Response surface analysis of structural, mechanical, and permeability properties of polyethylene/Na⁺-montmorillonite composites, prepared by slurry-fed melt intercalation

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Abstract. Samples were produced by injecting Na⁺-montmorillonite (Na⁺-MMT) slurry into a co-rotating twin-screw extruder. Na⁺-MMT was modified inside the extruder, in an in-situ process, and blended with the LDPE/LLDPE in melt state. Three different types of alkyl ammonium salt (ALAMS) were used as modifier to study the effect of chemical composition and chain length of ALAMS on the dispersion of nanoparticles. Also, the effect of nanoclay content on structural, mechanical, and permeability properties of the samples was investigated. To translate the data into intelligible trends, response surface method was utilized to analyze the effects of the factors on the results. Moreover, transmission electron microscopy was implemented to observe the dispersion of nanoclay platelets. The results suggested that the chain length of ALAMS dramatically affects its ability to modify nanoclay platelets. What is more, while nanoclay increase deteriorates nanoparticles dispersion, it brings about better mechanical and gas barrier properties. The improvement in the properties was higher than those of nanocomposites prepared by conventional method. By studying the effects of feeding rate on nanoclay dispersion, we proved that unlike conventional melt intercalation, water-assisted melt intercalation is controlled by diffusion rather than shear stress. In the end, we proposed a mechanism for this process.

Keywords: nanocomposites, nanoclay slurry, melt intercalation, polyethylene

1. Introduction

Low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) blends have gained remarkable attention in packaging film industries. Although these two polymers and their blends are among the most multi-purpose polymers, their lack of strength and stiffness along with poor heat resistance are problematic [1]. To eliminate these drawbacks and to prepare materials with improved properties, varieties of inorganic nanoparticles have been added to these polymers, among which nanoclay platelets have gained special interest [2, 3]. This special interest is an outgrowth of two particular characteristics of nanoclay particles: first is the ability to disperse into individual layers, the second is the ability to engineer their surface chemistry through ion exchange reactions [4, 5]. When compared to their unloaded counterparts, polymeric nanocomposites demonstrate drastic improvements in physical and mechanical properties. Adding nanoclay also brings forth better gas barrier and flame retardancy properties [6, 7]. There are various methods to prepare nanocomposites, among which melt intercalation has attracted a lot of attention. Melt
intercalation involves annealing, mainly under shear stress, a mixture of polymer and nanoclay particles above the softening point of the polymer. Owing to the absence of organic solvents, this method is environmentally benign and also compatible with current industrial process, such as extrusion and injection molding [8]. A major modification to melt intercalation method was carried out by Korbee and Van Geenen [9], in which the pristine nanoclay particles and PA6 pellets were introduced into the extruder, and water was then injected directly into the extruder downstream. After interactions with the melt compound, water was evacuated further downstream via a vacuum pump. The presence of water weakens the interaction between the nanoclay platelets and brings forth an increase in the gallery spacing. In case of high surface energy polymers, e.g., polyamides, water can also reduce matrix viscosity and thus add to the chain mobility. Both of these effects facilitate polymer chain penetration between the nanoclay platelets. This modification makes the need for the use of nanoclay modifiers unnecessary for high surface energy polymers. Even if the use of modifiers is unavoidable, i.e., in case of hydrophobic polymers like polyamides, this method still brings about improved, if not similar, results and offers *in-situ* nanoclay modification, which is less cumbersome and costly than pre-modification process and provides us with more process flexibility and less health hazard [10].

Water-assisted melt intercalation can be employed in three different ways: slurry injection, solution injection, and water injection. According to Mola-javadi and Garmabi [11], using slurry injection for nanocomposite production would result in the best mechanical properties. Plus, this method can be used to produce nanocomposites from a wide range of polymers and modifiers. But, it requires slurry preparation process and higher amount of water; higher amount of injected water may cause technical problems. There is also a limit for nanoclay content, 5 wt%, and feeding rate, 2 kg/h in this study. Moreover, the slurry may even stick to the screw and cause other technical difficulties. Solution injection, on the other hand, requires relatively less amount of water. Because the modification process occurs in water [12], this method provides better chance for nanoclay modification [13]. The addition of more amount of nanoclay is possible and higher outputs can be achieved. But, modifier solution process is required; and, this process is limited only to modifiers that are water-soluble under ambient conditions. Interestingly, water injection method does not need slurry nor solution preparation processes and requires less amount of water [14]. The addition of more amount of nanoclay is possible and higher outputs can be achieved. But, it brings forth lower chance for nanoclay modification. As a result, this method is best used only for high surface energy polymers [15, 16]. It should also be noted that the use of water in producing polymeric nanocomposites is not only limited to polymer/nanoclay composites; this method can be employed to produce polymeric composites from other particles as well [17]. Table 1 summarizes these findings, based on which we decided to utilize slurry injection method for this study.

The slurry-fed melt intercalation process has not been used to produce LDPE/LLDPE nanocomposites. In this study, Octadecyl trimethyl ammonium chloride (OTAC), dodecyl trimethyl ammonium chloride (DTAC), and dodecyl trimethyl ammonium bromide (DTAB) were used to study the effect of chemical composition and chain length of modifiers on the dispersion of nanoparticles. By comparing the results between DTAC- and DTAB-modified samples, the effect of chemical composition, chlorine or bromine, can be studied. Similarly, the comparison between DTAC- and OTAC-modified samples will show the effect of modifier chain length on the dispersion of nanoparticles. Table 2 presents some information regarding the three alkyl ammonium salt (ALAMS) types.

Furthermore, Hasegawa et al. [18] and Kato et al. [12] claimed that water-assisted melt intercalation process is quite different from conventional one: In conventional melt intercalation, polymer chains intercalate into the galleries of the stacked layered silicates and the silicate layers exfoliate into polymer matrix; this largely occurs under shear stress. On the other hand, in water-assisted process the exfoliated silicate layers in water are fixed into the polymer matrix without aggregation; this means that shear stress has no consequential role in the dispersion of the nanoparticles, and diffusion plays the important role. To examine this theory, we decided to study the effect of feeding rate on the nanoclay dispersion and the properties of samples.
Because, by changing feeding rate, we can change the imposed shear stress on and the residence time of the materials inside the extruder; the inverse relationship between the shear stress and the residence time should be noticed. To get a notion on how feeding rate affects the residence time of the materials, the effect of feeding rate on the residence time of LDPE/LLDPE is gathered in Table 3. For this theory to hold true, i.e., the process is diffusion-controlled rather than shear-controlled, better nanoclay dispersion must emerge from lower feeding rates, i.e., higher residence time and higher chance for

Table 1. Schematic view, advantages, and disadvantages of the three different types of water-assisted melt intercalation

<table>
<thead>
<tr>
<th>Method</th>
<th>Schematic view of the process and advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>slurry injection</td>
<td><img src="image" alt="Schematic view of slurry injection" /> 1 – better nanoclay dispersion and mechanical properties 2 – can be used for a wide range of polymers and modifiers</td>
<td>1 – higher amount of water is needed 2 – nanoclay content limit in slurry (up to 5 wt%) 3 – slurry may stick to the screw 4 – slurry preparation process is needed 5 – only low outputs are available</td>
</tr>
<tr>
<td>solution injection</td>
<td><img src="image" alt="Schematic view of solution injection" /> 1 – better chance for nanoclay modification 2 – better results than water injection 3 – less water is needed than slurry injection 4 – higher outputs and nanoclay contents are available</td>
<td>1 – more water is needed than water injection 2 – limited only to modifiers that are water-soluble under ambient conditions 3 – solution preparation process is needed</td>
</tr>
<tr>
<td>water injection</td>
<td><img src="image" alt="Schematic view of water injection" /> 1 – less amount of water is needed 2 – neither slurry nor solution preparation processes are needed 3 – higher outputs and nanoclay contents are available</td>
<td>1 – lower chance for nanoclay modification 2 – best suited for high surface energy polymers, for which no chemical modification is needed</td>
</tr>
</tbody>
</table>

Table 2. General information of the studied ALAMS types

<table>
<thead>
<tr>
<th>ALAMS type</th>
<th>Chemical Formula</th>
<th>More information</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTAC</td>
<td><img src="image" alt="Chemical structure of OTAC" /> $C_{21}H_{40}N\cdot Cl$</td>
<td>Synonyms: Steartrimonium chloride; Stearyl trimethyl ammmonium chloride; Trimethyloctadecylammonium chloride; Aliquat 7  Molecular weight: 348.05  Soluble in hot water</td>
</tr>
<tr>
<td>DTAC</td>
<td><img src="image" alt="Chemical structure of DTAC" /> $C_{12}H_{25}N\cdot Cl$</td>
<td>Synonyms: N,N,N-Trimethyl-1-dodecanaminium chloride; Trimethyl-1-dodecanaminium chloride; Laurtrimonium chloride  Molecular weight: 263.89  Water soluble</td>
</tr>
<tr>
<td>DTAB</td>
<td><img src="image" alt="Chemical structure of DTAB" /> $C_{12}H_{25}N\cdot Br$</td>
<td>Synonyms: Lauryltrimethylammonium bromide; Dodecyltrimethylammonium bromide; Laurtrimonium bromide  Molecular weight: 308.34  Water soluble</td>
</tr>
</tbody>
</table>
diffusion. Lastly, the role of nanoclay content on the properties of the samples and nanoclay dispersion is worth studying.

For the sake of proper interpretation and integration of all the data, a designed set of experiments is required. By using experimental design, it will be much simpler to analyze the effects of the factors on the morphology, mechanical, and permeability properties of the samples, to observe the trends, and to draw conclusions. Among the variety of experimental designs, response surface method was best compatible with our experimental and material conditions.

For these reasons, in this study, we produced LDPE/LLDPE/nanoclay samples in a co-rotating twin-screw extruder equipped with slurry injection system from LDPE/LLDPE blends, polyethylene maleic anhydride (PEMA), three different types of ALAMS, and Na⁺-montmorillonite (Na⁺-MMT) dispersed in water. The objective of this paper is to analyze, by means of response surface method, the effect of three key factors, i.e., modifier type, feeding rate, and nanoclay content, on the structural, mechanical, and permeability properties of the samples.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE, 2101TN47), density = 0.921 g/cm³, was kindly provided by Laleh Petrochemical Co. (Mahshahr, Khuzestan, Iran). Linear low density polyethylene (LLDPE, 0209AA), density = 0.920 g/cm³, was purchased from Amirkabir Petrochemical Co. (Mahshahr, Khuzestan, Iran). The melt flow index (MFI), measured at 190°C with 2.16 kg load, was 0.85 g/10 min for both LDPE and LLDPE. Maleic anhydride modified linear low density polyethylene (PEMA, Orevac® 18302N), density = 0.912 g/cm³, with a maleic anhydride content of 0.2 wt% was supplied by Arkema Inc. (Paris, France) to be used as compatibilizer, the MFI of PEMA used was 1.2 g/10 min. Na⁺-montmorillonite (Na⁺-MMT, Cloisite® Na⁺), density = 2.86 g/cm³, was purchased from Southern Clay Products (Gonzales, Texas, USA). The cation exchange capacity of Na⁺-MMT was 95 meq/100 g. Alkyl ammonium salts were purchased from Xiamen Pioneer Technology Inc. (Xiamen, Fujian, China). All the materials were used as received.

2.2. Design of experiments

Response surface methods are used to examine the relationship between one or more response variables and a set of factors. These methods are often employed after ‘vital few’ controllable factors are identified. In addition to process optimization, which is not discussed in this paper, these methods enable us to produce an approximate continues surface for the discrete results. This will help us to integrate the effects of two factors into one 3D plot, making it easier to observe the trends and possible to detect the interaction between the factors. Among different response surface methods, Box-Behnken method was found to be best compatible with our experimental criteria [19–22].

We considered feeding rate, nanoclay content, and ALAMS type as ‘vital few’ controllable factors. The properties used as responses include: tensile-modulus increase, reduction in oxygen permeability, and d-spacing of nanoparticles in the samples. A quadratic model was used to approximate the responses continuously. Throughout this paper, samples will be named the way below:

1 – The letters indicate the ALAMS type. OC, DC, and DB will stand for OTAC, DTAC, and DTAB, respectively.
2 – The figure on the left-hand side of the forward slash will represent nanoclay content in [wt%].
3 – The figure on the right-hand side of the forward slash will represent feeding rate in [kg/h].

Note: Samples No. 7, 9, and 11 have exactly the same design and are for reproducibility analysis. The extra figure that is added to the end of their names is simply for distinction.

Example: DB5/1.5 is the name of the sample that contains 5 wt% nanoclay and has been prepared at 1.5 kg/h feeding rate with DTAB as nanoclay modifier.

The full list of the samples and their compositions is gathered in Table 4.

<table>
<thead>
<tr>
<th>Feeding rate [kg/h]</th>
<th>Color change initiation time [s]</th>
<th>Color change termination time [s]</th>
<th>Average residence time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>350</td>
<td>265</td>
</tr>
<tr>
<td>1.5</td>
<td>110</td>
<td>240</td>
<td>175</td>
</tr>
<tr>
<td>2</td>
<td>96</td>
<td>152</td>
<td>124</td>
</tr>
</tbody>
</table>

Table 3. The effect of feeding rate on the residence time of the LDPE/LLDPE blend
2.3. Preparation of the samples using nanoclay slurry

Nanoclay slurry was prepared by dispersing Na⁺-MMT powder into distilled water using an overhead mechanical stirrer for 30, 60, and 90 minutes for 1, 3, and 5 wt% nanoclay contents, respectively. During the process, a magnetic stirrer was employed to prevent the slurry form being precipitated. A lab-scale co-rotating intermeshing twin-screw extruder from Brabender DSE25 (Duisburg, Germany) was used to prepare samples. The screw diameter was 2.5 cm, its length/diameter was 32, and the distance between the two axes was 20.87 mm. Figure 1 shows the screw configuration and the order of mixing according to which the samples were prepared. LDPE/LLDPE uniform mixture with 60/40 ratio together with PEMA was added to the extruder through hopper using a granule feeder. ALAMS was first homogeneously diluted in LDPE/LLDPE (60/40) powder and then added to the extruder through hopper using a powder feeder. The ratio of ALAMS to nanoclay equivalent was kept at 1.5:1. Because nanoclay content in the slurries and their respective samples were equal, the slurry injection rate was set equal to its respective feeding rate. The screw rotation speed was kept constant at 200 rpm. Temperature profile within the extruder for zones one to six was kept at 160, 170, 180, 185, 185, and 180°C, respectively. The residence times for the pure LDPE/LLDPE, measured by introducing black pellets into the extruder, are reported as the average time of initiation and termination of color change in the output. Residence time for each feeding rate was measured at least three times. Table 3 summarizes the average values of these results. The water was removed by vacuum in degassing section. The obtained strands were then pelletized.

2.4. Characterization

Tensile test measurements were performed on compression-molded sheets at room temperature using a tensile test machine (Z050, Zwick, Germany), based on ASTM-D638 [23], on dumbbell-shaped tensile bars of type I with a cross-head speed of 50 mm/min. At least three specimens of each sam-

<table>
<thead>
<tr>
<th>Table 4. Samples designs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
</tr>
<tr>
<td>1) OC1/1.5</td>
</tr>
<tr>
<td>2) OC3/1</td>
</tr>
<tr>
<td>3) OC3/2</td>
</tr>
<tr>
<td>4) OC5/1.5</td>
</tr>
<tr>
<td>5) DC1/1</td>
</tr>
<tr>
<td>6) DC1/2</td>
</tr>
<tr>
<td>7) DC3/1.5-1</td>
</tr>
<tr>
<td>8) DC5/1</td>
</tr>
<tr>
<td>9) DC3/1.5-2</td>
</tr>
<tr>
<td>10) DC5/2</td>
</tr>
<tr>
<td>11) DC3/1.5-3</td>
</tr>
<tr>
<td>12) DB1/1.5</td>
</tr>
<tr>
<td>13) DB3/1</td>
</tr>
<tr>
<td>14) DB3/2</td>
</tr>
<tr>
<td>15) DB5/1.5</td>
</tr>
<tr>
<td>16) Reference</td>
</tr>
</tbody>
</table>

*a in the nanocomposite and the respective injected slurry

*b LDPE/LLDPE+PEMA+ALAMS, also identical to the rate of slurry injection.
ple were tested to establish testing reproducibility. For the sake of better response surface analysis, the average values of tensile modulus of the samples were normalized by the value of the reference, and the values are given for tensile-modulus increase in percent. The tensile modulus of the reference was 207±11.55 N/mm².

Nanoclay dispersion was investigated by X-ray diffraction (XRD) using a Holland Philips Xpert X-ray diffractometer with Co Kα radiation (λ = 1.789 Å) generated at 40 kV and 30 mA, scanning from 1 to 12° at a step value of 0.02°/s at room temperature. The compression-molded sheets at 190°C with 2 mm thickness were used for XRD studies. The transmission electron microscopy (TEM) micrographs were obtained using a JEOL 2010F transmission electron microscope operating at an accelerating voltage of 120 kV. TEM samples for particle characterization were cryogenically cut into ultra thin sections (30–50 nm thick) with a diamond knife at a temperature of −40°C using a Reichert-Jung Ultra cut E microtome.

Oxygen permeability of the samples was measured using an apparatus illustrated in Figure 2. The oxygen pressure was set at 3 bars and the compression-molded films thickness was 350±30 μm. The oxygen purity was 99.99%. The rate of oxygen permeation was recorded during steady-state phase of the permeation process, according to

\[
P = \frac{d \cdot \left( \frac{J}{\Delta p} \right)}{
\]

where \( J \) is the gas volumetric flow rate per unit area of the film, \( d \) is the thickness of the film, \( \Delta p \) is the pressure difference across the film, and \( P \) is permeability. To reduce error, the permeability of each sample was then normalized by the permeability of the reference and reported as reduction in oxygen permeability in percent.

Nanoclay contents were measured by thermogravimetric analysis (TGA) under nitrogen at a flow rate of 20 mL/s using a Perkin Elmer Pyris-1 (USA) instrument. Measurements were conducted at 600°C with 10°C/min heating rate.

3. Results

Mechanical and permeability measurements were performed to explore the effect of nanoparticles and their dispersion on the properties of the composites. Tensile-modulus increase, gas-permeability reduction, and \( d \)-spacing of nanoclay platelets in the samples are gathered in Table 5. It can be seen that the addition of nanoclay improved the tensile modulus and gas barrier properties of all the composites. The results also imply that the addition of water into the molten polymer had no damaging effect, i.e., hydrolysis, on the polymer.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile-modulus increase [%]</th>
<th>Oxygen permeability reduction [%]</th>
<th>( d )-spacing [Å]</th>
<th>Nanoclay content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC1/1.5</td>
<td>33.9</td>
<td>18.3</td>
<td>80.0</td>
<td>0.76</td>
</tr>
<tr>
<td>OC3/1</td>
<td>84.2</td>
<td>31.8</td>
<td>40.2</td>
<td>2.91</td>
</tr>
<tr>
<td>OC3/2</td>
<td>42.4</td>
<td>22.5</td>
<td>33.5</td>
<td>2.79</td>
</tr>
<tr>
<td>OC5/1.5</td>
<td>93.4</td>
<td>41.0</td>
<td>18.8</td>
<td>4.57</td>
</tr>
<tr>
<td>DC1/1</td>
<td>22.2</td>
<td>10.9</td>
<td>13.9</td>
<td>0.80</td>
</tr>
<tr>
<td>DC1/2</td>
<td>12.3</td>
<td>7.7</td>
<td>13.9</td>
<td>0.78</td>
</tr>
<tr>
<td>DC3/1.5-1</td>
<td>31.2</td>
<td>15.4</td>
<td>13.1</td>
<td>2.75</td>
</tr>
<tr>
<td>DC5/1</td>
<td>47.4</td>
<td>24.4</td>
<td>12.1</td>
<td>4.73</td>
</tr>
<tr>
<td>DC3/1.5-2</td>
<td>35.9</td>
<td>16.0</td>
<td>13.2</td>
<td>2.67</td>
</tr>
<tr>
<td>DC5/2</td>
<td>41.5</td>
<td>17.2</td>
<td>12.0</td>
<td>4.57</td>
</tr>
<tr>
<td>DC3/1.5-3</td>
<td>32.0</td>
<td>17.1</td>
<td>13.2</td>
<td>2.81</td>
</tr>
<tr>
<td>DB1/1.5</td>
<td>13.9</td>
<td>7.4</td>
<td>13.9</td>
<td>0.78</td>
</tr>
<tr>
<td>DB3/1</td>
<td>17.1</td>
<td>12.9</td>
<td>13.0</td>
<td>2.62</td>
</tr>
<tr>
<td>DB3/2</td>
<td>15.3</td>
<td>9.1</td>
<td>13.0</td>
<td>2.56</td>
</tr>
<tr>
<td>DB5/1.5</td>
<td>22.0</td>
<td>13.6</td>
<td>12.0</td>
<td>4.52</td>
</tr>
</tbody>
</table>

![Figure 2](image-url). The schematic cross-section view of the apparatus used for oxygen permeability measurements.
Figure 3 shows XRD patterns of Na⁺-MMT (a), samples prepared with OTAC (b), and DC1/1 and DB1/1.5 (c). The numbers indicate the angles and their corresponding d-spacing.

Figure 3 shows XRD patterns of Na⁺-MMT (a), samples prepared with OTAC (b), and DC1/1 and DB1/1.5 (c). Na⁺-MMT has an intense diffraction peak at 2θ = 8.69° and a small peak at 2θ = 10.69° that correspond to basal spacing of 1.18 and 0.96 nm, respectively. This suggests that most of Na⁺-MMT were hydrated by one layer of water molecules between platelets. An increase in the d-spacing of nanoclay stacks results in 001 diffraction peak to shift to lower 2θ and to weaken in intensity.

To study the effect of ALAMS type on the dispersion of nanoparticles, mechanical, and gas barrier properties of the samples, surfaces of tensile-modulus increase, reduction in permeability, and d-spacing of nanoclay particles in the samples are plotted as a function of feeding rate and nanoclay content in Figure 4. As can be seen, OTAC produces the best results, i.e., higher mechanical and permeability properties and also d-spacing. On the other hand, DTAC-modified samples demonstrate only slightly better results than DTAB-modified ones. An obvious interaction between ALAMS type and feeding rate can be observed in these graphs.

To better demonstrate the effect of feeding rate and nanoclay content on the dispersion of nanoparticles, mechanical, and gas barrier properties of the samples, surfaces of tensile-modulus increase, reduction in permeability, and d-spacing of nanoclay particles in the samples are plotted as a function of feeding rate and nanoclay content in Figure 5. As can be seen, nanoclay increase and feeding rate decrease cause both tensile modulus and reduction in permeability to rise. In a similar trend, feeding rate decrease causes the d-spacing of the nanoparticles to rise as well; nanoclay increase, however, causes the d-spacing of the nanoparticles to fall. Furthermore, no significant interaction between nanoclay content and feeding rate can be observed.

To scrutinize the dispersion of nanoclay platelets, the compression-molded samples modified with OTAC were microtomed under liquid nitrogen, and the prepared thin sections were observed by TEM micrographs. The dark lines in Figure 6 are cross section of silicate layers, which show a homogeneous distribution of nanoclay platelets in the polymeric matrix. As can be seen, OC1/1.5 is largely exfoliated; whereas, other samples show some small stacks of nanoclay layers. Still, these samples show appropriate level of nanoclay dispersion, i.e., intercalated structure. All the samples show acceptable level of distribution and dispersion of silicate layers. The increase in nanoclay content and feeding rate causes the exfoliated structure to vanish and the intercalated structure to appear.

4. Discussion

4.1. The effect of ALAMS type

Mechanical and gas permeability properties of nanocomposites depend on many factors, including aspect ratio of nanoparticles, degree of nanoparticles dispersion in matrix, nanoparticles content, nanoparticles orientation, adhesion at nanoparticle-matrix interface, crystallinity etc. An increase in nanoclay content and improvement in its dispersion will enhance tensile modulus and reduce gas permeability.
In Figure 4, a marked difference in $d$-spacing, mechanical, and permeability properties between OTAC-modified samples and samples modified with DTAC and DTAB can be observed. There are few noticeable properties improvements in case of DTAC- and DTAB-modified samples. XRD results show that the $d$-spacings of nanoparticles in DTAC- and DTAB-modified samples are almost the same.

Figure 4. Response surfaces of (a) Reduction in permeability, (b) Tensile-modulus increase, (c) $d$-spacing for samples prepared with different ALAMS types as a function of feeding rate. The graphs are plotted for samples containing 3 wt% nanoclay and were altered manually for better clarification.

Figure 5. Response surfaces of (a) Reduction in permeability, (b) Tensile-modulus increase, (c) $d$-spacing as a function of feeding rate and clay content. The graphs are plotted for OTAC-modified samples. For clarification purposes, the graphs were altered manually and the axes of graph (c) are drawn in reverse order.
as that of pristine nanoclay, suggesting the samples to be close to microcomposites rather than nanocomposites. OTAC-modified samples, on the other hand, show a good rise in tensile modulus and perceptible improvement in gas barrier properties. The $d$-spacing increased as high as about 8nm, suggesting even the existence of exfoliated structure [24, 25] at low nanoclay contents, which is hard to achieve in case of polyolefins [26]. TEM micrographs also proved the existence of exfoliated structure for OC1/1.5 and intercalated structure for other OTAC-prepared samples. The similarity of the results for DTAC and DTAB suggests that the difference in halogen element, chlorine or bromine, barely changes the ALAMS ability to properly modify nanoclay platelets; on other hand, because chain length is the only difference between OTAC and DTAC, it can be concluded that chain length is the key factor.

Throughout this paper, we use the term ‘nanocomposite’ only to refer to OTAC-modified samples. Several factors can influence ALAMS ability to improve nanoclay dispersion, e.g., structure, density, number of alkyl tails, chain length, packing density, polymeric matrix etc. [27–29]. Very often, the effect of each of these factors may be influenced by other co-existing factors. For example, ALAMS with one alkyl tail was proved to produce better results in case of Nylon 6 [30]; whereas, ALAMS with two alkyl tails produced better results in case of PE [31]. Therefore, the effect of these factors on the dispersion of nanoparticles may vary depending on the specific material and processing conditions that are being investigated. Anyway, the effect of chain length on the interlayer spacing of nanoclay platelets has been the subject of several studies. In general, longer ALAMS chain length and higher

**Figure 6.** TEM micrographs of (a) OC1/1.5 (b) OC3/1, (c) OC3/2, (d) OC5/1.5
charge density of nanoclay is considered to result in further nanoclay interlayer spacing [32]. In a study on PE nanocomposites, Wang et al. [33] have found that the interlayer spacing increases with an increase in the size of ALAMS chain length; they also found that this parameter may change the degree of interaction between nanoclay and polyethylene. Balazs and coworkers [34, 35] have found that longer ALAMS chain length favors the layers separation by allowing the polymer to adopt more conformational degrees of freedom. According to Ginzburg et al. [36], for short ALAMS molecules, the polymer is unable to penetrate inside the gallery between nanoclay surfaces, and the equilibrium morphology becomes immiscible for most values of the Flory-Huggins parameter and nanoclay volume fraction. Only in case of large negative $\chi$ can such a composite become exfoliated.

The quality of nanoclay dispersion in a system is determined by the relationship between entropy and energy changes. During melt intercalation, the loss in entropy of polymer due to confinement in the gallery space can be reduced by an increase in interlayer spacing, which allows more conformational changes. The entropy change associated with the ALAMS length increases until nanoplatelets separation is equal to the fully extended length of the ALAMS chain [37]. Some of these studies, however, also suggested that there might be an optimum ALAMS chain length or nanoclay interlayer spacing, which results in optimum nanoclay dispersion. This notion has to be approached with care, since, as mentioned, specific polymer/nanoclay systems demonstrate specific characteristics; ergo, the value of this optimum spacing or the very existence of it may be dependent on the system that is being investigated. The interlayer distance also depends on the way the ALAMS chains organize themselves in the modified nanoclay [38]. One factor that directly affects ALAMS chain organization is ALAMS packing density inside nanoplatelets. This will be discussed in the next section.

4.2. The effect of feeding rate

As demonstrated by Figures 4–6, feeding rate increase had a detrimental effect on the dispersion of nanoclay particles in the samples. Considering the extruder as a plug reactor would suggest that the residence time is an important factor in this process. Providing enough time for the OTAC to diffuse into water and react with nanoclay surface would ensure successful modification of nanoclay platelets, which leads to better stabilization of nanoclay platelets inside the matrix; thus, better dispersion can be achieved. This is the reason why samples prepared at higher feeding rates manifest lower $d$-spacing, gas barrier, and mechanical properties. Nonetheless, we should pay attention to the fact that lower feeding rate imposes lower shear stress on the materials inside the extruder. In conventional melt intercalation process, shear stress is vital for breaking down nanoclay agglomerates [39–41]. Interestingly, it seems that in this method the effect of shear stress is rather undermined. This finding shows that in water-assisted melt intercalation, the mechanism that affects the dispersion of nanoparticles is different from that of conventional melt intercalation. In other words, this process is diffusion-controlled rather than shear-controlled; this finding is in agreement with Hasegawa et al. [18] and Kato et al. [12] studies. We should, however, emphasize that one ought not to infer that higher shear stress does not have a positive effect on this process; but rather, shear stress effects, vis-à-vis residence time, are comparatively inconsequential. Moreover, the interaction between feeding rate and ALAMS type should be pointed out. The reason for this interaction to exist is that due to DTAC and DTAB inability to effectively modify nanoclay platelets, a change in feeding rate does not really affect the dispersion of nanoparticles in these samples; whereas, in case of OTAC-modified samples, feeding rate affects the dispersion through changing the residence time of materials inside the extruder. This is why an interaction between feeding rate and ALAMS type can be observed.

The effect of feeding rate on nanoclay dispersion can be further explained through ALAMS packing density inside nanoclay platelets; in this work, an increase in feeding rate decreased the average ALAMS packing density inside nanoplatelets. At low packing density, ALAMS chains have been considered to lie parallel to the silicate layer, in mono- or bi-layer formations, but, as packing density and/or chain length increases they are more likely to radiate away from nanoplatelets surface, organized in mono- or even a bi-molecular tilted ‘paraffinic’ formations. It is suggested that ALAMS
chains form liquid-like structures at low packing density or short ALAMS chain length. But, when the packing density and/or the chain length of ALAMS is within a certain range, the chains are not completely disordered but retain some orientational order similar to that in the liquid crystalline state; this increases the interlayer spacing of nanoclay particles [2].

Ginzburg et al. [36] showed that as ALAMS packing density increases, the miscibility between nanoclay platelets and polymer is improved and the resulting mixture can exhibit exfoliated structure for a range of nanoclay volume fractions. Similar conclusions have been drawn by Balazs and coworkers [34, 35] when they devised a theoretical model to study the effects of ALAMS packing density and chain length. Nonetheless, very high amounts of ALAMS packing density is suggested to make intercalation and exfoliation unfavorable, based on their model. This finding has been corroborated by Vaia and Giannelis [37] as well. They have also suggested that an optimal ALAMS packing density exists that favors optimum nanoclay dispersion.

4.3. The effect of nanoclay content
XRD results and TEM micrographs indicate that an increase in nanoclay content works to the detriment of nanoparticle dispersion. The decrease in the \( d \)-spacing of the nanoparticles at higher nanoclay content is a proof to this finding. TEM micrographs also show an increase in the existence of intercalated structure and disappearance of exfoliated structure as the nanoclay content increases. The reason for this finding is that at higher nanoclay contents, more OTAC must first diffuse into the slurry and then react with the nanoclay surface. This simply means more time is required for the cation exchange reaction to take place. Hence, at a given feeding rate, i.e., given residence time, an increase in nanoclay content decreases average ALAMS packing density inside nanoclay platelets. The other reason is the spatial hindrance imposed on nanoclay platelets by the surrounding nanoparticles. This hindrance is more profound at higher nanoclay contents and deteriorates the dispersion of the nanoparticles. Nevertheless, the effect of nanoclay content on gas barrier and mechanical properties of the samples is rather complicated. An increase in nanoclay content triggers two opposing trends: On the one hand, nanoclay increase worsens its dispersion, which in turn works to the detriment of nanocomposite properties; on the other hand, the introduction of more rigid material, i.e., nanoclay, which has much higher modulus and almost zero gas permeability improves these properties. By taking a look at Figure 5a and 5b, it is obvious that the second trend is more dominant. In the end, it is interesting to mention that the increase in the tensile modulus and gas barrier properties of OTAC-modified nanocomposites prepared by slurry-fed melt intercalation are quite higher than those of the same nanocomposites prepared by conventional melt intercalation [42].

4.4. Permeability
Some would argue that the permeability properties of the OTAC-modified nanocomposites are poor and do not correspond to the expected values for a polymer nanocomposite. In response to this objection, it should be kept in mind that the films used in our barrier property measurements were compression-molded from which no noticeable nanoplatelets orientation can be achieved. Moreover, interfaces between different phases of nanocomposites, especially the polymers and the inorganic particles, could deteriorate the barrier properties by creating voids. Plus, adding nanoclay may alter polymer chains packing and increase free volume inside the matrix. Polymeric matrix polarity is also higher in case of composites. These reasons may lead to solubility enhancement in the matrix, which may work to the detriment of gas barrier properties of the composites. Lastly, our DSC results, not shown here, indicate that introducing nanoclay particles changes the crystallinity of the PE matrix. The effect of nanoclay on crystallinity behavior is complicated and requires to be addressed in another study. However, it is possible that this alteration in crystallinity may be in a way that causes the permeability to rise.

In this study, the permeability measurements were intended only to be used for comparative study of nanoclay dispersion in the samples; thus, the detailed study of permeability is not the focus of this paper. We, therefore, refuse to prove or disprove any of the mentioned probable causes because an all-inclusive elaboration on this subject will add considerable length to this paper. We, however, only demonstrate that how nanoparticles orientation
affects gas barrier properties by using model of Maksimov et al. [43]. This model, shown in Equation 1, is an empirical equation that relates the permeability of a composite with random nanoclay orientation to the permeability of a composite with nanoclay orientation perpendicular to the direction of diffusion. The relation has been stated as shown in Equation (1):

\[
K_c = \frac{1}{3}[K || + 2K_m(1 - \phi)]
\]

(1)

where \( K_c \) is the permeability of a composite with 3D random orientation, \( K || \) is the permeability of the composite when nanoplatelets are oriented normal to the direction of transversing gas. The second term on the right-hand side of the equation corresponds to the permeability of the composite when nanoplatelets are oriented parallel to the diffusion direction and it is assumed to be equal to the permeability of the matrix corrected for its volume fraction. After manipulation the equation can be written as shown in Equations (2–4):

\[
\frac{K ||}{K_m} = 3\frac{K_c}{K_m} - 2(1 - \phi)
\]

(2)

\[
\phi = \frac{\Delta \% \text{ wt}, \rho_c}{\rho_l}
\]

(3)

\[
\frac{100}{\rho_c} = \frac{\Delta \% \text{ wt}, \rho_l \text{LDPE}}{\rho_l} + \frac{\Delta \% \text{ wt}, \rho_l \text{LLDPE}}{\rho_l} + \frac{\Delta \% \text{ wt}, \rho_l \text{PEMA}}{\rho_l}
\]

(4)

Here, \( \phi \) is the volume fraction of nanoclay in the composites that can be calculated from Equation (3). The density of composite (\( \rho_c \)) can be calculated from Equation (4), where \( \rho_l \) is nanoclay density, \( \rho_l \text{LDPE} \) is LDPE density, \( \rho_l \text{LLDPE} \) is LLDPE density, and \( \rho_l \text{PEMA} \) is PEMA density. Based on Equation (2), gas permeability of composites with nanoplatelets normal to the diffusion direction can be estimated from composites with random orientation. This estimation offers an impression as to how nanoclay orientation affects gas barrier properties. The results are demonstrated in Figure 7; as can be seen, if our samples had nanoclay orientation completely normal to the diffusion direction, gas barrier property would be higher.

5. Mechanism

Figure 8 illustrates the schematic view of the four-step mechanism that we proposed to justify the role of water in the dispersion of nanoparticles during extrusion. Our proposed mechanism is as follow:

1. Nanoclay suspension is injected into the molten compound under high pressure. Molten compound consists of LDPE, LLDPE, PEMA, and OTAC.
2. During blending, nanoclay slurry would disperse in finer drops under shear field and OTAC would diffuse into the drops and would start a cation exchange reaction with the Na\(^+\) cation, binding with silicate layers [12]; at the same time, water would begin to evaporate because of high compound temperature.
3. As water evaporates it also would get into finer drops and is dispersed more uniformly within the compound. The evaporated water is removed by vacuum [18].

![Figure 7](image1.png)

**Figure 7.** Estimated reduction in oxygen permeability for the hypothetical composites with nanoclay orientation perpendicular to diffusion direction (light color), compared to the results of the prepared samples (dark color)

![Figure 8](image2.png)

**Figure 8.** The schematic view of the four-step mechanism that illustrates the role of water in the dispersion of the nanoparticles
Finally, although water is completely evaporated, the silicate layers are stabilized by OTAC and are uniformly dispersed by PEMA. The layers are fixed and they maintain their formation, as proved by TEM micrographs.

In the end, it should be noted that LLDPE, due to being more elastic than LDPE, has greater segmental motion; as a result, LLDPE chains have to submit to larger entropy reduction to diffuse into nanoclay galleries. Plus, the amount of PEMA is not high in the matrix, compared to LDPE. Hence, nanoclay platelets must be largely intercalated by LDPE chains [42]. It is also probable that PEMA reacted with PE during the high temperature blending in air, forming a graft copolymer in which MA units are attached to the PE chains [44].

6. Conclusions
We prepared samples by injecting Na⁺-MMT slurry into a co-rotating twin-screw extruder, in a designed set of experiments based on response surface method. After investigating the effects of modifier type, feeding rate, and nanoclay content on the structural, mechanical, and permeability properties of the samples, we found out that (1) chain length and packing density of ALAMS modifiers were key factors in producing composites with better nanoclay dispersion and properties; (2) although high nanoclay content was proved to have a deleterious effect on nanoclay dispersion, it brought about an evident enhancement in mechanical and gas barrier properties for OTAC-modified nanocomposites: 93 and 41% enhancement in tensile modulus and oxygen permeability reduction were recorded, respectively; (3) an increase in residence time was more effective in producing better nanocomposites than an increase in shear stress.

Additionally, the existence of intercalated/exfoliated structures in the nanocomposites was proved by XRD and TEM. Interestingly, the improvement in the properties of the nanocomposites prepared in this work was higher than those of prepared with conventional method. Our study indicates that, contrary to conventional melt intercalation, water-assisted melt intercalation process is largely diffusion-controlled rather than shear-controlled. For this reason, a new mechanism was proposed to justify this finding and also to describe the role of water in the dispersion of nanoparticles.

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References
DOI: 10.1021/ma991324e

DOI: 10.1021/ma9514333

DOI: 10.1002/1439-2054(20000601)279:1<1::AID-MAME1>3.0.CO;2-Q

DOI: 10.1016/S0032-3861(01)00473-6

DOI: 10.1016/S0032-3861(01)00552-3

DOI: 10.1016/j.matdes.2011.03.017

DOI: 10.1002/cjce.20377

DOI: 10.1007/s11029-008-9041-x

DOI: 10.1016/S0141-3910(02)00398-1