

EFFECTS OF NANOPARTICLE MORPHOLOGY ON THE PERMEATION AND PHYSICAL PROPERTIES OF POLYMER NANOCOMPOSITES

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Abstract

Exfoliated graphite nanoparticles (EGN) have the potential to be a low cost, high performance reinforcement for polymers due to their platelet structure and predicted physical properties. Thermoplastic films were prepared containing different EGNs at different loading levels. Barrier and physical properties of these EGN/polymer nanocomposite films were then compared to similar nanocomposite films having either comparable filler morphology, such as smectite clays, or similar chemical composition, such as carbon nanotubes and conventional carbon black. Barrier testing included permeation of selected organic permeants, water vapor, and oxygen utilizing a number of different vapor and liquid permeation methods. Relationships between the properties of the nanocomposites and the nanoparticle composition and morphology are presented.

Introduction

Researchers [1-4] have found that polymer composites containing small amounts of nanosize clay particles (silicates, e.g. montmorillonite) possess unusual mechanical properties relative to their parent materials. In addition, these hybrid materials were found in many cases to tolerate higher temperatures than traditional polymer/particle composites. Nanoparticle reinforcement increases the polymer-particle interfacial surface area by orders of magnitude relative to conventional reinforcing particle sizes. The increased surface area increases the volume fraction of polymer that may have decreased segmental motion due to surface pinning (formation of a constrained layer). It has been hypothesized that the polymer close to the particle surface has an effective shift in the polymer's glass transition temperature, leading to lower permeability and altered thermomechanical properties.

The incorporation of nanoscale clays (silicates) into polymeric matrices has been shown to yield improved barrier properties, increased mechanical properties, and better fire resistance properties, relative to the unfilled

polymer. However, these materials typically require chemical treatments of the clays to provide the exfoliated dispersions that are critical to achieve the noted improved properties. Development of successful surface treatment of silicate nanoparticles is non-trivial, and must be specifically tailored to each polymer type.

Graphite is widely used as a filler to control electrical and thermal conductivity of normally non-conducting or poorly conducting materials, in addition to improving mechanical properties. However, there is a limit to improvement of these properties using natural or synthetic graphite in a flake or powder form due to particle size and morphological characteristics of the particles. Using nanoscale exfoliated particles, much better dispersion in polymeric matrix systems can be achieved. This is expected to lead to significant increases in thermal and electrical conductivity, mechanical properties, and chemical resistance in nanocomposites using these materials. Specific properties can be adjusted by filler content, matrix polymer type, and processing techniques.

A new process has been recently developed to produce nanoscale graphitic platelets through the exfoliation of monolithic graphite (**Figure 1**). These particles can be used as fillers in polymer composites, and hold the promise of improved material properties in several areas. These include mechanical properties, barrier properties, electrical properties and thermal stability. These nanoscale exfoliated graphite platelets may not require any pretreatment prior to processing, similar to conventional carbon blacks. They are also of lower density (20% or more) when compared to the silicates and thus result in lower density composites. In addition, graphite has electrical properties that the silicates do not, which offers additional functionality in the target materials such as EMI shielding, electrostatic dissipation and potential signature management applications. This paper describes the initial efforts carried out to incorporate this unique form of carbon into thermoplastics and elastomers and characterize the properties of interest.

Experimental

Three different morphology carbon nanoparticles were utilized as reinforcements in polycarbonate (PC) (Makrolon 2405, Bayer): platelet exfoliated graphite nanoparticle (EGN, mechanically comminuted graphite from Cornerstone Technologies), multiwall carbon nanotube (CNT, CVD grown from Nanolab, Inc. and MER Corp.), and spherical carbon black (AG, Vulcan 9 from Cabot Corp.). The nanocomposite dispersions were prepared through melt processing in a twin-screw extruder (DACA conical) and dispersion assessed by transmission electron microscopy (TEM). The nanoparticles were typically added at a 5 weight % level. Test specimens were prepared through injection molding, compression molding, or extrusion of the dispersions. Mechanical testing was carried out using standard specimens on Instron 55R4201 and 55R 4204 instruments. Dynamic mechanical analysis (DMA) was carried out on a TA Instruments Model 983. Electrical properties were measured utilizing a four-point probe technique.

The EGN, CNT, and AG nanoreinforcements were also incorporated into polyethylene (Dow LDPE 683I) through melt processing. In addition to the carbon-based particles, a nanoclay filler (alkyl quaternary ammonium montmorillonite from Southern Clay Products) was also included for comparison. Water vapor and oxygen permeation measurements were carried out on polyethylene samples with nanoclay and AG using MOCON instrumentation. Organic molecule penetration was measured with a permeation cell developed at the Natick Soldier Center using an automated data collection system and a flame ionization detector (FID).

Results & Discussion

Significant differences were found in the ease of dispersion of the various morphology particles in the PC matrix. The CNT was found to be the easiest to disperse (Figure 2) followed by the AG with the EGN the most difficult. Mechanical property evaluations (in tension and compression) show that in tension, EGN can produce increases in modulus and strength superior to those obtained with carbon nanotubes as shown in Table 1. Carbon nanotubes appear to produce superior properties in compression. These results are consistent with simple models of reinforcing mechanisms that have been presented by other researchers, but not verified until now. The absolute values of mechanical property enhancement fall short of what has been anticipated for CNT and EGN reinforcement, based on the properties of individual particles, and more work needs to be done to address this issue. Preliminary results of electrical conductivity measurements on PC/carbon nanocomposites have also

been inconsistent with expectations (conductivities are very low) and give rise to questions about the state of the nanoparticles in this particular matrix.

Unanticipated difficulties were encountered with compounding EGN and CNT in polyethylene. Good dispersion of relatively low amounts of these nanoparticles was difficult to achieve. Permeation experiments have not been carried out on these materials to date. Further processing trials of these materials are underway to produce samples suitable for testing. Water and oxygen permeation results on a series of polyethylene-based materials with nanoclays and AG are shown in Table 2. The clays show superior resistance to permeation when compared to the AG composites.

Organic permeation was also carried out on a number of polyethylenes with clay and AG nanoparticles using dichlorohexane (DCH). This organic solvent is used as a simulant for the chemical warfare agent, sulfur mustard. Representative results from this testing are shown in Figure 3 as plots of DCH flux versus time. Generally, increasing the level of clay increases the time to breakthrough and lowers the equilibrium flux level. Figure 3 also shows faster flux through AG when compared to clay at similar loading levels (7.5%). However, fairly significant scatter was observed for multiple runs of similar materials making differentiation of the particles difficult, especially for the equilibrium flux levels achieved at the latter stages of the test.

Because of the difficulties encountered with the dispersion of EGN and CNT in melt processed polyethylene, another effort was initiated to formulate these nanomaterials into elastomers through roll mill processing. Significantly better dispersion has been achieved, but experimental measurements were not complete at the time of preparation of this paper. These results will be the subject of a future paper.

Summary

Three different morphology carbon nanoparticles and a nanoclay have been investigated as fillers in thermoplastic films. Preliminary results have shown increases in mechanical properties associated with EGN and CNT nanoparticles in polycarbonate. Electrical properties have been surprisingly observed as little affected with the inclusion of the relatively conductive carbon nanoparticulates. The nanoclay/polyethylene nanocomposites show significant improvement in barrier properties for water and oxygen when compared to similar AG materials. Further work is currently underway to improve the processing of the polyethylene-based nanocomposites with EGN and CNT nanoparticulates and

to complete the characterization of a series of elastomer formulations incorporating EGN, CNT, AG, and clay.

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References

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Key Words

Nanoparticles, exfoliated graphite, carbon nanotubes



Figure 1 Micrograph of EGN

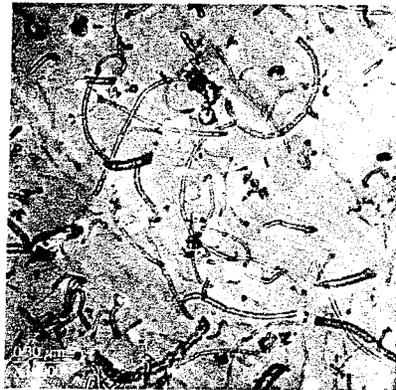


Figure 2 Micrograph of CNT dispersion in polycarbonate

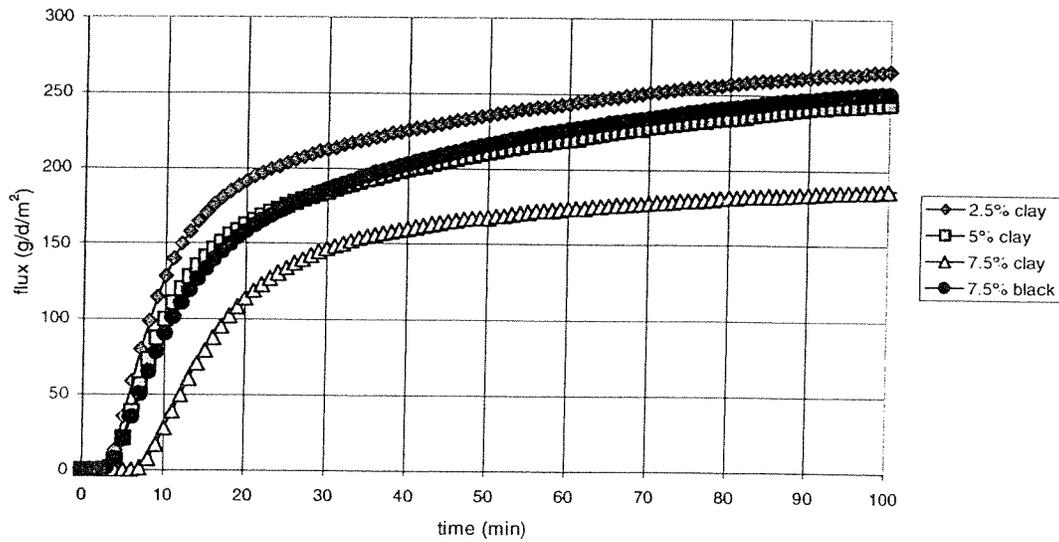


Figure 3 DCH permeation of low density polyethylene nanocomposites

Table 1 Quasi-static test summary for polycarbonate with 5% nanoparticles

MPa	Control	AG	CNT	EGN
Tensile [T] Modulus	833	917	1027	1262
Compression [C] Modulus	1694	1711	1657	1689
Stress to Yield [T]	42	43	45	47
Stress to Yield [C]	86	82	83	76
% Strain to Yield [T]	8.5	8.0	7.9	7.6
% Strain to Yield [C]	9.4	8.5	8.5	8.5

Table 2 Low density polyethylene nanocomposite water and oxygen permeation

Sample I.D.	Screw (rpm)	WVTR (g*mil/d/m²)	O₂TR (cc*mil/d/m²)
Control	40	15.49	“fail”
2.5% clay	40	19.19	6181
7.5% clay	40	11.9	4318
7.5% clay	200	10.5	3703
2.5% black	60	21.65	9528
5% black	60	20.53	“fail”
7.5% black	60	25.63	“fail”