Preparation of a Novel Microporous HDPE/Zeolite Composite Film

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Abstract: Novel microporous film of the zeolite filled HDPE composites prepared by a conventional compounding procedure using a twin-screw extruder and followed by a simple stretching in a tensile test machine. Zeolite particles are well dispersed in HDPE matrix without a significant aggregation. The Young's modulus values gradually increase, but the yield stress, impact strength, and elongation at break decrease with zeolite contents in composite. Dewetting phenomenon is predominant around the zeolite particles, thereby zeolite seems to be acting as non-adhering filler. In addition, the X-ray diffractometer measurement reveals that the crystallinity extremely reduced with zeolite contents. Thus, enlargement of the air holes upon stretching and merging between the neighboring air holes, and the reduced crystallinity is responsible for poor mechanical properties. It is suggested that the size, number, and aspect ratio of the micropores should be controlled due to the zeolite contents in matrix and the degree of stretching.

Keywords: zeolite, HDPE, composite

Introduction

Many of commercial polymeric materials consisting of two or more components are used for composites. In most cases, fillers are added to polymer matrix to reduce the production cost or acquire desired properties such as improved mechanical, morphological or thermal properties of the materials. Both organic and inorganic fillers are used for reinforcing or non-reinforcing purposes. Some of the most frequently used fillers are CaCO3, talc, carbon black, clay, various fibers (carbon, glass, wood, and cellulose), metal powders (zinc, aluminum, iron, and nickel) and so on [1-16]. Since the properties of a composite material depend on those of individual components, it is important to choose the most suitable filler for desired purposes [3,17,18].

Growing attention has been paid in using zeolite as the choice of filler in polymer composites. These works include a membrane production using poly(dimethylsiloxane) [19-21], an increase in thermal stability of epoxy resin [22] and curing of epoxy resin by means of zeolite filled polyaniline [23]. Recently, it has been reported by several authors regarding on making a porous structured composite film using zeolite in polyolefin matrix [24,25]. Özmihiç and coworkers [24] prepared a 2~4% natural zeolite filled polypropylene (PP) composite film where the surface of the zeolite particles was treated by polyethylene glycol (PEG) 4000 in order to enhance a dispersion and adhesion of zeolite in the matrix. On the other hand, Upadhyay [25] used synthetic zeolite in PP matrix since it has a narrower particle size distribution than that of natural ones.

In our previous works on the preparation of calcium carbonate (CaCO3) filled porous PE and PP composite films, CaCO3 was chemically treated by stearic acid in order to provide a better dispersion and easier processing [26-28]. However, it has been found that a significant number of cavities were generated due to the hydrophilic characteristics of stearic acid treated-CaCO3 which deteriorates the physical performance of the composites. In this study, therefore, we have attempted to develop a novel porous high density polyethylene (HDPE)/zeolite composite film since zeolite can adsorb and desorb moisture by varying temperature. Generally, zeolites are classified in A-type, X-type, Y-type, L-type, ZSM-5 and silica molecular sieve according to their particle size, pore size and Si/Al ratio in framework. And the basic property of zeolite on moisture is determined based on the content of Al component [29]. The more content of Al component, the closer to hydrophilic nature is observed. The choice of zeolite in this system is based on the following two expected reasons; One is a role of zeolite as the loci of stress concentration upon stretching.
in manufacturing air-permeable film, and the other is a role as a moisture adsorbent for applications in sports wears, diapers, and other hygienic wears. Therefore, the goals in this work are: 1) to utilize zeolite as a potential filler source and to explore its effects on composite properties, and 2) to understand the mechanism in the production of porous film in terms of dewetting and air hole formation (or crack propagation) induced by incorporation of zeolite particles upon stretching.

Experimental

Materials

High density polyethylene (HDPE, 3300) supplied by SK Corporation, Ulsan, Korea was used as a matrix and it has a specific gravity of 0.954, melt index of 0.8 g/10 min, heat distortion temperature (HDT) of 123°C, and tensile strength of 350 kg/cm². A-type synthetic zeolite containing the greatest amount of Al was employed as a filler since it is the most sensitive to moisture as mentioned earlier. Zeolite was provided from Zeobuilder Co., Korea and used. The zeolite possesses an average particle size of 0.5-3 μm, pore size of 4 Å, and BET surface area of 600 m²/g, respectively.

Zeolite Master Batch and Compounding

The previously prepared 50:50 wt% HDPE/zeolite master batch was used to make composites containing various amounts of zeolite. For the master batch, 50:50 wt% dry blended HDPE and zeolite were fed into the hopper of a Brabender twin-screw extruder (PL 2000) with L/D of 16 in a screw dimension. The mixed compounds extruded through a round die immediately passed through a cold water bath. Solidified long strands of composite were then pelletized. A temperature gradient maintained in the twin-screw extruder was 170°C in a feeding zone, 200°C in a compression zone, 210°C in a metering zone and 220°C in the die. The rotation speed of the screw was set at 70 rpm throughout the preparation of whole samples. By controlling the amount of the master batch in pure-linear low density polyethylene (LLDPE), 5 to 40 wt% zeolite filled HDPE composites were prepared.

Sample Preparation for Tensile Test

Two types of specimens, dumbbell and film, were prepared for the measurements of mechanical properties. Dumbbell shaped sample was compression molded in a Carver laboratory hot press at 5 × 10⁶ Pa and at 200°C. The hot mold was allowed to anneal at ambient temperature. The dimension of dumbbell bar was 13 × 3 × 165 (mm)³ following the ASTM D638M type M-L. Film type specimens were also made by using a slit die in 100 × 0.5 (mm)² dimension, fixed at the end of the extruder. Extruded sheets were uniaxially drawn by using a take-up device maintaining the film thickness about 400 micrometers. The dimension of the film was 15 × 0.4 × 165 (mm)³ by cutting with a sharp knife according to the ASTM D882 for a tensile testing.

Characterizations

The complex melt viscosity of the pure HDPE and zeolite filled composites was measured using a Torsion Rheometer Mk III of Polymer Laboratory, Great Britain. The complex viscosity of all samples was measured in a parallel plate (D = 38 mm) over a frequency range of 0.03–200 rad/sec and strain amplitude of 4%. The round 2 mm thick samples were molded from a hot press at 200°C. Prior to molding process, the pelletized samples were kept in vacuo at 110°C for 6 hrs for the removal of moisture.

The dumbbell bar and film specimens were measured using Instron 4465 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 stiffness was also determined from the tensile graph. The initial grip distance was maintained at 50 mm and the strain rates were 5 and 50 mm/min for dumbbell bar and 50 and 500 mm/min for film specimens.

The slow strain rate at 5 mm/min and an initial grip distance with 2 mm were employed for morphological study. Dewetting and change in size of air hole between the zeolite and matrix were investigated. The draw ratio was varied from 50 to maximum stretching according to a sample's ultimate behavior.

Dispersion of fillers and its agglomeration in the matrix were visualized from the cryogenically fractured surface. Stretched films and cryogenically fractured surface of 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 test in SEM.

The crystallinity variance between the pure HDPE resin and the filled composite with zeolite was characterized using a Philips X’pert MPD X-ray diffractometer (XRD) with Ni-filtered Co-Kα radiation at room temperature. The scanning rate was 0.08/°sec over a range of 2θ = 5°–35° and the film thickness was approximately 0.4 mm.

Izod impact strength values were evaluated using a CEAST Instrument according to ASTM D256 with a notch depth of 2.5 mm and a notch angle of 45°. Average impact values were collected after testing about ten specimens at ambient temperature.

Results and Discussion

Basic Properties of Zeolite and Dispersion of Zeolite in HDPE Matrix

Figure 1(a) exhibits the SEM microphotograph of zeolite
Figure 1. Comparison of SEM photographs (2000 magnification) of zeolite and the cryogenically fractured surface of the zeolite filled HDPE composites with dumbbell shape. (a) zeolite, (b) 5%, (c) 10%, (d) 20%, (e) 30%, (f) 40%, and (g) 50%.
particles at 5000 of magnification. Zeolite is crystalline inorganic material possessing an infinitely extending three-dimensional network of AlO₄ and SiO₄ linked to each other. It is seen that Na-A type zeolite used in this study has a polydisperse spherical shape with an approximate particle size range of 0.5–3 μm as shown in Figure 1(a). Figures 1(b) through (g) exhibit the SEM photographs of cryogenically fractured surfaces of HDPE composites filled with various amounts of zeolite. Zeolite particles are well dispersed without agglomeration since a good distributive mixing was achieved during compounding by means of a twin-screw extruder. As expected, the number of zeolite particles in the matrix increases as filler concentration increases from 5 to 50 wt%. However, it is observed that there exists void around zeolite particles in the matrix since adhesion of zeolite to HDPE matrix is not fair, implying that the interaction between them is not good. This might affect mechanical properties of the composites.

Rheological Measurements
The complex melt viscosity (η*) of pure HDPE and the composites filled with various contents of zeolite is plotted against log frequency in Figure 2. All the samples including pure HDPE exhibit a power law behavior following a non-Newtonian behavior in the frequency span operated. Viscosity value is the lowest for pure HDPE and increases with zeolite content. In particular, 50 wt% zeolite filled HDPE composite shows a significant leap than the other compositions.

Mechanical Properties
Dumbbell and film types of the sample were used for the measurement of mechanical properties of pure and zeolite filled HDPE system. Figures 3(a) and 3(b) represent the strain-stress curves of HDPE composites in dumbbell shape measured at a crosshead speed of 5 and 50 mm/min, respectively. It should be noted that the tensile test machine could stretch a sample for 20 min only, then stops automatically. As usual, the higher the strain rates, the higher the stress was observed. In addition, yielding behavior was observed for all compositions of the composite regardless of the strain rates. As shown in Figures 3(a) and (b), the majority of the samples is not broken up to the machine limit.

It is seen that the pure HDPE shows the highest stress and that the stress decreases with zeolite content in composite. As mentioned earlier in investigation of dispersion, the poor adhesion and dewetting between the zeolite particles and the matrix might be one of the reasons for the reduced stress in zeolite filled HDPE system. Similar results reported in the case of PP/zeolite composite by Upadhyay [25]. In their work, synthetic zeolite was added up to 40 wt% in PP matrix where the tensile strength and the elongation at break decreased with the zeolite content. In our previous study on the calcite filled HDPE composite [26], it was also observed that the yield stress decreased from 24 MPa for pure HDPE to 15 MPa for 50 wt% filled LLDPE composite. The possible explanation for the reduced stress is the fact that the enlarged air holes upon stretching due to increased contents of zeolite are weakened by the stress of
the matrix. This phenomenon will be observed in the section of morphological study, later. However, in the case of calcite filled LLDPE where the crystallinity of the matrix was lower than that of HDPE, the yield stress is not affected by the addition of filler [27].

The stress-strain curves of the film stretched at 50 and 500 mm/min are plotted in Figures 4(a) and (b). The shape of stress-strain curves for film is similar to those of dumbbell shape. However, the yield stress of the film is higher than that of dumbbell type. The faster the crosshead speed, the slightly higher the yield stress is observed as seen in dumbbell samples. The limits in maximum strain (200% for dumbbell type and 1000% for film type) maintain up to 20% zeolite filled system regardless of the strain rate, then the elongation at break of 30, 40 and 50% zeolite filled composites gradually decreases. It means that the increased filler contents and simultaneous stretching accelerate dewetting phenomenon with enlarged air holes.

Figure 5 exhibits the experimental Young’s modulus obtained by using Figures 3 and 4. Modulus for dumbbell bar at 5 and 50 mm/min and film at only 50 mm/min increased with the zeolite content. Since the modulus is obtained from the initial slope between the stress and strain, 500 mm/min for film specimen is too fast to calculate accurately. Thus, experimental results in Figure 5(a) and those for 50 mm/min only in Figure 5(b) are used for the next step.

Two common equations that are frequently used to estimate the modulus of particle-filled composites are:

\[ E_c = E_p \phi_p + E_f \phi_f \]  \hspace{1cm} (1)

\[ E_c = \frac{E_p E_f}{E_p \phi_f + E_f \phi_p} \]  \hspace{1cm} (2)

where \( E_c \) is the modulus of the composite, \( E_p \) and \( E_f \) are the moduli of the polymer matrix and filler, respectively, \( \phi_p \) and \( \phi_f \) are the volume fraction of the polymer and filler, respectively. The densities of HDPE matrix and zeolite are 0.954 and 2.3 g/cm³, respectively. Equation (1) is appropriate when strong adhesion exists between the filler and polymer and the filler has higher aspect ratio, for example fiber type filler, whereas Equation (2) is applicable to rigid spherical particles.

The modulus of the zeolite is extrapolated by putting the experimental modulus value and the volume fraction and the modulus of zeolite obtained is 2700 MPa. As shown in Figure 6, the experimental value lies between the Equation (1) and Equation (2). Although the geometry of zeolite particles is close to the latter case, it does not exactly fit to an ideal model suggested in the both...
the yield stress of whole compositions decreases with the filler content. In Figure 7(b), the elongation at break for 30, 40, and 50% filled specimens are broken at 918, 907, and 630% strain at 50 mm/min, and 5, 10, 20, 30, 40, and 50% filled specimens are broken at 989, 984, 670, 631, 611, and 401% at 500 mm/min, respectively. Based on the mechanical properties, the yield stress and the elongation at break decreased and this may be due to reduced interfacial interaction between the zeolite and the matrix upon stretching.

Air Hole Formation and its Growth upon Stretching

In order to study dewetting and followed by the formation and growth of air holes upon stretching, the SEM microphotographs of the surface of film specimens are displayed in Figures 8 through 10 for whole compositions of zeolite/HDPE composites at various elongations. All the samples were elongated at a crosshead speed of 5 mm/min with an initial grip distance of 2 mm.

Figures 8(a)~8(d) exhibit the photographs of the 5 wt% zeolite filled HDPE composite from 50, 100, 300, and 500% of elongation. The dewetting phenomenon occurs at the surface of filler due to reduced interfacial adhesion between the filler and the matrix at 50% strain shown in Figure 8(a), then air holes are formed from the dewetted particles or by the separation of zeolite particles from the air holes in Figure 8(b). The growth of air holes by means of merging of neighboring air holes is accelerated due to further elongations after 200% of strain. The approximate aspect ratio of the air holes increases from 2.32 at 100% strain to 10.72 at 500% strain. Similar behavior for the 10% zeolite filled HDPE composite is observed in the Figures 8(a') to 8(d').

For the 20 and 30% zeolite composites, the similar morphological behavior is observed in Figure 9. As the filler content increases, the number of air holes abruptly increase and the merging air holes are predominant above 30 wt% zeolite composites as seen from Figures 8 to 10. In particular for 50 wt% zeolite filled HDPE system as seen in Figure 10(a') to 10(d'), more than 50% of the film surface is covered with air holes, implying that the loading will be weakened. Through the SEM photographs for the 100, 300 and 500% of strain, approximately calculated number of air holes is 8~18 for 5 wt%, 15~35 for 30 wt%, and 20~42 for 50 wt% zeolite filled HDPE system. In addition, the aspect ratio of the 5, 30, and 50 w% zeolite filled composite varies from 2.3 to 10.7, 3.2 to 9.6 and 2.7 to 10.6, respectively. This means that the HDPE composite stretched from 50 to 500% makes five times bigger aspect ratio. Thus, a porous zeolite filled HDPE composite material is successively achieved; and the porosity of the film can be controlled by varying the filler content and the degree of the applied strain.

Figures 7(a) and (b) show the summarized mechanical properties of the yield stress and the elongations at break as a function of zeolite content in HDPE. In Figure 7(a),
Figure 8. SEM photographs (2000 magnification) of the 5% and 10% zeolite filled HDPE with 2 mm of initial grip distance and at 5 mm/min of cross-head speed at various strains; zeolite (5%)/HDPE: (a) 50% (b) 100% (c) 300% (d) 500%, zeolite (10%)/HDPE: (a’) 50% (b’) 100% (c’) 300% (d’) 500%.
Figure 9. SEM photographs (2000 magnification) of the 20% and 300% zeolite filled HDPE with 2 mm of initial grip distance and at 5 mm/min of cross-head speed at various strains; zeolite (20%)/HDPE: (a) 50% (b) 100% (c) 300% (d) 500%, zeolite (30%)/HDPE: (a’) 50% (b’) 100% (c’) 300% (d’) 500%.
Figure 10. SEM photographs (2000 magnification) of the 40% and 50% zeolite filled HDPE with 2 mm of initial grip distance and at 5 mm/min of cross-head speed at various strains; zeolite (40%)/HDPE: (a) 50% (b) 100% (c) 300% (d) 500%, zeolite (50%)/HDPE: (a’) 50% (b’) 100% (c’) 300% (d’) 500%.
Figure 11. SEM photographs representing (a) dewetting between the zeolite particles and matrix resin and (b) enlargement of the air holes due to stretching and merging of neighboring air holes between fibril structures.

With the zeolite filled HDPE composite, two figures are collected to propose the formation and growth of air holes. At a low strain in the beginning of elongation, air holes were generated due to dewetting around filler particles as seen in Figure 11(a). As the strain increased, the size and aspect ratio of the air holes increased with the presence of fibril structure of the matrix as seen in Figure 11(b). Subsequently, the air holes grow not only the further elongation of the film, but also through merging neighboring air holes between the fibril structures of the matrix. The mechanism of the formation of porous film upon stretching was also proposed using the calcite filled PP [26] and PE [27] composites. In the case of PE system, the migration of calcite particles onto the PE surface upon stretching was observed [27].

X-ray Diffractometer Measurements

Figures 12(a) shows the intensity vs. $2\theta$ between 5° and 35°, and Figure 12(b) represents the strong peak area of which $2\theta$ is 20° and 25°. As seen in Figure 12(a), pure HDPE exhibited the biggest main peak at 21.7° and 24.2° of $2\theta$ without any noticeable noise. However, as the zeolite content increases, the above peak intensity abruptly decreases with an appearance of small peak at various places as seen in Figure 12(b). This implies that the crystallinity of HDPE composite is dramatically reduced upon incorporation of zeolite. This may correspond with the reduced yield stress and Izod impact strength. Mechanical and SEM photographs of PP/nanocomposite with calcite reported are slightly different with our results [30].

Impact Properties

Figure 13 is the graphical representation of the Izod
impact strength of both pure and filled HDPE composites (error bar indicates the experimental deviation). The impact strength decreased constantly with zeolite content. This is similar behavior to the reduced yield stress with zeolite content and may be due to the increased air holes upon stretching with decreased crystallinity.

**Conclusions**

We have developed a novel HDPE/zeolite composite having a microporous structure. The composite was prepared by a conventional compounding procedure using a twin-screw extruder and by a following simple stretching in a tensile test machine.

Zeolite particles are well dispersed in HDPE matrix without a significant aggregation. However, it seems that the adhesion of zeolite particles to HDPE matrix is not fair, implying that interfacial interaction between them is poor.

In the view point of mechanical performance, the Young's modulus gradually increases but the yield stress and the elongation at break decrease with zeolite content since incorporated zeolite particles act as a non-adhering filler and relatively large portion of air holes weakens the stress of the matrix upon loading.

The mechanism of the formation of porous film upon stretching was investigated based on morphological study. Void air holes are generated due to dewetting around filler particles at low strain. As the strain increases, the enlarged air holes and increased aspect ratio of the air holes may be due to not only the increased dewetting behavior, but also merging of the neighboring air holes between fibril structures. Thus the size, number, and aspect ratio of the air holes can be strongly controlled by the zeolite contents and the degree of the applied strain.

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