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Abstract

The ability to achieve enhanced mechanical properties through in-plane orientation of platelet-like nanofillers is a challenge for nanocomposite fabrication and performance. Here we use forced assembly to orient graphene nanoplatelets in PMMA/PMMA-graphene films produced through multilayer coextrusion. Electron microscopy confirms the alternating layer structure of PMMA and PMMA containing oriented graphene. Relative reinforcement of 11\% at a concentration of 0.2 wt\% graphene in the total film was achieved without loss of toughness. The reinforcement is attributed to the planar orientation and improved dispersion of the graphene as the layer thickness decreases.

Key Words: multilayer coextrusion, forced assembly, graphene, planar orientation, nanocomposites, reinforcement

Introduction

Graphene-based nanofillers, such as graphene, graphene oxide and graphene nanoplatelets have aroused significant research interest in recent years [1,2]. Dispersion of graphene-based nanofillers in polymer matrices, has been a major strategy to enhance materials’ mechanical properties [3,4] and electrical conductivities [5]. By solution mixing, graphene polymer nanocomposites have been made with excellent mechanical reinforcement at low loadings (< 1 wt\%) [3,4,6]. In addition, graphene nanoplatelets can also be dispersed into a polymer matrix via melt mixing methods, e.g. in most cases through extrusion [7-11].

Incorporation of platelet-like fillers with high aspect ratio ($A_f = \text{length} / \text{thickness}$) provides the possibility of two-dimensional mechanical reinforcement and enhanced gas barrier properties [12, 13, 14], if the nanofillers can be aligned in a plane of the polymer matrix. However, most graphene polymer reinforced nanocomposites have been made in ways that only emphasize good dispersion, without heavily exploring the possibility of creating oriented structures. Therefore, a useful method to create such structures is desirable and important.

As an advanced polymer processing technique, multilayer coextrusion can produce up to thousands of layers in films with individual layer thicknesses from 50 $\mu$m to 10 nm [15,16]. In pioneering work, Baer and coworkers used this “forced assembly” technique to force immiscible polymer pairs and filled/unfilled polymers to combine into unique multilayer structures. As the layer thickness approaches the nano-scale, such designed architectures lead to interesting confined crystallization effects [17], optical properties [18] and gas barrier properties [19].

Because of the strong confinement effects and since multilayer coextrusion is scalable to industrial processing, it offers an attractive approach to orient high aspect ratio nanoparticles in the layer plane. Although orienting anisotropic nanofillers such as talc microplatelets [20] and carbon nanotubes [21,22] through multilayer coextrusion has been investigated, to our knowledge, multilayer coextrusion has not been exploited to orient platelet-like nanofillers, such as graphene, to create a biaxially reinforced medium in polymer matrixes. Figure 1 shows a schematic of the multilayer coextrusion method of forced assembly [23] and how it can create the oriented graphene layers in the multilayer film. At large number of layers, the thickness of the filled layers can approach the nano-size scale.
The purpose of the present work is to use forced assembly by multilayer coextrusion to create a new class of polymer nanocomposites with oriented graphene nanoplatelets. To this end we studied the nanocomposites of amorphous polymer poly(methyl methacrylate) (PMMA), and specifically mechanical properties of alternating PMMA/PMMA-graphene films. The reinforcement and dispersion of the graphene nanoplatelets were also investigated, as a function of the layer thickness.

Experiments

Poly(methyl methacrylate) was provided by Altuglas International (PMMA V920T) and was dried in a dry air dryer at 80 °C for 4 hours before extrusion. A lab-made PMMA-20 wt % graphene master batch was prepared from the Altuglas PMMA and ACS Materials graphene nanoplatelets (aspect ratio between 1000 and 5000), following a solution mixing method described previously [23].

The PMMA-graphene formulations (0.5, 1.0 and 2.0 wt %) to be used in extruder 2 (see Figure 1) were prepared by diluting the master batch with the neat PMMA using a Thermo Haake PTW 16-40D co-rotating twin-screw extruder at 600 rpm and 215 °C as described previously [23].

In this study, PMMA films containing respectively 3, 129 and 2049 alternating layers were prepared using the multilayer coextrusion process described previously [23](Figure 1). The PMMA melt and the PMMA-graphene melt were extruded from two single-screw extruders (Mapre, 30 mm diameter screw with a barrel of length-to-diameter ratio of 33 and a screw speed fixed at 37 rpm; Scamex, 20 mm diameter screw with a barrel of length-to-diameter ratio of 20 and a screw speed between 30 and 45 rpm), combined in a classical three layer coextrusion feed block. The three-layer melt block flows through a series of mixing elements shown in Figure 1 to produce $2^n+1$ layers (n being the number of mixing elements. Here n is 0, 6 and 10). These are then spread through a flat die and onto a chill roll maintained at 80 °C to allow the PMMA chains to relax. Mixing elements and die were set to 225 °C. The percentage of PMMA-graphene layers in the film was kept constant at 10 wt % and the final concentration of graphene nanoplatelets was 0.05, 0.1 and 0.2 wt % in the PMMA/PMMA films.

To establish a reasonable viscosity match in the extrusion [16], the apparent steady shear viscosities of the PMMA and the PMMA-graphene formulations were determined using an ARES Rheometer (TA Instruments) with 25 mm diameter parallel plate fixture.

Transmission electron microscopy (TEM) was used for morphological analysis: Approximately 50 nm thick sections were microtomed for TEM imaging.

Optical microscopy: 20 µm thick slices of film were observed by transmission optical microscopy using an Olympus BH2-UMA. Images were analyzed using ImageJ (an open source image processing software developed by the National Institutes of Health).

Mechanical properties were studied using an Instron 4301 testing machine and a TA Instruments Q800 DMA: Quasi-static mechanical properties were determined in uniaxial extension using the Instron 4301, and at least five specimens of each sample (0.3×10×110 mm$^3$) were tested at ambient temperature at a cross head speed of 5 mm/min. The dynamic modulus at a single frequency of 1.0 Hz was determined by DMA with a rectangular specimen (0.3×5 ×20 mm$^3$). Three specimens of each sample were tested at 40 °C.

Fracture toughness was determined in a compact tension test as follows: due to the small thickness of the films, a modified ASTM standard procedure [24] was used. At least five specimens of each sample (rectangular 0.3×10×10 mm$^3$) were tested at ambient temperature. For the pre-crack, a heated fresh razor blade was used to make a cut approximately 1 mm long perpendicular to the extrusion flow direction and an optical image was taken to measure the actual pre-crack length. The cross head speed was 1 mm/min.

Results and Discussion

Multilayer coextrusion requires a reasonable viscosity match between the polymer melt streams [16]. In our study, since formulations with different amounts of graphene nanoplatelets were used to produce the films, the viscosity ratio $\eta_{\text{graphene filled PMMA}} / \eta_{\text{PMMA}}$ could not be
maintained constant. The viscosity ratios were obtained from the apparent steady shear viscosities of all polymer and graphene formulations as a function of temperature to choose acceptable operating conditions and 225 °C was chosen for the processing considering both viscosity match and degradation. Figure 2 shows that adding of graphene doesn’t increase the zero shear rate viscosity of the formulation significantly, possibly due to potential degradation of PMMA in the twin-screw extrusion. At high shear rates, the graphene enhances shear thinning relative to the neat PMMA.

![Figure 2. Shear viscosity of PMMA and PMMA-graphene at 225 °C.](image)

Multilayer coextrusion produces polymer films with alternating layers, and the thickness of the graphene filled layers is controlled from 30 nm to 30 µm by varying the number of layers and keeping the total thickness of the films constant (around 0.3 mm). The layers, as they approach to the nano-scale thickness, provide the geometric constraints to orient the graphene nanoplatelets. In the 2049-layer PMMA/PMMA-graphene films, electron microscopy was used to confirm the existence of the layer structure, graphene orientation and aspect ratio (see Figure 3).

![Figure 3. TEM images of 2049-layer PMMA/PMMA film filled with (a) 1.0 wt % graphene showing a single aligned graphene particle; (b) 2.0 wt % graphene showing graphene confinement (dashed lines represent the tentative positions of the thin PMMA layers)](image)

Electron microscopy supports our hypothesis that the forced assembly method is able to orient, to some extent, the graphene in the plane of the layers. Therefore, enhanced stiffening of the composite films should be expected in the plane directions where the graphene platelets are aligned.

Our previous work found that for PMMA/PS-graphene films, there is a concentration limitation of approximately 2 wt % of graphene in polystyrene layers to maintain the nano-scale layer structure [23]. Here the concentration of 2 wt % graphene in PMMA thin layers appears to reach, similar to the PMMA/PS system, an upper limit which starts to perturb the nanostructure. Although the 2 wt % graphene nanoplatelets appear mostly oriented in the plane of the thin layers (dashed lines in horizontal direction in Figure 3b), many small wrinkled graphene nanoplatelets confined within the thin PMMA layers are also observed.

Since the process of extrusion is known to lead to the shortening and breakage of nanofibers [25] and nanoplatelets [26], it is not surprising that the lengths of the graphene nanoplatelets become much smaller than the initial, supplier provided length, after twin-screw extrusion and multilayer coextrusion. Here to estimate the aspect ratio, we assume the graphene thickness is still 2-10 nm as given by the provider. Therefore the aspect ratio $A_f$ can be estimated to range from 5-25 (wrinkled/small particles) up to 80-400 (flattened particles).

![Figure 3. TEM images of 2049-layer PMMA/PMMA film filled with (a) 1.0 wt % graphene showing a single aligned graphene particle; (b) 2.0 wt % graphene showing graphene confinement (dashed lines represent the tentative positions of the thin PMMA layers)](image)

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The addition of stiff nanofillers to polymers has been widely examined as an effective approach to enhance mechanical properties. [3, 4, 13] We first examine the stiffening of films versus layer thickness at a given graphene concentration to study the influence of layer thickness on the orientation and dispersion. By increasing the number of layers, the thickness of the confining layer decreases and should confine the graphene nanoplatelets more efficiently, giving enhanced reinforcement, which is the case as shown in Figure 4.

![Figure 3. TEM images of 2049-layer PMMA/PMMA film filled with (a) 1.0 wt % graphene showing a single aligned graphene particle; (b) 2.0 wt % graphene showing graphene confinement (dashed lines represent the tentative positions of the thin PMMA layers)](image)

We also used optical microscopy to compare the dispersion of the graphene nanoplatelets for varying the number of layers. To quantify the dispersion of the graphene nanoplatelets, the fraction $R$ of the total aggregates with circle equivalent diameter $> 5 \mu$m over the total area of the sample was determined following the work of Pötschke [25, 27]. It is observed in Figure 4 that
the large aggregation fraction R decreases as the number of layers increases. Therefore the degree of dispersion of the graphene nanoplatelets and the possible breakage of aggregates in the polymer matrix appear to increase upon decreasing the layer thickness.

![Figure 4](image.png)

Figure 4. Relative reinforcement of PMMA/PMMA-1 wt % graphene from DMA at 40 °C and aggregation fraction R vs. layer thickness

To confirm the microscopic observations, we investigated the modulus of the multilayer films, and analyzed the experimental results within the Mori-Tanaka model[28] to obtain an additional estimate of the graphene platelet aspect ratio. Since the graphene in the 2049 layer films shows better dispersion and this leads to a higher reinforcement, we studied this film system versus graphene concentration. Figures 5 shows the relative reinforcement E/E\textsubscript{m} of the 2049 layer PMMA films along the extrusion flow direction, versus weight fraction of graphene in the full film. E\textsubscript{m} is the modulus of unfilled PMMA (2.89 GPa). From the quasi-static tension tests, we observe an 11.0 % reinforcement for the 2049-layer film (E= 3.21 GPa), for a 0.2 wt % graphene in the total film. These results are close to the predictions from the Mori-Tanaka model [28, 29] with A\textsubscript{f} =225. This aspect ratio is similar to values estimated from the electron microscopy images described above for the flattened nanoplatelets.

In addition, fracture toughness, the ability of a material to resist fracture in the presence of cracks, is also a mechanical property of interest. As we know, incorporation of some stiff nanofillers such as carbon nanotubes may increase or maintain the polymer brittleness depending on the dispersion [22], and silica nanoparticles can enhance the fracture toughness of epoxy.[30] The crack propagation of PMMA films at room temperature occurs in the linear elastic region, and fracture toughness K\textsubscript{IC} can be obtained from the following equation [24]:

$$K_{IC} = \frac{P_c}{\pi W^{0.5}} Q$$  \hspace{2cm} (1)

where P\textsubscript{c} is the load at crack propagation obtained from the load-displacement curve, t is thickness, w is width, and Q is a dimensionless function of pre-crack length over width. Figure 5 also shows the fracture toughness results for the 2049-layer PMMA/PMMA–graphene films. No change in fracture toughness was observed. Therefore the addition of graphene can reinforce the PMMA films without loss of toughness.

![Figure 5](image.png)

Figure 5. Relative reinforcement and fracture toughness K\textsubscript{IC} in the extrusion flow direction for 2049L PMMA/PMMA-graphene films from quasi-static tension tests at 23 °C.

**Conclusion**

We have used forced assembly through multilayer coextrusion to create alternating PMMA/PMMA-graphene multilayer films with different layer thicknesses. A combination of morphological analysis of the multilayer films and mechanical property measurements provides evidence that the reinforced films contain oriented graphene. The reinforcement is attributed to the planar orientation and improved dispersion of the graphene as the layer thickness decreases.

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