

A STUDY OF LABORATORY AND PILOT SCALE EXTRUDED LDPE NANOCOMPOSITE FILMS

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Abstract

A nanocomposite formulation consisting of low density polyethylene (LDPE), montmorillonite layered silicates (MLS), and a compatibilizer were compounded and extruded into blown films on laboratory and pilot scale extruders. This study evaluates the compounded pellets and extruded films for their morphological, thermal, mechanical and barrier properties. Wide angle x-ray diffraction and transmission electron microscopy experiments confirmed an intercalated morphology in all the samples. Thermogravimetric analysis revealed slightly higher degradation temperatures in the laboratory scale film samples than the pilot scale films. Mechanical and barrier properties were comparable for films produced by laboratory and pilot scale. Overall, this was a successful transition from laboratory scale to pilot scale processing, allowing the Army to consider this nanocomposite for the outer pouch of the Meals Ready-To Eat (MRE) package.

modulus^[1,2]. More importantly for food packaging applications, these high aspect ratio nanolayers force gas and water molecules to follow a more tortuous path in the polymer matrix around the silicate layers.

Polypropylene and polyethylene nanocomposites with compatibilizers have been widely studied in the literature prepared by a variety of preparation methods.^[3,11] Achieving exfoliation and significantly improving the properties of a polyolefin is a challenge. Currently, there are minimal studies specifically focused on LDPE blown film nanocomposites by melt processing. In this study, blown films of the nanocomposites are produced at the laboratory and pilot scale level to determine the level of compatibility between the montmorillonite and the pure polymer as well as to compare the properties of the nanocomposite films in relation to the pure polymer films. Morphological, barrier, thermal and mechanical properties of the films are evaluated and compared for the different trials.

Background

Nanocomposites containing small amounts of clay (1-5%) have been shown to yield large improvements in barrier properties, as well as in physical properties such as tensile strength, tensile modulus and heat distortion temperature.^[1] A doubling of tensile modulus and strength without a sacrifice in impact resistance has been achieved for nylon 6/clay nanocomposites containing as little as 2 wt. % of clays.^[1,2]

The nanoparticle commonly used in these nanocomposites is organically modified montmorillonite, a mica-type silicate, which consists of sheets arranged in a layered structure. These montmorillonite layered silicates (MLS) are used for their high cation exchange capacity and high surface area. The silicate platelets are 1nm in thickness and 100-200 nm in length.

The large aspect ratio of the silicate layers has many benefits for several polymeric applications. The interface between the tremendous surface area of the MLS and the polymer matrix minimizes the chain mobility, creating a reinforcement effect. In addition, this interface facilitates stress transfer to the reinforcement phase, thus improving physical properties such as tensile strength and tensile

Experimental

Materials

The MLS was supplied by Southern Clay Products, under the trademark Cloisite 20A. Low Density Polyethylene 683 I was supplied by Dow Chemical Company. The compatibilizer was Polybond (PB) 3109 supplied by Crompton Chemical.

Processing

Laboratory Scale

Compounding

The MLS at 7.5% loading was compounded with LDPE using a Zenix ZPT-30 30mm co-rotating twin screw extruder using a standard mid shear configuration for additive blending. Temperature was varied across the nine zones from 165°C in the feed section to 215°C at the die. Extruded strands were pelletized for secondary processing.

Film Processing

Blown films were prepared with a Haake® Polylab twin-screw extruder, 24:1 L/D. The screws were conical, counter-rotating and intermeshing with a diameter of 31.8mm and a length of 300mm. The die has an interior

diameter of 24 mm and outer diameter of 25 mm with an adjustable ring gap. Screw speeds ranged from 40-200 rpm and processing temperatures varied from 215 to 235°C.

Pilot Scale

Compounding

Foster Corporation processed the same LDPE nanocomposite formulation that was used with the laboratory scale trial with a 30 mm twin-screw extruder at temperatures varying from 160 to 215°C, and a screw speed of 300 rpm. Melt temperature was measured at 234°C.

Film Processing

Alcan Packaging conducted a trial production run of low density polyethylene (LDPE) nanocomposite film. The LDPE nanocomposite pellets that were compounded at Foster were shipped to Alcan's Neenah Technical Center in Neenah, WI. Several hundred linear feet of pure LDPE film and LDPE nanocomposite film were successfully processed on a 5-layer blown film pilot plant coextrusion line. Films were fabricated at 2 mil and 6 mil thicknesses.

Characterization

The morphologies of the nanocomposites were determined by transmission electron microscopy (TEM). The samples were prepared in a mixture of epoxy and hardener to enable slicing of the samples in the ultramicrotome, using a diamond knife. The microtomed samples were then observed under Philips EM400 Transmission Electron Microscope at 120kV at various magnifications. Tensile properties were evaluated with an Instron® 4200 series instrumentation in accordance with ASTM D882. The load cell weight was 50 Kg and the cross head speed was 2.0 mm/min. Rectangular samples with a gauge length of 2 inches were used. Each result was based on the average of 10 replicates. Measurements were made in both the machine and transverse directions.

Differential Scanning Calorimetry (DSC) was used to evaluate the melting and crystallinity of the LDPE in the pure LDPE films as well as the nanocomposite. A Perkin Elmer DSC-7 at a scan rate of 20°C/min was used.

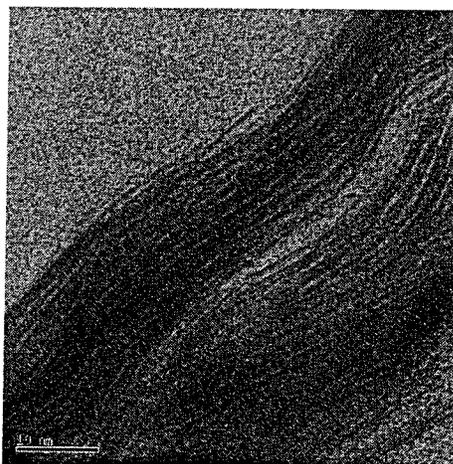
Thermogravimetric analysis (TGA) was used also to determine the thermal stability of the pure LDPE as well as the LDPE nanocomposites films. A TA Instrument TGA 2190 was used from ambient temperature to 700° at a scan rate of 20°C/minute.

Oxygen transmission rates (O₂TR) were established in accordance with ASTM D3985 using the Mocon® Ox-Tran 2/20 at a temperature of 23°C and 50% RH.

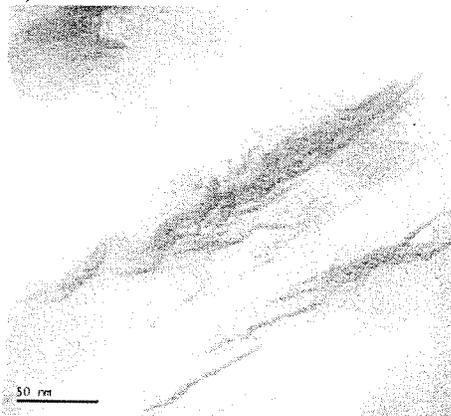
Results and Discussion

Morphology

The nanocomposite blown films were more translucent and yellow in color than the pure LDPE films. They do appear similar in ductility. TEM and X-ray diffraction was used to determine the morphology and interaction of the polymer and MLS. TEM data are shown below. Figure 1 is a representative TEM of the LDPE/MLS nanocomposite with 7.5% MLS for the laboratory and pilot scale films. The threadlike strands in the high magnification photograph in Figure 1a represent the MLS stacked platelets. It is difficult to determine the spacing in between the platelets as it is clearly an intercalated morphology. Figure 1b is at a lower magnification that shows the aggregates of MLS in the polymer matrix. A series of photographs have been taken for both the trials to show the degree of dispersion at the lowest magnification and the degree of intercalation at the highest magnification. Both laboratory and pilot scale films show similar dispersion and intercalation from the TEM photographs.



a.)



b.)

Figure 1a and b. Typical TEM images for LDPE nanocomposite with 7.5% MLS.

Thermal Properties

Thermogravimetric analysis (TGA) data of the laboratory and pilot scale trials were compared. The TGA data representing the laboratory scale samples showed an 80°C improvement in thermal stability while the pilot scale data showed a 50°C improvement. The calculated residue after heating the samples in the TGA does show that the pilot scale film samples have slightly less MLS than the laboratory scale samples which may have influenced these results. Possible variations in the degree of dispersion and orientation of the platelets may have influenced this difference in thermal stability. Figure 2 shows the onset of degradation temperature for the pure LDPE and LDPE nanocomposites for the pilot scale trial. Both the 2 and 6 mil thickness samples have similar onset temperatures for the pure LDPE and vary slightly for the LDPE/MLS nanocomposite.

The melting temperatures determined from DSC for the pure LDPE and the LDPE/MLS nanocomposite films were equivalent. These values remained constant from the laboratory to the pilot scale blown film trial.

Mechanical Properties

The Young's modulus increased in the machine direction by approximately 80% for the 7.5% montmorillonite nanocomposite in both laboratory and pilot scale trials in comparison to the pure LDPE. Figure 3 showed even greater improvements in the transverse direction than seen in the machine direction of the films for the pilot scale trial. The results showed that the pure LDPE transverse direction films had about a 30% improvement in Young's modulus over than the pure LDPE machine direction films. Mechanical properties such as modulus usually increase in the direction of orientation of polymer molecules. However, these films are blown films with biaxial orientation. The improvement in modulus can be seen in both machine and transverse directions for the nanocomposites, since there is orientation in both the parallel and perpendicular directions as well as random orientation of the MLS platelets throughout the matrix. For the laboratory scale trial, only machine direction samples could be analyzed due to the size of the films.

Barrier Properties

The oxygen barrier performance improved with the 7.5% nanocomposite films having almost twice the barrier of the pure LDPE films. Table 1 shows this data for both the laboratory and pilot scale trials. These results are also attributed to the degree of exfoliation in the LDPE nanocomposites. For both trials, the water vapor transmission rates show approximately 40% improvement for the LDPE nanocomposites films as compared to the pure LDPE films.

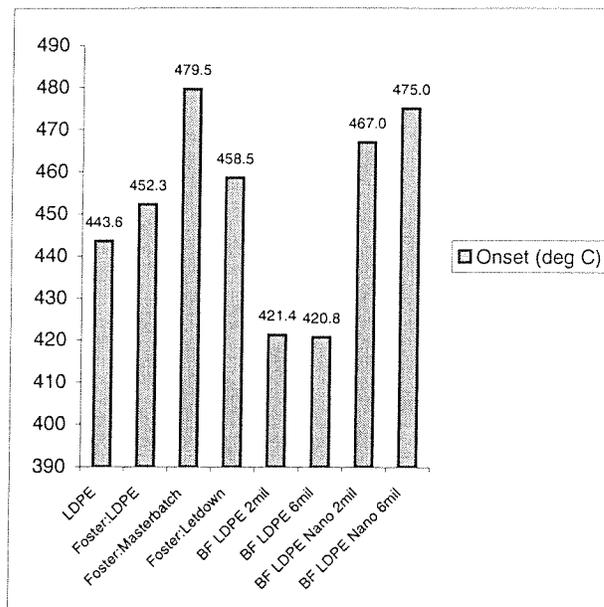


Figure 2. Onset degradation temperatures for the pilot trial of the various pure and LDPE/MLS nanocomposites.

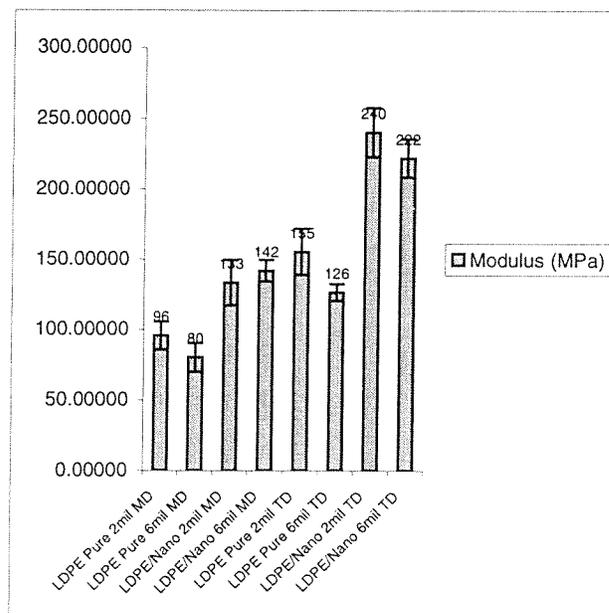


Figure 3. Young's Modulus data for the pilot trial of LDPE and LDPE/MLS nanocomposite films. (MD = machine direction and TD = transverse direction)

Table 1: Oxygen Transmission Rates

Trial	Oxygen Transmission Rates (cc-mil/m ² -day)	
	Laboratory	9095
Pilot	40.54	6270

Conclusions

Recyclable nanocomposites consisting of low density polyethylene (LDPE) and montmorillonite are potential materials for military food packaging. The organically modified montmorillonite is combined at low loadings (7.5%) with a compatibilized LDPE and processed as a blown film to give improved thermal, mechanical and barrier properties. Transmission electron microscopy (TEM) of the films at various processing parameters shows that the 7.5% loading has a high degree of intercalation and dispersion. The Young's modulus increased by 80% for the 7.5% montmorillonite nanocomposite in comparison to the pure LDPE. The oxygen barrier improved also with the 7.5% nanocomposite having almost twice the barrier of the pure LDPE. The ability of the LDPE nanocomposite to significantly improve the properties of the pure LDPE was consistent between both laboratory and pilot scale trials. With all these improvements over pure LDPE, an application targeting the military ration pouches is being investigated. Further tests with regard to military specifications are underway.

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1. Giannelis, E.P. (1996), "Polymer Layered Silicate Nanocomposites", *Advanced Materials*, Vol.8, PP. 29-35.
2. LeBaron, Peter C., Wang, Zhen et al. (1999), "Polymer-layered Silicate Nanocomposites: An Overview", *Applied Clay Science*, Vol. 15, pp 11-29.
3. O'Neil, Charles, J., Acquarulo, Lawrence A., et al., (2000), "Optimizing Nano Filler Performance in Selected Nylons", *Antec 2000 Proceedings*.
4. Hambir, Sangeeta, Bulakh, N., Jog, J.P., (2002), "Polypropylene/clay Nanocomposites: Effect of Compatibilizer on the Thermal, Crystallization and Dynamic Mechanical Behavior", *Polymer Engineering and Science*, Vol. 42, No. 9 1800-1807.
5. Alexandre, Michael, Dubois, Philille, Sun, Tao, Garces, Juan, Jerome, Robert, (2002) "Polyethylen-layered Silicate Nanocomposites Prepared by the Polymerization-filling Technique: Synthesis and Mechanical properties", *Polymer*, Vol 4, 2123-2132.
6. Jeon, H., Jung, H., Lee, S. Husdon, S., (1998) "Morphology of polymer/silicate Nanocomposites", *Polymer Bulletin*, 4, 107-113.
7. Jeon, H., Jung, H., Lee, S. Husdon, S., (1998) "Morphology of polymer/silicate Nanocomposites", *Polymer Bulletin*, 4, 107-113.
8. Hotta, S., Paul, D.R., (2004) "Nanocomposites formed from linear low density polyethylene organoclays", *Polymer*, 45(22) 7639-7654.
9. Pandey, Jitendra, Singh, Ray P., (2004, "On the durability of low density polyethylene nanocomposites", *e-Polymers* http://www.e-polymers.org/papers/singh_140804.
10. Bae, J. H., Ryu, S. H., Chong, Yong, W., (2004), "Characterization of LLDPE/montmorillonite nanocomposites", *ANTEC*, 62nd, Vol. 2 2196-2200.
11. Zhang, Jinjuo, Wilke, C. (2003), "Preparation and flammability properties of polyethylene clay nanocomposites", 80(1), 163-169.
12. Wang, K. H., Cheng, M., Chung, I. J. (2003), "Physical properties of polyethylene silicate nanocomposite films", *J. of Appl. Polym. Science*, 89(8) 2131-2136.