Selective localization of organic montmorillonite nanoparticles in multilayered high-density polyethylene/polyamide 6 composites

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Abstract
To achieve a selective localization of nanoparticles in multilayered two-component polymer blends, an intentional two-step process, first pre-compounding and then co-extruding, was employed to prepare multilayered high-density polyethylene (HDPE)/polyethylene-grafted maleic anhydride (PE-g-MAH)/organic montmorillonite (OMMT)-polyamide 6 (PA6) nanocomposites. The dispersion of OMMT was evaluated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results showed that the localization of OMMT was tunable with different content of PE-g-MAH. By comparing the localization of OMMT in a single-layered nanocomposite with that in the multilayered nanocomposites, as well as by theoretically calculating wetting coefficients of the multilayered nanocomposites, the migration mechanism of OMMT was revealed. As demonstrated by differential scanning calorimetry (DSC), transmission rate measurement and tensile test, the selective localization of OMMT in the multilayered nanocomposites could increase crystallinity degree of the two-polymer components, enhancing oxygen barrier property and tensile strength of the nanocomposites.

KEYWORDS
high-density polyethylene, migration of nanoparticles, multilayered composites, polyamide 6, selective localization

1 | INTRODUCTION

Selective localization of nanoparticles in a two-component polymer blend has attracted much attention because of its potential for improving electrical, mechanical, and thermal properties of nanocomposites. However, selective localization of nanoparticles cannot be easily achieved, because the dispersion behavior of nanoparticles may be influenced by many factors, including affinity of nanoparticles to each polymer, mixing sequence, processing methods, viscosity of each polymer melt, chemical reaction, and so on. Many works have been carried out to tune the localization of nanoparticles in two-component blends. Liebscher et al. reported that, through varying mixing sequence and melt-mixing parameters, different states of dispersion and different localizations (in the polycarbonate [PC] or poly(styrene-acrylonitrile) [SAN] component or at the blend interface) of graphene nanoplatelets were achieved. Huang et al. found that, by grafting polystyrene chain to the surface of silica nanoparticles and changing the chain length of grafted polymers, silica nanoparticles were selectively located at the interfaces or at the poly(methyl methacrylate) domains. Similarly, Wiwattananukul et al. found that, because of a large difference in the surface tension between polyethylene (PE) and multi-walled carbon nanotubes (MWCNTs), MWCNTs moved from PE to PC during the annealing treatment in the laminated sheets. However, in the case of melt-mixing, MWCNTs transferred from PC to PE, attributed to the grafting of PE chains on MWCNTs. Further, Wu et al. discussed...
suggested that the selective location of carbon black (CB) in polymer blends did not always depend on the surface tension (or surface roughness) of polymers, but seemed to be largely governed by the flexibility of the polymer chains. To reveal the correlation of the aspect ratio of nanoparticles and their localization in immiscible blends during melt-mixing, Göldel et al.\textsuperscript{[18]} compounded MWCNTs or CB in PC/SAN blends for comparison. It was found that the introduction of some reactive components could also induce the migration of nanoparticles, and the localization of nanoparticles could be controlled by changing the content of reactive components. With this method, Sun et al.\textsuperscript{[19]} successfully changed the localization of MWCNTs in PC/acrylonitrile-butadiene-styrene (ABS) blends. They noticed that MWCNTs migrated from the PC phase to the ABS phase when the rubber content of ABS was varied from 5% to 60%. In addition, Gultner et al.\textsuperscript{[20]} found that the addition of maleic anhydride grafting polymer could lead to the migration of amino-functionalized MWCNTs (AFMWCNTs) from PC phase to SAN phase in SAN/PC/AFMWCNTs composites, presumably because of a chemical coupling or strong interactions between maleic anhydride groups and amino groups of AFMWCNTs. However, despite many above-mentioned efforts have been devoted to the selective localization of nanoparticles in single-layered two-component polymer blends, reports on tuning the localization of nanoparticles in a multilayered two-component polymer blend are quite limited.

Multilayered two-component polymer blends were conventionally produced by a multilayered co-extrusion process, whose special channel structure could lead to the formation of special microstructure of the blends. Furthermore, the incorporation of nanoparticles into polymer blends has been utilized as an effective means to prepare multilayered nanocomposites with high performances, such as improved gas barrier and water resistance properties,\textsuperscript{[120–22]} as well as enhanced mechanical properties\textsuperscript{[23]} and thermal stability.\textsuperscript{[24]} However, because of their unique multilayered structure, selective localization of nanoparticles in a multilayered two-component blend is more complicated than that in a single-layered one. Therefore, the development of an effective way to tune the localization of nanoparticles in multilayered nanocomposites still remains a challenge.

In the present work, a two-step process (first pre-compounding and then co-extruding) was developed to incorporate organic montmorillonite (OMMT) nanoparticles and different content of polyethylene-grafted maleic anhydride (PE-g-MAH) into a typical immiscible high-density polyethylene (HDPE)/polyamide 6 (PA6) blend, forming multilayered nanocomposites. The dispersion and localization of OMMT nanoparticles in the multilayered nanocomposites as a function of PE-g-MAH content, as well as their thermal, barrier and mechanical properties were investigated. To understand the dispersion behavior of OMMT nanoparticles in the multilayered nanocomposites, the dispersion and localization of OMMT nanoparticles in a single-layered HDPE/PA6/PE-g-MAH/OMMT nanocomposite prepared by conventional extrusion, as well as theoretical calculation of wetting coefficients of HDPE/PE-g-MAH/OMMT-PA6 systems were also studied. We expect that this work can offer an effective way to tune the localization of nanoparticles in polymer matrices and then obtain the nanocomposites with good gas barrier and mechanical properties.

\section{EXPERIMENTAL}

\subsection{Materials}

HDPE (5200B) pellets (MFI = 0.35 g/10 min, density = 0.96 g/cm\textsuperscript{3}) was purchased from Yanshan Petrochemical Co. Ltd., (China). OMMT (I.31PS) modified by octadecylamine/γ-aminopropyltriethoxysilane with the cation exchange capacity of 145 meq/100 g was supplied from Nanocor Inc. (USA). HDPE-g-MAH with MAH content of 0.5% was supplied by Shanghai Sunny New Technology Development Co., Ltd. PA6 (1030B) was a commercially available product from Ube Co. (Japan), with a weight-average molecular weight of 30,000 g/mol, a density of 1.14 g/cm\textsuperscript{3}, a melting point of 220°C, and a glass transition temperature of 67°C.

\subsection{Preparation of nanocomposites}

Before mixing and melt-blending, OMMT was dried in a vacuum oven at 80°C for 24 hr, HDPE-g-MAH was dried in a vacuum oven at 50°C for 2 hr, PA6 pellets were dried at 90°C for 8 hr to reduce the moisture-induced thermal degradation.

A two-step process was intentionally designed to prepare multilayered nanocomposites: firstly, HDPE (100 phr), OMMT (3 phr) and PE-g-MAH (0, 1, 3, 5 or 7 phr) were pre-compounded using a twin-screw co-rotating extruder (\textit{L/D} = 40, \textit{D} = 20 mm, Coperion Keya Machinery Co., Ltd., Nanjing, China) with a temperature program of 140, 205, 210, 215, 215, and 210°C and a screw speed of 280 rpm. Secondly, the pre-compounded HDPE/PE-g-MAH/OMMT (100/\textit{x}/3, \textit{x} = 0, 1, 3, 5, 7) master batches (dried at 80°C for 5 hr) were co-extruded with PA6 using a multilayered co-extrusion system similar to the one reported in the literature,\textsuperscript{[25]} as shown in Figure 1a. HDPE/PE-g-MAH/OMMT (100/\textit{x}/3, \textit{x} = 0, 1, 3, 5, 7) and PA6 were simultaneously extruded from extruder A and extruder B, whose temperatures and screw speeds were set from 180 to 250°C, 150 rpm and from 190 to 240°C, 25 rpm, respectively, and combined as a two-layered melt in the co-extrusion block, then flowed through a series of layer multiplying elements (LMEs). The temperatures of the LMEs and the extruder die were kept at 245 and 240°C respectively. In one LME, the melt was sliced into two left and right sections by a divider, and then recombined vertically as shown in Figure 1b. An assembly of \textit{n} multiplying elements produced a tape with 2\textsuperscript{(\textit{n}+1)} layers, where \textit{n} was the number of multiplying elements. In
this work, the multilayered sheets were prepared by the alternating multilayered membranes with a thickness of 0.6 ± 0.1 mm, a width of 20 ± 0.5 cm and a layer number of 2,048.

In comparison with the multilayered sheets, HDPE (70 phr), OMMT (3 phr), PE-g-MAH (3 phr) and PA6 (30 phr) were extruded in only one extruder without LME to form a single-layered HDPE/PE-g-MAH/OMMT/PA6 nanocomposite, with the same temperature and screw speed setting. The thickness and the width of the single-layered sheets were also controlled at 0.6 ± 0.1 mm and 20 ± 0.5 cm respectively.

2.3 | Characterization

The degree of exfoliation was examined by means of X-ray diffraction (XRD) at 40 kV and 35 mA (Bruker D8 Advance, Bruker Co., Germany), using a nickel filtered Cu-Kα radiation source (λ = 1.5406 Å). The scanning 2θ angle range was 1°–60° and the scanning rate was 10°/min.

The distribution of OMMT in the obtained sheets was observed by Quanta 250 FEG scanning electron microscopy (SEM) (FEI, Hillsboro, USA) at an anaccelerating voltage of 10 kV and JEM-200CX transmission electron microscopy (TEM) (JEOL Ltd., Japan) at an accelerating voltage of 120 KV. Ultrathin sections (60–80 nm) were cut from Izod bars perpendicular to the flow direction under cryogenic conditions using a LKB-5 microtome (LKB Co, Switzerland).

Contact angle measurement was taken at room temperature using sessile drop method on DSA 100 (Kruss, Germany). Hot-pressed sheets were prepared at 245°C for PA6 and 250°C for HDPE and HDPE/PE-g-MAH blends respectively. Surface-free energy of the component was calculated using the Young’s equation:

\[
\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV}
\]

where \(\gamma_{SL}, \gamma_{LV}, \text{ and } \gamma_{SV}\) represent the interfacial energy of the solid/liquid, liquid/air, solid/air interface, respectively, and \(\theta\) is the contact angle.

Differential scanning calorimetry (DSC) (Q10, TA Instruments, Inc., New Castle, DE) was used to study the thermal properties of the obtained sheets. All measurements were carried out under a nitrogen atmosphere. The samples were first heated to 240°C at a constant rate of 10°C/min and held for 5 min at this temperature to eliminate possible thermo-mechanical histories. Then, they were cooled to 40°C at a constant rate of 10°C/min. The crystallization (\(T_c\)) and melting (\(T_m\)) temperatures, as well as the melting enthalpy value were obtained from crystallization and melting curves, respectively. The degree of crystallinity (\(X_c\)) of HDPE or PA6 component in the nanocomposites was determined from the area under the exothermic melting peak in the first melting cycle.

\[
X_{c-HDPE} = \frac{\Delta H_{m-HDPE}^0}{\Delta H_{m-HDPE}^0 \times \omega_{HDPE}} \times 100\% \tag{2}
\]

\[
X_{c-PA6} = \frac{\Delta H_{m-PA6}^0}{\Delta H_{m-PA6}^0 \times \omega_{PA6}} \times 100\% \tag{3}
\]

where \(\Delta H_{m-HDPE}^0\) and \(\Delta H_{m-PA6}^0\) are the melting enthalpies of HDPE and PA6 of the samples (J/g), \(\Delta H_{m-HDPE}^0\) and \(\Delta H_{m-PA6}^0\) are the enthalpy values of melting of a 100% crystalline form of HDPE (293 J/g)\(^{[26]}\) and PA6 (190 J/g),\(^{[27]}\) \(\omega_{HDPE}\) and \(\omega_{PA6}\) are the mass fractions of HDPE and PA6 of the samples respectively.

FIGURE 1  Scheme of a multilayered co-extrusion system (a and b: single screw extruder; c: co-extrusion block; d: layer multiplying elements; e: die)
The composition of multilayered sheets was measured by extraction experiment according to the previous literature.\cite{28} A certain amount of sample was weighted and performed by Soxhlet extraction in hot formic acid for 48 hr. Then the left unsolved substance was dried until its weight was constant. The mass fraction of PA6 (\(\omega_{\text{PA6}}\)) and HDPE (\(\omega_{\text{HDPE}}\)) were calculated as the following equations:

\[
\omega_{\text{PA6}} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (4)
\]

\[
\omega_{\text{HDPE}} = (1 - \omega_{\text{PA6}}) \times \frac{100}{103 + n_{\text{PE-g-MAH}}} \times 100\% \quad (5)
\]

where \(W_1\) is the weight of sample before extraction experiment and \(W_2\) is the weight of dried unsolved substance after extraction experiment, \(n_{\text{PE-g-MAH}}\) is the addition (phr) of PE-g-MAH. It is hypothesized that OMMT nanoparticles in the PA6 phase did not run off during the extraction experiment.

Oxygen transmission rate (OTR) was determined using an Ox- Tran Model 2/21 oxygen permeability MD Module from MOCON (USA) at 23°C and 0% RH. The 100% dry oxygen test gas concentration was used as the driving force and all the tests were done under barometric pressure 760 mmHg. According to the definition, to obtain the permeability coefficient, all measured OTR values were normalized (multiplied) by the thickness of the sheets.

Water vapor transmission rate (WVTR) was also measured by a Permatran-W 3/33MA instrument from MOCON (USA) at 23°C and 100% RH. The 100% water vapor was injected to one side to produce a saturated vapor, and then WVTRs of the samples were obtained as a function of time.

The tensile properties were carried out according to GB 1040.2-2006 at room temperature and humidity, by using a tensile machine (CMT6104; Shenzhen Xinsansi Co. Ltd., China) at a cross-head speed of 200 mm/min. The specimens were all cut from sheets along the extrusion direction, and the tensile properties were determined from the recorded load-displacement curves. A minimum of five specimens was tested for each reported value.

3 | RESULTS AND DISCUSSION

3.1 | Exfoliation of OMMT in multilayered nanocomposites

The X-ray diffraction (XRD) profiles for the multilayered nanocomposites are shown in Figure 2. As can be seen, the multilayered HDPE/PE-g-MAH/OMMT(100/1/3)-PA6 nanocomposite showed an obvious diffraction peak at 2\(\theta\) \(\approx 6.9^\circ\) (Figure 2a). When the content of PE-g-MAH increased, the intensity of diffraction peak decreased. The multilayered HDPE/PE-g-MAH/OMMT(100/7/3)-PA6 nanocomposite even showed no diffraction peak, indicating the destruction of the ordered structure of OMMT nanoparticles in the composite. This result also implies that the OMMT nanoparticles were well dispersed in the PA6 phase because of the good interaction between polymer and clay, which was consistent with the study of Das et al.\cite{23}
further was increased to 5 and 7 phr (Figure 3c,d), implying that a portion of OMMT nanoparticles migrated across the interfaces, from the HDPE layers to the PA6 layers. Consequently, the localization of OMMT nanoparticles in the multilayered HDPE/PA6 composites could be tuned by adding different content of PE-g-MAH.

As we know, the migration of nanoparticles can be induced by chemical coupling,\textsuperscript{[13]} interfacial thermodynamics\textsuperscript{[29]} or high viscosity ratio between two polymers.\textsuperscript{[30]} To reveal the exact mechanism of the migration of OMMT nanoparticles in the multilayered HDPE/PA6 composites, a single-layered HDPE/PA6/PE-g-MAH/OMMT (70/30/3/3) nanocomposite prepared by a conventional extrusion process was also studied. Figure 4 shows TEM micrographs of the single-layered sample. It can be seen that shuttle-like PA6 domains with different sizes dispersed in the HDPE matrix phase (Figure 4a). Furthermore, the TEM image at higher magnification (Figure 4b) clearly indicated that exfoliated OMMT platelets preferred to stay in the PA6 domains. This can be explained by the fact that the polar OMMT preferentially disperses in the polar polymer (PA6), but not the nonpolar polymer (HDPE), as reported by Mallick et al.\textsuperscript{[6]}

Theoretical prediction for the distribution of OMMT in HDPE/PA6 blends was also carried out. As we know, the localization of nanoparticles in an immiscible polymer blend can be predicted by the wetting coefficient ($\omega_a$), according to Young’s equation\textsuperscript{[31,32]},

$$\omega_a = \frac{\gamma_{\text{OMMT-A}} - \gamma_{\text{OMMT-B}}}{\gamma_{\text{A-B}}}$$

\textbf{FIGURE 3} Transmission electron microscopy (TEM) micrographs of the multilayered HDPE/PE-g-MAH/OMMT-PA6 nanocomposites: (a) HDPE/PE-g-MAH/OMMT(100/1/3)-PA6, (b) HDPE/PE-g-MAH/OMMT(100/3/3)-PA6, (c) HDPE/PE-g-MAH/OMMT(100/5/3)-PA6, (d) HDPE/PE-g-MAH/OMMT(100/7/3)-PA6. HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride.

\textbf{TABLE 1} Mass fraction of HDPE and PA6 in the multilayered HDPE/PE-g-MAH/OMMT(100/x/3, x = 1, 3, 5, 7)-PA6 nanocomposites with different content of PE-g-MAH.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass fraction/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/1/3)-PA6</td>
<td>54.3</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/3/3)-PA6</td>
<td>53.7</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/5/3)-PA6</td>
<td>53.0</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/7/3)-PA6</td>
<td>53.5</td>
</tr>
</tbody>
</table>

HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride.
where $\gamma_{\text{OMMT-A}}$, $\gamma_{\text{OMMT-B}}$ and $\gamma_{A-B}$ are the interfacial energies between OMMT and polymer A, OMMT and polymer B, polymer A and polymer B respectively. The $\omega_a$ value can be used to predict the localization of OMMT. The values of $\omega_a$ above 1, below −1, and in between mean that OMMT would preferentially be located in polymer B phase, in polymer A phase, and at the interface respectively.

The interfacial energy between two different materials ($\gamma_{12}$) can be calculated based on the surface-free energy of each component using the geometric mean equation (Equation 7) or the harmonic mean equation (Equation 8):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d}\right)^{0.5}$$  \hspace{1cm} (7)

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1^d}{\gamma_1^d + \gamma_2^p} + \frac{\gamma_2^p}{\gamma_1^d + \gamma_2^p}\right)^{0.5}$$  \hspace{1cm} (8)

Where $\gamma_1$ and $\gamma_2$ are the interfacial energies of components 1 and 2, $\gamma_1^d$ and $\gamma_2^d$ are the dispersive parts, and $\gamma_1^p$ and $\gamma_2^p$ are the polar parts of the interfacial energies of components 1 and 2 respectively.

In this work, the surface-free energies of PA6, HDPE, and HDPE/PE-g-MAH with different PE-g-MAH content were calculated from the contact angle of each materials by using Equation (1), and the surface-free energy of OMMT was obtained from reference.[31] Then these values were extrapolated to the processing temperature of 245°C, using temperature coefficients ($-d\gamma/dT$) extracted from references (see Table 2),[32–34] with the simplifying hypothesis that the polarity is independent of temperature. The interfacial energies between pairs of components according to geometric mean and harmonic mean equations were calculated and summarized in Table 3. Then the $\omega_a$ value was obtained according to the Equation (6), by setting polymer A as HDPE or HDPE/PE-g-MAH blend and polymer B as PA6 respectively.

As can be seen in Table 3, the value of interfacial energy between HDPE (or HDPE/PE-g-MAH) and PA6 ($\gamma_{23}$), which

### TABLE 2  Surface-free energies (SFE) of OMMT and polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature coefficient $d\gamma/dT$(mN/(mK))</th>
<th>SFE at 23.5°C (mN/m)</th>
<th>SFE at 245°C (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Dispersive part</td>
</tr>
<tr>
<td>OMMT</td>
<td>0.1$^a$</td>
<td>48.34</td>
<td>33.59</td>
</tr>
<tr>
<td>PA6</td>
<td>0.065$^b$</td>
<td>36.09</td>
<td>31.65</td>
</tr>
<tr>
<td>HDPE</td>
<td>$-0.057^c$</td>
<td>35.40</td>
<td>35.40</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH(100/1)</td>
<td>$-0.057^d$</td>
<td>36.51</td>
<td>36.42</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH(100/3)</td>
<td>$-0.057^d$</td>
<td>34.57</td>
<td>33.73</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH(100/5)</td>
<td>$-0.057^d$</td>
<td>37.73</td>
<td>36.83</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH(100/7)</td>
<td>$-0.057^d$</td>
<td>34.81</td>
<td>34.46</td>
</tr>
</tbody>
</table>

HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride.

$^a$Value for L31PS reported in Ref. [33].

$^b$Value for PA6 reported in Ref. [32].

$^c$Value for HDPE reported in Ref. [34].

$^d$Value for HDPE/PE-g-MAH assumed to be the same as that for HDPE reported in Ref. [34].
is calculated from whether the geometric mean equation or the harmonic mean equation, decreased with the increase of PE-g-MAH content, indicating that the compatibility between HDPE and PA6 was improved. Meanwhile, the obtained $\omega_a$ value increased and all the $\omega_a$ values were larger than 1, implying that the tendency of the location of OMMT in the PA6 phase in a HDPE/PA6 blend was enhanced. Therefore, with the increase of PE-g-MAH content, the OMMT nanoparticles, which located in the HDPE layers of the multilayered composites at the very beginning, should migrate to the PA6 layers under the thermodynamic driving force.

<table>
<thead>
<tr>
<th>Material</th>
<th>Interfacial energy (mN/m)</th>
<th>Wetting coefficient, $\omega_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Geometric mean equation</td>
<td>Harmonic mean equation</td>
</tr>
<tr>
<td>HDPE/OMMT(100/3)-PA6</td>
<td>$\gamma_{12} = 8.03$</td>
<td>$\gamma_{12} = 8.38$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{13} = 1.33$</td>
<td>$\gamma_{13} = 2.48$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{23} = 2.84$</td>
<td>$\gamma_{23} = 3.01$</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/1/3)-PA6</td>
<td>$\gamma_{12} = 6.88$</td>
<td>$\gamma_{12} = 8.48$</td>
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<tr>
<td></td>
<td>$\gamma_{13} = 1.33$</td>
<td>$\gamma_{13} = 2.48$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{23} = 2.19$</td>
<td>$\gamma_{23} = 3.03$</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/3/3)-PA6</td>
<td>$\gamma_{12} = 5.56$</td>
<td>$\gamma_{12} = 7.56$</td>
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<td></td>
<td>$\gamma_{13} = 1.33$</td>
<td>$\gamma_{13} = 2.48$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{23} = 1.46$</td>
<td>$\gamma_{23} = 2.54$</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/5/3)-PA6</td>
<td>$\gamma_{12} = 4.58$</td>
<td>$\gamma_{12} = 7.21$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{13} = 1.33$</td>
<td>$\gamma_{13} = 2.48$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{23} = 1.08$</td>
<td>$\gamma_{23} = 1.99$</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT(100/7/3)-PA6</td>
<td>$\gamma_{12} = 4.38$</td>
<td>$\gamma_{12} = 6.64$</td>
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<tr>
<td></td>
<td>$\gamma_{13} = 1.33$</td>
<td>$\gamma_{13} = 2.48$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{23} = 0.89$</td>
<td>$\gamma_{23} = 1.57$</td>
</tr>
</tbody>
</table>

HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride.

3.3 | Thermal properties of multilayered nanocomposites

To study the effect of selective localization of OMMT on thermal properties of the multilayered HDPE/PE-g-MAH/OMMT (100/x/3, x = 1, 3, 5, 7)-PA6 sheets, DSC experiments were carried out. Figures 5 and 6 show the melting and crystallization curves of all the multilayered sheets respectively. Table 4 summarizes the melting and crystallization data of the samples. To calculate the crystallinity degree of each polymer component, the composition of multilayered sheets was determined.

**FIGURE 5** Differential scanning calorimetry (DSC) melting curves of the multilayered HDPE/PE-g-MAH/OMMT(100/x/3, x = 1, 3, 5, 7)-PA6 nanocomposites with different content of PE-g-MAH. HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride

**FIGURE 6** Differential scanning calorimetry (DSC) crystallization curves of the multilayered HDPE/PE-g-MAH/OMMT(100/x/3, x = 1, 3, 5, 7)-PA6 nanocomposites with different content of PE-g-MAH. HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride
by an extraction experiment. The mass fraction and the crystallinity degree were also listed in Table 4. It can be seen that the melting temperature ($T_m$), crystallization temperature ($T_c$) and half-width of crystallization peaks of PA6 and HDPE in all the multilayed sheets remained almost unchanged, implying that the selective localization of OMMT had no effect on the crystalline lamellar thickness the crystallization behavior of the two-polymer components.\[35\] Furthermore, it is found that the crystallinity degree of HDPE increased when the content of PE-g-MAH increased from 1 phr to 5 phr, which can be ascribed to the improved dispersion of OMMT nanoparticles, which act as nucleating agents. However, the crystallinity degree of HDPE/PE-g-MAH/OMMT(100/5/3)-PA6 is lower than that of HDPE/PE-g-MAH/OMMT(100/5/3)-PA6. This observation can be attributed to the migration of OMMT nanocomposites from the HDPE phase to the interfaces or the PA6 phase, which weakens the nucleating effect of OMMT. Also, the results of TEM observation showed that the content of OMMT nanoparticles in the PA6 layers increased with the increase of PE-g-MAH content, so the crystallinity degree of PA6 should be increased. Indeed, the crystallinity degree of PA6 increased when the addition of PE-g-MAH increased from 1 phr to 5 phr. However, in contrast to that of HDPE/PE-g-MAH/OMMT(100/5/3)-PA6, the crystallinity degree of PA6 in HDPE/PE-g-MAH/OMMT(100/7/3)-PA6 reduced, possibly because of the increased viscosity of PA6 phase with increase of OMMT nanoparticles, which could restrict the crystallization of PA6.\[36\] Anyway, it is concluded that the crystallization properties of the multilayered sheets would be influenced by the dispersion and selective localization of OMMT.

### 3.4 Barrier properties of multilayered nanocomposites

The barrier properties of the multilayered nanocomposites were also studied. As we know, the barrier property of a polymer sheet is greatly influenced by the intrinsic characteristics of the polymer sheet itself and the permeating molecule. In general, a polar polymer sheet is strongly resistant to a nonpolar gas or solvent, but easily permeated by a polar gas or solvent.\[28\] Moreover, the transmission of gas or solvent is influenced by the crystallization property of a certain polymer. Gas or solvent molecules tend to permeate through an amorphous area rather than a crystallization region of polymer sheets. It was demonstrated that addition of impermeable nanoclays could improve the barrier properties of nanocomposites,\[27\] because the addition of nanoclays induced a direct tortuosity effect, which was closely related to volume fraction, aspect ratio and orientation of the impermeable nanoclays, restricting the permeation of gas or solvent molecules. Besides, the addition of nanoclays may modify the crystallinity index of polymer matrices, and then change the barrier property of the composites indirectly.

Figure 7 describes the oxygen and water vapor transmission rate of the multilayered sheets. It can be seen that the oxygen transmission rate of all the multilayered nanocomposites decreased with the increase of PE-g-MAH content. This can be ascribed to the improved dispersion of OMMT in the

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m/°C$</th>
<th>$T_c/°C$</th>
<th>$\Delta W/°C$</th>
<th>$\Delta H_m/(J/g)$</th>
<th>$X_c/%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
<td>PA6</td>
<td>HDPE</td>
<td>PA6</td>
<td>HDPE</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT (100/1/3)-PA6</td>
<td>136.18</td>
<td>223.54</td>
<td>114.74</td>
<td>187.67</td>
<td>9.53</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT (100/3/3)-PA6</td>
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<td>223.79</td>
<td>115.13</td>
<td>187.59</td>
<td>9.24</td>
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<tr>
<td>HDPE/PE-g-MAH/OMMT (100/5/3)-PA6</td>
<td>137.73</td>
<td>224.30</td>
<td>114.69</td>
<td>186.59</td>
<td>9.26</td>
</tr>
<tr>
<td>HDPE/PE-g-MAH/OMMT (100/7/3)-PA6</td>
<td>137.99</td>
<td>223.09</td>
<td>113.29</td>
<td>185.32</td>
<td>10.11</td>
</tr>
</tbody>
</table>

HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride.

**FIGURE 7** Oxygen transmission rate and water vapor transmission rate of the multilayered HDPE/PE-g-MAH/OMMT(100/x/3)-PA6 nanocomposites with different content of PE-g-MAH. HDPE, high-density polyethylene; PA6, polyamide 6; MAH, maleic anhydride
multilayered nanocomposites, which enhanced the tortuosity effect of OMMT platelets. Meanwhile, the increasing crystallinity degree of the two polymers with the increase of PE-g-MAH content suggested that their crystalline regions were expanded, resulting in decreased permeable part of the polymer matrices. Consequently, the passing way of oxygen (illustrated in Figure 8a) in the multilayered sheet was lengthened. Different from oxygen transmission, it is found that the water vapor transmission rate increased at first and then decreased slightly with the increase of PE-g-MAH content. The slightly decreased water vapor transmission value at 7 phr PE-g-MAH can also be explained by the fact that, the increase of OMMT nanoparticles in the PA6 phase may restrict the motion of PA6 molecules, and then limit the diffusion of water molecules. The completely opposite barrier properties for oxygen and water may be attributed to the different passing ways of the two molecules. Given that both PE-g-MAH and OMMT platelets have good affinity with water, the solubility and diffusion of water molecule in these parts are unimpeded. Thus, the passing way of water molecules (illustrated in Figure 8b) in the multilayered sheets should be shorter than that of the oxygen molecules. In other words, the water vapor barrier property of the multilayered sheets is determined by the dispersion degree of OMMT and the content of PE-g-MAH. We have demonstrated that the dispersion of OMMT in the multilayered sheets was improved with the increase of PE-g-MAH content. As a result, the water vapor transmission rate should be increased.

3.5 Mechanical properties of multilayered nanocomposites

Tensile tests were performed to evaluate the mechanical properties of the nanocomposites. For comparison, the tensile properties of neat HDPE-PA6 and HDPE/OMMT(100/3)-PA6 multilayered sheets were also tested. Figure 9 depicts the tensile strength and elongation at break of all the sheets. It is shown that the neat HDPE-PA6 multilayered sheet exhibited a low tensile strength of 17.0 MPa and a moderate elongation at break. Admittedly, the bad mechanical strength occurred because of the bad compatibility between HDPE and PA6. When 3 phr OMMT was added, a 23% increase in the tensile strength was obtained but with a slight sacrifice of the elongation at break. The improvement of tensile strength with addition of OMMT can be ascribed to the reinforcing effect of rigid inorganic clays. Intriguingly, the tensile strength of the composite with addition of 3 phr OMMT and 1 phr PE-g-MAH was enhanced significantly, with a 78% increase compared to that of neat HDPE-PA6. However, the elongation at break was reduced at the same time. The improved tensile strength may be attributed to the
better dispersion of OMMT nanoparticles in the HDPE layers with addition of few PE-g-MAH. However, the content of PE-g-MAH was too low to improve the interfacial compatibility between HDPE and PA6. Therefore, compared with HDPE/OMMCT(100/3)-PA6, the elongation at break of the HDPE/PE-g-MAH/OMMCT(100/1/3)-PA6 nanocomposite decreased with the increase of the tensile strength, which is similar to some previous works.[38–40] When the content of PE-g-MAH was increased from 1 to 7 phr, as the OMMT nanoparticles migrated to the interfaces and the PA6 layers and their dispersion became more homogeneous, the tensile strength of the nanocomposites continued to increase but the increasing rate became smaller. On the other hand, the elongation at break of the multilayered nanocomposites continued to increase, attributed to the improved compatibility between HDPE and PA6.

4 CONCLUSIONS

In this paper, commercial OMMT nanoparticles and a compatibilizer PE-g-MAH were incorporated into multilayered HDPE/PA6 immiscible system by an intentional two-step process: at first OMMT, PE-g-MAH and HDPE were melt-extruded and the prepared master batches, after being cut into pellets, were then co-extruded with PA6 by using a special multilayered co-extrusion system. We have demonstrated that the dispersion and localization of the OMMT nanoparticles can be tuned by adding different contents of PE-g-MAH. The results of TEM and XRD showed that the OMMT nanoparticles exclusively localized in the HDPE layers when 1 phr PE-g-MAH was added. However, when the content of PE-g-MAH was increased to 3, 5 or 7 phr, a portion of highly exfoliated OMMT nanoparticles migrated to the interfaces and the PA6 layers gradually. The localization of OMMT in the single-layered HDPE/PA6/PE-g-MAH/OMMCT (70/30/3/3) nanocomposite, as well as the theoretical calculation of the wetting coefficient, demonstrated that the migration of the OMMT nanoparticles can be ascribed to the thermodynamic factors, including the enhanced tendency of the location of OMMT in the PA6 phase of the HDPE/PA6 blends and the improved compatibility between HDPE and PA6. Through a series of characterization methods, it is concluded that the homogenous dispersion and selective localization of OMMT in the nanocomposites would result in increased crystallinity degree of the two-polymer components, enhanced oxygen barrier property and improved tensile strength of the nanocomposites, but the water barrier property would be decreased. The opposite barrier properties for oxygen and water results because of the different passing ways of the two molecules. It is believed that this work can provide an effective way to tune the localization of nanoparticles in multilayered nanocomposites.

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REFERENCES


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