Comparative Study of Zeolite-Filled LLDPE and HDPE Composite Films

Jagannath Biswas, Hyun Kim, Sang Eun Shim, Geon Joong Kim, Dai Soo Lee, and Soonja Choe†

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea

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Abstract: A comparative study of zeolite-filled LLDPE and HDPE composite films has been performed in terms of the filler dispersion, morphology, and the mechanical, rheological, and impact properties. The SEM morphology showed a good dispersion and adhesion of the filled zeolite in the LLDPE and HDPE systems. The HDPE/zeolite composite presents the higher draw ratio and aspect ratio, and has a larger number and bigger area of air holes than appear in the LLDPE system, which shows the most effective composition for diapger applications with a 40 wt% zeolite loading at a 300% draw ratio. The tensile and yield stress increased with the zeolite content in the LLDPE system, but the inverse behavior was observed in the HDPE system. The Young’s Modulus gradually increased, whereas the elongation at break was constant up to a certain draw ratio, but decreased at high contents of zeolite in both the LLDPE and HDPE systems. The impact properties of the LLDPE composite improved at up to 40% zeolite content, but they decreased in the HDPE system, implying a weak interfacial interaction in the HDPE system. Morphological observations strongly support the differences in the mechanical properties between the LLDPE and HDPE systems. Based on various properties, zeolites can be good candidates for fillers in each LLDPE and HDPE system for particular purposes.

Keywords: polyethylene, zeolite, composite film

Introduction

Polymeric materials already occupy a supreme position with regard to total usage and have replaced other conventional materials, like metals, glass, and wood, in a number of applications. Some distinct properties can be achieved when polymers are mixed with other extenders, fillers, and additives rather than using solely the virgin resin. The use of various types of fillers incorporated into polymers has become quite a common practice as a means of reducing the cost and imparting certain desirable mechanical, thermal, electrical, or magnetic properties to various polymers [1-10]. Extensive studies have been reported on filled polyolefin composites and their thermal, mechanical, and rheological properties in the presence of metallic filler have been described [11-17]. However, filled polymer systems normally offset these advantages to some extent by the increased complexity of their processing that is introduced by the inclusion of the fillers.

Because of the energy crisis and the high prices of petrochemical feedstocks (raw materials for polymers), there is a great demand for the increased use of fillers to cheapen polymeric systems while maintaining or improving their performance. In this respect, researchers are continuously searching for new types of fillers and their suitable applications as composites. Some of the most commonly used fillers for making composites include metal oxides, metal powders, carbon black, silica, spherical or fibrous glass, talc, calcite, kaolin, and mica [18]. The size, shape, filler modification [19,20], and quantity of loaded fillers all play an important role in the final systems. In this study, our work was confined to using LLDPE and HDPE as composite matrices and zeolite as a common filler.

In general, zeolites are crystalline inorganic polymers comprising an infinitely extended three-dimensional network of AlO4 and SiO4 linked to each other [21]. Zeolites are porous materials, whose pore sizes can be controlled

† To whom all correspondence should be addressed. (e-mail: sjchoe@inha.ac.kr)
by synthetic methods.

In our earlier work on calcite-filled polyolefin systems, where the filler was fixed to 50 wt% calcite, the mechanical and rheological properties of the pure polymer were compared against those of their corresponding composites [22,23]. Moreover, Kim and coworkers tried to unravel the influence of mixing cycle variations of 50 wt% calcite-filled composites where the second mixing yielded better performance among the first, second, and third compounding process in terms of the mechanical properties and filler dispersion in the matrix [24].

To date, there have been several reports on zeolite-filled thermoplastics. Among these, Upadhyay and Kale and coworkers [25] described the effects of the addition of synthetic sodium aluminum silicate (SSAS) in Nylon-6 and PP. Composites of nylon-6 filled up to 15 wt% and PP up to 40 wt% by SSAS showed increased flexural strength and flexural modulus. In addition, Kim and coworkers reported the mechanical, morphological, and rheological properties of the zeolite-filled microporous HDPE composites. Most of the mechanical properties, such as yield stress, impact strength, and elongation at break, decreased with increasing zeolite content and this finding was rationalized by a dewetting phenomenon that was predominant around the zeolite particles; thereby, the zeolite seems to be acting as a non-adhering filler [26].

In this study, linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) were compounded with zeolite in a twin-screw extruder by using a melt extrusion process and we compared the properties of the composite films in detail. Thus, the purposes of this work were: 1) to utilize zeolites [27-29] as potential fillers, 2) to discover the effects of the zeolites on the properties of the composite films, 3) and to find the acceptability of zeolites as conventional fillers in thermoplastics by considering the results obtained in this study.

Experimental

Materials

The polyolefins used in this study are linear low-density polyethylene (LLDPE: FT810) and high-density polyethylene (HDPE: 3300) supplied by SK Corporation, Ulsan, Korea. The respective physical properties for LLDPE and HDPE afforded by the supplier are as follows: density, 0.918 and 0.954 gm/cm³; melt flow index (MFI), 2.1 and 0.8 g/10 min; heat deflection temperature, 98 and 123°C. The synthesized zeolite has an average agglomerate size of 2–3 μm; the pore size and BET surface area are 4 and 600 m²/g, respectively. The zeolite was produced from Zeobuilder Co. Ltd., Chungnam, Korea.

Zeolite Master Batch and Compounding

To induce better mixing between the common zeolite filler and LLDPE or HDPE, a 50:50 wt% resin/zeolite master batch was prepared in advance by feeding 50:50 wt% resin and dry zeolite into the hopper of a Brabender twin-screw extruder (PL 2000) with L/D of 16 as a screw dimension. The mixed compounds, extruded through a round die, were immediately passed through a cold-water bath and then the solidified long strands of composite were pelletized. A temperature gradient, maintained in the twin-screw extruder, was 170°C in the feeding zone, 180°C in the compression zone, 190°C in the metering zone, and 200°C in the die zone for LLDPE system. For the HDPE system, these temperatures were 180, 190, 200, and 210°C, respectively. The rotation speed of the screw was maintained between 60 and 70 rpm. By controlling the amount of the master batch in the pure resins, 5 to 40 wt% of zeolite-filled composites were prepared.

Film Preparation

Film specimens were prepared by fixing a slit die (dimensions: 100 × 0.5 mm) at the end of the extruder in order to measure the mechanical and morphological properties. The dimensions of the film were 15 × 0.4 × 165 mm according to the ASTM D882-97 for tensile testing. The extruded film was drawn uniaxially using a take-up device while maintaining a film thickness ca. 400 micrometers.

Characterization

The dispersion of the zeolite in the matrix and the particle agglomeration were visualized from the cryogenically fractured surface. Cryogenically fractured surfaces of the composites were analyzed using a Scanning Electron Microscope (SEM), Hitachi S-4300, Japan. All specimens prepared for SEM analysis were coated with platinum using a sputter coater prior to analysis by SEM.

Tensile properties of the film specimens were measured using an Instron 4465 apparatus at 25°C and 30% humidity. Tensile properties, such as yield stress, elongation at break, and maximum stress, were enumerated from a stress-strain curve. The Young’s Modulus, as a measure of the stiffness, was also determined from the tensile graph. The initial grip distance of the film was maintained at 50 mm and the strain rates varied between 50 and 500 mm/min.

Izod impact strength was obtained using notched samples on a CEAST instrument (Italy) according to ASTM D 256 (dimensions: 3.64 × 12.7 × 3.17 mm) with a notch depth of 2.5 mm and a notch angle of 45°. Pure LLDPE and HDPE, as well as their composites (at least ten specimens), were tested and average values were collected. All tests were performed at ambient temperature.
**Results and Discussion**

**Zeolite Particles and their Dispersion in Both Matrices**

Figure 1(a) represents the SEM microphotograph of zeolite particles at 2000 times magnification. Zeolites are crystalline inorganic materials possessing an infinitely extended three-dimensional network of AlO₄ and SiO₄ units linked to each other. The Na-A-type zeolite used...
in this study has a polydisperse cube-like shape with an approximate particle size range of 0.5–3 μm [Figure 1(a)]. To confirm the uniform dispersion and wetting behavior of the zeolite particles in all compositions, SEM microphotographs of zeolite-containing LLDPE and HDPE systems, taken using their cryogenically fractured surfaces, are shown in Figures 1(b) to 1(e) and Figures 1(b'') to 1(e''), respectively.

We observe a good dispersion of the zeolite and a higher population density of the zeolite particles at the higher filler loading. In addition, the zeolite particles in the LLDPE matrix seem to be discrete, i.e., without filler agglomeration. Thus, a fair adhesion and a good wetting between the zeolite and LLDPE, resulting an improved mechanical properties, are suggested.

Figures 1(b') through 1(e') are the SEM photographs of HDPE composites filled with various amounts of zeolite and display their cryogenically fractured surfaces. Zeolite particles are well dispersed without agglomeration because a good distributive mixing was achieved during the compounding by means of a twin-screw extruder. However, some of the zeolites seem to have poor adhesion at the interface between the zeolite and HDPE matrix.

The comparative morphology of the film surfaces of 30 wt% zeolite-filled LLDPE with draw ratios of 50, 100, 200, and 300% are shown in Figures 2a-d, respectively, and in Figures 2a'-d', with same draw ratios, for the HDPE system. Between the two systems, we observe

Figure 2. A comparison of the SEM photographs of the film surfaces of 30% zeolite-filled LLDPE (a-d) and HDPE (a'-d') composites with draw ratios of 50, 100, 200, and 300%, respectively.
that the zeolite is better wetted in the LLDPE matrix (left side of the Figure) than in the HDPE system (right side of the Figure). In addition, for the same content of zeolite and the same elongation with the same strain rate, the HDPE system provides a greater number of air holes due to dewetting behavior between the zeolite and the polymer matrix. At 50% of the strain, dewetting is initiated between the zeolite particles and the matrix in both the LLDPE and HDPE systems (Figures 1a, a'). However, as the applied strain increases, the enlargement, the number, and the size of the formed air holes were completely different in two systems; the initially formed air holes are continuously enlarged along the machine direction upon stretching the specimen in the LLDPE system, whereas the enlargement, the number, and the size of the formed air holes increased dramatically in the HDPE system relative to the LLDPE one. The appearance of a fibril structure and some agglomeration of the zeolites upon stretching were predominant in the HDPE composite film.

**Mechanism of Air-hole Formation and Growth**

To analyze the morphological properties between the LLDPE and HDPE composites, the comparative values of the aspect ratio and the number and total area of the air-holes are plotted in Figures 3(a)-(c) and 3(a')-(c'), respectively, in terms of the various zeolite contents and draw ratios. In Figures 3(a) and 3(a'), the values of the aspect ratio increase gradually with the draw ratio, whereas the content of the zeolite does not influence it remarkably. The observed aspect ratio induced by dewetting is different; it varied from 3.7 to 4.9 at the 350% maximum draw ratio for the LLDPE system and from 3.5 to 6.9 at the 500% maximum draw ratio for the HDPE system. The higher aspect ratio, along with the higher draw ratio, for the HDPE system is probably induced by the formation of fibril structures, followed by a merging effect that originated from the structural difference [18] between the nearest air holes in the HDPE system.

The number of air holes plotted in Figure 3(b) shows no distinct increase between 5~20% zeolite content, but shows a maximum (ca. 600) at a 40% zeolite content and then a dramatic decrease at a 50% zeolite-filled LLDPE composite. However, there is no considerable effect of the draw ratio on the increase in the number of air holes.
The number of air holes plotted in Figure 3(b') shows a maximum at a 50% zeolite content at 50–300% draw ratios, but it decreased abruptly at a 500% draw ratio in the HDPE system. In addition, no distinct difference in the number of air holes with respect to draw ratio is observed for the HDPE system.

In Figure 3(c), for the LLDPE system, the total area of the air holes as a function of the zeolite content and the draw ratio shows no remarkable change, but then they increased abruptly and maximized at 40% zeolite and 300% draw ratio. In contrast, for the HDPE system, the phenomenon is quite different. The total areas of the air holes in the 20, 30, 40, and 50% zeolite-filled HDPE composites increased linearly with the draw ratio up to 300%. Compared to the LLDPE system, the number and total area of the air holes in the HDPE system are much larger because of the fibrous structure and enlargement of the air holes upon stretching.

Although the values of the aspect ratio and the number and total area of the air holes are different upon changing the zeolite content and draw ratio, the optimum conditions for the highest aspect ratio and number and total area of air holes are the same in both the LLDPE and HDPE systems: the highest values were obtained at 40% zeolite content and 300% draw ratio. However, in application for diapers, the film properties of the HDPE/zeolite system with a high loading of zeolite (40 and 50%) is much better than in the LLDPE/zeolite systems in terms of giving better properties in the aspect ratio and the number and total area of air holes.

**Tensile Properties**

To compare the tensile properties of the various zeolite-filled composites, specimens of the LLDPE and HDPE films were prepared. Figure 4 exhibits the stress-strain curves of the films of pure LLDPE and various compositions of zeolite-filled LLDPE at 50 mm/min (Figure 4a) and 500 mm/min (Figure 4b). As usual, the higher the strain rates, the higher the tensile stress, as seen in Figures 4a and 4b. Moreover, the tensile stress increases with the zeolite content and this finding may be due to a reinforcement effect of the zeolite. The yielding behavior was observed using the LLDPE/zeolite composite films prepared at 50 and 500 mm/min. In addition, the elongation at break exceeds 1000% (due to the machine limit, which was fixed to stretch the specimen to up to 50 mm) for the pure LLDPE and the up-to-30-wt%-zeolite-filled films at 50 mm/min, but then it declines at higher zeolite contents.

Figures 4(a') and 4(b') represent the stress-strain curves.
of the HDPE composite films measured at crosshead speeds of 50 and 500 mm/min, respectively. As shown in these Figures, the higher the strain rate, the higher are the observed tensile and yield stresses. In addition, as the zeolite content increased, the tensile stress decreased. As mentioned earlier in the investigation of dispersion, the poor adhesion due to the large number of air holes upon stretching, and, thereby, a detwetting between the zeolite particles and the matrix, may cause the reduced stress in the zeolite-filled HDPE system. Similar results have been reported by Upadhyay for PP/zeolite composites [25]. In their work, synthetic zeolite was added up to 40 wt% in a PP matrix, and the tensile strength and the elongation at break decreased with increased zeolite content.

The Young’s modulus, which is a characteristic of a material’s rigidity, is represented in Figures 5(a) and 5(b) for the LLDPE and HDPE systems, respectively. By increasing the zeolite loading from 5 to 50 wt% in the LLDPE system, corresponding progressive increments in modulus from 120 to 247 MPa at 50 mm/min and from 127 to 179 MPa at 500 mm/min were observed. The increment in modulus is higher in the 50 mm/min sample than in the 500 mm/min one, implying that the crosshead speed influences the Young’s modulus during the tensile test. On the other hand, the Young’s modulus of the HDPE film increased from 457 to 1052 MPa for the 50 mm/min sample, but decreased from 378 to 219 MPa for the 500 mm/min one. The latter phenomenon may have arisen from the fast stretching, which induces fast propagation of detwetting due to the weak interface between the zeolite and the HDPE matrices, and fibrous structures of HDPE.

The yield stress of the LLDPE film (Figure 6(a)) increased continuously from 6.5 to 9.7 MPa at 50 mm/min and from 9.8 to 11.2 MPa at 500 mm/min. The augmentation of the yield stress with increased zeolite contents indicates that reinforcement was introduced by incorporating the zeolite. On the other hand, the yield stress of the HDPE film (Figure 6(b)) decreased with increased zeolite content upon stretching; they decreased from 18.0 to 13.1 MPa and from 22.2 to 12.2 MPa for the 50 and 500 mm/min samples, respectively. This behavior is totally opposite to that of the LLDPE system. In our previous study on calcite-filled HDPE composite [19], we also observed that the yield stress decreased from 24 MPa for pure HDPE to 15 MPa for the 50-wt%-filled composite. This reduced yield stress may arise from the fact that the matrix is weakened as a result of the increased number and total area of air holes formed upon stretching.

The elongations at break of the LLDPE and HDPE systems are presented in Figures 7(a) and 7(b), respectively. The elongation at break of the LLDPE film is > 100% (due to the machine limit) for loadings up to 30 wt.% zeolite at the 50 mm/min crosshead speed, as seen in Figure 7a, but then it decreases to 931% and 160% at 40 and 50 wt% zeolite contents, respectively. No big difference in the elongation at break was observed at the 500 mm/min crosshead speed. In addition, for the zeolite-filled HDPE (Figure 7b) film at 50 mm/min, the elongations at break for the 0, 10, 20, 30, 40, and 50% zeolite-filled specimens are 1000, 1000, 1000 (due to machine limit), 918, 907, and 630% respectively. For the
500 mm/min crosshead speed, these values were 989, 984, 670, 631, 611, and 401%, respectively. Although the aspect ratio in the HDPE system was higher than in the LLDPE one, an inverse behavior was observed in the yield stress and elongation at break; this behavior can be interpreted as being caused by the reduced interaction between the rigid zeolite and the HDPE matrix upon stretching.

Impact Properties

Figures 8(a) and 8(b) are graphical representation of the impact strength of both the pure and zeolite-filled (error bar indicates the experimental deviation) LLDPE and HDPE composite films, respectively. As seen in Figure 8(a), the impact strengths of the composites having up to 40% zeolite content were increased relative to that of the pure LLDPE, but then it decreased dramatically at 50% zeolite content. This result is consistent with the mechanical properties. In contrast, the zeolite-filled HDPE systems show decreased impact strength upon increasing the zeolite content. This phenomenon corresponds to the reduced yield stress and elongation at break upon increasing the zeolite content.

X-Ray Diffractometer Measurements

Figures 9(a) and 9(b) represent the strong peak intensity area, between 2θ values of 20 and 25°, for the LLDPE and HDPE systems, respectively. Pure LLDPE and HDPE exhibit their main peaks at 2θ = 21.7° and 24.2°, depicting 110 and 200 reflections without any noticeable
noise. Moreover, the highest peak intensities at $2\theta = 21.7^\circ$ for the pure LLDPE and 5, 10, 20, and 30 wt% zeolite-filled composite films all remained unaffected, but then they decreased abruptly for the 40 and 50 wt% zeolite-filled ones, as seen in Figure 9(a). However, in the HDPE systems, as the zeolite content increases, the corresponding peak intensity decreases abruptly with an appearance of the small peak at various places in Figure 9(b). This observation implies that the crystallinity of the HDPE composite reduced dramatically upon incorporation of the zeolite. This effect may correspond with the reduced yield stress and Izod impact strength. The XRD measurements suggest no appreciable differences exist between the LLDPE and HDPE composite films. The mechanical behavior and SEM photographs of PP nanocomposites with calcite, which have been reported earlier, differ slightly from our results [22].

Conclusions

We have attempted to develop LLDPE and HDPE composites using a novel inorganic filler, zeolite with a conventional compounding procedure by applying a twin-screw extruder. The mechanical properties of pure LLDPE and HDPE and their composites having various amounts of zeolite have been analyzed thoroughly using film specimens. In general, the higher the strain rate, the higher the observed stress. Improved Young’s Moduli were observed upon successive increments in the amount of filler in both systems, except at 500 mm/min in the HDPE system. The yield stress of the LLDPE films gradually increased, but the inverse behavior was observed in the HDPE system. The elongation at break is almost constant up to a certain draw ratio, but it reduced at higher draw ratios in both systems. The impact strength of the composites containing the LLDPE matrix increased linearly up to a critical zeolite concentration, whereas that of the HDPE matrix decreased. Based on the various properties we have investigated, zeolites are good candidates as filler materials in both LLDPE and HDPE systems for use in particular applications.

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