

THE EFFECT OF MALEIC ANHYDRIDE COUPLING AGENT ON MELT PROCESSED SEMI-CRYSTALLINE PET NANOCOMPOSITE FILMS

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Abstract

Semi-crystalline PET/montmorillonite nanocomposite films were processed by melt-extrusion along with 0.5% maleic anhydride as a coupling agent. Mechanical, thermal, barrier and morphological properties of the nanocomposite films with and without the coupling agent were examined. The nanocomposites have demonstrated an intercalated/exfoliated morphology with the montmorillonite acting as a crystal-nucleating agent in all of the nanocomposite film samples. DSC experiments show this effect through faster nucleation rates and an increased overall degree of crystallization. A depressed glass transition temperature is observed in all nanocomposite samples along with an increased Young's modulus and decrease in film toughness.

Introduction

The improvement of polymer properties through composite systems is a common practice in today's industrial and academic research. From wood flour and talc, to carbon black and glass-fiber, polymer fillers and reinforcements have been used to modify polymers for the desired end-use of the manufacturer and customer¹. Polymer nanocomposites are a fairly new type of composite system that has demonstrated significant improvements in polymer properties such as tensile modulus, tensile strength, heat distortion temperature, and barrier to liquids and gases². Although not completely understood at this time, significant progress has been made in analyzing and developing polymer nanocomposite systems^{2,3,4,5,6}.

Montmorillonite layered silicate (MLS) has been a popular choice as the inorganic nanoparticle in polyimide³, polypropylene⁴, nylon⁵, polylactide⁶, and many other polymer systems^{7,8}. Loading levels of these nanoparticles are significantly lower than amounts typically used in conventional composites. Substantial improvements in material properties are observed at loading levels of 1-5% MLS⁹. When the MLS is dispersed sufficiently, the majority of the polymer chains will be located near an inorganic surface, causing restrictions in chain mobility. These restrictions alter polymer properties such as relaxation behavior, free volume, and thermal transitions².

Montmorillonite is classified as a mica-type silicate that consists of sheets arranged in a layered structure. The crystal structures of these silicates are made up of two silica tetrahedra fused to an edge-shared octahedral sheet of either alumina or magnesia. A regular van der Waals gap is formed between layers of these silicates. Ion-exchange reactions with cationic surfactants alter the normally hydrophobic surface of the silicate. This counter-ion produces hydrophilic character on the silicate surface. Thus, the surface becomes organophilic, which makes interaction with many polymers possible¹⁰. Maleic anhydride is often used as a compatibilizer for the polymer and MLS. It assists in developing a system in which a more hydrophobic end (PET) is tied to a more hydrophilic end (maleic anhydride). This polarizes the polymer, which aids in MLS dispersion.

A particular system that has been examined is polyethylene terephthalate (PET)-layered silicate nanocomposites. Through compression molding methods, Ke et al. prepared PET/MLS nanocomposites that exhibited a 40°C increase in heat deflection temperature (HDT) and a 250% enhancement of Young's Modulus. The MLS played a strong nucleating-role in the polymer and had strong interactions with the PET polymer chains¹¹. Fang Ou et al. also observed similar results in PET/MLS nanocomposites prepared through solution mixing techniques. The PET exhibited heterogeneous nucleation and an increased crystallization rate in the presence of MLS¹². Sanchez-Solis et al. made PET/MLS bottles through the injection-stretch blow-molding process. Thermal, mechanical, and rheological properties of PET were all affected by the addition of 2% MLS into the blow-molded bottles. A mixed intercalated/exfoliated structure was present in all blow-molded samples¹³.

This study concentrated on the production of PET/MLS films, with and without maleic anhydride coupling agent, through twin-screw extrusion. It is our hope that we will produce highly intercalated/exfoliated nanocomposite films that demonstrate improved physical, thermal, and barrier properties over the neat PET film.

Experimental

Materials

The polymer used in this study was a semi-crystalline, extrusion grade of PET (KOSA 1101) supplied by KOSA. Organically modified MLS (Cloisite 20A and 30B) provided by Southern Clay were used to process a series of PET/MLS nanocomposites. MLS percentages in the nanocomposites varied from 2 to 5% by weight. One half percent by weight maleic anhydride, supplied by Avocado Research Chemicals, was incorporated into the nanocomposites as a polymer-MLS coupling agent.

MLS Selection

Determination of the proper MLS to use in the nanocomposite was accomplished by mixing 25g of the dried PET resin with 0.5g of MLS 20A. This mixture was mechanically mixed by hand for 5 minutes and fed into a DACA micro-compounder to mimic a twin-screw extrusion system. The mixture was compounded for 1 minute at screw speeds of 150 rpm and 200 rpm at a temperature of 255°C before being extruded into strands. The same procedure was done using MLS 30B in the PET polymer. Each set of strands was pelletized and analyzed to determine which system demonstrated better MLS dispersion and intercalated/exfoliated morphology.

Pelletizing

Once the proper PET/MLS system was determined, it was possible to compound the PET/MLS nanocomposites. KOSA PET was dried overnight at 65°C in a vacuum oven and fed into the feeding zone of a Thermoprism TSE-16 co-rotating, twin-screw extruder (16mm-bore, 24:1 L/D) using a volumetric feeder. A PET/MLS nanocomposite master batch was pelletized at a concentration of 10% MLS by hand feeding the MLS into the second zone of the extruder. Nanocomposite pellets with MLS percentages of 2, 3, and 5% 30B, by weight, were processed using the master batch and a measured amount of pure PET. 0.5% by weight maleic anhydride was added during this final extrusion to compatibilize the polymer and MLS. Control samples were also processed in this way without maleic anhydride. Extruder temperatures ranged from 270°C in the feed zone, to 290°C in the die. The screw speed of the extruder was 65 rpm. The PET strand was pulled through a water bath and pelletized using a Thermoprism mechanical pelletizer.

Film Processing

The compounded PET/MLS pellets, with and without maleic anhydride, were extruded into films by way of a ThermoHaake Polydrive Single Screw Extruder. A PET melt-temperature of 250°C provided the proper melt viscosity for quality film extrusion. Chill rolls set at a temperature of 17.5°C were used to form the film.

Characterization Methods

Morphology

A Siemens D500 X-ray Diffractometer was used to study the diffraction behavior of the PET/MLS nanocomposites. All the experiments were carried out between 2θ equal to 2° to 60°. Sample films were analyzed and experiments were carried out at room temperature.

Transmission electron microscopy (TEM) was carried out to also determine the interaction of the MLS and polymer. The samples were prepared in a mixture of epoxy and hardener in order to slice the samples in the ultra-microtome, using a diamond knife. The microtomed samples were then examined under a Philips EM400 transmission electron microscope at 120kV and various magnifications.

Mechanical Properties

Tensile testing was performed using an Instron instrument (model: 5500) with a Series IX (v. 7.50.00) Automated Materials Testing System. A 50-kg load cell with 1112 N pneumatic grips was used to test the film samples. The samples were tested according to ASTM D882.

Thermal Properties

Differential scanning calorimetry (DSC) was performed with a TA Instruments Q100 system. Two scanning cycles were run from 15 to 270°C at a heating and cooling rate of 10°C/minute. Samples of 10-15mg were analyzed using TA hermetic pans.

Thermogravimetric analysis (TGA) was performed with a TA Instruments Hi-Resolution 2950 TGA. Samples were heated from room temperature to 1000°C at a rate of 10°C/minute to determine the thermal stability and inorganic content of the nanocomposites.

Results and Discussion

Morphology

Presented in Figure 1 are the WAXD patterns for the MLS samples before compounding, along with the patterns for the nanocomposite pellets formed from PET and 2% by weight of the MLS. As indicated by the shifts in the pattern peaks, the d-spacing of the MLS 20A has increased from 24.4Å to 34.1Å after processing with PET in the twin-screw extruder. This indicates that polymer is penetrating between MLS platelets, but it is an intercalated system. However, examination of the WAXD pattern for the PET/MLS 30B sample shows that the MLS peak is primarily absent from the scan. This indicates a shift toward a more intercalated/exfoliated nanocomposite sample. TEM images listed in Figure 2 show the aligned structure of the PET/MLS 20A sample

while the PET/MLS 30B image shows a slightly better dispersion confirming the intercalated structure. Therefore, it was decided that Cloisite 30B would be the best choice for our nanocomposite. Figure 3 shows a TEM image of a PET/MLS 30B nanocomposite sample after the pelletization process. Notice the intercalated structure as well as a small degree of exfoliated platelets.

Thermal Analysis

DSC analysis of the films provided an interesting glimpse into the thermal properties of the PET/MLS nanocomposites. Figure 4 shows an overlay of a DSC scan in which the films are being cooled at a controlled rate of 10°C/min from the melt state. The peaks shown represent the crystallization onset temperature and the degree of crystallization in the films. The scans indicate that the degree of crystallization is higher in the nanocomposites and that the maleic anhydride did not substantially affect this. The onset of crystallization was also observed at higher temperatures indicating that the MLS were acting as nucleating agents for crystal formation within the films. These values are listed in Table 1 along with other transition temperature data for each sample. The glass-transition temperature of the films dropped by 1-4°C with the addition of the MLS.

Another important property of the films that was examined was thermal stability. Through TGA experiments, it was possible to determine how the MLS and maleic anhydride agent affected the polymer's degradation temperature. Figures 5 and 6 show an overlay of numerous TGA experiments. It is important to note the temperature at which the sample begins to significantly lose weight and degrade. The neat PET film appears to demonstrate the highest thermal stability of all samples tested. The addition of MLS alone causes a depression in degradation temperature and thermal stability. A chemical reaction between the PET and MLS treatment may be the cause of this depressed stability. A similar effect is observed in the maleated PET samples without clay. Again, the thermal stability of the samples is depressed by as much as 10°C when 0.5% maleic anhydride is incorporated into the system. In this set of experiments, the maleated PET without the MLS additive displays the least thermal stability. The degradation mechanism of PET and maleic anhydride is currently under investigation.

Mechanical Properties

Mechanical analysis of the nanocomposite films shows that the mechanical properties of the PET were substantially altered by the incorporation of MLS and maleic anhydride to the polymer. Young's Modulus of the nanocomposite was enhanced by 11% at a 5% MLS loading. The maleated samples showed slightly lower modulus values when compared to their non-maleated counterparts. The greatest effect of the MLS and maleic

anhydride on the PET appears upon examination of the toughness and ultimate strain properties of the film. While neat PET and maleated PET samples show similar toughness and strain values, nanocomposite samples with and without the maleic anhydride show a tremendous loss in these properties. Figure 7 illustrates the dramatic effect that the MLS had on the ultimate strain of the PET films. Possible causes for this behavior include inadequate MLS modification or polymer degradation. Analysis of the film molecular weight through gel-permeation chromatography (GPC) will support this hypothesis.

Conclusions

An intercalated PET/MLS film has been produced through film extrusion processing. WAXD analysis and TEM microscopy has shown that the d-spacing of the MLS platelets has increased as a result of melt processing, but layered-structures are still present in the samples. The PET/MLS systems with and without the maleic anhydride-coupling agent demonstrate an increased Young's Modulus along with a substantial loss in film toughness and strain. Maleated PET/MLS systems do not show any improvement in mechanical properties over the non-maleated PET/MLS films.

Maleated and non-maleated PET/MLS films show an increased degree of crystallization and crystallization rate over the neat PET films. It is believed that both the maleic anhydride and MLS act as nucleating agents for crystallization to occur upon cooling of the nanocomposites from the melt state. No substantial differences were found between the maleated and non-maleated systems in relation to crystallization properties. The MLS also appears to plasticize the PET as the Tg of the PET/MLS systems is lower than the neat PET film. This effect is not observed in the maleated PET sample; therefore it is assumed directly related to the MLS additive.

Further analysis of the PET/MLS film's barrier properties is planned along with GPC analysis of the sample's molecular weight. A deeper understanding of the reaction between maleic anhydride and montmorillonite is needed to determine cause of mechanical property loss and possible polymer degradation. There are various grades of MLS that may be examined in relation to this system in order to find an optimum polymer/MLS nanocomposite.

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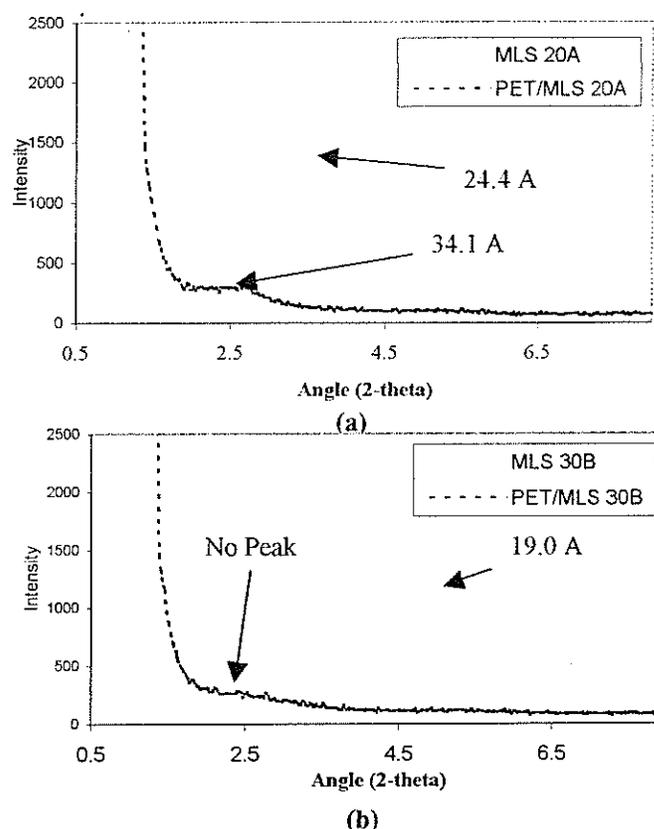


Figure 1: WAXD patterns for MLS 20A (a) and 30B (b) before and after compounding with KOSA PET.

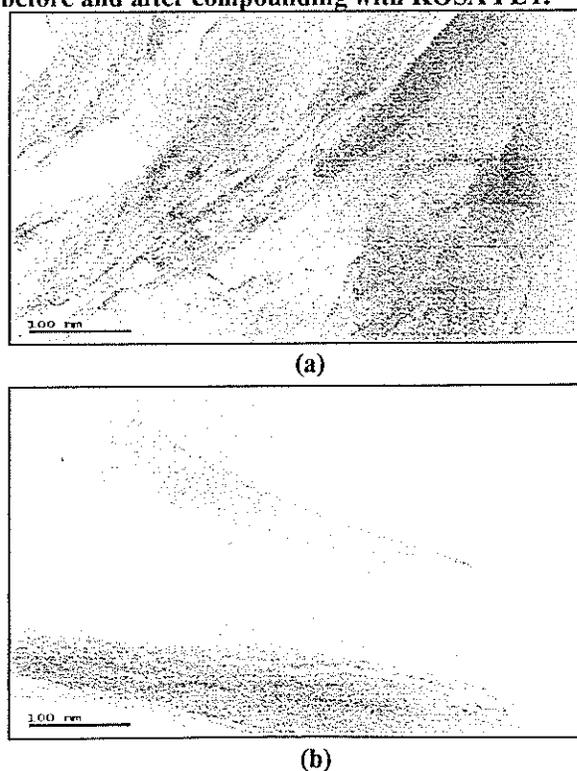


Figure 2: TEM Images of PET/MLS 20A (a) and PET/MLS 30B (b) pellets.



Figure 3: TEM image of an intercalated PET/MLS 30B nanocomposite.

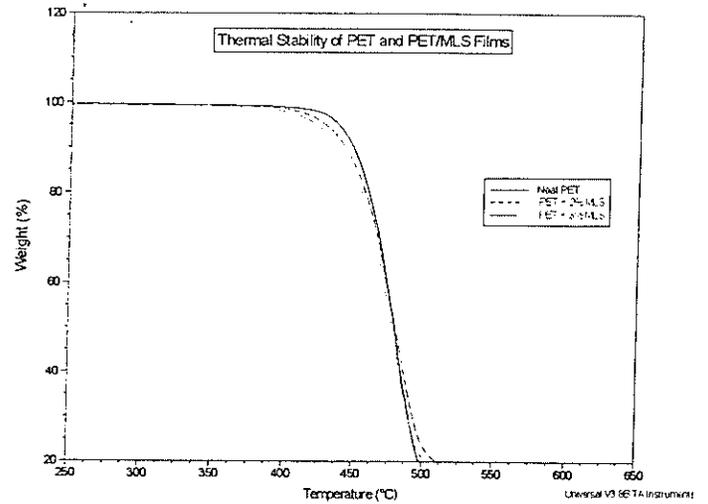


Figure 5: Thermal stability of PET/MLS nanocomposite films.

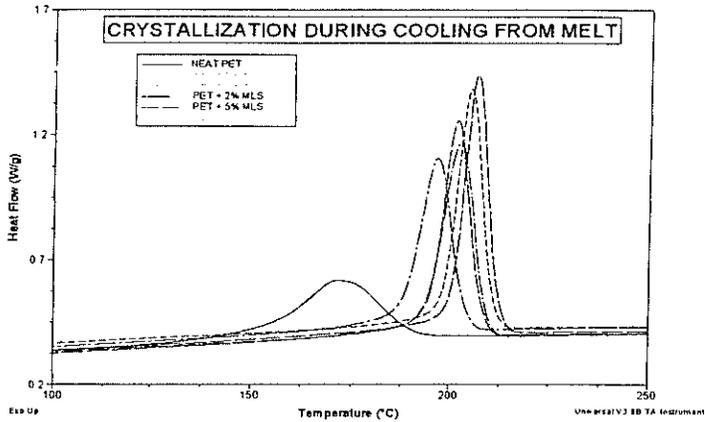


Figure 4: Nucleating effect of maleic anhydride and MLS on PET films.

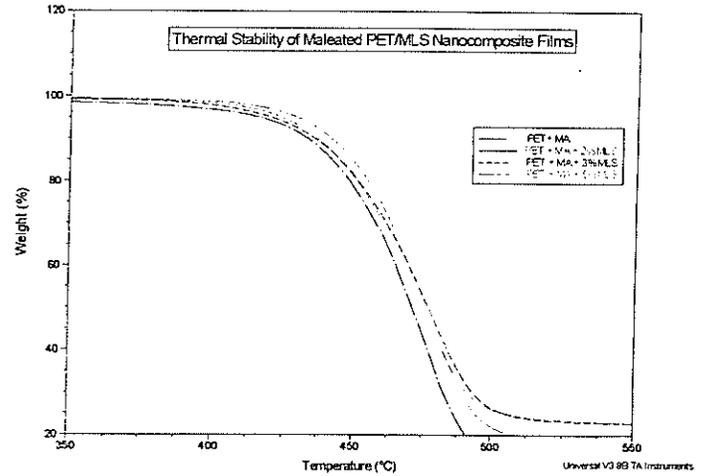


Figure 6: Thermal stability of maleated PET/MLS nanocomposite films.

Table 1: DSC Experimental Data

Sample	Tg (°C)	ΔH (J/g)	Tc (°C)
Neat PET	81.9	32.8	190.3
PET + MA	80.3	44.6	203.6
PET + 2% MLS	78.2	47.5	209.0
PET + 5% MLS	76.2	49.3	211.9
PET + MA + 2% MLS	78.4	48.5	207.8
PET + MA + 5% MLS	77.5	49.8	210.5

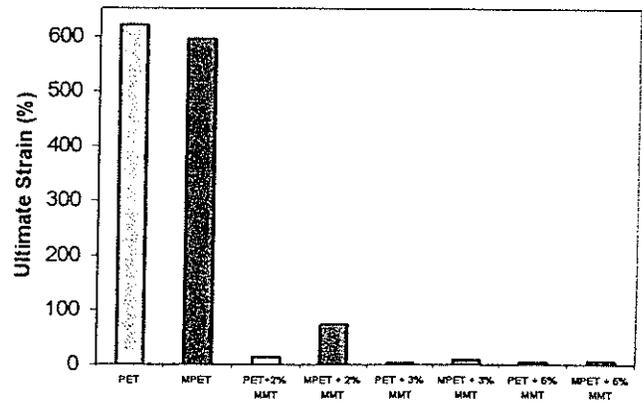


Figure 7: The effect of MLS and maleic anhydride on the ultimate strain of PET films.

Keywords: Nanocomposite, PET, Film, Extrusion