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Factors affecting the dispersion of montmorillonite in LLDPE nanocomposite

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Summary

Physical properties, such as gas permeability, tensile modulus, and dispersion behavior of nanopowder in linear low density polyethylene/ montmorillonite nanocomposite were investigated as a function of compatibilizer and processing conditions. Nanocomposites were prepared using twin screw extruder and internal mixer under various processing conditions. XRD and TEM were used to evaluate the degree of intercalation/exfoliation of montmorillonite. Significant changes of dispersion behavior of montmorillonite and physical properties were observed depending on the processing conditions and concentration of compatibilizer.

Introduction

Montmorillonite (MMT) is one of widely used layered silicates and it consists of layers separated by van der Waals gap called gallery or interlayer. These interlayers are occupied by metal cations and those make difficult to disperse MMT in polymer matrix. Replacing the metal cations with alkylammonium cation is well known method to improve the dispersion of the MMT in polymer matrix. Various polymer systems are used to form polymer-MMT nanocomposites [1,2]. Linear low density polyethylene (LLDPE)/MMT nanocomposite has been prepared by means of melt compounding [3-5] or in-situ polymerization [5]. In melt compounding, chemical structure of polymer and processing conditions, such as screw speed and throughput rate, are important factors to determine the degree of dispersion of MMT [6-12]. Dennis et al showed that type of extruder and screw design affected the dispersion and delamination of MMT [12].

Polypropylene (PP), a typical nonpolar polymer, is thought that homogeneous dispersion of the silicate layers in PP is difficult due to its nonpolar characteristic. Recently, functional oligomer or comonomer was used as a compatibilizer to improve the dispersion of silicate layers and maleic anhydride (MAH) grafted polyolefin has been widely used as a compatibilizer [6-12]. Kato et al. used MAH grafted PP oligomer to improve the dispersion of MMT in PP and reported that number of repeating units per polar group of MAH played a critical role for the exfoliation of MMT in MMT/PP nanocomposite [7]. Kawasumi showed that low concentration of

MAH in MAH grafted PP oligomer resulted in better exfoliation behavior in MMT/PP nanocomposite [8]. Improvements of exfoliation are attributed to the enhanced miscibility between PP and MAH grafted PP oligomer. Recently, Zhang et al. reported that MAH grafted PP polymer also enhanced the dispersibility of MMT [11]. Improved tensile strength and modulus were observed in LLDPE/MMT nanocomposite. Wang et al studied the effect of maleic anhydride grafted polyethylene (PEMA) in MMT/LLDPE mixture and found that the grafting level of maleic anhydride of PEMA is crucial factor for the exfoliation of MMT [2].
This study investigates the effects of compatibilizer and processing conditions on the intercalation/exfoliation behavior of MMT/LLDPE system. LLDPE and MMT are melt blended in internal mixer or co-rotating twin screw extruder. PEMA with different maleic anhydride contents are used as compatibilizer.

Experimental

Materials

Linear low density polyethylenes (LLDPE SN318, Hyundi Petrochemical Co.) with octene comonomer were used as a matrix polymer. Dimethyl dioctadecyl ammonium-modified montmorillonite (Cloisite^{TM} 15A) was supplied by Southern Clay Products Inc and it was used as received. 0.5 wt% maleic anhydride grafted PEMA (Aldrich) and 1 wt% maleic anhydride grafted PEMA (Polybond^{TM} 3009, MI= 5g/10 min, Uniroyal) were used as a compatibilizer and those were designated as PEMA-05 and PEMA-10, respectively.

Nanocomposite Preparation

LLDPE, PEMA and MMT were mixed simultaneously and compounded using internal mixer or co-rotating twin screw extruder. Concentration of MMT was varied from 1 to 5 wt%. For internal mixer, rotor speed was 80 rpm and mixing time was 20 min. Processing temperature was 170 °C. For twin screw extruder (D= 25 mm and L/D=30), barrel temperatures were 150 – 170 °C under various throughput rate. The amount of PEMA was based on LLDPE, while MMT concentration was based on PEMA/LLDPE mixture.

Characterizations

Degree of intercalation/exfoliation was evaluated using X-ray diffractometer (XRD). The thin film of nanocomposite was prepared by pressing at 170 °C. X-ray diffraction patterns of the nanocomposite film were obtained by using M18XHF-SRA diffractometer with CuKα radiation (Macscience Inc). It was scanned from 1.5-12o and scanning speed was 2o/min. The dispersibility of MMT in the nanocomposite was observed directly using transmission electron microscopy (TEM). A transmission electron micrograph was obtained with a JEOL 200CX using an acceleration voltage of 200kV. Young's modulus was measured using tensile tester (Tensilon/UTM-III, Toyo-Baldwin) and crosshead speed was 50 mm/min. Test specimen was prepared by pressing at 170 °C for 1 min. 10 different specimens were used to obtain the properties and results were quite reproducible. Gas permeability of N_2, O_2, CO_2 at 35 °C was measured with gas permeation analyzer (GPA 2001, BS Chemical Co.) under 4 atm. pressure. Sample thickness was 0.1 mm.

Results and discussion

The interlayer distance of MMT/LLDPE/PEMA nanocomposites is measured using X-ray and its values at various concentrations of PEMA-05 and PEMA-10 are shown in Fig. 1. The concentration of MMT is 5 wt% and nanocomposites are prepared using internal mixer. Little increase of interlayer distance is observed for MMT/LLDPE nanocomposite without compatibilizer and it indicates that intercalation of MMT is not significant. Maleic anhydride grafted polyolefin's have been known as an excellent compatibilizer to improve the dispersion of MMT in polyolefin/MMT systems. The role of maleic anhydride grafted polypropylene (PP-g-MA) in polypropylene/MMT nanocomposite has been studied by several investigators. Kato et al. proposed that PP-g-MA molecules diffused into the galleries first and it induced the easy diffusion of following polypropylene molecules [7]. Increasing interlayer distance of MMT is observed with the concentration of PEMA's. It is observed that degree of exfoliation of MMT is strongly dependent on the concentration of PEMA and the concentration of grafted maleic anhydride in PEMA. Improved intercalation is obtained with increasing concentration of PEMA's, while exfoliation begins at different concentration of PEMA depending on the concentration of grafted maleic anhydride. For PEMA-10 exfoliation behavior is observed at 10 wt%, while PEMA-05 still shows intercalation behavior up to 20 wt%. Wang et al also showed that concentration of maleic anhydride is important for the exfoliation of MMT in MMT/LLDPE nanocomposite [4].

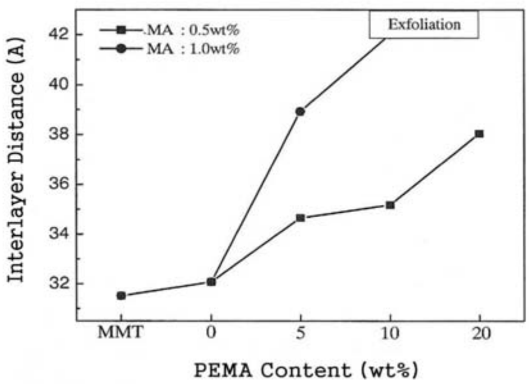

Figure 1 Interlayer distance of LLDPE/MMT/PEMA nanocomposite with various PEMA content.

Tensile modulus of MMT/LLDPE nanocomposites with various concentration of PEMA-10 is shown in Figure 2. Tensile modulus increases 40-50% by the addition of PEMA-10 and it tends to level off from 5 wt% PEMA-10. Increasing tensile modulus can be attributed to the improved dispersion of MMT by the addition of compatibilizer. Ranade et al., also showed the increase of ultimate tensile strength and modulus by the addition of maleic anhydride grafted LLDPE in MMT/LLDPE nanocomposite [3]. Figure 3 shows the effect of grafted maleic anhydride concentration in PEMA on the tensile modulus. PEMA concentration is 5 wt%. Higher tensile modulus is observed for PEMA-10 and it also can be attributed to the better dispersion of MMT for PEMA-10 than PEMA-5.

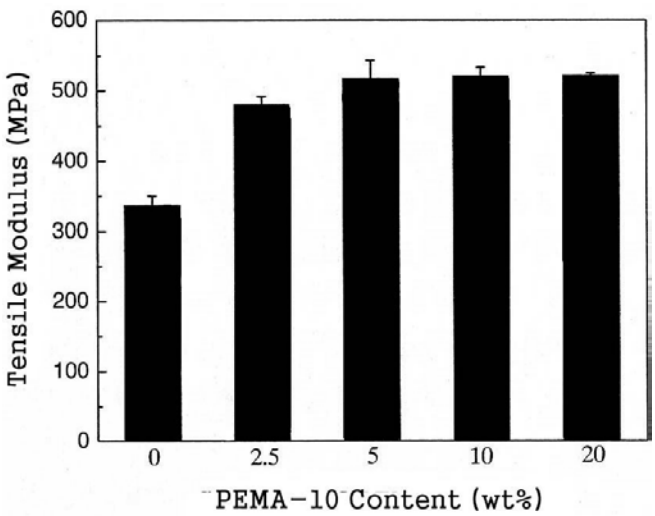

Figure 2 Tensile modulus of LLDPE/MMT/PEMA-10 nanocomposites with various PEMA content.

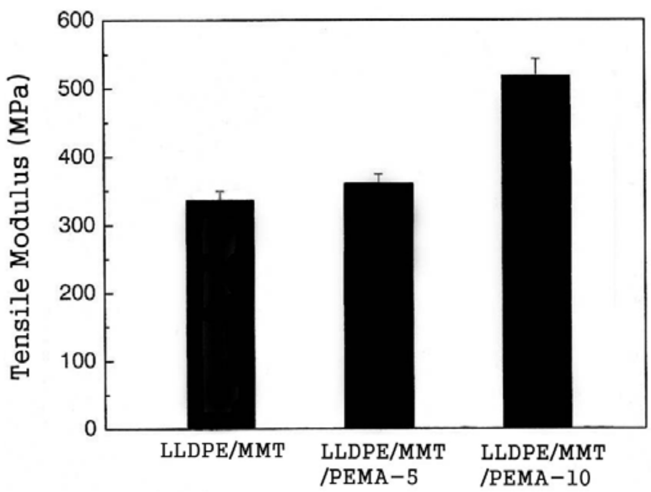

Figure 3 Effect of grafted maleic anhydride concentration on the tensile modulus of LLDPE/MMT/PEMA.

Nitrogen, oxygen and carbon dioxide barrier characteristics of nanocomposite with various concentration of MMT are shown in Figure 4. Barrier property is improved with increasing concentration of MMT. Figure 5 shows the effect of concentration of PEMA-10 on the gas barrier property. Gas barrier property is improved with increasing concentration of PEMA-10 for all gases and it is attributed to the improved dispersion of MMT. Improved gas barrier characteristic due to exfoliation/ intercalation is also reported in Nylon/MMT nanocomposite [13]. For nanocomposite materials, gas permeability is strongly affected by tortuosity factor and constraining

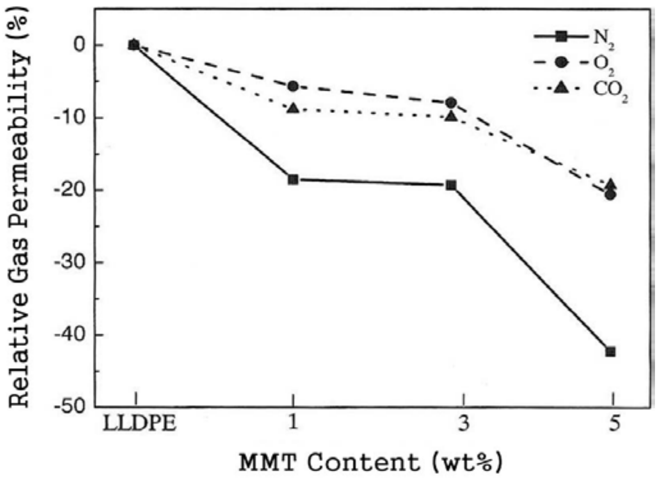

Figure 4 Gas barrier characteristics of LLDPE/MMT nanocomposites at various MMT content.

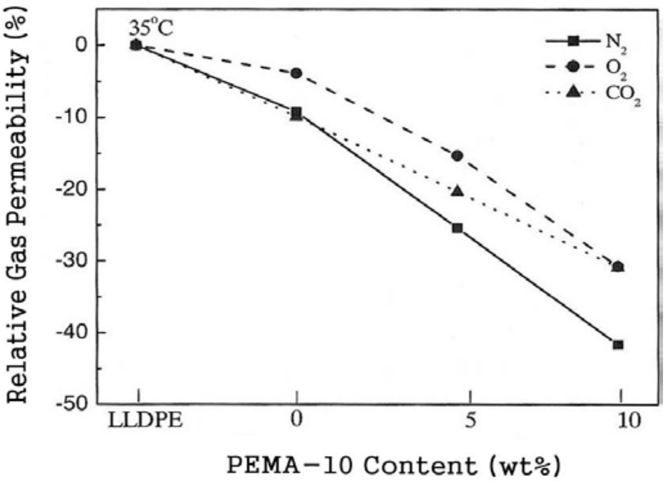

Figure 5 Gas barrier characteristics of LLDPE/MMT/PEMA nanocomposites at various PEMA-10 content.

effect of nanoparticles on the amorphous chains and diffusion coefficient can be expressed by those factors [14]. The diffusion coefficient is kinetic in nature and largely determined by polymer-penetrant dynamics and it depends on not only the nature of polymer but also the penetrant size. Kinetic diameters of N_2, O_2 and CO_2 are 3.64Å, 3.46Å, 3.3Å, respectively [15]. Thus increasing tortuosity path and restriction of chain mobilization due to the presence of MMT have more profound effect on the movement of larger size penetrant, N_2, than O_2 and CO_2.

Figure 6 shows the effect of mixing equipment and processing condition on the intercalation/exfoliation behavior of LLDPE/MMT nanocomposites. No compatibilizer is added for these experiments. The mean residence times in co-rotating twin

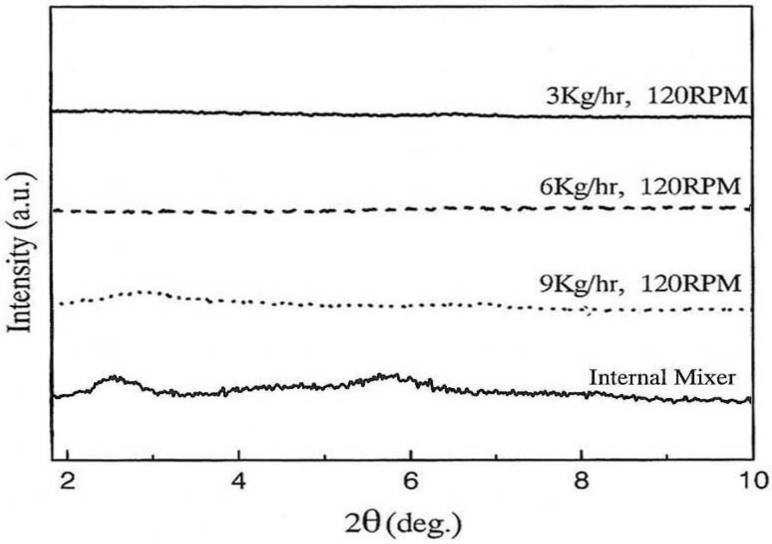

Figure 6 XRD patterns of LLDPE/MMT at different processing conditions.

screw extruder are 61, 52 and 38 seconds for 3, 6 and 9 kg/hr throughput, respectively, while residence time in internal mixer is 20 min. For internal mixer, distinct (001) peak is observed and it shows that little dispersion of MMT is achieved by melt compounding, while intercalation or exfoliation behavior is observed for twin screw extruder depending on the throughput. This is an interesting result. Even though residence time in internal mixer, i.e. mixing time, is 20 – 30 times longer than that of twin screw extruder, performance of twin screw extruder is better than that of internal mixer. Dennis et al. observed that delamination of MMT in MMT/nylon nanocomposite using the single screw extruder was worse than that in co-rotating or counter-rotating twin screw extruders in spite of relatively long residence time of single screw extruder and that was attributed to the presence of back mixing in the single screw extruder [12]. He also demonstrated that shear intensity was an important factor to decide the delamination and dispersion of MMT.

At 9 kg/hr throughput rate in twin screw extruder, little dispersion of MMT is observed, while exfoliation behaviors are observed at 3 and 6 kg/hr throughput rate as shown in Fig 6 and this is confirmed by TEM micrographs as shown in Fig 7 in which the dark lines are the MMT layers each of which is dispersed homogeneously in a matrix. These results can provide two facts: 1) MMT can be exfoliated with LLDPE without compatibilizer using appropriate equipment and processing condition and 2) processing condition, i.e. residence time in our study, is one of crucial factors to induce sufficient exfoliation.

Specific energy consumption (SEC) represents the amount of energy required to extrude per unit mass of material and it has been known as an important parameter to determine the measure of the total deformation that the material is exposed during the extrusion process and a decrease of SEC with increasing feed rate was reported [16]. Thus low deformation of material at high throughput rate can cause poor delamination of stacks of MMT particles. Mean residence time in extruder is also an important factor to establish an exfoliation. Diffusion of polymer chain into the MMT galleries was proposed as a intercalation/exfoliation mechanism of MMT [17]. It means that sufficient time is needed to allow the penetration of polymer molecules into MMT galleries. Thus, short residence time, i.e. high throughput rate, can not be enough for the diffusion of LLDPE molecules into MMT galleries. Dennis et al. reported that intercalation was strongly dependent on the residence time and shear intensity. Increasing the mean residence time in the extruder generally improved the delamination and dispersion of MMT [12].

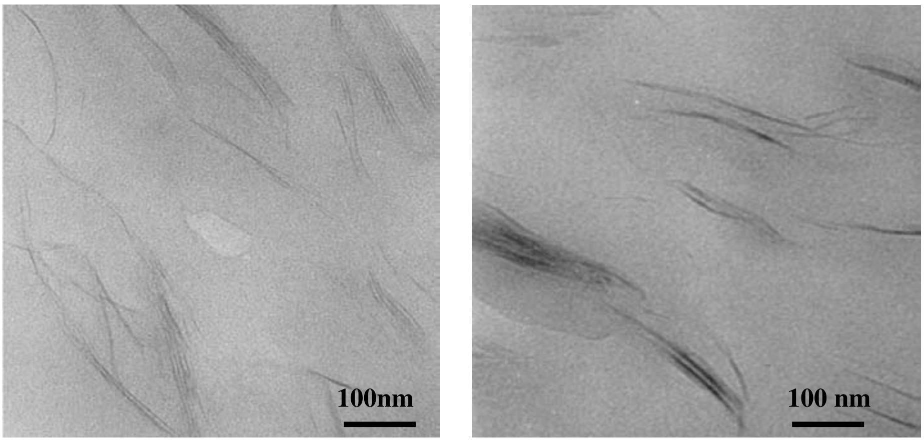

Figure 7 TEM micrographs of 3 kg/hr (left) and 9 kg/hr (right) throughput rate in twin screw extrusion.

Conclusions

LLDPE/montmorillonite nanocomposites with/without maleic anhydride grafted polyethylene are prepared using melt blending. Melt blending is done by internal mixer or co-rotating twin screw extruder. Interlayer distance of MMT increases with concentration of PEMA and also concentration of grafted maleic anhydride of PEMA. Tensile modulus is increased and gas barrier property is enhanced with increasing concentration of PEMA and it is attributed to the improved intercalation/exfoliation. Twin screw extruder induces better intercalation/exfoliation behavior than internal mixer and critical residence time exists to induce intercalation/exfoliation in twin screw extruder.

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