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# Oxygen Barrier LDPE/LLDPE/Organoclay Nano-Composite Films for Food Packaging

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**Summary:** This study intends to replace polyethylene multi-layer films used in food packaging industry with single-layer polyethylene nanocomposites films. Nanocomposites of LDPE/LLDPE/ montmorillonite organoclay were prepared by melt compounding in a twin extruder and then film blown to prepare thin films. LLDPE-g-MA was used as compatibilizer to achieve better interaction between the blend and organoclay. Various compositions of organoclay and compatibilizer were prepared. The structure of nanocomposites was characterized by XRD and TEM. Permeability properties were measured using a permeability measuring set-up and aspect ratio of the particles was evaluated using permeability data. The results showed that addition of organoclay even at low level (below 5 phr) had significant effect on barrier properties of the nanocomposites. Oxygen permeability decreased by 50% by adding only 3 phr of nanoclay into the blend. Crystalline structure of the nanocomposites was studied by DSC. Addition of clay also led to increase in melting point and somewhat decrease in the crystalline level. Given the fact that crystals are effectively non-permeable, the concomitant reduction in crystallinity of the blend with decrease in permeability suggests that barrier properties arise from tortuousity of nanoparticles in the blend.

**Keywords:** gas barrier properties; LDPE; LLDPE; montmorillonite; nanocomposites

## Introduction

Improvements in poor barrier properties of polyethylene will be beneficial for the current applications and should also lead to applications in pharmaceuticals, electronic packaging and particularly packaging of food products which are sensitive to oxygen. Most schemes to improve polyolefins gas barrier property involve either addition of higher barrier plastics via a multilayer structure or high barrier surface coatings, however, these approaches are not cost effective. The emerging field of polymer-layered nanocomposites is unique in that it addresses shortcomings of polyolefins for both packaging and engineered applications requiring desirable mechanical, thermal as well as good barrier properties.[1–16] The most common mineral used in nanocomposites is montmorillonite. To improve the interaction between non-polar polymer and clay, montmorillonite is treated usually with ammonium alkyl compounds and the treated clay is called organoclay. Many approaches have been tried to prepare organoclay/polyolefin nanocomposites, including in situ polymerization of ethylene in the presence of layered silicates,[14] solvent blending[15] and melt compounding.[1–13] However, melt blending is the most convenient process for preparation of the nanocomposites. Although in situ polymerization may form an exfoliated nanocomposite but the clay platelets would recover the stacked structure in the subsequent melt forming process and mechanical properties would not significantly improved.[14]

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In this study nanocomposites of LDPE/ LLDPE/ montmorillonite organoclay were prepared by melt compounding in a twin extruder and then film blown to prepare thin films. The effect of nanoclay content and compatibilizer on the state of dispersion and oxygen barrier properties polyethylene blends was discussed.

## Experimental Part

LDPE with MFI = 2g/10min and LLDPE with MFI = 1.12g/10min were domestic petrochemical products. The nanoclay used in this study was Nanolin DK4 which is an alkyl ammonium modified montmorillonite. The blend of LDPE/LLDPE was mixed with various amounts of organoclay in a Brabender twin extruder. In some of the samples, LLDPE-g-MA was used as compatibilizer to achieve better interaction between the polyethylenes blend and the organoclay. Also irganox 1010 , an antioxidant from Ciba Specialty Chemicals, was used in some samples as an additional compatibilizer between polyethylene and nanoclay.[17] The content of LDPE was fixed at 70 wt% and the total content of LLDPE and LLDPE-g-MA remained 30 wt% where the amount of LLDPE-g-MA was 5 or 7 wt%. The organoclay content was varied from 3 to 7 parts per hundred polymer (phr). So the sample designation as 70/25/5 + 3phr means 70 wt % LDPE, 25 wt% LLDPE, 5 wt% LLDPE-g-MA and 3 phr nanoclay. To determine Oxygen transmission rate of nanocomposite membranes, pure gases were fed from high pressure bottles via steel tubing to a stainless steel membrane cell. The gases then entered the cell with internal diameter of 90mm. Permeability of gases calculated from $P = l\frac{J}{\Delta p}$ where $J$ is the gas volumetric flow rate per unit area of the membrane, l is thickness of membrane and $\Delta p$ is pressure difference across the membrane and $p$ is the permeability. The degree of nanoclay dispersion was determined using wide-angle x-ray diffraction (XRD) and transmission electron microscopy (TEM). Effect of nanoclay on crystallinity and melting temperature of polyethylene blends was investigated by DSC.

## Results and Discussion

XRD spectra nanocomposites with various contents of nanoclays are shown in Figures 1–3. XRD measures the degree of dispersion by estimating the distance between individual platelets after mixing with polymer. A shift to lower angles of the characteristic diffraction peak suggests an increase in interlayer spacing or gallery of the clay, which is referred to as intercalation. A disappearance of the clay interlayer

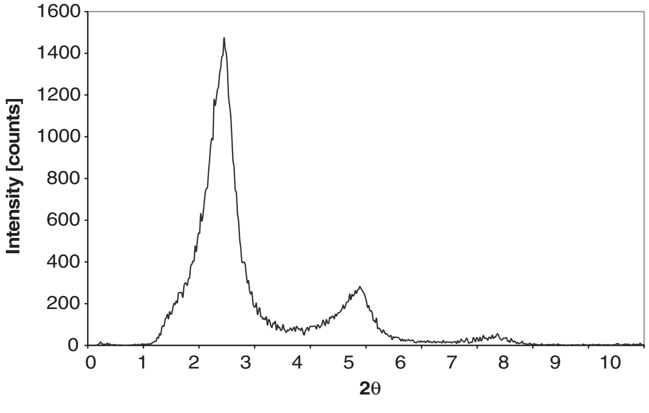

***Figure 1.***
XRD spectra of the nanoclay.

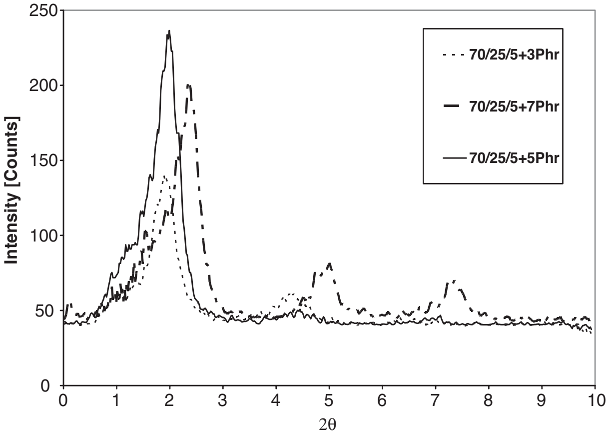

*Figure 2.*
XRD spectra of nanocomposites with LLDPE-g-MA as compatibilizer.

diffraction peak indicates possible exfoliation of the clay platelets and a broadening of the peak is considered to be the result of partial exfoliation. The peak angle $2\theta = 2.50^\circ$ for neat organoclay has shifted to $2\theta = 1.97^\circ$ in the nanocomposite containing 3phr organoclay.

The measured diffraction angles for different samples were used to calculate the distance between nanoclay layers using

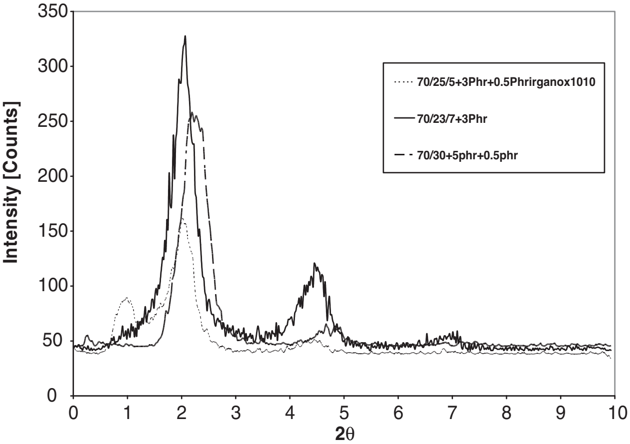

*Figure 3.*
XRD spectra of nanocomposites with and without LLDPE-g-MA and irganox as compatibilizers.

*Table 1.*
XRD calculations of nanocomposites.

| Organoclay content of nanocomposites | Peak angle of nanoclay ($2\theta$) | Distance between platelets of nanoclay (nm) |
|---|---|---|
| 3 phr | 1.97 | 4.48 |
| 5 phr | 2.08 | 4.24 |
| 7 phr | 2.4 | 3.68 |

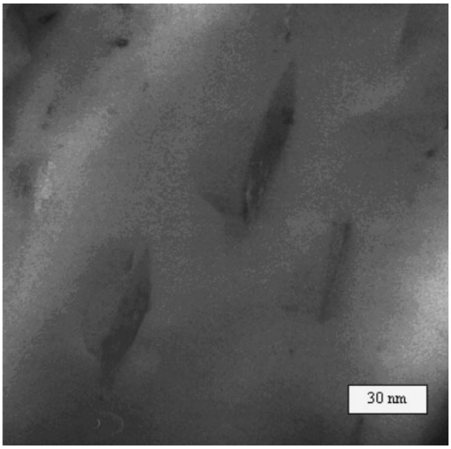

*Figure 4.*
TEM of 3 phr sample.

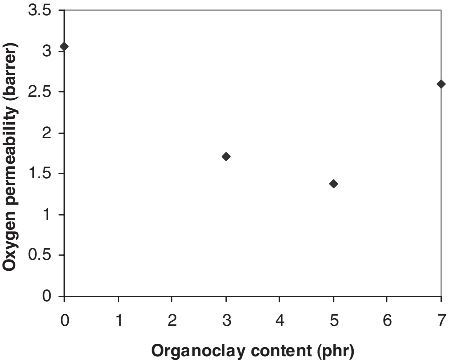

*Figure 5.*
$O_2$ permeability of nanocomposites.

Bragg's law and are shown in Table 1. The details of calculations are explained in reference 17. As the amount of organoclay increases to 5 and 7 phr, the peak angle distances from that of 3 phr sample and approaches to that of neat organoclay. The result suggests that the optimum intercalation occurs at 3 phr organoclay and further increase in organoclay results in repacking of the platelets.

In Figure 4 a TEM micrograph of the 3 phr sample is shown. It must be mentioned that the ultratoming of samples for TEM observations was very difficult to do because of low modulus of polyethylene. There is no indication of agglomeration of nanoclay at 3 phr content.Oxygen permeability measurement data are shown in Figure 5. Upon addition of only 3 phr organoclay the permeability of polyethylene decreases down to half.Using permeability in the Equations 1–3, the aspect ratios of nanoclay in the nanocomposites were estimated and depicted in Table 2.[17]

$$\frac{P_m}{P_c} = 1 + \frac{\alpha^2 \phi^2}{1 - \phi} \tag{1}$$

$$\phi = \frac{wt\%}{100} \frac{\rho_c}{\rho_f} \tag{2}$$

$$\frac{100}{\rho_c} = \frac{wt\%}{\rho_f} + \frac{100 - wt\%}{\rho_m} \tag{3}$$

where $\phi$ is the volume percent of nanoclay in the nanocomposites and $\alpha$ is aspect ratio, and $P_m/P_c$ is the ratio of permeability of neat polymer ($P_m$) to the nanocomposite ($P_c$). Density of nanoclay ($\rho_f$) and polyethylenes ($\rho_m$) were taken as 1.77g/cm$^3$ and 0.918 g/cm$^3$ respectively and the density of nanocomposite ($\rho_c$) was calculated from Equation 3. It is found that for the sample with 3 phr nanoclay, the aspect ratio is as high as 57.

The DSC thermograms are shown in Figure 6. The melting temperature of nanocomposites showed an increasing trend with increase in nanoclay content. The measured melting points from DSC thermograms are depicted in Figure 7. The

*Table 2.*
Permeability and aspect ratio of nanoclay platelets in the nanocomposites.

| | | | | |
|---|---|---|---|---|
| Organoclay content (phr) | 0 | 3 | 5 | 7 |
| Organoclay content (wt%) | 0 | 2.91 | 4.76 | 6.54 |
| Organoclay content (vol%) | 0 | 1.53 | 2.53 | 3.50 |
| Permeability of samples with 5 phr LLDPE-g-MA (barrer) | 3.41 | 1.71 | 1.38 | 2.59 |
| $P_m/P_c$ (permeability ratio) | 1 | 1.78 | 2.20 | 1.18 |
| Aspect ratio $\alpha$ of nanoclay | – | 57 | 43 | 12 |

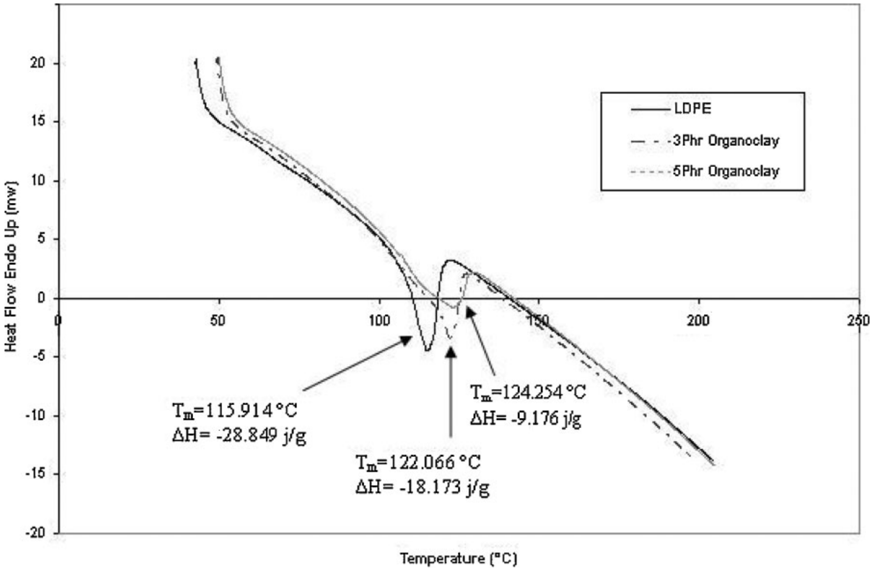

***Figure 6.***
DSC thermograms of polyethylene and nanocomposites.

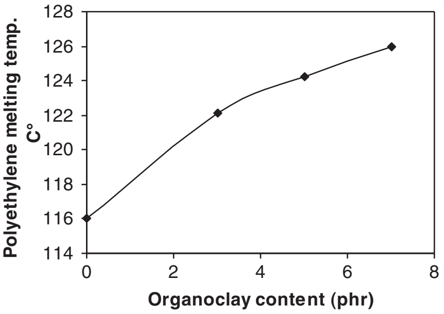

***Figure 7.***
Melting temperature of nonocomposites.

increase in Tm could result from the fact that the platelets dispersed in the matrix could shield the conduction of heat to crystallites to some extent until at higher temperatures the heat flow is enough to melt down the crystallites. However, enthalpy of melting of polyethylenes followed an opposite trend indicating decrease in crystallinity content as shown in Figure 6. It seems that exfoliated/intercalated layers of organoclay hinder the growth of polyethylene spherulites.

It is assumed that crystalline regions of a polymer are essentially impermeable to gasses. Thus the loss of crystallinity should result in higher permeability. However, the decrease in permeability (Figure 5) with the addition of organoclay suggests that the extent of dispersion of nanoclay platelets in the blend play a major role in creating a tortuous path for the diffusion of gas molecules through the polymer matrix. Indeed the good barrier properties of nanocomposites suggest a good dispersion of nanoclay in the blend which was also verified by TEM micrographs and XRD measurements.

## Conclusion

The permeability measurements showed that addition of organoclay even at low level had significant effect on barrier properties of the nanocomposites. Oxygen permeability decreased by 50% by introducing only 3 phr of nanoclay into the blend. Addition of clay also led to increase in melting point and decrease in the crystallinity. The fact that crystals are effectively non-permeable, the decrease in permeability suggests that improvement in barrier properties arise from tortuousity of nanoparticles in the blend.

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