Maleic Anhydride Grafting onto HDPE by In situ Reactive Extrusion and its Effect on Intercalation and Mechanical Properties of HDPE/Clay Nanocomposites

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Received 30 May 2009; accepted 14 September 2009

Nanocomposites based on high-density polyethylene-grafted maleic anhydride (HDPE-g-MA) were prepared by in situ reactive melt mixing using a twin-screw extruder. The effects of different modified clays and maleic anhydride content on intercalation and mechanical properties were studied. The nanocomposites were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy techniques and tensile testing. The results show that clay I.30TC is suitable for preparation of HDPE-g-MA/clay nanocomposites. Grafting HDPE with MA contributed to higher degree of intercalation in clay particles and increases the tensile modulus of nanocomposite. MA content should be maintained at a certain level to improve the extent of intercalation. During the process, grafted maleic anhydride groups on HDPE backbone are converted to acid pendant groups. In order to determine the extent of cross-linking as a function of MA content, the gel content of the samples were measured. A significant improvement in the tensile modulus of the HDPE/clay nanocomposites was observed without changes in tensile strength and elongation-at-break values.

INTRODUCTION

Polymer nanocomposites have attracted great interest, because they exhibit enhanced mechanical, thermal, and barrier properties at low clay content [1]. Interest in polyolefin nanocomposites has emerged due to their promised improvement in packaging and engineering performance and application. Chemical modification of these resins has been used successfully to overcome problems associated with poor phase adhesion in polyolefin/clay systems [2].

Polyethylene as the most commonly used polyolefin has no polar group in its backbone. Therefore, it is expected that some difficulties would be encountered in preparing its homogeneous dispersion with hydrophilic silicate layers. The situation is improved somehow, when layered silicate is modified with alkylammonium functions to facilitate its interaction with polyethylene, because alkylammonium groups make the hydrophilic silicate surface to become organophilic. However, the organic modification of the silicate is
insufficient to achieve a good dispersion in highly hydrophobic polyethylene [3]. For this reason, functionalization of polyethylene through grafting has gained interest as an approach for the synthesis of polyethylene/clay nanocomposites [4-8]. The monomers grafted onto polyethylene are usually unsaturated functional monomers, such as maleic anhydride (MA) and acrylic acid (AA) and its derivatives [9]. This functionalization lowers the hydrophobicity of polyethylene, imparting polarity which makes it more compatible with hydrophilic clay.

Maleic anhydride is suitable for grafting onto polyethylene because MA has low reactivity towards itself and it grafted onto the polymer. Generally, one MA unit is attached onto the polymer backbones [4,5]. It is believed that grafting reaction starts with hydrogen abstraction by the alkoxyl radical upon decomposition of the peroxide initiator. The formed polyethylene macro-radical subsequently reacts with maleic anhydride monomer. Experimental results have shown that the incorporated MA unit is predominately a single succinic anhydride group [10-12] due to the poor homopolymerization capability of MA monomer. Many side reactions also take place during this free radical grafting reaction. For example, secondary formed macro-radicals undergo a coupling reaction to produce a cross-linked product. The detail of the grafting mechanism of MA onto polyethylene with peroxide initiator may be found in various reports [5,10].

Jeon et al. [13] reported that an intercalated clay structure was obtained in HDPE nanocomposites prepared by mixing HDPE with modified clay and dodecylamine, in solution. Exfoliation could be obtained only with in situ polymerization of HDPE and clay [14,15]. Wang et al. [16] suggested that when polyethylene has a higher grafting level of maleic anhydride (MA) than a critical level (0.1 wt%) and when the number of methylene groups in the alkylamine chains exceeds 16, polyethylene/clay nanocomposites may be completely exfoliated. Recent works on maleated polyethylene indicates that clay could be exfoliated in maleated polyethylene [17-19].

Polyethylene/maleic anhydride grafted polyethylene/organoclay nanocomposites were studied by Liang et al. [20]. They found that montmorillonite (MMT) intercalation in PE/PE-g-MAH/organo-MMT could be enhanced by increasing the content of PE-g-MAH, while using MMT modified with a cationic surfactant with a benzyl group or long alkyl chain. Mehrabzadeh et al. studied the melt preparation of high density polyethylene (HDPE)/clay, HDPE/polyamide (PA-6)/clay and HDPE/PA-66/clay nanocomposites [21,22]. Their results showed that exfoliation was likely to occur, under appropriate processing condition (e.g., sufficient shear force, mixing and residence time) and when suitable modification has been used.

The flammability properties of polyethylene/clay nanocomposites were evaluated, using a cone calorimeter [23,24]. The reduction in peak heat release rate was about 30-40%, for nanocomposite with low silicate loading (3-5 wt%). HDPE/clay nanocomposites show significant increases in complex melt viscosity, storage modulus, and loss modulus under shear [25]. Michael et al. [26] found that with ethylene-vinyl acetate copolymer as modifier in HDPE/clay nanocomposites, significant delamination of the intercalated clay occurred in thin stacks. The improved dispersion led to significant increases in the stiffness and flame resistance of the nanocomposite. It was found by Swain et al. [27] that ultrasonic treatment enhanced the intercalation of HDPE between the layers of clay and increased d-spacing up to 50%. Mechanical properties such as elongation-at-break, yield stress, toughness, and impact strength of ultrasonically treated nanocomposites, increased in comparison with the untreated nanocomposites. Choonghee et al. [28] evaluated the effect of strain rate on mechanical properties of semi-crystalline polymer/clay nanocomposites such as HDPE/clay nanocomposite. They reported that the rate of increase in the modulus was blunted as strain rate increased. The modulus increased gradually with increasing the strain rate, but the rate of increase diminished as crystallinity increased. HDPE/clay foams exhibit improved mechanical properties [29,30]. Flexural strength and modulus increase by adding only a small amount of clay (0.1-1 wt%).

Hwang et al. [31] reported that LDPE grafted maleic anhydride (LDPE-g-MA) nanocomposites containing up to 5 wt% clay exhibited better tensile
strength and wear resistance than their neat equivalents, using either the conventional or microcellular injection moulding process. Maleic anhydride and other related modifiers such as polyolefin elastomer grafted maleic anhydride (POE-g-MA) [32], propylene grafted maleic anhydride (PP-g-MA) [33,34] and POE elastomer (Engage 8150) [35] were used to improve the dispersion of organoclay in polypropylene.

In the present work, the effects of unmodified and various organically modified montmorillonite clays and maleic anhydride-grafting levels on the intercalation/exfoliation of high density polyethylene/clay nanocomposites are evaluated. The nanocomposites are prepared by reactive melt extrusion in a twin screw extruder.

EXPERIMENTAL

Materials
High density polyethylene Scalir 58A, $M_w = 142,200$ g/mol, density 0.957 g/cm$^3$ and MFI 0.43 g/10 min at 190°C was obtained from NOVA Chemicals (Calgary, Canada). Sodium montmorillonite clay (MMT), Cloisite 15A modified with dimethyl dehydrogenated tallow quaternary ammonium and Cloisite 30B modified with methyl tallow bis-2-hydroxy ethyl quaternary ammonium were provided by Southern Clay Product, Inc., USA. Nanomer I.30TC modified with octadecyl amine was obtained from Nanocor (USA). Maleic anhydride (MA) and dicumyl peroxide (DCP, initiator) were supplied by Aldrich.

Sample Preparations
High density polyethylene grafted maleic anhydride (HDPE-g-MA) samples with and without clay were produced by melt compounding in Berstorff corotating twin screw extruder (screw diameter: 17 mm, L/D = 25) at a constant rotating speed and feeding mass flow rate of 200 rpm and 2 kg/h, respectively. The temperature setting of six heating zones and the long slit die were 180, 180, 185, 190, 195, 200°C and 200°C (die). The clay was dried at 80°C for 18 h to remove any absorbed water. The concentration of the clay in the samples was 5 wt% and the clay was added using a separate feeder. MA and DCP were mixed with polyethylene, prior feeding into the extruder.

Characterization
X-ray diffraction was performed at room temperature using X-ray diffractometer, Rigaku Rotaflex, in the 2θ angle range 1-10 degree, in order to determine the extent of intercalation or exfoliation in the nanocomposites. The X-ray beam was Cu $k_\alpha$ ($\lambda = 0.1541$ nm), radiation operated at 45 kV and 130 mA. The interlayer spacing was calculated from the diffraction peak in the X-ray diffraction curve, using the Bragg equation [9].

Sections of samples with each having a thickness of 70 nm were prepared by ultra microtomy with a diamond knife. Transmission electron microscopy (TEM), Jeol, JEM 200 FX (Japan), was used to evaluate the dispersion, intercalation, and exfoliation of the clay in the nanocomposites. Dumb-bell specimens were cut from the extruded ribbons in extrusion direction for tensile testing. At least three and typically five replicated samples were tested for tensile data. Tensile bars conformed to ASTM D-638 type V procedure. Testing was conducted at a crosshead speed of 5 mm/min using an Instron model 4500 (Canton, MA, USA) Universal Testing Machine.

Fourier transform infrared spectroscopy (FTIR) was used to measure the relative MA grafting level in MA-grafted polyethylene prepared by melt extrusion. FTIR spectra were recorded on a Bomem Michelson Series-100 FTIR spectrometer from 400 to 5000 cm$^{-1}$. The relative peak height of the anhydride absorption band between 1860 and 1710 cm$^{-1}$ to the CH stretching peak (719 cm$^{-1}$) was taken as an approximate indicator of the extent of MA grafting. The samples were prepared using a Carver laboratory press at 200°C with 10 ton force to form thin films. The films were washed for 6 h and then dried in an oven at 90°C for 12 h prior to characterization in order to remove the unreacted MA monomers.

The gel content of the samples was determined based on ASTM D238 by an extraction procedure in boiling xylene for 5 h [36]. Around 1.5 g of crude sample was cut into a rectangular shape and placed within a steel cage. The exact weights of both the PE sample ($w_1$) and the PE sample and the steel basket
(w₂) were determined, and thus the gel content could be determined later. The steel basket containing crude PE sample was then immersed in boiling xylene, and the PE was allowed to dissolve for 5 h. The sample was placed in a vacuum chamber and allowed to dry for 12 h at room temperature. Then, the specimen was dried in an oven at 90°C for 1 h to remove any residual solvent. Once the sample was completely dry, it was reweighed (w₃). The gel content was then determined, using the following equation:

\[ Gel(\%) = 100 - \left( \frac{w_2 - w_3}{w_1} \right) \times 100 \]

**RESULTS AND DISCUSSION**

**Effect of Clay Modification**

Figure 1 shows the XRD patterns obtained for the organoclays 15A, 30B and I.30TC and their corresponding nanocomposites containing 0.2 wt% DCP and 1 wt% MA. Clay peaks shifted towards higher angle of 2θ are observed for HDPEA-g-MA/clay 15A (Figure 1a) and HDPE-g-MA/clay 30B (Figure 1b). In both cases, the d-spacing decreased, indicating some collapse in the structure. In the case of HDPE-g-MA/I30TC (Figure 1c), there is a shift of the d-spacing to a lower angle (2θ = 2.85º). This suggests some intercalation due to a higher level of compatibility between maleated PE and the clay modifier. Clay I.30TC is modified with octadecyl ammonium that has a more linear structure, compared to the other two clay modifiers (15A and 30B), therefore it does not introduce significant steric hindrance to intercalation.

The results regarding mechanical properties show that clay I.30TC improved the tensile modulus of its nanocomposites relative to the other types of clays. Figure 2 shows the tensile modulus of the nanocomposites samples with 1 wt% MA, 0.2 wt% DCP and 5 wt% of one type of clay for each sample. It can be seen that clay I.30TC yields the highest improvement in tensile modulus. The tensile modulus is increased by about 38% over the unmodified HDPE. Also the nanocomposites with 30B show a significant improvement of 26%. Although clay 30B is collapsed, the samples are still micro-composite and clay with high modulus can improve the modulus
of the samples.

Based on XRD and tensile test results, the rest of the experiments are reported only for clay 1.30TC systems.

Effect of MA Content on HDPE/Clay Nanocomposites

Figure 3 shows XRD patterns of samples with organoclay 1.30TC. The original d-spacing reflection peak of 1.30TC splits into two peaks in all the samples containing MA: one peak (lower 2θ angle) indicating some intercalation of polymer chains within the galleries, and the other peak (higher 2θ angle) corresponding to some collapse of the organoclay in the polymer matrix. The d-spacing peak of sample with 4 wt% MA shows the highest shift to

Figure 3. XRD patterns of organoclay 1.30TC and samples containing different amounts of MA with 5 wt% organoclay 1.30TC and 0.2 wt% DCP.

Figure 4. TEM micrographs of HDPE/Clay 1.30TC (5 wt%) with 4 wt% MA, and 0.2 wt% DCP: (a) uniform distribution of tactoids, (b) very small tactoid with few clay layers, and (c) its intercalated structure.
a lower angle, resulting in a $d_{001} = 3.92$ nm or 1.66 nm greater than the d-spacing of the clay. Above this level, e.g., 6 wt%, the interlayer spacing is reduced ($d_{001} = 3.75$ nm). This suggests that 4 wt% MA content is near the optimum level needed in order to achieve a higher level of intercalation.

TEM micrographs for HDPE/clay with 4 wt% MA content show a uniform distribution of small tactoids in HDPE (Figure 4a). At higher magnification one of the very thin tactoid with few clay layers can be seen (Figure 4b). At much higher magnification the micrograph shows the intercalated structure of the tactoid (Figure 4c). However, in the case of the HDPE/clay sample without MA, the distribution of the clay is not as uniform as that of the sample containing MA and with no sign of intercalation. This means that grafting of MA groups onto PE chains lowers the interfacial tension and increases the interfacial adhesion between the modified clay and the polymer existing in nanocomposite.

The above results are supported by the improvement obtained in tensile modulus (Figure 5). The highest increase in modulus over that of the unfilled polyethylene (1226 MPa) was obtained with MA content of 4 wt% (1854 MPa), representing an increase of 51%. The improvement of the modulus can be attributed to the presence of polar anhydride group, which promotes dipole and/or hydrogen bonding between the organoclay I.30TC particles and the maleated polyethylene, thus leading to improved dispersion, intercalation, and adhesion of clay in polymer matrix. Above 4 wt% concentration, MA probably interacts no longer with PE or clay, but reacts with itself (oligomerization of MA to PMA). Also, some phase separations could occur between polymer matrix and PMA, which make the sample weaker.

Other results of this study also indicate that the tensile strength and elongation-at-break of the HDPE/clay nanocomposites with 4 wt% MA content remain unchanged compared with those of the unfilled polyethylene. The tensile strengths of HDPE and HDPE/clay (5%)/MA (4%) were 24.2 and 24.5 MPa, and the values for elongation-at-break were 102% and 100%, respectively.

Infrared Spectroscopy
Figure 6 shows the FTIR spectra of HDPE and HDPE-g-MA (without organoclay) obtained by reactive extrusion. It is found that new peaks appear at 1718 and 1790 cm$^{-1}$ when MA is grafted successfully onto HDPE. The band at 1790 cm$^{-1}$ is due to asymmetric stretching modes of carbonyl (C=O) of saturated maleic anhydride, while the band at 1718 cm$^{-1}$ belongs to the symmetric stretching of carbonyl (C=O) of maleic acid [8,37,38]. Figure 6 also shows the relative peak heights of the anhydride absorption bands to the C-H stretching peak (719 cm$^{-1}$) of HDPE, which is a measure of the extent of MA grafting onto the PE backbone [39,40]. The relative peak height increases at 2 wt% MA, then it remains practically constant up to 6 wt% MA and
beyond that it decreases.

FTIR spectra of HDPE-g-MA/clay I.30TC are shown in Figure 7. There are two main observations made from Figures 6 and 7: (i) only one peak is observed in the carbonyl region at 1718 cm⁻¹, and not two peaks; (ii) a new peak appears at 3620 cm⁻¹. It is possible that the organoclay I.30TC interacts with maleic anhydride components to form maleic acid grafts, which results in only one absorbance peak at 1718 cm⁻¹; an indication that the carbonyl groups were changed to hydroxyl groups, as the new peak appears at 3620 cm⁻¹ which corresponds to O-H stretching. This MA ring opening could be due to an increase in water content within the extruder. Since the organoclay I.30TC is hygroscopic, some absorbed moistures could be released by the organoclay to hydrolyze maleic anhydride grafts, which result in a single peak at 1718 cm⁻¹. Another possibility is that the hydroxyl group (OH) in the clay and/or the hydrogen substituent of the organic modifier could change the maleic anhydride group to maleic or succinic acid groups.

The new characteristic band at 3620 cm⁻¹ corresponds to the O-H stretching [41] of the maleic acid groups. This peak is also observed at very low intensity in Figure 6. This is because the presence of organoclay I.30TC increases the grafts due to maleic acid while it reduces them due to maleic anhydride, resulting in a higher content of OH groups. The relative peak height of the maleic acid absorption band (1718 cm⁻¹) to the C-H stretching (719 cm⁻¹) of the HDPE reaches a maximum at 4 wt% MA (0.40). Therefore, the optimum amount of MA needed to achieve the highest grafted content is 4 wt%. This is in accordance with the tensile modulus results obtained from the sample with 4 wt% MA and is confirmed by XRD.

Cross-linking Analysis

In order to determine the extent of cross-linking in the samples, as a function of MA content, the gel contents of the samples were measured. Figure 8 shows the fractions of samples insoluble in xylene for different contents of MA, with or without clay. The extent of cross-linking of PE decreases to 3.73% with MA content of up to 4 wt%, and yet it increases above 4 wt% MA. There is a possibility that at lower concentration, the PE radical sites exceed the PMA (polymer-MA.) radicals. The PE macro-radicals couple with each other, since the cross-linking is a dominant reaction [4]. As the amount of MA increases the PE radicals decrease and the PMA radicals increase. Since MA is a strong electron acceptor, MA radicals would be expected to undergo disproportionation rather than coupling reactions [5,10,12]. At a higher MA concentration (4 wt %), MA no longer interacts with PE, as it reacts with itself, forming poly(MA) which is not soluble in xylene; leading to increased xylene insoluble fractions [42]. This is in agreement with the mechanical and XRD results obtained for nanocomposite samples with 6 and 8 wt% MA in
which some phase separations may occur between poly(MA) and HDPE.

**CONCLUSION**

XRD patterns and TEM micrographs show an intercalation structure and uniform distribution of small clay (I.30TC) tactoids in the HDPE matrix. Among the organoclays considered, I.30TC was the suitable clay in HDPE and HDPE-g-MA matrices. Higher degrees of intercalation and tensile modulus were obtained in the presence of MA, suggesting that the polar anhydride groups promote dipoles and/or hydrogen bonding between the organoclay I.30TC and polyethylene. Thus, MA grafting leads to improved dispersion and adhesion of the clay in polymer matrix. An optimum level of MA (ca. 4 wt%) is needed to achieve the desirable degrees of dispersion and adhesion, in addition to good intercalation levels. The grafted anhydride groups on the PE backbone appear to change to acid pendant groups in the presence of organoclay I.30TC.

**ACKNOWLEDGEMENTS**

This work was supported by grant from the Natural Sciences and Engineering Research Council of Canada. The Authors wish to extend their appreciations to NOV A Chemical of Canada for Supplying HDPE.

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