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Fabrication and Properties of Blown Films Based on Polypropylene-Clay Nanocomposite

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INTRODUCTION

It is well known that the incorporation of a relatively low content (less than 5% by weight) of layered silicate reinforcement into a polymeric matrix can result in significant improvements in a range of properties, provided that the clay particles are sufficiently exfoliated into their basic layers, of thickness about 1 nm [1]. Achievement of a high degree of exfoliation remains a major challenge in producing commercial products, particularly when the polymer matrix is hydrophobic like polypropylene (PP) whereas the clays are naturally hydrophilic. This problem is usually attacked by two approaches: (i) treatment of the natural clay with organic intercalants like onium salts, which replace the metal ions located between the layers and increase the interlayer spacing, thus facilitating further separation; and (ii) incorporating into the hydrophobic polymer matrix a compatibilizing agent (CA) which resembles the matrix but also contains polar groups that lead to better interaction with the clay. Maleic-anhydride-grafted polypropylenes (MA-g-PP) are often used as CAs for PP. This paper describes the results of a study covering a range of compositions based on polypropylene, a commercial treated clay, and two different MA-g-PP compatibilizing agents.

EXPERIMENTAL

Materials. The PP used was Pro-fax PDC1274 from Basell Polyolefins. The clay was Cloisite 15A from Southern Clay Products, Inc.; it consists of montmorillonite treated with dimethyl di(hydrogenated tallow) ammonium salt to give an organic content of about 40% and an interlayer d_{001} spacing of 3.15 nm. The two MA-g-PPs were: (i) Epolene 43 from Eastman Chemical Company, with a low molecular weight ($M_w = 9000$) but high MA content (3.8 wt%), henceforth designated "MA9k", and (ii) Polybond 3150 from Crompton Corp., with a high molecular weight ($M_w = 330,000$) and low MA content (0.5 wt%), henceforth designated "MA330k".

Processing. Masterbatches containing 10 wt% or 15 wt% clay in PP were prepared by processing in a Leistritz 34 mm twin screw extruder at 200°C. These were then processed under the same conditions together with appropriate amounts of PP and CA to give mixtures containing 0 or 4 wt% CA in combination with 0, 2, 5, or 10 wt% clay. Some mixtures with 2% clay and higher levels of CA (20% or 38%) were also prepared. The mixtures were injection-molded on a BOY machine at 200°C. Blown films with a take-up ratio of 24 and a blow-up ratio of 2.6 were prepared on a Killion machine. The typical sample designation PP-4MA9k-2C denotes a composition containing 4 wt% of compatibilizing agent MA9k and 2 wt% Cloisite 15A.

Characterization. The samples obtained were characterized by means of various techniques making use of standard instrumentation and procedures: X-ray diffraction, scanning electron microscopy, infrared spectroscopy, differential scanning calorimetry, tensile properties, optical properties, permeability to oxygen of the air. In the case of infrared spectroscopy, the "tilted film" method [2] was used to obtain spectra of the blown films with polarization corresponding to each of the three orthogonal directions: MD (machine = longitudinal or "take-up" direction), TD (transverse = circumferential or "blow-up" direction), and ND (normal or thickness direction). The spectra were used to determine the orientation of both the polymer matrix and the clay platelets.

RESULTS AND DISCUSSION

X-ray diffraction curves measured on injection-molded specimens indicated that the clay was intercalated but not completely exfoliated. The measured d_{001} spacings are given in Table 1. When no CA is present, the spacing is similar to, or even slightly lower than, that of the starting clay (3.15 nm), which suggests that some collapse may occur during processing. This could be because the Cloisite 15A contains an excess of intercalant (based on the cation exchange capacity of the clay), and the excess may be more easily lost during the processing. When MA9k is present, even at only 4 wt%, the spacing increases to ~3.8 nm and does not change on going to 20 wt%. When MA330k is present at 4 wt%, however, there is little change in the spacing, but it does increase to ~4 nm when the content of MA330k is high. Of course, these results only pertain to the intercalated clay and do not give a good indication of the amount of exfoliated clay that is present.

Table 1. Values of the d_{001} Spacing Obtained from X-ray Diffraction Curves

Sample	d-spacing (nm)
PP-2C	2.81
PP-5C	2.83
PP-10C	2.90
PP-4MA9k-2C	3.84
PP-4MA9k-5C	3.75
PP-4MA9k-10C	3.84
PP-20MA9k-2C	3.88
PP-4MA330k-2C	3.21
PP-4MA330k-5C	3.03
PP-4MA330k-10C	2.99
PP-20MA330k-2C	3.99
PP-38MA330k-2C	3.96

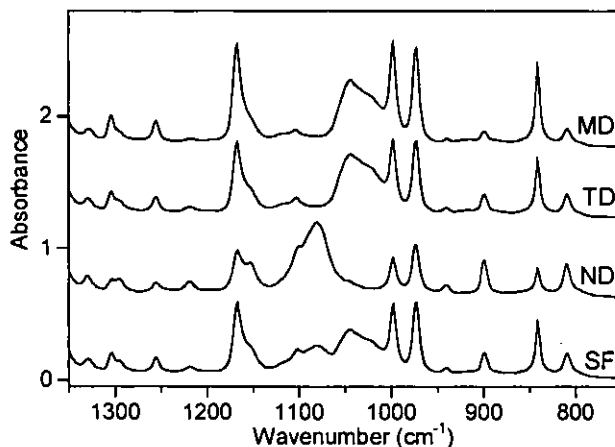


Figure 1. Trichroic infrared spectra obtained by the "tilted film" method for the blown film with composition PP-20MA330k-2C, corresponding to machine direction (MD), transverse direction (TD), normal direction (ND), and structural factor (SF).

Figure 1 shows a typical example of the trichroic infrared spectra obtained, in this particular case for the blown film with composition PP-20MA330k-2C. Many of the peaks arise from the crystalline phase of PP. The vibrational mode at 841 cm^{-1} is known to have its transition moment (L.m.) parallel to the polymer chain direction [3], and the one at 1167 cm^{-1} shows similar behavior. It can be seen that these peaks are strongest in the MD spectrum, weaker in the TD spectrum, and weaker still in the ND spectrum. This confirms that the PP orientation is biaxial, as expected for a blown film, and that the molecular chains are more strongly oriented in the take-up direction than in the blow-up direction, as expected for a high take-up ratio. Also of interest are the

strong and broad clay peaks occurring in the 1150-1000 cm^{-1} region. Farmer and Russell [4] have pointed out that montmorillonites show four Si-O stretching bands in this region, of which three (near 1120, 1048, and 1025 cm^{-1}) have their t.m. lying in or close to the plane of the silicate layers and the fourth (near 1080 cm^{-1}) has its t.m. perpendicular to the plane. It can be clearly seen in Figure 1 that the bands at 1048 and 1025 cm^{-1} are quite strong in the MD and TD spectra but very weak in the ND spectrum, whereas the opposite is true for the perpendicular band at 1080 cm^{-1} . (The band at 1120 cm^{-1} is too weak to see clearly.) This behavior indicates a strong orientation of the clay layers in the plane of the film. The method does not distinguish between individual layers and platelets containing stacked layers.

The orientation of both polymer and clay can be quantified by comparing the MD, TD, and ND spectra to the average or "structural factor" spectrum, which corresponds to the isotropic state. The Hermans orientation function f_{ij} describing the degree of orientation of the axis i corresponding to the t.m. of a given vibrational mode with respect to the direction J ($J = M, T, \text{ or } N$) is given by:

$$f_{ij} = \frac{1}{2} \left[\frac{A_j}{A_0} - 1 \right]$$

where A_j/A_0 is the ratio of the intensities of said peak in the J -direction spectrum and the structural factor spectrum. This ratio is determined by interactively subtracting the two spectra and adjusting the factor until the peak in question disappears. The orientation functions determined in this manner for some of the blown films with 2% clay are given in Table 2. For the PP, they were determined from the 1167 and 841 cm^{-1} peaks, corresponding to the polymer chain axis, and for the clay, they were determined from the 1080 cm^{-1} peak, corresponding to the axis normal to the silicate layers. It can be seen that the biaxial orientation is similar in all the films and that the clay layers are rather highly oriented ($f = 1$ corresponds to perfect orientation).

Table 2. Orientation Functions for Blown Films

Composition	Polypropylene			Clay
	f_{CM}	f_{CT}	f_{CN}	
PP	+0.15	+0.02	-0.17	—
PP-2C	+0.20	-0.02	-0.18	+0.78
PP-4MA9k-2C	+0.17	-0.04	-0.12	+0.78
PP-4MA330k-2C	+0.22	0.00	-0.21	+0.80
PP-20MA330k-2C	+0.24	+0.02	-0.25	+0.74
PP-38MA330k-2C	+0.20	+0.02	-0.21	+0.75

Figures 2 and 3 show the tensile properties and oxygen permeation coefficients as a function of clay content for formulations with no CA, 4% MA9k, and 4% MA330k. With no CA, at 2% and 5% clay the tensile properties are improved but the permeability is not significantly reduced. Increasing the clay level to 10% reduces the permeability but at a cost in tensile performance. The low-MW CA (MA9k) is very obviously detrimental to the properties, as it both greatly increases the permeation coefficient and generally lowers the mechanical performance. The best results are obtained with the high-MW CA (MA330k). Although it does not appear to reduce the permeability at the 2% clay level, it does so at 5% and 10% while at the same time improving the tensile properties. Thus, the formulation with 4% MA330k and 5% Cloisite 15A reduces the permeability by about 25% compared to pure PP, while increasing the tensile modulus by 50% and the rupture stress by 15%. The formulation with 4% MA330k and 10% Cloisite 15A, on the other hand, reduces the permeability by about 35% but with less improvement in the tensile properties, although they are at least maintained.

In conclusion, it has been demonstrated that the incorporation of highly oriented nanoclay particles in blown PP films can reduce the oxygen permeability by at least 35% compared to pure PP and at the same time improve the mechanical performance, but the choice of compatibilizing agent is very important. Further improvements may be achievable if the degree of exfoliation can be improved through optimization of the processing conditions.

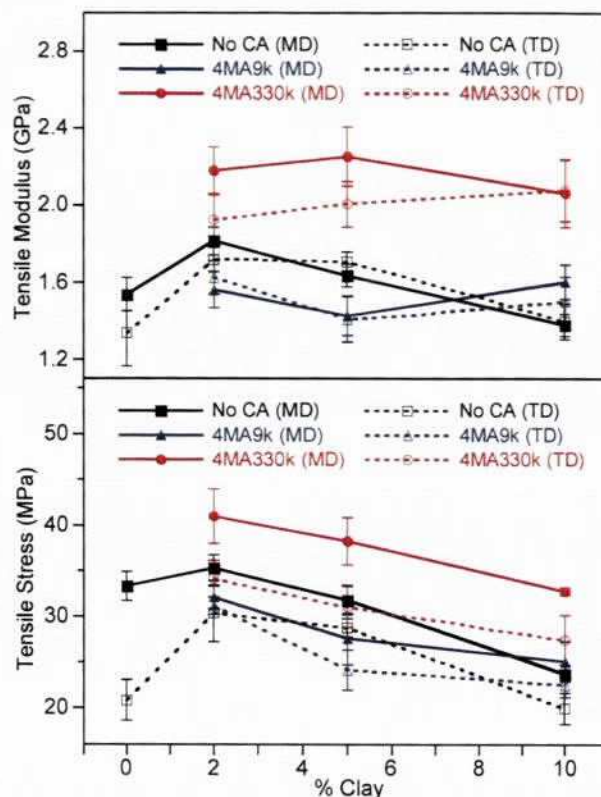


Figure 2. Tensile properties of different blown films.

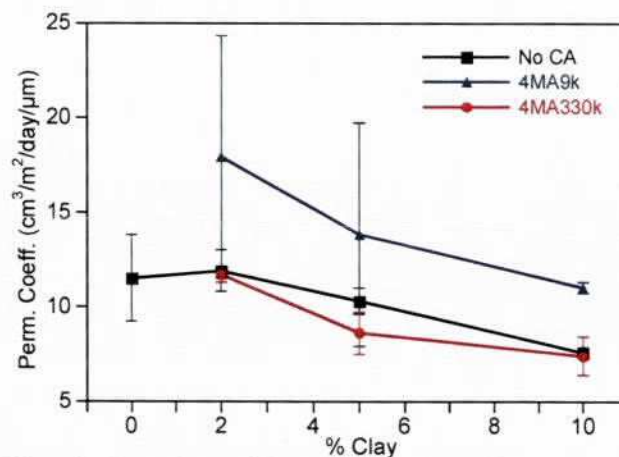


Figure 3. Permeation coefficients of different blown films.

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