

Barrier and Mechanical Properties of Nanocomposites Based on Polymer Blends and Organoclays

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ABSTRACT: Nanoclays (NCs) impart highly effective barrier properties to polymers due to their platelet structure, provided that the NCs are exfoliated and form a parallel array relative to the product surface. High barrier films with enhanced mechanical properties were developed and studied using blends of polyamide (PA) or ethylene vinyl alcohol (EVOH) with polyethylene (PE) and compatibilizing copolymer, and with incorporated NC. Permeability measurements indicated that by increasing the active polymers concentration up to 30%, however, reducing the barrier layer thickness comprising the active polymers (PA or EVOH), resulting in reduction of the oxygen transmission rate (OTR) by more than 7- to 8-folds. When NC was incorporated in the concentrated active polymer layer, the barrier to oxygen was further increased. This resulting in equal or even better barrier properties compared to the case where the active polymers are at 95% concentration. The increase in barrier properties was attributed to the laminar structure

of the incompatible active polymer in addition to the orientation of the NC with its additional effects due to nucleation and enhancement of the amorphous phase barrier. The mechanical properties of the concentrated active layer (CAL) films were better or comparable with respect to the high barrier reference films. Furthermore, a nucleation effect, leading to increased crystallinity, was identified in the cases where PA compositions contained NC, whereas selective nucleation was obtained in the case where EVOH compositions contained NC. These observations, on oxygen barrier and mechanical properties, were further supported by the results obtained from thermal analysis (differential scanning calorimetry [DSC]), X-ray diffraction (XRD) measurements, and transmission electron microscopy (TEM) imaging studies carried out on the hybrid films. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 72–83, 2010

Key words: barrier; blends; clay; coextrusion; composites

INTRODUCTION

Polymer blends offer a cost-efficient route to design plastic component properties.¹ An additional dimension to design the end product characteristics can be achieved by the recently commercialized technology based on nanoclays (NCs).

Organoclays are layered aluminosilicates bound by ions. In nature, they form a closed structure. To be useful, the closed structure has to be exfoliated. When exfoliated effectively, single platelets are obtained, having a thickness of 1 nm size, with lateral dimensions of $0.5 \times 0.5 \mu\text{m}$. The surface area of exfoliated organoclays is $700 \text{ m}^2/\text{g}$. This enormous surface area gives rise to large interfacial interactions with the polymer matrix, provided that sufficient compatibility is tailored. Because of its cost-effective advantages, applications based on NC have been a proposed for reinforcement, barrier, and fire retardancy.^{2–8} In addition to blends, multilayer structures (coextruded films) containing single material or mul-

timaterial in each individual layer are commonly used for packaging applications. In the latter cases, polyamide 6 (PA-6) or ethylene vinyl alcohol (EVOH) is incorporated with polyethylenes (PE).⁹ PA-6 and EVOH are characterized by their high barrier properties for gases, whereas PE is known for its high barrier properties to humidity. Consequently, combinations of PA or EVOH with PE are used commercially to yield both high barrier films for both gases and humidity. Furthermore, incorporation of NC into PE and PA has demonstrated reduced permeability to gases and humidity. This has been attributed to the “tortuous path” mechanism due to the platelet morphology of the NC.^{10,11} It should be emphasized that a similar plate-like morphology can be obtained when blending incompatible polymers like PE and PA under optimized processing conditions.¹²

The increase of the tortuous path length is estimated by using Nielsen’s model [eq. (1)]³:

$$P/P_0 = [1 + pf/2] - 1 \quad (1)$$

where P_0 is the pure polymer permeability coefficient, P is the organoclay polymer composite permeability, f the volume fraction of organoclays, and

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TABLE I
The Precompounds Composition in Wt %

| Precompound designation | LLDPE | LDPE | EVOH | PA6 | LLDPE-g-MAH | MMT 15A | MMT 30B | Pre-1 |
|-------------------------|-------|------|------|-----|-------------|---------|---------|-------|
| Pre-1 | 59 | 29 | | | 12 | | | |
| Pre-2 | | | | | | 20 | | 80 |
| Pre-3 | | | 96 | | | | 4 | |
| Pre-4 | | | | 96 | | | 4 | |

p the organoclay aspect ratio. This model is also applied for polymer blends having a plate-like morphology in similar manner. The model quantitatively states that the aspect ratio and not the particle size is the most significant parameter determining the permeability in blends and in organoclay hybrid composites. In the case of $p = 500$ (estimated NC aspect ration) and $f = 0.03$ (5 wt % of NC) the expected decrease of permeation is close to 9-fold. Because organoclays are high aspect ratio particles, their orientation with respect to the film surface will determine the barrier as well as the mechanical properties. In extrusion blown films, the orientation of the clay platelets is controlled by the axial extension, as well as the blow-up ratio. These two types of flows are of an elongation type and hence are effective in determining the state of orientation and in turn the final film properties.³

Previous studies carried out by Kenig³ and Kenig and Ophir⁴ dealt with two systems of PE hybrids: the first was based on PE/organoclay nanocomposite blown films and the second on blown film containing PE/PA and/or PE/EVOH blends. The latter approach led to the present investigation where the barrier layer contains both PA or EVOH and NC in a concentrated layer. The so-called "concentrated active layer (CAL)" led to improved barrier as well as enhanced mechanical properties. Consequently, the objectives of the present research are to investigate the hybrid system based on organoclay composites of PE/PA-6 and/or PE/EVOH blends processed by film extrusion, to give either a monolayer or a trilayer film based on the CAL technology.

EXPERIMENTAL

Materials

The materials used for the film preparation were as follows:

LLDPE—butene-LLDPE resin with melt flow index (MFI) of 1.0 g/10 min and specific gravity (SG) of 0.918 g/cm³ (LL1001.32, Exxonmobil).

LDPE—LDPE resin with MFI of 2.0 g/10 min and SG of 0.920 g/cm³ (Ipethene 320, Carmel Olefins).

EVOH—EVOH resin with MFI of 3.2 g/10 min containing 32 mol % of ethylene comonomer (Soaranol DC3203F Nippon Gohsei).

PA6—medium viscosity PA6 resin having viscosity no. of 195 cm³/g and SG of 1.13 g/cm³. (Ultrad B35. BASF).

LLDPE-g-MAH—1 wt % of MAH-modified LLDPE MFI of 1.5 g/10 min and SG of 0.930 g/cm³ (Fusabond MB226D, DuPont).

Organoclay 1—2M2HT quaternary ammonium-modified montmorillonite organoclay with surfactant concentration of 125 meq/100 g (Cloisite 15A, from Southern Clays).

Organoclay 2—MT2EtOH quaternary ammonium-modified montmorillonite organoclay with surfactant concentration of 90 meq/100 g (Cloisite 30B, from Southern Clays).

Precompounds composition and preparation

Precompounds (Pre) were prepared using a corotating twin-screw compounder (APV DL 23) with an L/D ratio of 40 : 1, operated at 350 rpm. Pre-1, pre-2, and pre-3 were processed at melt temperature of 210°C and pre-4 at 235°C.

Table I summarizes the compositions of the precompounds.

Films structure, composition, and preparation

Monolayer and trilayer coextruded films, having an "A-B-C" layer structure, were produced by film blowing using a three layer blown film lab scale coextrusion system (BETOL BT38), operated in blow-up ratio of 3.5 and draw down ratio of 5.0. Pre-1, pre-2, and pre-3 extruded each at melt temperature of 210°C and pre-4 at 235°C. The total film thickness for each of the films produced was 100 μm. In Table II, the various films composition and structure are detailed, where M—denotes monolayer, T—denotes tri-layer, PE, OH—EVOH, PA—PA, c—organoclays contained in the specific polymer, and %—denotes percentage of the layer from the total film thickness. Coex-refOH—denotes coextruded film containing a layer of pure EVOH in 10% of the film total thickness, and Coex-refPA—denotes coextruded film containing a layer of pure PA6 in 10% of the film total thickness.

TABLE II
Material and Layer Composition of the Films

| Film designation | Layers structure and relative thickness | Material and Layer Composition of the Films | | | | | | | |
|------------------|---|---|------|------|-----|-------------|-----------------|-------------------|-----------------|
| | | LLDPE | LDPE | EVOH | PA6 | LLDPE-g-MAH | PRE-2 (15A, PE) | PRE-3 (30B, EVOH) | PRE-4 (30B, PA) |
| MPE | A—25% | 70 | 30 | | | | | | |
| | B—50% | 70 | 30 | | | | | | |
| | C—25% | 70 | 30 | | | | | | |
| MPEc | A—25% | 56 | 24 | | | | 20 | | |
| | B—50% | 56 | 24 | | | | 20 | | |
| | C—25% | 56 | 56 | | | | 20 | | |
| MPEOH | A—25% | 60 | 25 | 10 | | 5 | | | |
| | B—50% | 60 | 25 | 10 | | 5 | | | |
| | C—25% | 60 | 25 | 10 | | 5 | | | |
| MPEcOH | A—25% | 48 | 21 | 10 | | 3 | 18 | | |
| | B—50% | 48 | 21 | 10 | | 3 | 18 | | |
| | C—25% | 48 | 21 | 10 | | 3 | 18 | | |
| MPEcOHc | A—25% | 48 | 21 | | | 3 | 18 | 10 | |
| | B—50% | 48 | 21 | | | 3 | 18 | 10 | |
| | C—25% | 48 | 21 | | | 3 | 18 | 10 | |
| MPEPA | A—25% | 60 | 25 | | 10 | 5 | | | |
| | B—50% | 60 | 25 | | 10 | 5 | | | |
| | C—25% | 60 | 25 | | 10 | 5 | | | |
| MPEcPA | A—25% | 48 | 21 | | 10 | 3 | 18 | | |
| | B—50% | 48 | 21 | | 10 | 3 | 18 | | |
| | C—25% | 48 | 21 | | 10 | 3 | 18 | | |
| MPEcPAc | A—25% | 48 | 21 | | | 3 | 18 | | 10 |
| | B—50% | 48 | 21 | | | 3 | 18 | | 10 |
| | C—25% | 48 | 21 | | | 3 | 18 | | 10 |
| TPEOH50 | A—25% | 65 | 30 | | | 5 | | | |
| | B—50% | 53 | 22 | 20 | | 5 | | | |
| | C—25% | 65 | 30 | | | 5 | | | |
| TPEcOHc50 | A—25% | 65 | 30 | | | 5 | | | |
| | B—50% | 43 | 18 | | | 3 | 16 | 20 | |
| | C—25% | 65 | 30 | | | 5 | | | |
| TPEOH30 | A—35% | 65 | 30 | | | 5 | | | |
| | B—30% | 45 | 20 | 30 | | 5 | | | |
| | C—35% | 65 | 30 | | | 5 | | | |
| TPEcOHc30 | A—35% | 65 | 30 | | | 5 | | | |
| | B—30% | 37 | 16 | | | 3 | 14 | 30 | |
| | C—35% | 65 | 30 | | | 5 | | | |
| TPEPA50 | A—25% | 65 | 30 | | | 5 | | | |
| | B—50% | 53 | 22 | | 20 | 5 | | | |
| | C—25% | 65 | 30 | | | 5 | | | |
| TPEcPAc50 | A—25% | 65 | 30 | | | 5 | | | |
| | B—50% | 43 | 18 | | | 3 | 16 | | 20 |
| | C—25% | 65 | 30 | | | 5 | | | |
| TPEPA30 | A—35% | 65 | 30 | | | 5 | | | |
| | B—30% | 45 | 20 | | 30 | 5 | | | |
| | C—35% | 65 | 30 | | | 5 | | | |
| TPEcPAc30 | A—35% | 65 | 30 | | | 5 | | | |
| | B—30% | 37 | 16 | | | 3 | 14 | | 30 |
| | C—35% | 65 | 30 | | | 5 | | | |
| Coex-ref.OH | A—45% | 65 | 30 | | | 5 | | | |
| | B—10% | | | 95 | | 5 | | | |
| | C—45% | 65 | 30 | | | 5 | | | |
| Coex-ref.PA | A—45% | 65 | 30 | | | 5 | | | |
| | B—10% | | | | 95 | 5 | | | |
| | C—45% | 65 | 30 | | | 3 | | | |

Testing and characterization of films

The blown films were characterized for their barrier properties, mechanical, and thermal properties, as well as their microstructure and morphology.

Oxygen transmission rate (OTR) measurements were carried out with an OTR testing instrument (SYSTECH 8000) according to ASTM D3985. Tensile mechanical testing was carried out with a mechanical tester (Instron 3300) according to ASTM D882. Dart

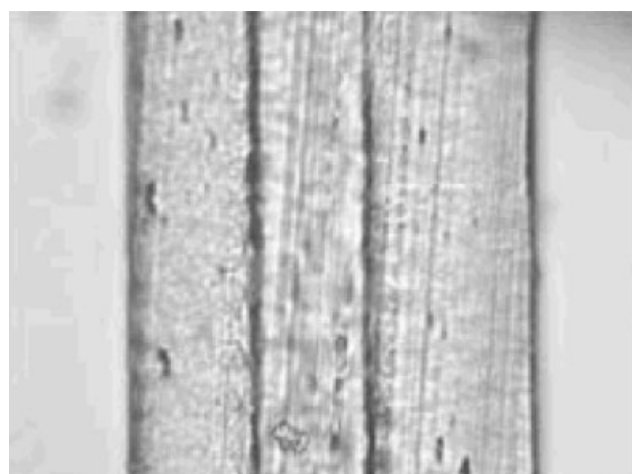


Figure 1 Microscopic image of a film cross section in an A-B-C tri-layer configuration.

drop impact test was carried out with Free Falling Dart testing device, according to ASTM D1709. Thermal properties of the blends were studied by differential scanning calorimetry (DSC) (Q200, TA, USA) under nitrogen atmosphere. Samples of about 10 mg were first heated from 25°C to 250°C and then cooled back to 25°C at a heating/cooling rate of 10°C/min.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to examine the exfoliation, dispersion, and orientation morphology of the layer nanocomposite films. The XRD was carried out on an X-ray diffractometer (Rigaku, Japan) with a CuK α tube source ($\lambda = 1.5404 \text{ \AA}$) scanning from 1.5

to 8° at a continuous scan rate of 0.6°/min. The generator tension was 50 KV and the current 20 mA. TEM images of the nanocomposites were obtained with a TEM (100CX, JEOL, Japan) operated with an accelerating voltage of 100 kV and equipped with an Olympus BH-2 digital camera (Japan). Also an optical microscopy was carried out on cross section of the films, to get an image of the trilayers structure.

METHODOLOGY

The objective of the present study was to investigate the combined effects of oriented clays exerting tortuous path morphology in layers containing blends of the barrier polymers: PA or EVOH in a consecutive increasing concentration (CALs). Accordingly, the films were prepared in a form of A-B-C layer configuration, as demonstrated in Figure 1, where layers A and C are the two sides outer layers of the film (both are always in the same composition), and layer B is the core one.

As can be seen in Table II, the first set of films with the first letter designation “M” have identical composition in all the three layers. These are actually may seen as “mono-layer” film. In all cases, the NC concentration in the film was kept constant at 4%. The compatibilizing copolymer concentration, whenever present, was also kept at a constant concentration of 5%. In cases where a barrier polymer was used, it was at 10% weight concentration. The second series of experiments with the first letter designation “T” comprise trilayer film where the

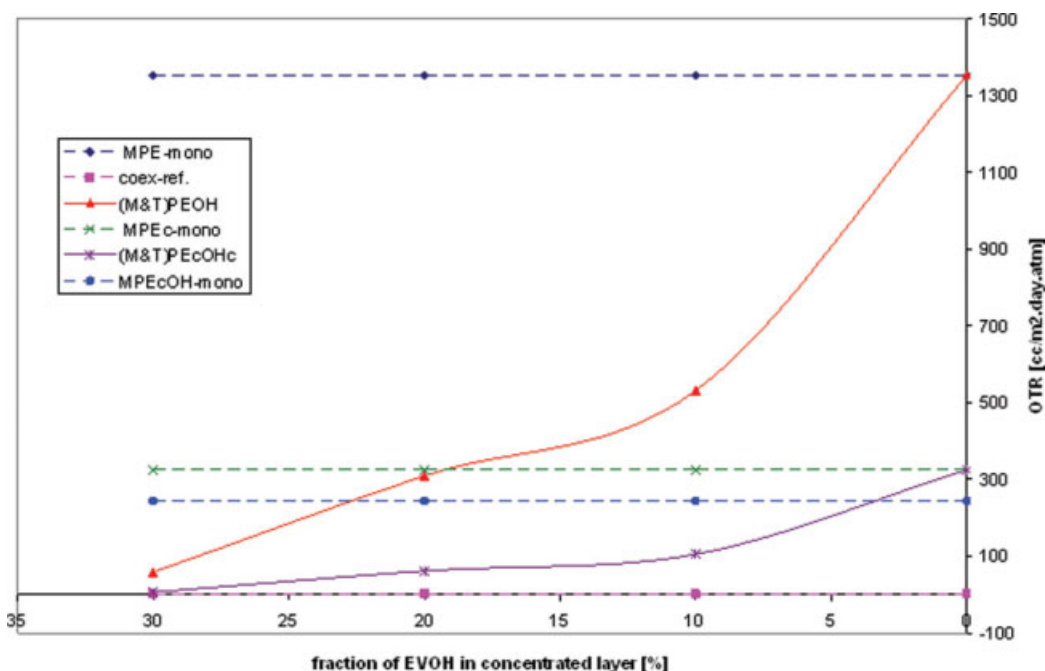


Figure 2 OTR of PE-EVOH based blends (with and without clays)—the effect of “concentrated active layer”. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

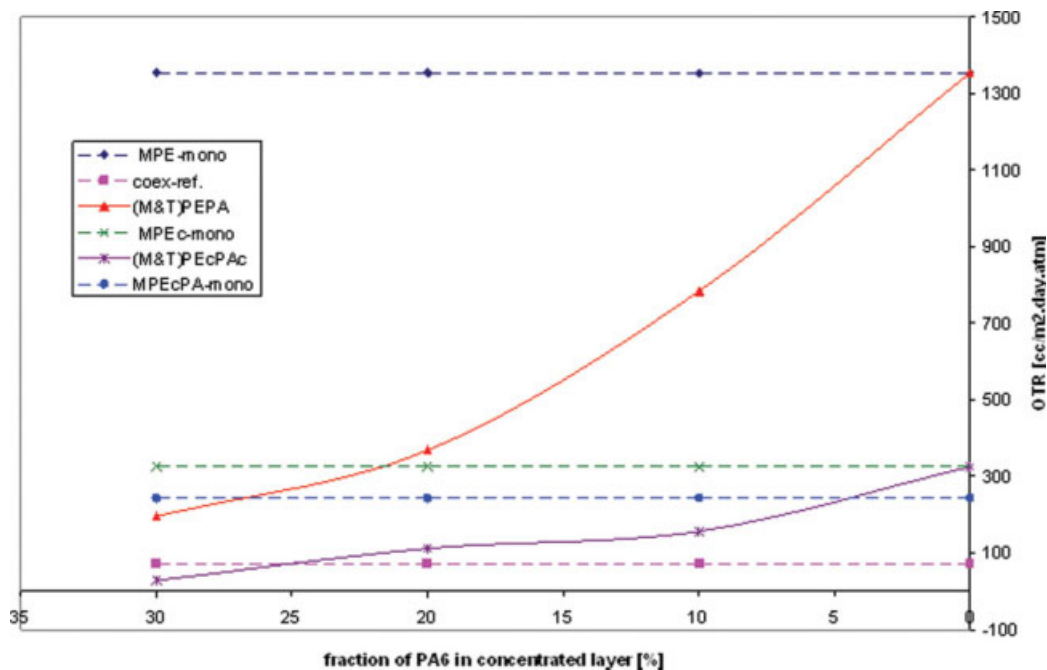


Figure 3 OTR of PE-PA6 based blends (with and without clays)—the effect of “concentrated active layer”. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composition of Layer A and Layer C is different than that of Layer B. The Layer B consists of the barrier elements namely barrier polymer and/or NC. Layers A and C are a blend of LDPE and LLDPE. The thickness of the active layer “B” was initially 50% of the total film thickness and then was reduced to 30% of the total thickness. In the trilayer films, the concentration of the barrier polymer was kept at 10% with respect to the total film thickness. Thus, when the thickness of the layer “B” was reduced,

the concentration of the active polymer in the layer was increased accordingly, to keep the concentration constant with respect to the total film thickness. The last two films were produced with a concentration of 95% of EVOH or PA in layer “B” having a thickness of 10% and serve as a reference. It should be emphasized that the fact that the active polymers are blended with polyolefin polymers in Layer B it is saving the need for an addition of tie layers. Consequently, the “tie-layer-less” approach is more

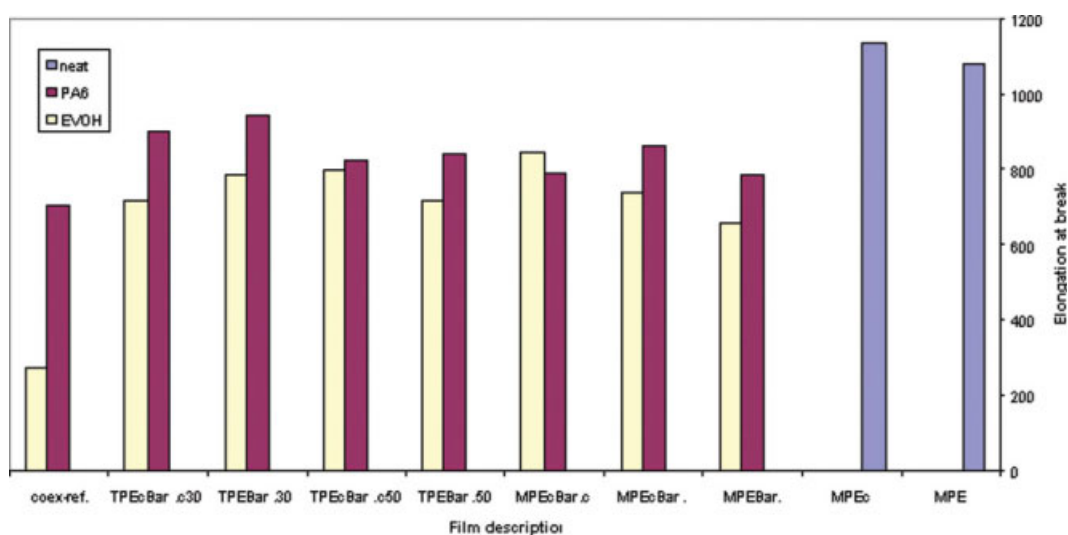


Figure 4 Films elongation at break (from tensile test). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

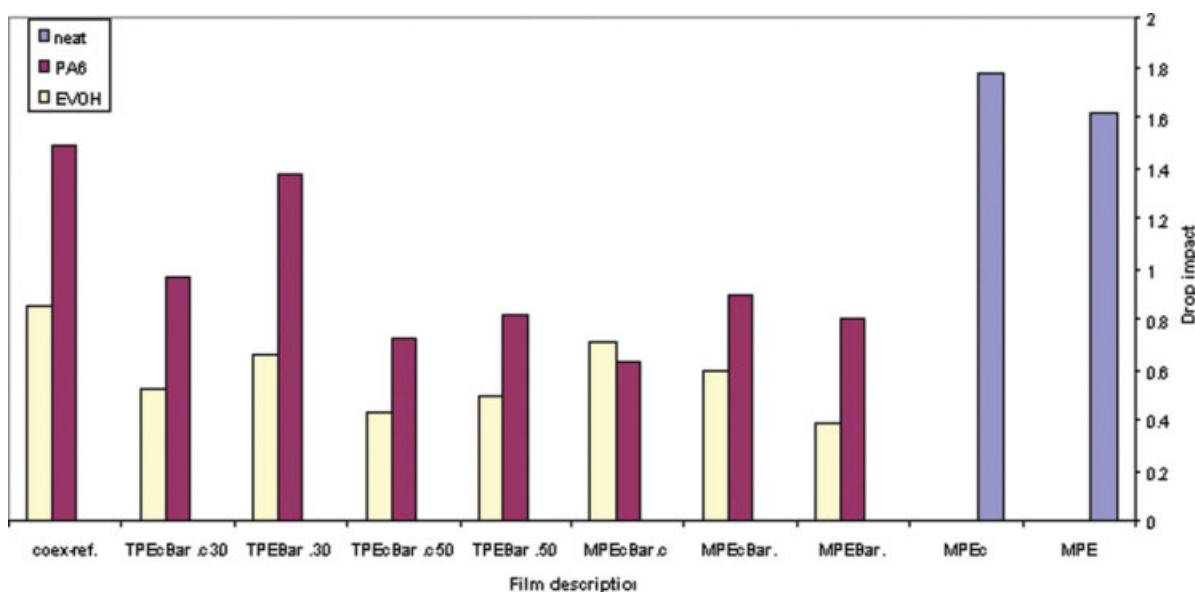


Figure 5 Films drop impact (from Free Falling Dart test). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

economical compared to the traditional five layer barrier films, which include two symmetrical tie layers in an A-tie-B-tie-C configuration.

RESULTS AND DISCUSSION

Oxygen transmission barrier properties

Figures 2 presents the various effects of film composition and layer configuration on the OTR barrier properties, for films containing EVOH and organoclays, in the form of the CAL approach.

The upper base line for oxygen barrier is the monofilm based on PE blend (MPE). The lower base line is the 95% EVOH containing trilayer film (Coex.ref.OH). As can be seen, the addition of 4% NC reduces the OTR of the monofilm by a factor of 4.5 compared to the upper base composition. An addition of 10% of pure EVOH to the above com-

pound system improved slightly the barrier compared to the case where only NC was added. A profoundly distinct behavior was observed in the cases where the concentrated trilayer approach was used. As can be seen, the EVOH containing T films exhibited a close to 7-fold reduction in OTR compared to the upper base when increasing the concentration of the EVOH to 30%. The most outstanding result took place when NC was added to the active layer. As can be observed, the OTR was reduced from 300 cc/m²/day.atm for 4% NC at zero content of EVOH to the lower reference value at 30% EVOH. It should be emphasized that in the latter case, the concentration of the NC was only 1.2% based on the total film thickness.

Figure 3 depicts, in similar manner, the OTR results for the case of PA active polymer.

As can be observed, the same phenomenon was identified in the case of the PA. Addition of 10% PA

TABLE III
Thermal Properties of Hybrid Compositions

| Sample code | T_m (°C) | ΔH_m (J/g) | ^a ΔH_m (J/g) | T_c (°C) | ΔH_c (J/g) | ^a ΔH_c (J/g) |
|-------------|------------|--------------------|---------------------------------|------------|--------------------|---------------------------------|
| MPEPA | 217.8 | 5.8 | 58.0 | 117.3 | 1.3 | 13.4 |
| MPEcPAc | 218.1 | 7.6 | 79.2 | 175.3 | 6.7 | 70.0 |
| TPEPA30 | 218.4 | 19.1 | 63.7 | 134.4 | 8.0 | 26.7 |
| TPEcPAc30 | 218.5 | 21.7 | 75.4 | 176.4 | 21.7 | 75.4 |
| CoexPA | 219.3 | 47.8 | 50.3 | 180.6 | 69.8 | 73.5 |
| MPEOH | 181.1 | 7.2 | 72.0 | 145.0 | 6.1 | 61.0 |
| MPPEcOHc | 180.2 | 7.1 | 74.0 | 160.4 | 6.2 | 64.6 |
| TPEOH30 | 178.7 | 21.9 | 73.0 | 153.1 | 20.1 | 67.0 |
| TPEcOHc30 | 181.6 | 28.7 | 99.7 | 159.8 | 26.1 | 90.6 |
| CoexOH | 181.2 | 73.6 | 77.5 | 156.8 | 73.2 | 77.1 |

^a Transition specific enthalpy normalized to the barrier polymer concentration in the blend.

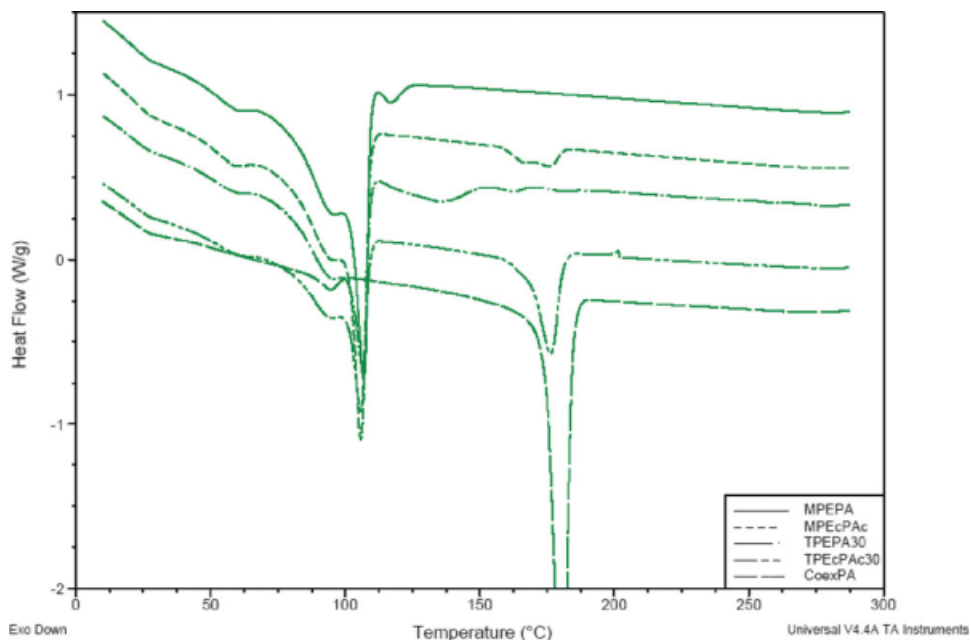


Figure 6 Crystallization DSC curves of PA containing compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

improved slightly the barrier compared to the case where only NC was added. A profoundly distinct behavior was observed in the cases where the concentrated trilayer approach was used. As can be seen, the PA containing T films exhibited a close to 7-fold reduction in OTR compared to the upper base when increasing the concentration of the PA to 30%. The concentrated trilayer approach exhibited superior properties compared to the monolayer approach

at the same total PA concentration. Furthermore, at 30% PA concentration and NC the OTR level was below that of the lower reference film. Also, in this case, the concentration of the NC was only 1.2% based on the total film thickness.

The significant change of barrier properties in the case of the CAL technology is attributed to the mutual orientation effect of both the active polymer and the NC, and also due to the nucleation effect of the

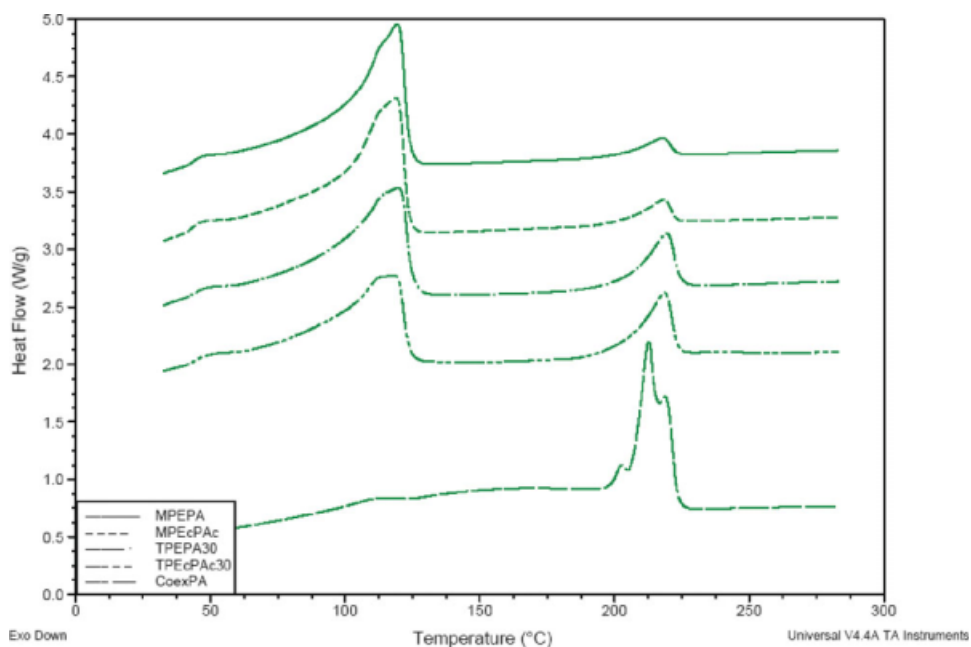


Figure 7 Melting DSC curves of PA containing compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

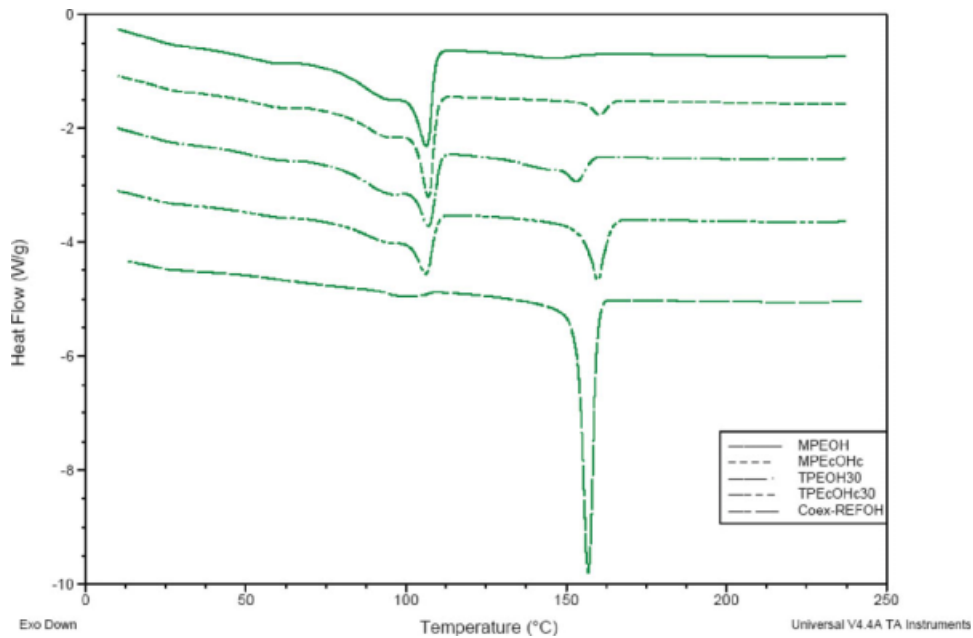


Figure 8 Crystallization DSC curves of EVOH containing compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

clay particles on the crystallization behavior of the active polymer when cool from melt (will be discussed in more detail further ahead). In the case of the active polymers (EVOH and PA), both of which incompatibility with the host PE results in laminar morphology development, whereas the orientation of which increases with reduction with layer thickness. In the case of the high aspect ratio NC plate-

lets, the orientation development is enhanced with the reduction in layer thickness. In both cases, the orientation of the laminar structure of the active polymer parallel to the film surface, as well as the orientation of the NC, results in an increase of the tortuous path for oxygen. Also, it is worth noting from the results that the basic natural advantage of EVOH copolymer over PA6, in terms of oxygen

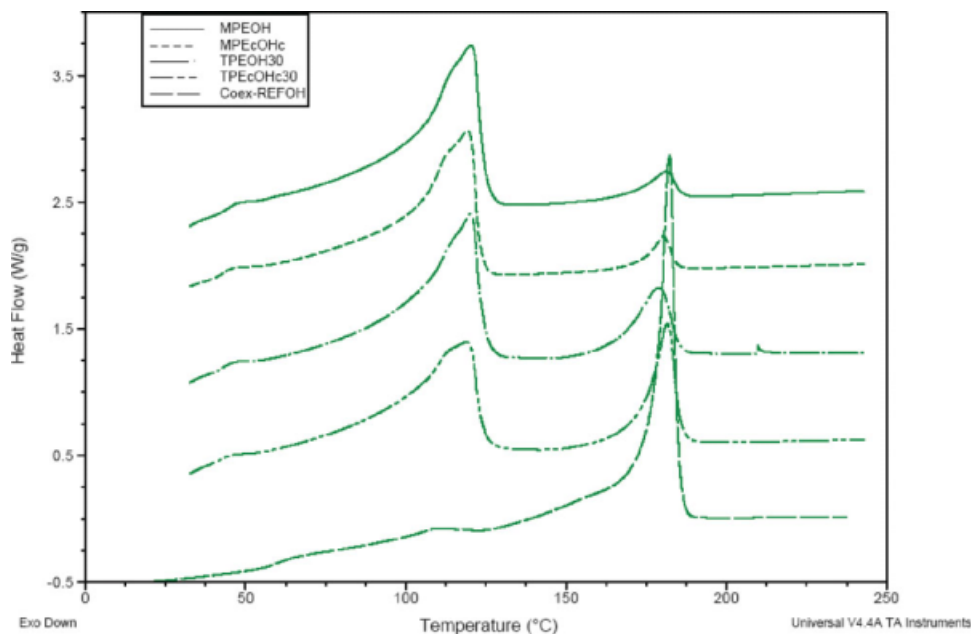


Figure 9 Melting DSC curves of EVOH containing compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

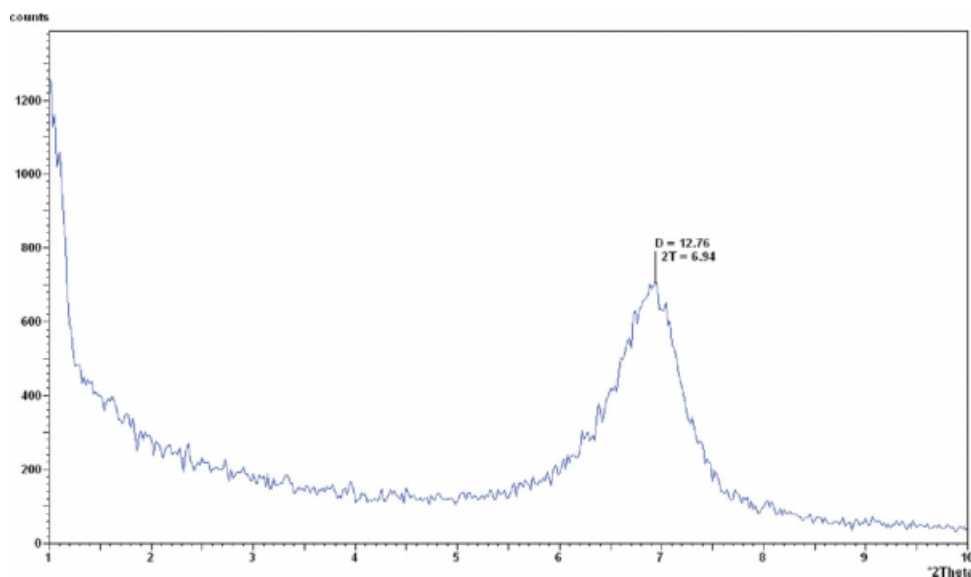


Figure 10 XRD pattern of hybrid PE/clay film with compatibilizing agent system-(MPEc). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

barrier properties, expressed considerably in those films with CAL that not containing any organoclays. However, this figure is changed significantly when the clays are added to the system, in which the OTR properties of films containing PA6 become very close to those of similar films containing EVOH. This distinct phenomenon may be related to the better exfoliation, dispersion, and nucleation effect achieved in the hybrid systems containing PA6 over those containing EVOH. This is evidently supported further by DSC thermal analysis, XRD, and TEM morphology imaging study.

Mechanical properties

Figure 4 summarizes the results for tensile elongation of the various mono- and trilayer for the EVOH and PA containing films. As is evident, elongation at break of most hybrid blend is superior in relation to the low reference base (high barrier) films. As the compositions are changed toward the trilayer cases, the elongation to break is improved.

Figure 5 presents the results for the Dart impact test of the mono- and trilayer films containing EVOH and PA. As can be noticed that compared to

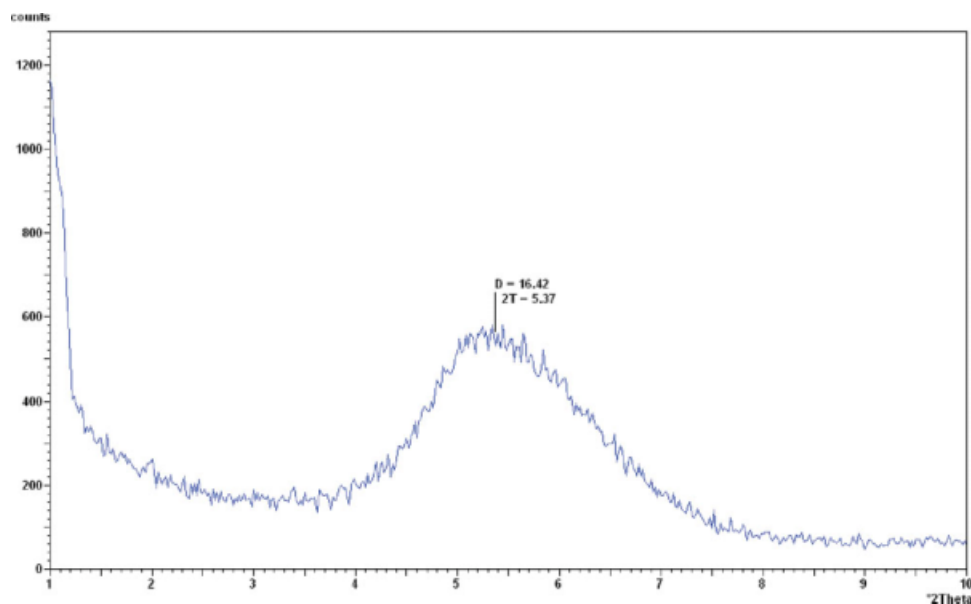


Figure 11 XRD pattern of PE/clay film (reference sample) without compatibilizing agent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

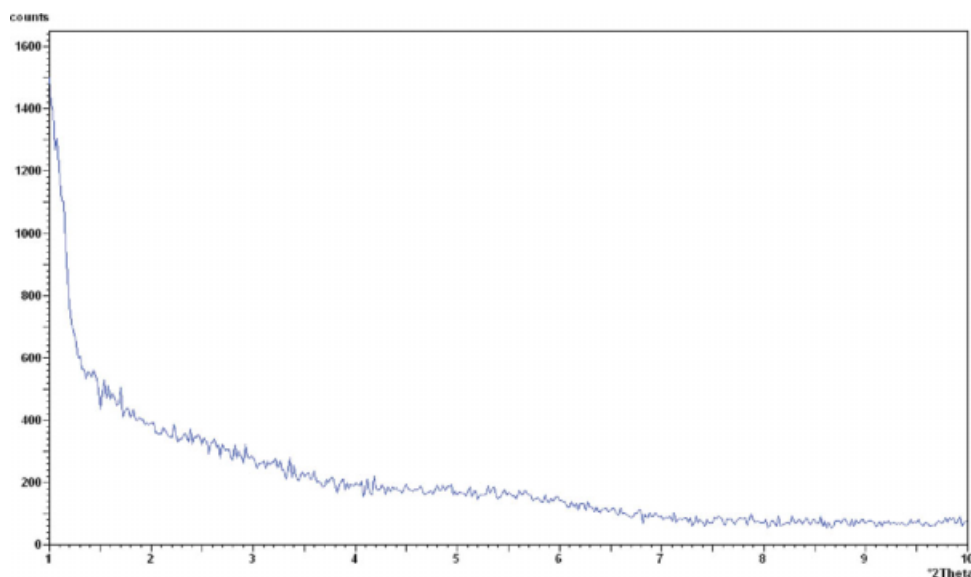


Figure 12 XRD pattern of hybrid PE/PA6/clay film of “concentrated active layer” system- TPEcPAc30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the reference films the Dart impact properties are better in the hybrid films containing PA6 but inferior in those containing EVOH, while improved with increase the barrier concentration.

Thermal properties

Because the NC resides in the active polymers, its nucleation effect on crystallinity of the barrier polymers was investigated, using DSC thermal analysis. Table III and Figures 6 and 7 summarize the melting and crystallization temperatures and the respective enthalpies of the various PA compositions. As can be noticed, the melting point of the PA is relatively

unchanged (217–219°C) and the melting enthalpies (normalized with respect to PA concentration) of the NC containing compositions, increased by 25% to 75–79 J/g, compared to the NC-free compositions. Large changes in the crystallization temperature were recorded in the case where NC was incorporated into the PA. Crystallization temperatures as high as 175°C were obtained in the latter cases with corresponding crystallization enthalpies of 70–75 J/g compared to 13 to 27 J/g, in cases where NC was absent. It should be noticed that in the case of the Coex-ref. composition (95% PA and 5% LDPE), a crystallization temperature of 180°C with a corresponding enthalpy of 73 J/g, were obtained.

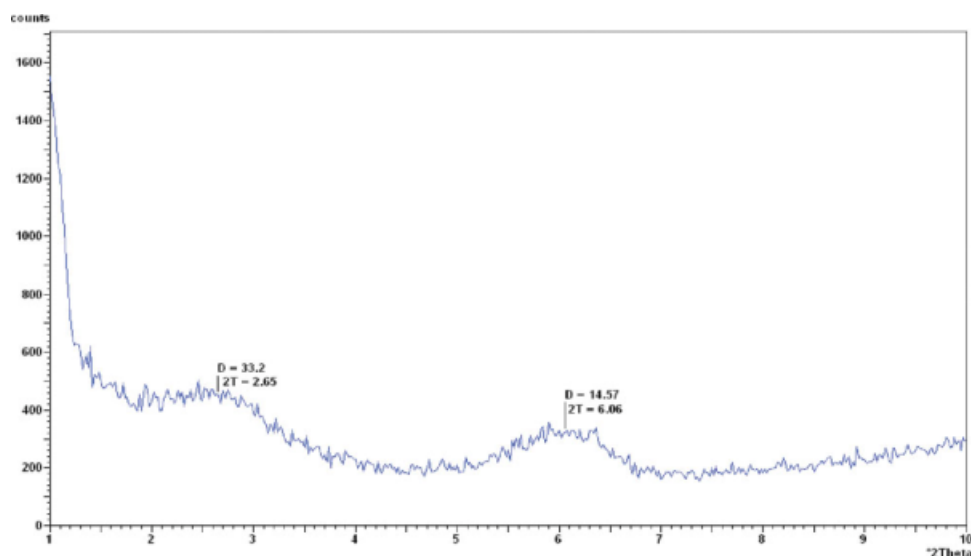


Figure 13 XRD pattern of hybrid PE/PA6/clay film of “concentrated active layer” system—TPEcOHc30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Figure 14 TEM micrograph on the core layer in the hybrid PE/PA6/clay film of “concentrated active layer” system—TPEcPac30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the case of EVOH-containing compositions, the changes caused by the presence of the NC was not as pronounced in the case of the PA-containing compositions. As can be seen in Table III and Figures 8 and 9, the melting temperatures of the EVOH containing blends (178–182°C) did not change significantly and so was the situation of the corresponding melting enthalpy (72–78 J/g). Similarly, the crystallization temperatures changed in a narrow range of 145 to 160°C and the crystallization enthalpy between 61 and 67 J/g. The composition containing NC in a 30% EVOH exhibited a distinct behavior with an increased melting as well as crystallization enthalpies (~ 90 J/g). This may be due to considerable nucleation effect of the NC in this highly CAL hybrid film.

The general figure evident from the DSC analysis obtained for the hybrid films, indicating the considerable nucleation effect of the NC, leading to increased crystallinity. This may in turn affect the barrier and mechanical properties of the NC-containing compositions and is vastly significant in the hybrid films containing PA6.

X-ray diffraction study

XRD was performed at selected samples in an attempt to get certain measure for the degree of intercalation/exfoliation obtained of the layered silicate organoclay within the polymer components of the various hybrid films. The shift in the “2 θ ” axis to the left and the change in the “D-spacing” values (related to the interlayer gallery height of the organoclay particles) can give an indication of the intercalation/exfoliation being obtained. From the peaks height, a quantitative indication can be obtained also, of the amount of organoclay that has or has not intercalated/exfoliated. Figure 10 shows

the XRD pattern for a PE/clay film (reference sample) containing 4 wt % of Cloisite 15A without compatibilizing agent, in which strong prominent peak observed at $2\theta = 7$ with $d = 12.76 \text{ \AA}$. This figure indicates that the organoclay moieties have nearly not experienced any intercalation or exfoliation in this PE system (layers did not separate at all or crushed).

Figure 11 shows the XRD pattern for a hybrid PE/clay film sample containing 4 wt % of Cloisite 15A with compatibilizing agent (MPEc). The left shifting of the peak toward $2\theta = 5.37$, with increased ‘D-spacing’ to $d = 16.42 \text{ \AA}$ and some decrease in the peak height, indicates that considerable degree of intercalation has taken place in the dispersed clay particles, which also were even accompanied with small amount of exfoliation. The nearly flat XRD pattern (in Fig. 12) observed for the hybrid PE/PA6/clay film sample containing 4 wt % of Cloisite 30B + Cloisite 15A and PA6, in a form of CAL (system—TPEcPac30), indicates almost complete exfoliation that taken place and high dispersion of the organoclays layer particles. Conversely, the XRD pattern observed in Figure 13 for the hybrid PE/EVOH/clay film sample containing 4 wt % of Cloisite 30B + Cloisite 15A and EVOH, in a form of CAL (system—TPEcOHc30), indicates advanced intercalation and partial exfoliation that taken place, corresponding to the small left shifted peak related to PE/clay at $2\theta = 6.06$ with increased D-spacing of $d = 14.57 \text{ \AA}$ and also to the smaller left peak related to EVOH/clay at $2\theta = 2.65$ with increased D-spacing of $d = 33.20 \text{ \AA}$.

The observed view from the XRD measurements supporting most of the results and conclusions obtained above in relation to oxygen barrier (OTR) and thermal analysis (DSC) properties.

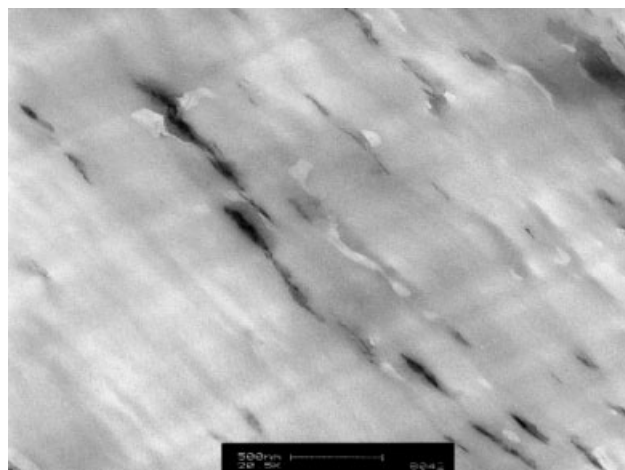


Figure 15 TEM micrograph on the core layer in the hybrid PE/EVOH/clay film of “concentrated active layer” system—TPEcOHc30.

Transmission electron microscopy

The morphology of selected samples was studied using TEM. The TEM images reveal a significant impact on the morphology of the samples when the organoclays, the barrier polymer, and the compatibilizing copolymer were added to the film in a form of CAL. Figure 14 showed the TEM image of the hybrid PE/PA6/clay film sample containing 4 wt % of Cloisite 30B + Cloisite 15A and PA6, in a form of CAL (the core layer of system—TPEcPac30). The microstructure observed in this micrograph indicates largely advanced exfoliation of the NC particle platelets, well dispersed in the polymer matrix and highly elongated parallel to the film surface. This observation is in agreement with the results obtained by the XRD measurements which supported the measured results of oxygen barrier (OTR) and thermal analysis (DSC) properties.

Figure 15 showed the TEM image of the hybrid PE/EVOH/clay film sample containing 4 wt % of Cloisite 30B + Cloisite 15A and EVOH, in a form of CAL (the core layer of system—TPEcOHc30). The microstructure observed in this micrograph indicates partial exfoliation that taken place, having an exfoliated NC particle platelets mixed with intercalated clay bands, highly elongated parallel to the film surface. This observation has also in agreement with the results showed and discussed above and is further supporting the general view obtained for the systems investigated in this study.

CONCLUSIONS

High barrier films with enhanced mechanical properties were developed and studied using blends of PA or EVOH with PE and compatibilizing copolymer, and with incorporated NC. Permeability measurements indicated that by increasing the active polymers concentration up to 30%, however, reducing the barrier layer thickness comprising the active polymers (PA or EVOH), resulting in reduction of the OTR by more than 7- to 8-folds. When NC was incorporated in the concentrated active polymer layer, the barrier to oxygen was further increased. This resulting in equal or even better barrier properties compared to the case where the active polymers are at 95% concentration. The increase in barrier

properties was attributed to the laminar structure of the incompatible active polymer in addition to the orientation of the NC with its additional effects due to nucleation and enhancement of the amorphous phase barrier. The mechanical properties of the CAL films were better or comparable with respect to the high barrier reference films. Furthermore, a nucleation effect, leading to increased crystallinity, was identified in the cases where PA compositions contained NC, whereas selective nucleation was obtained in the case where EVOH compositions contained NC. These observations, on oxygen barrier and mechanical properties, were further supported by the results obtained from thermal analysis (DSC), XRD measurements, and TEM imaging studies carried out on the hybrid films. The concept of CAL, with the incorporation of NC, comprising three layers was shown to give high barrier films having equal or better barrier properties with improved mechanical compared to the conventional five layer films barrier film. This concept may lead to reduced capital as well as materials cost for the production of high barrier films.

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