

IMPROVEMENT OF BARRIER PROPERTIES OF POLYESTERS USING NANOCCLAY

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1 Introduction

Polyethylene terephthalate (PET) is a semi crystalline engineering polymer extensively used for packaging applications. In the recent years, a biopolymer, poly(lactic acid) (PLA), has been intensively studied as a suitable, more environmentally acceptable substitute for PET. However, gas permeability for both polymers is a major issue for applications such as soft drink, beer and wine bottles. In this presentation we will summarize key results obtained on the development of PET and PLA nanocomposites using an organo-modified clay, as a part of a major project funded three years ago by the Natural Science and Engineering Council of Canada (NSERC) entitled: "Polyester Nanocomposites for Greener Transportation, Construction and Packaging Applications". Significant improvements of the barrier properties of PET and PLA have been achieved and we hope to do better in the near future by improving the exfoliation of the nanocomposites via twin-screw extrusion. Many challenges still need to be solved, in particular the control of the thermal degradation of both matrices during processing. Promising results with that respect using chain extenders will be presented.

2 Experimental

In the case of PET nanocomposites, an experimental grade high viscosity PET Selar PTX 295 (DuPont) and a low viscosity general purpose PET 9921 (Eastman Chemical Co.) were blended at a ratio of 4:1 (low: high viscosity) [1]. A commercial ammonium modified clay (Cloisite 30B, Southern Clay Co.) was compounded with the PET blend (in powder form) at 3 wt% nominal level of clay. Melt compounding was carried out in an intermeshing co-rotating twin screw extruder (TSE) (Leistritz, Germany). The clay was premixed with the grounded PET and then fed to the extruder hopper.

Different screw geometries were used to prepare the PET films.

The poly(L-lactide) (PLA) used was supplied by NatureWorks (PLA 4032D). The organically modified Cloisite30B was mixed to the PLA using a small (18 mm) twin-screw extruder or an internal mixer (Brabender).

Three different chain extenders were used in this study. Polycarbodiimide (PCDI), a carboxyl-reactive chain extender, and Tris (nonylphenyl) phosphite (TNPP) were obtained from Sigma Aldrich. Joncryl ADR, supplied by BASF, is a modified acrylic copolymer with epoxy functions and it was found to be the most effective chain extender in this work.

3 Key Results

3.1 Properties of PET nanocomposites

Figure 1 presents the X-ray diffraction (XRD) measurements for the 4:1 PET blend containing 3 wt % Cloisite 30 B prepared using a severe screw geometry for five different conditions [2]. Two distinct peaks are observed for the films. The first (d -spacing ~ 3.6 nm) reflects intercalation of the clay layers and the second (d -spacing ~ 1.6 nm) implies the degradation or the exuding of the modifier or could be related to a reflection of the first peak. In all cases, including results for different screw geometries, the interlayer distance of the clay platelets is around 3.6 nm. Thus, the level of intercalation is somehow independent of the processing conditions and screw profile as observed by others for polypropylene (PP) nanoclay composites [3].

The transmission electron (TEM) graphs of Figure 2 for a PET film containing 3 wt.% C30B shows a partially exfoliated/intercalated structure plus dispersed tactoids. The individual dispersed silicate layers, observed at higher magnification, suggest

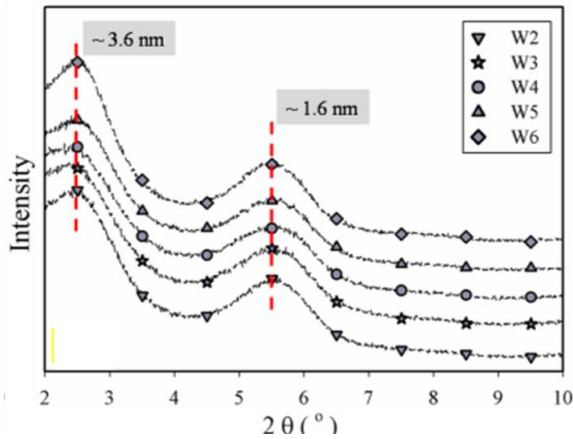


Fig. 1 X-ray diffraction (XRD) measurements for the 4:1 PET blend containing 3 wt % Cloisite 30 B prepared using a severe screw geometry for five different conditions [2].

compatibility of the PET chains and hydroxyl groups of C30B, although some of the organo modifier could have been decomposed at the processing temperature of 265 °C. The experimental relative permeability to oxygen was found to be equal to $K=0.77$. This value is quite close to predicted values from theoretical models using aspect ratios of clay obtained by image analysis of TEM graphs [1].

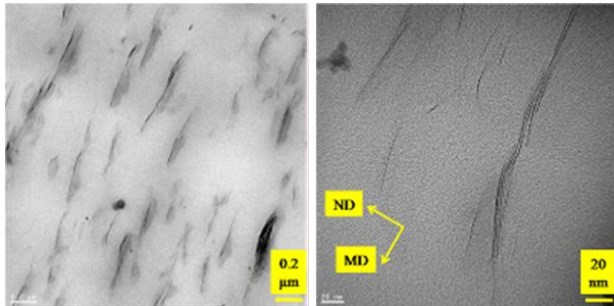


Fig.2 TEM graphs of the PET films containing 3% C30B at a draw ratio (65). Data from [1].

To quantify the dispersion level of silicate layers, the method proposed by Luo and Koo [4] was used. In this method, a random line (usually vertical or horizontal) is drawn to intercept the clay layers in a TEM graph. After measuring the free-path distance, x_i , between the platelets (more than 100 measurements), $D_{0.1}$ is defined as the probability of

the free-path distance distribution to be in the range of $\bar{x} \pm 0.1$). The $D_{0.1}$ value obtained for experiment W4 (optimal conditions with a rotational speed of 250 rpm and feed rate of 3.5 kg/h) was found to be 7.5 %, which is very close to the value of 8 %, criterion for a fully exfoliated system [4].

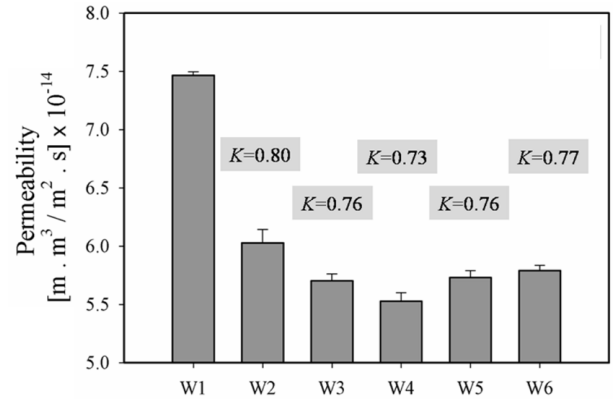


Fig.3 Oxygen permeability of PET films containing 3 wt % Cloisite 30B, prepared using the severe screw configuration. The K values ($K=P/P_0$) represent the relative permeability of the samples. (P and P_0 are the permeabilities of the sample with and without clay, respectively.) W1 corresponds to the neat PET. Data from [2], obtained at the atmospheric pressure.

The measured oxygen permeability values of the PET films containing 3 wt % Cloisite 30B are shown in Figure 3. For this screw profile, the lowest K (0.73) corresponds to 27% improvement of oxygen barrier properties. This result pertains to the sample prepared at the highest screw speed (W4). A comparison between the K values of the samples prepared at constant feeding rate (W2 and W4 in Figure 3) and constant screw speed (W5 and W6 in Figure 3) shows that the screw speed has a stronger effect than the feeding rate on the barrier properties. A comparison between the experimental data and the predictions of models was presented in [1] and it was shown that the maximum achievable reduction in oxygen permeability for fully exfoliated and well-aligned silicate layers in the flow direction is about 40% (at 1.8 wt% neat silicate layer content corresponding to a volume fraction of 0.009).

After 20 min annealing at 150°C, the oxygen permeability of the neat PET and the PET

nanocomposite films at the same draw ratio decreased by 40 and 46%, respectively. Besides the tortuosity, chain segment immobility due to confined environmental geometry should be taken into account. After annealing crystal lamellas introduce more confinement and entropic penalty into the matrix, which leads to less chain mobility and reduction of permeation.

The mechanical properties increase significantly with clay content, of the order of 30 % for the modulus in the machine direction for the best mixing conditions (W4). As expected the optical properties are somewhat affected by the presence of clay as shown in Figure 4. However, the increase in haze and decrease in clarity remain acceptable for most applications

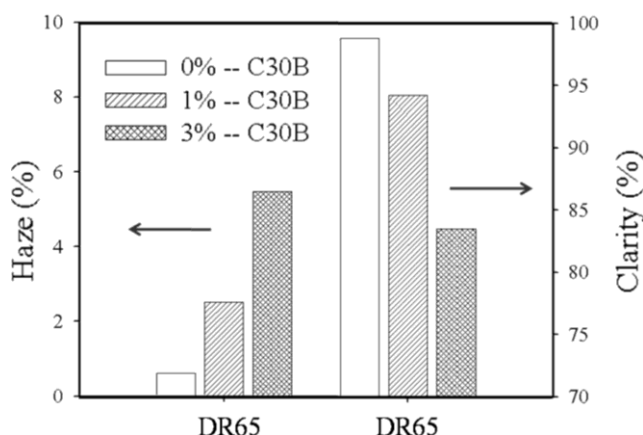


Fig.4 Haze and clarity of PET films containing 0, 1 and 3% C30B at a draw ratio (65). Data from [1].

3.2 Properties of PLA nanocomposites

Figures 5 and 6 show typical degradation tests carried in rheometry in small amplitude oscillatory shear flow for the neat PLA and the PLA containing up to 6 wt % of Cloisite 30B in presence or not of the chain extender, Joncryl. Figure 5 shows a rapid and significant degradation of the neat PLA with time during rheological tests carried out at 180 °C. The figure also reveals that the initial value of the complex viscosity is considerably reduced by the processing, indicating a serious degradation of the PLA when prepared using an internal mixer and more so using a twin-screw extruder. Note that in the presence of 3 wt % Cloisite 30B, the thermal degradation is more rapid. Figure 6 also reveals the

rapid decreases of the complex viscosity for PLA nanoclay composites. However, using a chain extender, especially 0.5 % Joncryl, the complex viscosity is stabilized, indicating that the thermal degradation is stopped by this chain extender. More over the molecular weight of the PLA is increased by the reaction of the chain extender with the PLA .

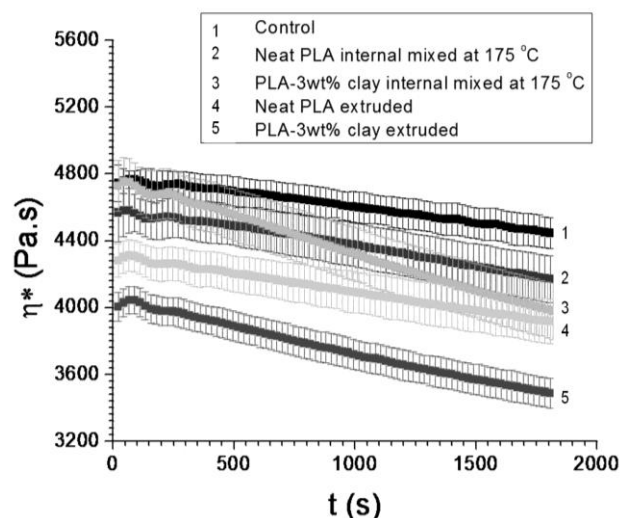


Fig. 5 Complex viscosity as a function of time for the neat PLA, as received (control) or prepared in internal mixer or extruded at 175 °C and PLA nanocomposites containing 3 wt % Cloisite 30B. Measurements were carried out at 0.1 Hz in the linear viscoelastic domain at 180 °C.

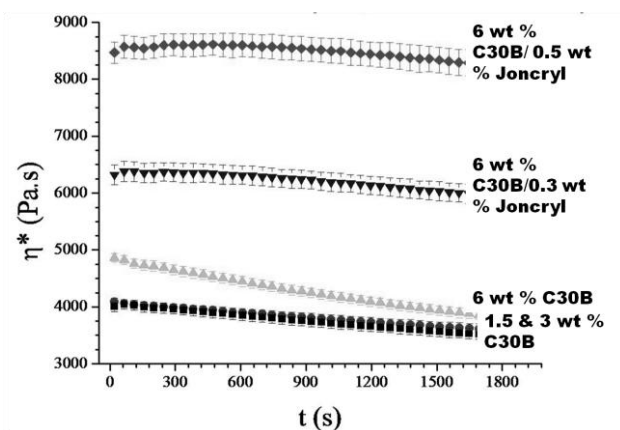


Fig. 6 Complex viscosity as a function of time for PLA/C30B nanocomposites containing or not Joncryl as a chain extender. The nanocomposites were prepared using a twin-screw extruder at 175 °C Measurements carried out at 0.1 Hz in the linear viscoelastic domain at 180 °C.

The effect of chain extenders is illustrated in Figure 7 that shows very large increases of the complex viscosity of the PLA/2 wt % Cloisite 30B nanocomposites containing a chain extender. The effect is more drastic for Joncryl with an increase of more than a decade at low frequencies. We note also that in presence of a chain extender the behavior becomes more shear-thinning (decreasing complex viscosity as a function of the angular frequency). This suggests stronger particle-particle interactions and a better dispersion of the clay. A refined analysis of the rheological data of PLA nanocomposites suggests that Joncryl reacts with PLA chains to form long branches [5]. Preliminary NMR results indicated possible cross-linking, but this could not be verified by dissolution.

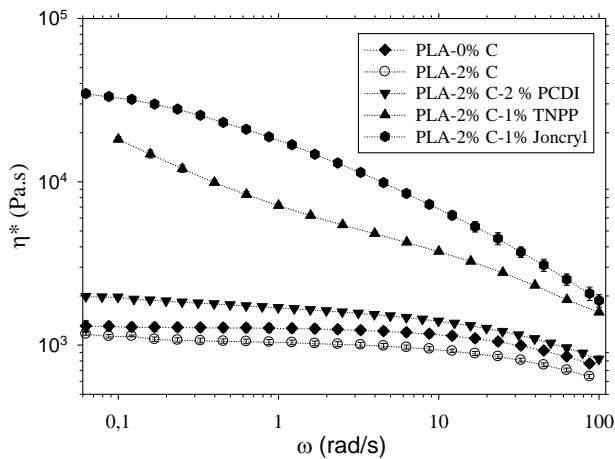


Fig. 7 Complex viscosity as a function of the angular frequency for the neat PLA and PLA/nanocomposites containing a chain extender or not. Data from [5] obtained at 190 °C.

Figure 8 presents the TEM morphology of two PLA/2 wt % Cloisite 30B nanocomposites at the largest magnification (scale bar of 20 nm). For the left sample (a) no chain extender was used, whereas for the right sample (b), 1 wt % Joncryl was added after an initial preparation of a masterbatch using an internal mixer. Both graphs show partial exfoliation, but the $D_{0.1}$ value based on the analysis of Luo and Koo [4] was found to be 6.84 and 7.86 % for the nanocomposite without Joncryl and with Joncryl, respectively. Note that a $D_{0.1}$ value of 8.0 % is considered to represent a totally exfoliated system [4]. By adding the Joncryl after the masterbatch was prepared, the considerably enhanced viscosity due to

the reaction of Joncryl with PLA is a major factor that favors delamination of tactoids and exfoliation.

The improvement of the barrier properties of PLA using Cloisite 30B is illustrated in Figure 9. We note that the addition of 3 wt % Cloisite 30B results into a decrease of 37 % of the permeability of the neat PLA. Adding 3 wt % more Cloisite 30B reduces the permeability by 48%. However, the use of 0.5 % Joncryl increases slightly the permeability of the 6 wt % nanocomposite. We have observed a significant increase of the permeability when Joncryl

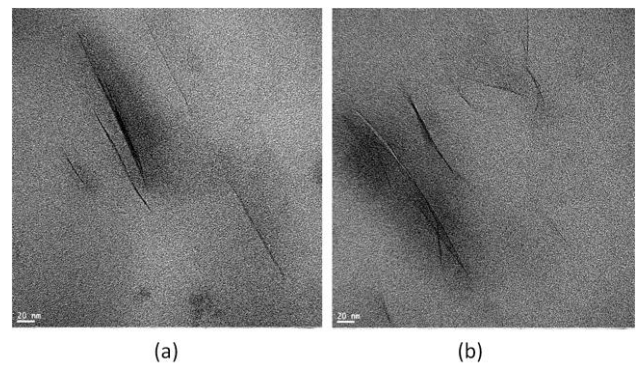


Fig. 8 TEM graphs two PLA/2 wt % Cloisite 30B nanocomposites, (a) sample without Joncryl; (b) sample containing 1 wt % Joncryl prepared via a masterbatch (scale bar of 20 nm).

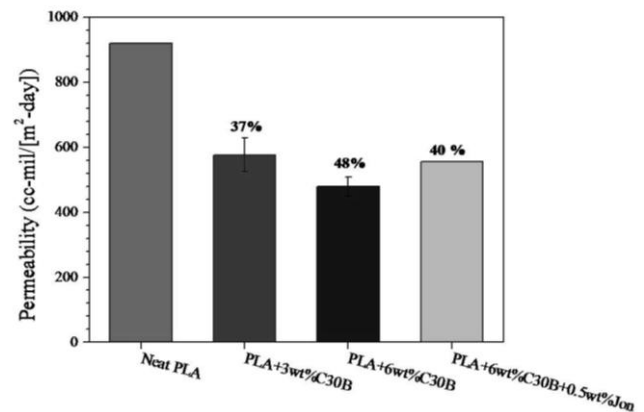


Fig. 9 Permeability data for the neat PLA and PLA/Cloisite 30B nanocomposite films, measured at the atmospheric pressure. The units are based on the film thickness taken in mil (10^{-3} inch, i.e. 0.0254 mm).

was added to the neat PLA. This is explained by a slight decrease of the crystallinity in the presence of Joncryl and possibly to the increase of the free volume of the PLA/Joncryl system. Finally, we note that the mechanical properties of PLA nanocomposites are considerably enhanced by using Joncryl, (data not reported here).

4 Concluding Remarks

The addition of an organo-modified clay in a small amount (2 - 6 wt %) leads to significant decrease of the permeability of PET and PLA. In this work we have shown improvements of the barrier properties of about 30 % for PET using 3 wt % Cloisite 30B and up to 58 % for PLA using 6 wt % Cloisite 30B. Better improvement could be obtained if one could achieve complete exfoliation of the nanoclay, possibly using more severe twin-screw configurations and faster rotational speeds of the screw. Unfortunately, this would lead to significant PET and PLA degradation and breakage of the clay particles. A smaller aspect ratio of the nanoparticles will reduce their efficiency for barrier properties. Optimal processing conditions have to be sought and possibly a more effective clay has to be used. We have investigated quite a variety of commercially available nanoclays and found so far that Cloisite 30 B is the best for PET and PLA.

We have shown that Joncryl (or other chain-extenders) in PET and PLA nanocomposites can control the thermal degradation of the matrix. Moreover, it increases the molecular weight of the polymer chains during melt processing and helps delamination (exfoliation). Other promising techniques are in-situ polymerization or the use of low molecular weight PET or PLA, followed by the use of chain extenders or solid-state polymerization that may lead to better mechanical and barrier properties.

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6 References

- [1] H. Ghasemi, P.J. Carreau, M.R. Kamal, and S.H. Tabatabaei, "Properties of PET Nanocomposite Films", in press, *Polym. Eng. Sci.*, 2011
- [2] H. Ghasemi, P.J. Carreau, M.R. Kamal, and N. Chapleau, "Effect of Processing Conditions on Properties of PET/Clay nanocomposite films", in press, *Intern. Polym. Proc.*, 2011
- [3] W. Lertwimolnun, B. Vergnes. "Influence of screw profile and extrusion conditions on the microstructure of polypropylene/organoclay nanocomposites", *Polym. Eng. Sci.*, **47**, pp 2100-2109, 2007
- [4] Z.P. Luo and J.H. Koo, "Quantification of the Layer Dispersion Degree in Polymer Layered Silicate Nanocomposites by Transmission electron Microscopy", *Polymer*, **49**, pp 1841-1852, 2008
- [5] N. Najafi C., M.C. Heuzey, P.J. Carreau, P.M. Wood-Adam, "Polylactic Acid (PLA) -Clay Nanocomposites Prepared by Melt Compounding in the Presence of Chain Extender", in preparation, 2011