by using chaotic mixing techniques [22] and sonication in our future work.

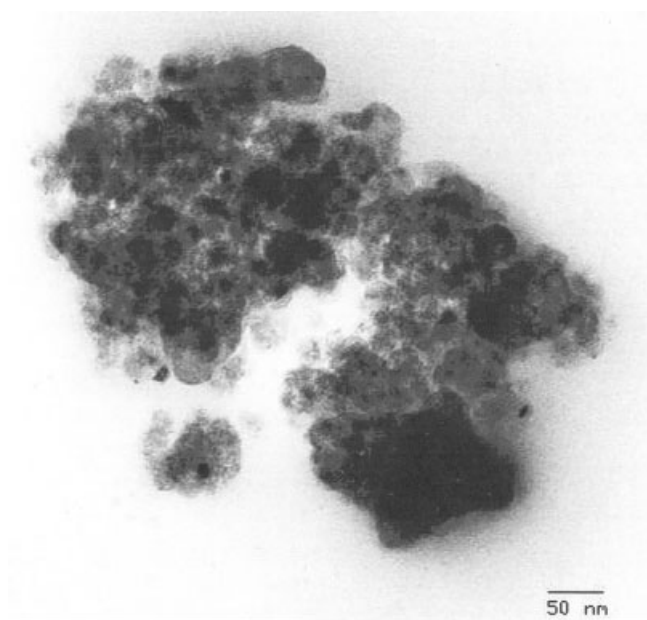


FIG. 6. TEM photomicrograph of graphite-nanoplatelet-containing polymer coating.

CONCLUSIONS

Dielectric properties of graphite-based polymer nanocomposites were studied. It was shown that with as little as 0.5 wt% graphite, the relative permittivity dramatically increased. The charge-storing capacity changed upon inclusion of graphite nanoplatelets. Then, a bimodal distribution of platelet sizes was observed, a result which strongly suggests the promise of graphite nanoplatelet materials for nano reinforcements. The structure–dielectric property relationships of such novel nanocomposites await future investigations.

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