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Effect of Mechanical Milling on the Thermal Behavior of Polyethylene Reinforced with Nano-sized Alumina

In the current study the dependency of morphology and thermal behavior of medium density polyethylene (MDPE) powder reinforced with 0, 5, 10 and 15 wt.% nano-sized Al₂O₃ particles on mechanical milling were studied. The effects of milling time on the morphology and the thermal behavior were investigated by Transition Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetery (DSC) and Thermo Gravimetric Analyzer (TGA). The TEM micrographs obtained from the nanocomposites proved that mechanical milling could be an adequate method to disperse nano-sized hard particles throughout the polymer. The SEM micrographs of pure MDPE showed that regular shape powder converted to the flake shapes as milling time increased. Also the results illustrated that an increase in milling time caused to decrease the agglomeration of alumina. The DSC profiles of samples elucidated that ball milling had little effect on crystalline temperature and melting point of all materials including MDPE and its nanocomposites. The nanocomposite exhibited more thermal stability than pure polyethylene proved by TGA tests.

1 Introduction

It is well known that properties of a polymer can be enhanced through the formation of a nanocomposite of that material. In addition, formation of polymer-matrix nanocomposite may promote heat distortion temperature, permeability and fire retardancy of polymers (Jordan, 2005; Paul, 2008; Hussain, 2006, Chen, 2005; Gacitua, 2005). The selection of nanoparticles depends on the desired thermal, mechanical and electrical properties of the nanocomposites. For example, Al nanoparticles are often selected due to their high conductivity; calcium carbonate particles are chosen because of the relative low cost of the material, and Al_2O_3 nanoparticles are used for increasing thermal stability.

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The preparation of polymer-matrix nanocomposites is a challenging area that makes considerable effort. Researchers (Hussain, 2006; Chen, 2005; Nicloais, 2005; Pomogalio, 2005) have tried a variety of processing techniques to fabricate them. The techniques include melt mixing, in-situ polymerization, sol-gel and ball milling technique.

In the case of organic–inorganic nanocomposites, the strength or level of interaction between the organic and inorganic phases is an important issue. Physical or simple mechanical mixing like melt mixing and ball milling causes a weak interface, e.g., van der Waals forces (Hussain, 2006). On the other hand, a strong chemical covalent or ionic–covalent bond between the organic and inorganic phases, such as sol gel technique, is the typical preparation method for the organic–inorganic nanocomposites (Chen, 2005).

High-energy mechanical milling is one of the effective processes for fabricating polymer-ceramic composite powders as it allows incorporation of the ceramic phases into the polymer particles. In this technique, polymer nanocomposites with nano-sized ceramic particulate reinforcement can be produced through numerous deformations, fracturing and cold welding events. After a certain period of milling, powder microstructure homogeneity can be achieved. In addition, simplicity, high efficiency and low cost of ball milling method has impressed scientist to attention. For instance, in 2005 Mangiacapra et al. considered the dispersion of the clay inside the pectin matrix. The process included the exfoliation of the clay sheets via ball milling. Through analyzing the physical properties such as: thermal degradation, elastic modulus, adsorption and diffusion of water vapor and oxygen, it was found that they all were improved in the nanocomposites (Mangiacapra, 2006). In other research, fumed silica nanoparticles with 14 nm of diameter were blended with poly methyl-methacrylate, PMMA, by means of a high energy ball milling process. AFM analysis revealed how the blending process allows obtaining a very homogeneous dispersion of the nanoparticles within the PMMA (Castrillo, 2007). In the study, Castrillo (2007) demonstrated the possibility of preparing transparent nanocomposites with excellent moldability. Vertuccio et al. (2009) showed that the structural organization and physical, mechanical, and thermal barrier properties of Nano clay reinforced PCL/starch blends correlated with the milling conditions. In the mentioned study, it was cleared that the milling process not only is a

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promising compatibilization method for immiscible PCLstarch blends, but it can be also used to improve the dispersion of nanoparticles into the polymer blends. Martínez-Gallegos et al. (2009) produced layered double hydroxides in poly ethylene terephthalate by in-situ polymerization and mechanical grinding. They reported that the exfoliation and dispersion of the inorganic-organic hybrid in the polymer phase was achieved and improved thermal properties (Martínez-Gallegos, 2009).

The mechanical and thermal properties of polymer-matrix composites by the presence of nano-sized filler were studied. It was demonstrated that well-dispersed nanoparticles in the polymer matrix can significantly enhance Young's modulus, impact strength and thermal barrier properties (Garcia, 2004; Lazzeri, 2005). In another work the role of addition of about 10 wt.% of nano-sized calcium carbonate to polyethylene on tensile properties, viscosity and dimensional stability has been investigated by some researches. For example, Lazzeri et al. (2005) showed that Young's modulus of PE can be promoted of about 70% as 10 vol.% nano-sized calcium carbonate was added.

Alumina is a ceramic metal oxide of great importance. The material is used as building material, refractory material, electrical and heat insulator, due to its high strength, corrosion resistance, chemical stability, low thermal conductivity, and good electrical insulation (Ridzuan Noordin, 2010). The incorporation of nano-scaled alumina in poly propylene (PP) has improved the mechanical properties (Jung, 2006) and increased the wear resistance of PP by nearly two times (Bhimaraj, 2005). Mohamad et al. reported that the presence of uniformly distributed alumina nanoparticles has efficiently hindered the polymer chains movement during deformation and contributes to the high stiffness of the composites (Mohamad, 2008).

Alumina presence thermoplastic and thermosetting polymeric materials are also gaining wide application as surface coatings. Generally, it has been found that the addition of alumina nanoparticles enhances the mechanical and thermal properties of polymers. It is required to disperse the nanoparticles uniformly throughout the polymer. At low volume fraction the nanoparticles could be distributed uniformly across the polymer (Ridzuan Noordin, 2010). Various methods have been adopted to facilitate good dispersion. The methods include mechanical milling of alumina nano fibers (Santos-Beltran, 2007) and mechanical milling followed by hot extrusion (Flores-Zamora, 2007).

Crystallinity is an important characteristic of semi-crystalline polymers which determines the mechanical and thermal properties such as yield stress, dimensional stability, elastic modulus, specific heat capacity and etc. (Yu, 2004).

Chan et al. (2002) showed that the degree of crystallinity of a polypropylene system changed very little with the addition of CaCO₃ nanoparticles. On the other hand, the peak crystallization temperature was increased by around 10 °C with the addition of the CaCO₃ particles. Scanning electron microscopy (SEM) showed that the spherulites in the pure system had an average size of around 40 μ m, but no spherulites could be seen when CaCO₃ nanoparticles were added to the system. It is possible that the spherulites were too small and they were not detected by SEM (Chan, 2002). Based on the literature survey, there is little evidence of study concentrated on polyethylene-alumina nanocomposites. Thus, the main goal of this study is to fabricate polyethylene-alumina nanocomposites by high energy ball milling as a new method. Also, it will be tried to elucidate the role of both ball milling and alumina nanoparticles on morphology, crystallinity index and thermal properties of medium density polyethylene.

2 Materials and Methods

2.1 Materials

Medium density polyethylene (MDPE) granules obtained from Scoopa Company, Korea was used as matrix. The specification of used MDPE was summarized in Table 1. Alumina powder was provided from Nanolin Company with average particle size of about 80 nm and used as reinforcement.

2.2 Experimental Procedure

The mixture of pure medium density polyethylene and different weight percent of alumina (0 to 15 wt.%) were put in to a stainless steel vial with stainless steel balls with different sizes (10, 12 and 15 mm in diameters). The ratio of ball mass to the powder was kept constant 20:1. Ball milling was carried out using planetary high energy ball milling machine (PM-200) at 250 min⁻¹, for 5, 10, 20 and 40 hours. Then the produced nanocomposites were characterized by SEM, TEM, DSC and TGA. The morphology and microstructure evolution of the powders during milling were observed by SEM (LEO 1450) and TEM (LEO 912 AB). A Perkin-Elmer DSC-60, interfaced to a PC was used to measure the thermal properties of samples. The heating rate of 10°C/min and sample weight of 1.5 to 2 mg was used to obtain results. The heating scan of the cycle: 30 to 200 °C (10 °C/min); 200 to 30 °C (100 °C/ min); 30 to 200 °C (10 °C/min), was selected for getting information. Thermo gravimetric analysis (TGA) experiments under air atmosphere were carried out in a TGA-50 Shimadzu. The sample weights varied from 4 to 4.5 mg. The heating rate for the dynamic conditions was 10°C/min, and the airflow was 60 ml/min.

| Physical properties | | | | | | |
|------------------------|-------------------------|--|--|--|--|--|
| Melting point | 127 °C | | | | | |
| Semi-solid temperature | 117°C | | | | | |
| Density | 0.937 g/cm ³ | | | | | |

Table 1. Physical properties of medium-density polyethylene

3 Results and Discussion

3.1 Morphological Analysis

To improve thermal properties through uniform dispersion of inorganic nanoparticles into the matrix, synthesize of MDPE/ Al_2O_3 through high energy ball milling method was carried out. Alumina nanoparticles as reinforcements are embedded in PE matrix via this method. The effects of ball milling on physical reactions are due to the high temperatures and pressures which develop during the scission in PE. Fig. 1 shows TEM micrographs taken from the nano-sized alumina powder used as reinforcement. It is indicated that the average particle size is about 80 nm.

Fig. 2 shows the effect of mechanical milling on the morphology of the unreinforced polyethylene powder. As Fig. 2A illustrates, the as-received powder exhibit semi-spherical shape with relatively broad size distribution. After 5 h milling, the in-



Fig. 1. TEM micrograph of nanoscaled alumina







B)

D)



Fig. 2. SEM micrographs of milled MDPE powders, (A) 0 h, (B) 5 h, (C) 10 h, (D) 20 h

itial particles were deformed and a change from spherical to irregular shape was noticed (Fig. 2B). The average size of particles was also increased slightly, because of cold drawing phenomenon. When longer milling time was applied, the polyethlene particles were flattened and flake like plate were formed (Figs. 2C and D). Micro-welding and fracture between the particles was also observed. At longer milling time of 20 h, the fragmentation of the flattened particles was detected, although the shape of particles was still flake-like and irregular (Fig. 2D).

TEM examinations provided information on the PE/Al₂O₃ nanocomposite. The good adhesion was also revealed from the TEM micrographs shown in Fig. 3. When hard particles are added to polyethylene powder, the chain scission occur earlier, the agglomerations are broken to smaller pieces, and their morphology changes because of nanodispersed alumina disrupts the ordered structure of polyethylene. This is because alumina is brittle and acts as a stress concentration point and causes to failure of crystallites. After 20 h milling, the initial particles were deformed and a change from irregular to bean shape was noticed (Fig. 3A, B). The experimental results indicate that increasing ball milling time enhances alumina dispersion and decreases size of particles. 40 h of milling was sufficient to reduce the alumina size to ~60 nm (Fig. 3C, D). Note that the fragmentation of the bean-like particles and distribution of nanoparticles may occur concurrently. It can be expected that for a given volume fraction (15 wt.%), the smaller mean size of particles and the narrower size distribution will enhance the homogeneity of the nanocomposite. The shape of the particles also plays a significant role. It can be said that particles with more regular shapes should be more effective at a given size and volume fraction. It is important to highlight here that particles with irregular shapes of alumina can be prepared from this method with a specific size, at least, as an average and with a homogeneous distribution in matrix.

C)



Fig. 3. TEM micrographs of MDPE-5 wt.%

3.2 Thermal-oxidation Stability

Fig. 4 shows the thermal degradation samples of the MDPE and the two nanocomposites under dynamic conditions in air flow. The established mechanisms for polyethylene pyrolysis involve steps of formation of free radicals and abstraction of hydrogen from the polymer chains leading to a molecular weight decrease and finally, to the formation of volatile products. The thermal oxidative degradation temperatures corresponding to a mass loss of 10% (T_{-10} %) and 50% (T_{-50} %) (Lu, 2006) respectively, are listed in Table 2. It can be seen that the nanocomposite exhibits higher thermal-oxidation stability in terms of T_{-10} % and T_{-50} % than that of either the pure polymer. As it is observed from Fig. 4, the polyethylene nanocomposite showed higher thermal-oxidative stability than that of pure MDPE, and there is a 14% reduction in mass loss for MDPE/15 wt.% Al₂O₃ in comparison with pure MDPE at the temperature range from 277 to 427 °C. The improvement in



Fig. 4. TGA dynamic runs in airflow of MDPE samples and its nanocomposites

 Al_2O_3 at various milling time, (A) and (B) 20 h, (C) and (D) 40 h

thermal stability may depend on the two facts; first one is related to formation of carbon-oxygen bonds during milling; therefore formation of this structure makes the degradation more difficult. The other is interaction among nanoparticles and matrix that causes to embed the reinforcements in polyethylene. Listed temperatures in Table 2 show the remarkable improvement in the thermal behavior of nanocomposite which results from PE oxidation without water and catalyst at sufficiently high temperature. This phenomenon especially will take place if alumina is present. Reinforcements with high aspect ratios are able to sustain high temperature and hinder the heat and mass transfer efficiently. That is the reason why the nanocomposite exhibits the lowest mass loss rate at the temperature range from 277 to 427 °C.

3.3 DSC Analysis

In Table 3 the evolution of thermal stability of neat MDPE and nanocomposite samples as a function of milling time and volume fraction of alumina is shown. It can be seen that the crystallization rate between neat MDPE and MDPE/15 wt.% Al₂O₃ decreases with increasing crystallization temperature as it increases from 113.8 °C to 115 °C in constant ball milling time. However, the crystallization rate increases with the increase of Al₂O₃ content. In addition, Fig. 5 shows cooling scan of samples at constant milling time of 10 h. The intensity and broadness of peaks has decreased as volume fraction of alumina increases. This result suggests that nanoparticles can serve as a heterogeneous nucleation agent for MDPE crystallization.

Using the mentioned above temperature program the following information can be achieved: T_m: The melting temperature of polymer, ΔH_m : Heat of melting, the amount of energy which

| Samples | Ball milling time h | T_10 % ℃ | T_50 % ℃ | Mass loss (277–427 °C) % | |
|--------------------------------------|------------------------|-------------|-------------|--------------------------------|--|
| Neat PE | 0 | 352 | 422.7 | 50 | |
| Neat PE | 10 | 340.5 | 432.5 | 43 | |
| PE/5 Al ₂ O ₃ | 5 | 398.8 | 438 | 38 | |
| PE/5 Al ₂ O ₃ | 10 | 399.5 | 442.8 | 37 | |
| PE/5 Al ₂ O ₃ | 20 | 412.8 | 443.1 | 36 | |
| PE/5 Al ₂ O ₃ | 40 | 425.1 | 449 | 11 | |
| PE/15 Al ₂ O ₃ | 5 | 407.14 | 441 | 36 | |
| PE/15 Al ₂ O ₃ | 10 | 407.6 | 452 | 29 | |
| PE/15 Al ₂ O ₃ | 20 | 415.5 | 451.1 | 27 | |
| PE/15 Al ₂ O ₃ | 40 | 426.6 | 452.5 | 9 | |

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Table 2. The thermal oxidative degradation temperatures corresponding to a mass loss

| Samples | Ball milling time h | T _m °C | T _c °C | $-\Delta H_m$ J/g | $\Delta H_{m}/(arphi_{PE})$ J/g | $-\Delta H_c$ J/g | Degree of crystallinity |
|--------------------------------------|------------------------|----------------------|----------------------|----------------------|------------------------------------|----------------------|----------------------------|
| Neat PE | 0 | 129.3 | 112.5 | 159 | 159 | 149.7 | 54.2 |
| Neat PE | 10 | 128 | 113.8 | 148.9 | 148.9 | 147.2 | 50.8 |
| PE/5 Al ₂ O ₃ | 5 | 128.1 | 114.3 | 144.66 | 152.3 | 148 | 51.9 |
| PE/5 Al ₂ O ₃ | 10 | 127.9 | 114.8 | 146 | 153.7 | 147 | 52.4 |
| PE/5 Al ₂ O ₃ | 20 | 127.7 | 114.9 | 137.6 | 144.8 | 142 | 49.4 |
| PE/5 Al ₂ O ₃ | 40 | 127.2 | 115.2 | 129.5 | 136.3 | 136.4 | 46.5 |
| PE/15 Al ₂ O ₃ | 0 | 128 | 114 | 130.7 | 153.7 | 141.5 | 52.4 |
| PE/15 Al ₂ O ₃ | 5 | 127.9 | 114.7 | 128.3 | 150.9 | 140 | 51.5 |
| PE/15 Al ₂ O ₃ | 10 | 127.7 | 115 | 126.4 | 148.7 | 140.1 | 50.7 |
| PE/15 Al ₂ O ₃ | 20 | 127.6 | 115.2 | 122.1 | 143.6 | 136 | 49 |
| PE/15 Al ₂ O ₃ | 40 | 127 | 115.3 | 120 | 141.1 | 129.6 | 48.1 |

Table 3. DSC data of MDPE and its nanocomposites

is consumed for melting, T_c : The crystallization temperature, ΔH_c : Heat of crystallization, the amount of energy which evolved during crystallization temperatures. The percentage of crystallinity of MDPE and its nanocomposites are calculated as:

 $X_{C} (MDPE) = \Delta H^{*}(MDPE) / \Delta H^{0}(MDPE),$

(1)

 X_{C} (Nanocomposite) = ΔH^{*} (Nanocomposite)/ ΔH^{0} (MDPE), (2)

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Fig. 5. DSC cooling curves of the neat MDPE and its composites in constant ball milling time

where Δ H*(MDPE) is the apparent enthalpy of fusion per gram of MDPE in the nanocomposite, Δ H⁰(MDPE) is the heat of fusion of 100% crystallinity MDPE, taken as 70 cal/g from what proposed by Wunderlich (1980) and Δ H*(nanocomposite) is the apparent enthalpy of fusion per gram of nanocomposite. The relationship between Δ H*(nanocomposite) and Δ H*(MDPE), X_c(MDPE) and X_c(nanocomposite) can be achieved by the following Eq. 3 and 4 respectively.

 $\Delta H^{*}(MDPE) = \Delta H^{*}(Nanocomposite)/W (MDPE), \qquad (3)$

 X_{C} (MDPE) = X_{C} (Nanocomposite)/W (MDPE), (4)

where the W (MDPE) is the weight fraction of MDPE in the nanocomposites.

The crystallization peak temperature shifts to higher temperature with the presence of alumina. This result indicates again the efficiency of Al₂O₃ as a nucleating agent for MDPE crystallization. One of the important factors in nucleation of crystals is surface energy of fillers. For instance, talc is one of the effective agents in PP matrix with small surface energy (140 mj/m^2) . However, alumina has surface energy 50 mj/m², but data shows that its nucleation effect is limited. Nevertheless, it should be noted that the nucleation effect of some fillers on polymer crystallization is limited compared to other good nucleation agent or increasing their volume fraction had no sensible effect. For example, Seo et al. (2005) investigated the crystallization kinetics of PP/MWNT composites and observed that the addition of 1 wt.% MWNTs increased the crystallization rate by as much as an order of magnitude or higher and the addition of 5 wt.% MWNTs. Furthermore, the melting temperature decreases partially for all samples. That is related to small decreasing of cystallinity, because increasing amorphous phase facilitates breaking bonds apart. In another study, polypropylene (PP) composites reinforced using a novel plant fiber, sunflower hull sanding dust (SHSD), were prepared using a twin-screw extruder (Sui, 2005). Thermal and mechanical properties of the SHSD/PP composites were characterized and compared to an organically modified clay (organo-clay)/PP composite. DSC analysis showed that the crystallization temperature and degree of crystallinity of PP exhibited changes with addition of SHSD and organo-clay. Sui et al. (2005) showed that the degree of supercooling required for the crystallization of PP was reduced with the presence of the fillers. As the 5 wt.% fillers were added to the PP matrix, the fillers were found to obstruct the mobilization of the PP macromolecular chain and prevent the macromolecular segment from obtaining ordered alignment of the crystal lattice. Thus, the degree of crystallinity of the specimens decreased, accordingly.

4 Conclusions

In the current study morphology and thermal behavior of MDPE/alumina nanocomposite produced using ball milling method were investigated. The results are summarized as follows:

- TEM micrographs show alumina can be dispersed uniformly throughout a MDPE matrix by ball milling process.
- Crystallization temperature of MDPE doesn't change significantly as milling time increases.
- Crystallization temperature of MDPE depends on alumina content.
- The degree of crystallinity of MDPE decreases as nanosized alumina increases.
- Thermal stability of polyethylene nanocomposite is better than that of pure polyethylene.

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