

# Morphology and Properties of Polypropylene/Exfoliated Graphite Nanocomposites

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## Introduction

Electrically conductive polymer composites are of special interest in the industry. Addition of various conducting fillers such as carbon black, graphite, and metal fiber or powder (1-3) into polymer matrix through melt mixing is an effective approach to fabricate the composites. Because large amount of the fillers, generally above 15 wt% (4), were required for the host polymer to become conductive, which resulted in both poor processability and declining mechanical properties. The application of these conventional composites was largely restricted.

In the meantime, the techniques of graphite intercalation compound (GIC) developed very quickly (5), paving the way for the research and advancement of polymer/graphite conducting composites. Recently, Pan et al. (6) prepared nylon 6/expanded graphite (EG) conducting nanocomposites by intercalation polymerization, which had a percolation threshold ( $\phi_c$ ) of 0.75 vol % and an electrical conductivity ( $\sigma$ ) of  $10^{-2}$  S/m at 2 vol % EG. This showed the tremendous potential and value of functional nanocomposites of polymer and delaminated graphite. In view of the successful preparation of layered silicate nanocomposites by solution intercalation, we attempted in this study to prepare maleic anhydride grafted polypropylene conducting nanocomposites with similar route. The results presented here are thermal and mechanical properties from dynamical mechanical analysis (DMA). The electrical properties were measured with a dielectric analyzer (DEA).

## Experimental

The method due to Hummers and Offeman (7) was adopted to prepare graphite oxide (GO) from graphite powder (10–20  $\mu\text{m}$ ) supplied by Aldrich Chemical. Alkylamine intercalated GO was prepared by the method due to Matsuo et al. (8), which involved dispersing GO powder with octadecylamine (ODA) by ultra-sonic in p-xylene. ODA treated GO was dispersed in p-xylene to prepare a suspending dispersion with certain GO content. PPgMA, trade name PB3150 from Chemtura, was dissolved in p-xylene by heating to about 110°C. The GO suspending dispersion was added drop by drop into the PPgMA solution. The blended mixture was precipitated by adding acetone, and then oven-dried at 90°C. The resulting loose powder was hot pressed to obtain plates for subsequent characterization.

The PPgMA/GO samples were examined using both TEM and SEM. A transmission electron microscope (JEOL JEM-1200CX II, Japan) was used to observe the microstructure of the composites. Scanning electron microscope (JEOL JSM-70000F, Japan) was used to observe the structures of graphite powder, GO, and ODA treated GO. Dynamic mechanical thermal tests were done on a DMTA (Perkin Elmer 7e). Dielectric measurements in the temperature range from 193 to 403 K at a constant frequency of 100 Hz were performed using a TA DEA 2970 high-performance dielectric spectrometer.

## Results and Discussion

### Morphology observatoion

Observation of the structure of the filler was carried out. SEM pictures of neat graphite, GO, and ODA treated GO are shown in Figs. 1a to c. It can be seen that pure graphite flake (Fig. 1a) was completely fragmented, resulting in graphite sheets with diameters ranging from about 1 to 10  $\mu\text{m}$ . Note that the GO flake (Fig. 1b) is apparently thicker than that of pure graphite due to the oxidation reaction. However, the intercalating effect of ODA can be clearly seen in Fig. 1c, where the stack of graphite sheet was exfoliated into thin plate thinner than 100 nm. Figs. 2a and b represent the repeatable and representative TEM micrographs of the nanocomposites of 1 and 3 wt% GO, carried out at different sites or observing fields of the sample. It can be found that there exist a group or several groups of parallel EG sheets with a thickness of ca. 50 nm on average, finely dispersed in the PPgMA matrix regardless of the GO content. This demonstrates the PPgMA/GO nanocomposites can also be obtained via solution intercalation.

### Dynamic Mechanical Thermal Analysis

Storage modulus spectra ( $E'$ ) of PPgAA/GO nanocomposites with 1 and 3 wt% GO contents are shown in Figure 3a. Clearly a moderate improvement in the storage modulus values is seen when the GO content increases. A general falling trend can easily be observed for all samples. Above glass transition temperature around 0 °C, the storage modulus values drop as the temperature increases. The loss modulus spectra ( $E''$ ) of the same specimens are shown in Fig. 3b. All the samples exhibit two major transitions. The first transition, which is seen around 0°C for neat resin, is the glass ( $\alpha$ ) transition. The glass transition temperature  $T_g$  are slightly shifted to higher temperatures as the GO content increases. There is

another transition is seen as a broad peak in the range of 60 to 80°C. This is the  $\alpha'$  transition, which usually seen in high crystalline polymers due to crystal-crystal slip. As it is seen, this transition was not very obvious in neat PB3150 but became more distinct in the case of the composites.

## Dielectric Spectroscopy Analysis

The dielectric measurements of the neat PB3150 and its 1 and 3 wt% GO nanocomposites, extending over a temperature range from -50 to 140°C at 10 Hz, are shown in Figs 4a and 6b for the dielectric constant  $\epsilon'$  and the loss factor  $\epsilon''$ , respectively. The  $\epsilon'$  of neat resin remains as a constant at 2.2, showing no dielectrically active relaxation process regardless of their low grafting degree of the polar group of maleic anhydride, but the  $\epsilon'$  of the nanocomposites increase with increasing temperature. It can be seen that a single relaxation process is observed as a step change for the hybrid systems in the  $\epsilon'$  curves. The temperature range of this relaxation process is much higher than the glass ( $\alpha$ ) transition. Since there seems no dielectrically active response of the neat resin, the polarization would be due to charge carriers accumulated at the interface between GO nanolayers and matrix polymer, referred to as Maxwell-Wager-Sillars (MWS) relaxation or interfacial polarization. Furthermore, the value of  $\epsilon'$  increases significantly as the GO content increases.

Next the isochronal plot of  $\epsilon''$  is given in Fig. 4b. Note that the  $\epsilon''$  of the neat PB3150 nearly vanishes, and it is not shown in the figure. Sample with higher GO content again shows higher  $\epsilon''$ . In addition, the peak of loss maximum, which is masked by high dc conductivity, is hardly to be seen. Finally, the large increase at high temperatures observed in both  $\epsilon'$  and  $\epsilon''$  was attributed to the charge carriers accumulating at interfaces within the bulk of the sample (interfacial polarization), and/or at the interface between the sample and the electrodes (electrode or space charge polarization).

## Conclusion

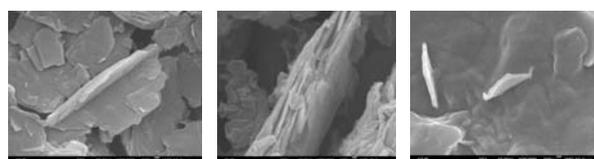
The solution blended PPgMA/GO materials were characterized by SEM and TEM. Compared to the neat PPgMA, the composite materials with 3 wt % GO loading exhibited higher glass-transition temperature, and higher storage modulus. The improvement of both the thermal properties and the mechanical properties could be attributed to the fact that the polymer chains were confined in the gallery of ODA treated GO. Moreover, a significant increase of the dielectric permittivity was observed for the hybrid system because the dispersive GO largely contributed to the space charge polarization, leading to significant increase in  $\epsilon'$  at high temperatures beyond Tg.

## Acknowledgement

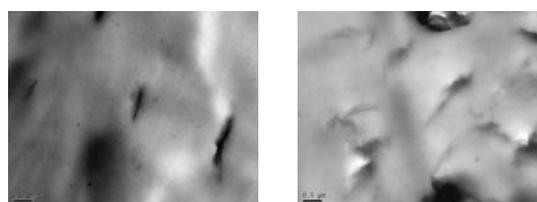
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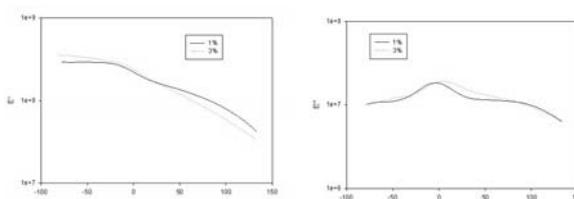
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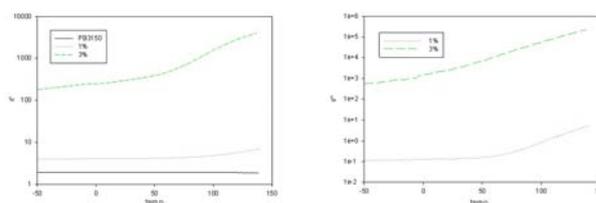
(a) Pure graphite (b) GO (c) ODA treated GO  
Figure 1. SEM micrographs of graphite fillers.



(a) 1 wt% GO (b) 3 wt% GO  
Figure 2. TEM micrographs of nanocomposite.



(a) Storage modulus (b) Loss modulus  
Figure 3. DMA measurements of the nanocomposites.



(a) Dielectric constant (b) Dielectric loss  
Figure 4. DEA measurements of the nanocomposites.