Available online at www.sciencedirect.com

SCIENCE DIRECT®

polymer

Polymer 47 (2006) 3981–3992

www.elsevier.com/locate/polymer

Effects of stearic acid coating on zeolite in LDPE, LLDPE, and HDPE composites

Hyun Kim, Jagannath Biswas, Soonja Choe *

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

Received 10 September 2005; received in revised form 13 January 2006; accepted 17 March 2006
Available online 18 April 2006

Abstract

In order to manufacture the microporous, breathable films applicable to absorbent articles, LDPE, LLDPE, and HDPE/zeolite composite films filled with zeolite, uncoated and coated with stearic acid, were prepared. The stearic acid is verified as a coupling agent by how much effect it has on the various properties such as mechanical, thermal, morphological, and rheological measurements. The incorporation of stearic acid on the zeolite surface improved the flexibility of polymer matrices. In particular in the LLDPE and HDPE composites, the increase in the area of the air holes and decrease in the number of the air holes by merging among neighboring air holes was prominent upon higher filler loading, therefore resulted in enhanced modulus, elongation and impact properties.

Keywords: Zeolite; Stearic acid coating; Composite

1. Introduction

Blending polymers or composites offers an attractive alternative in developing new polymeric materials. Particularly, compounding fillers with thermoplastic materials in order to introduce a desired property is a conventional practice and useful method [1–11]. Not only mineral fillers such as $CaCO_3$ [3,6], silica, clays, mica, talc, but also metallic fillers such as aluminum [9], chromium, copper, iron, nickel, silver [10] have been used in preparation of composites. In general, polymeric composite materials filled with fillers can lead to a loss in the mechanical properties of the polymer due to the incompatibility between the fillers and polymer. Therefore, a variety of coupling agents [12,13] can be used to bind solid surface to polymer resins.

Zeolite is a crystalline inorganic material possessing an infinitely extending three-dimensional net-work of AlO_4 and SiO_4 linked to each other. The composition of Al/Si in its structure is one of the important factors in determining the hydrophobicity and hydrophilicity [11]. The higher the relative composition ratio of the Si component in a zeolite, the higher the hydrophobicity of the zeolitis obtained.

There are many beneficial reports on chemically coated fillers that show a better adhesion with a polymer matrix than that of uncoated ones [14,15]. Simple surfactants such as stearic acid and maleic anhydride, which cannot form covalent bonds, have been used as coupling agents in filled polymer systems [16,17].

Nowadays, breathable polyolefin films used in personal care items, better comfort, and hygiene are widely utilized. Examples of those are baby diapers, sanitary napkins, incontinence garments, training pants, bandages, and health care-related items such as drapes, gowns and food packing, etc. The method for making microporous film is to uniaxially, or biaxially stretch polymer composites filled by inorganic or organic materials [18].

In our earlier studies on 50 wt% calcite filled PP composite systems using homo-PP (polypropylene), CoPP (poly(ethylene-*co*-propylene)), and TerPP (poly(ethylene-*co*-I-butene-*co*-propylene)) and PE (polyethylene) composites, the mechanism of air hole growth suggested that the neighboring air holes be merged with each other with increasing draw ratios [19–21]. In addition, the Young's modulus and complex melt viscosity enhanced with inorganic filler loading [19–21]. On the other hand, to the best of our knowledge to date, there are few reports on coated zeolite filled thermoplastics. Metin et al. [17] described the effects of the surface treatment of zeolite by various kinds of surface modifiers in polypropylene (PP)/natural zeolite composites. They also reported that the significant improvement of filler compatibility and mechanical

---

* Corresponding author. Tel.: +82 32 860 7467; fax: +82 32 876 7467.
E-mail address: sjchoe@inha.ac.kr (S. Choe).

0032-3861/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2006.03.068

properties could be attained by around 1 wt% of silane treatment [23].

In this article, the mechanical, morphological, and rheological properties on LDPE, LLDPE, and HDPE composites filled with zeolite uncoated and coated with stearic acid were studied. The main concerns are the followings; (1) the effects of stearic acid coated zeolite on three different matrices having the unique molecular structure, (2) the effects of stearic acid as a coupling agent on filler surface in respective composites, and (3) the different aspect of air hole property upon stretching.

2. Experimental

2.1. Materials

Three polymers used in this study are low density polyethylene (LDPE, FB3000), linear low density polyethylene (LLDPE, FT810), and high density polyethylene (HDPE, 3300), supplied by SK Corporation, Ulsan, Korea. The distinctive properties of the three selected resins are summarized in Table 1, which also includes their respective physical data. Inorganic zeolite powder was purchased from Zeobuilder Co. Ltd, Chungbuk, Korea. In addition, modified zeolite powder, coated by stearic acid, was manufactured in this laboratory in cooperation with Ecopro Co. Ltd, Chungbuk, Korea. The properties of respective fillers are tabulated in Table 2. The production of the stearic acid coated zeolite powder follows; for making a 0.1 M stearic acid solution by ethanol with the purity of 99%, the 28.4 g mol of stearic acid was taken in a steel pot and melted at 70 °C. Ethanol was then added in melted stearic acid and 1 l of stearic acid solution was made. Finally, stearic acid coating solution used for modification of the zeolite surface was prepared in the ratio of 1:0.6 in weight/volume (zeolite/stearic acid) basis by slowly adding in a mixer with constant stirring. The modified zeolite was dried in a vacuum oven for 6 h at 60 °C and then ground to form powder.

2.2. Compounding

Prior to mixing with resins, the uncoated zeolite was dried in an oven for 3 h at 130 °C and the stearic acid coated zeolite was done for 3 h at 60 °C, respectively (T_m of stearic acid is 69 °C). A Brabender PL 2000 twin-screw extruder with L/D of 16 in a screw dimension was used for compounding with two kinds of zeolites, uncoated and coated, and LDPE, LLDPE, and HDPE resins. The content of filler was fixed to 5–50 wt% for all the three matrices. Premixed respective fillers and polyolefins were fed into the extruder hopper and the compounded samples were extruded through extruder die. The mixed compounds extruded through a round die 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: 180 °C in a feeding zone, 190 °C in a compression zone, 200 °C in a metering zone and 210 °C in the die zone for the LDPE system and these variables were 190, 200, 210, and 220°C for the LLDPE system, and 200, 210, 220, and 230°C for the HDPE system, respectively. These variables were identically maintained for all the filler systems, irrespective of the specimen types such as pellet and film.

2.3. Film preparation

Film specimens were prepared using sheet extrusion installed with a slit die (100×0.5 mm^2), which was equipped at the end of the extruder. An extruded sheet was pulled out using a take-up device and the film thickness was maintained at 0.4 mm. The film specimen was prepared following ASTM D-882-97, which had a dimension of 15×0.4 mm^2.

2.4. Characterization

2.4.1. Tensile tests at constant strain rate

Tensile properties of the film specimens were measured using an Instron 4465 at 25 °C and 30% humidity. The initial gauge length of the film specimen was maintained at 50 mm, and the crosshead-speed was 50 mm/min. The Young's modulus, yield stress, and elongation at break were enumerated from stress–strain curves. For mechanical and morphological characterizations, at least ten specimens were used and the most probable results were averaged.

Table 1
Resins used in this study

Resins (grade name)	Density (g/cm^3)	MI (g/10 min)[a]	HDT (°C)[b]	Tensile strength (kg/cm^2)	Supplier
LDPE (FB 3000)	0.919	3.0	90	120	SK Co., Korea
LLDPE (FT 810)	0.918	2.1	98	350	SK Co., Korea
HDPE (3300)	0.954	0.8	123	350	SK Co., Korea

[a] Melt flow index.

[b] Heat distortion temperature.

Table 2
Properties of two kinds of zeolites in this study

Filler	Density (g/cm^3)	Particle size (μm)	BET area calculated (m^2/g)	Supplier	Code (comment)
Zeolite-uncoated	1.9	2–5	250–350	Zeobuilder Co., Korea	Untreated
Zeolite-coated	–	2–5	7.06	Ecopro Co., Korea	Treated by stearic acid

2.4.2. Morphology and analysis using an IA

The morphological investigation of the zeolite filled LDPE, LLDPE, and HDPE was carried out for observation of the matrix/filler interface status. The dispersion of pristine zeolite and after chemical treatment in three different matrices was visualized from the cryogenically fractured surface.

Film samples containing zeolite were slowly deformed at 5 mm/min of crosshead-speed and 2 mm of gauge length by a universal testing machine (UTM) for stretched surface morphology. The scanning electron microscopy (SEM), Hitachi S-4300, Japan, images were used for quantitative examination of the air hole diameters, aspect ratio, and area using the special image analyzer. All specimens prepared for SEM analysis were coated with platinum using a sputter coater prior to test using SEM. Images of drawn film of the uncoated and coated zeolite filled LDPE, LLDPE, and HDPE composites were analyzed identically by a Scion Image Analyzer (SIA) software. To avoid complication, the average diameter of the air hole was measured by converting all elliptical air holes to the corresponding spherical diameters.

2.4.3. Rheology

The complex melt viscosity of LDPE, LLDPE, and HDPE composites containing their pure resins was measured using a Torsion Rheometer Mk III of Polymer Laboratory, Great Britain. The complex melt viscosity of the samples was measured in a parallel plate ($D=38$ mm) geometry over a frequency range of 0.03–200 rad/s and the constant strain rate of 4%.

2.4.4. Thermal properties

In order to investigate the effect of inorganic zeolite fillers on crystals formed in the polymer matrix, the specimens were heated and cooled at a rate of 20 °C/min in the temperature range of 60–180 °C on a differential scanning calorimeter (DSC) (Perkin–Elmer, DSC-7). All the results were recorded from the second heating and cooling of the samples.

2.4.5. Impact properties

Izod impact strength was evaluated on V-shape notched samples on a CEAST instrument (Italy) in accordance with ASTM D 256 with a notch depth of 2.5 mm and a notch angle of 45° at ambient temperature. For composites, both the uncoated zeolite and coated zeolite filled as well as virgin LDPE, LLDPE, and HDPE, at least ten specimens were tested and the average values were collected.

3. Results and discussion

3.1. Geometry of inorganic fillers

Fig. 1(a) and (b) exhibits the geometric comparison and the degree of agglomeration by means of SEM photographs on the uncoated and coated inorganic zeolite particles (Na-A type) used in this study, respectively. It is seen that the uncoated zeolite has a spherical shape with an approximate particle size of 0.5–3 μm without particular agglomerations. However, the stearic acid coated zeolite comparatively has a slightly enhanced size distribution than the uncoated ones. It may be due to the stearic acid coated surface as a coupling agent for minimizing agglomeration among particles. In Table 2, the comparable BET surface area between the uncoated and coated zeolite shows how much the stearic acid affects the filler properties.

3.2. Dispersion of zeolite particles

In order to confirm the uniform dispersion, wetting, and dewetting behavior of the uncoated (in Fig. 2) and coated (in Fig. 3) zeolite in all compositions, SEM photographs were taken using a cryogenically fractured surface of 5, 30, and 50% zeolite filled LDPE, LLDPE, and HDPE composites, respectively. In addition, the SEM photographs of B, B′, B″ and C, C′, C″ of the last two rows in Figs. 2 and 3 represent four times magnified pictures of 30 and 50 wt% filled composites of LDPE, LLDPE, and HDPE, respectively. This closer view shows more distinct morphology of good wetted zeolite particles, especially in LDPE and LLDPE matrices. Between both filler systems, coated one shows slightly finer dispersion than uncoated one.

As the zeolite content increases, a higher increase of population density of the filler is observed in both filler systems. However, the stearic acid coated system shows enhanced dispersion compared to the uncoated system. It may be due to the addition of stearic acid [24–26]. In addition,

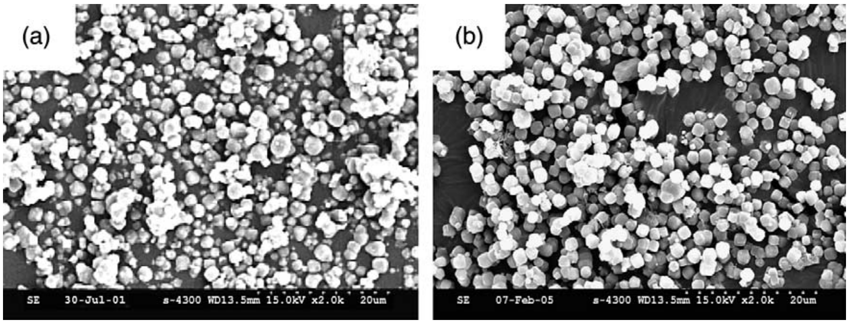

Fig. 1. SEM microphotographs of inorganic zeolite particles used in this study (a) uncoated zeolite and (b) coated zeolite.

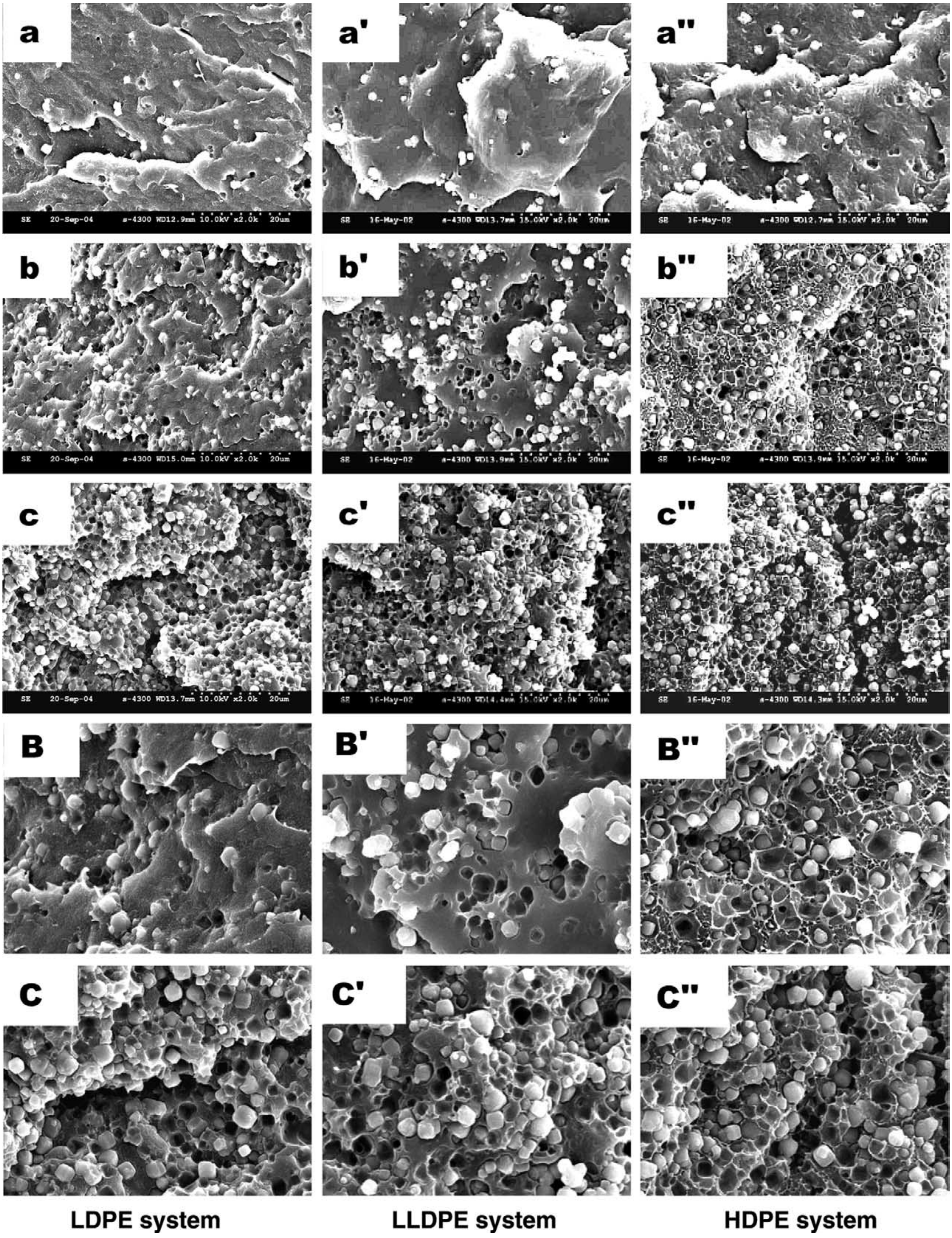

Fig. 2. SEM microphotographs (×2000) of cryo-fractured parts of uncoated zeolite filled LDPE, LLDPE, and HDPE composites. (a–c): LDPE system; (a′–c′): LLDPE system; (a″–c″): HDPE system: 5, 30, and 50 wt%. (B and C): LDPE system; (B′ and C′): LLDPE system; (B″ and C″): HDPE system: 30 and 50 wt% (four times magnified).

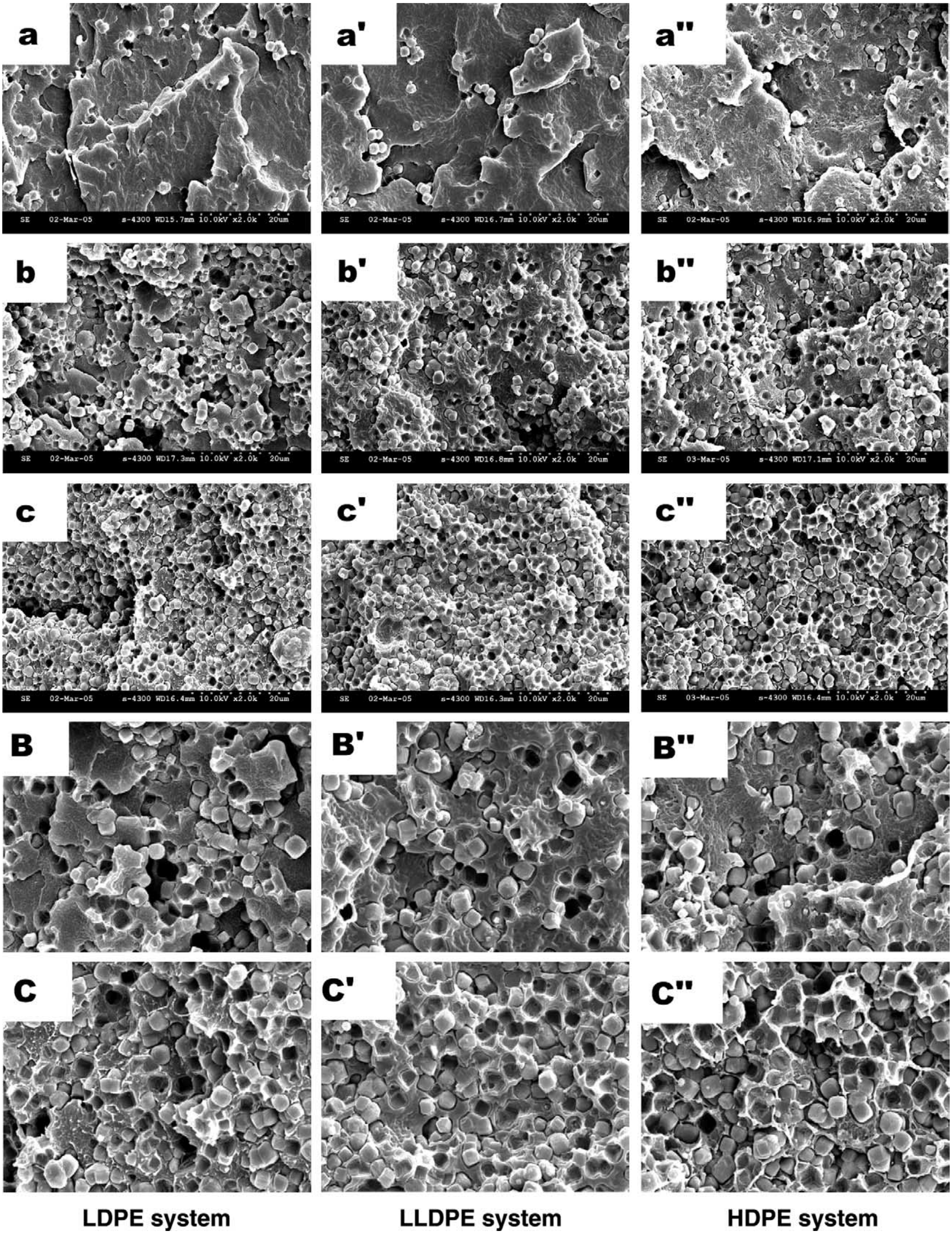

Fig. 3. SEM microphotographs (×2000) of cryo-fractured part of stearic acid coated zeolite filled LDPE, LLDPE, and HDPE composites. (a–c): LDPE system; (a′–c′): LLDPE system; (a″–c″): HDPE system: 5, 30, and 50 wt%. (B and C): LDPE system; (B′ and C′): LLDPE system; (B″ and C″): HDPE system: 30 and 50 wt% (four times magnified).

Table 3
Tensile and thermal properties of pure and various LDPE, LLDPE, and DHPE composites with zeolites

Filler	Uncoated zeolite system									Coated zeolite system								
Resin	LDPE			LLDPE			HDPE			LDPE			LLDPE			HDPE		
Filler content (%)	0	30	50	0	30	50	0	30	50	0	30	50	0	30	50	0	30	50
Tensile																		
modulus (MPa)	96	181	254	120	225	416	557	891	1056	96	193	316	120	277	419	557	1078	1374
Yield stress (MPa)	6.6	7.8	8.4	7.30	8.4	10	17.8	14.8	13.2	6.6	6.24	7.43	7.30	7.4	7.62	17.8	14.3	10.8
Elongation at break (%)	804	228	18	1000	1000	140	1000	918	626	804	278	30	1000	1000	654	1000	1000	847
Thermal																		
melting temperature (°C)	112	111	111	124	124	124	133	132	131	112	109	108	124	122	122	133	131	130
Crystallization temperature (°C)	89	90	91	102	106	108	109	112	113	89	88	88	102	98	97	109	108	107

the dewetting phenomenon is the most prominent in the HDPE matrix among three matrices systems.

3.3. Tensile and thermal properties

Table 3 exhibits the tensile properties such as the Young's modulus, yield stress, and elongation at break and thermal properties of the pure LDPE, LLDPE, HDPE, and their composites. Of composites with various filler contents, only three representative films were selected, which are 0, 30, and 50 wt% contents of uncoated and coated zeolite filled composites, respectively. In comparison of the above three values from S–S curves on both filler systems, the modulus proportionally increases by increasing the filler content from 0 to 50% in three matrices, induced from the reinforcement effect by filler loading. The degree of variation with respect to the modulus and elongation at break is more predominant in the coated zeolite system compared to the uncoated one. This would be the result of a lubricating effect by an addition of stearic acid as a coupling agent. In particular, the lubricating effect is outstandingly observed in the HDPE system, thus the stearic acid most strongly influences the mechanical properties of the HDPE composites. One may observe lubricating effect in many composites, if the filler/modifier ratio exceeds some critical content.

As HDPE has unique molecular structure with many short side chains, Young's modulus, yield stress, and elongation at break of the HDPE composites are higher than that of LDPE ones. On the contrary, since LDPE and LLDPE have long side and branch chains, the variation of molecular structure is also influenced on the morphological observation on stretched films: on SEM photographs of HDPE composites films, a great number of air holes with higher aspect ratio are appeared upon streching. In addition, fibril structure and merging phenomenon between air holes are greatly prominent, whereas, LDPE composite films with lower elongation show air holes with lower aspect ratio and the merging and fibril structure are rarely appeared.

In general, when the polymer films are stretched, main chains in polymer are apt to be aligned in parallel along with MD (machine direction). However, branch and side chains in LDPE and LLDPE interfere for maintaining these alignments, and results in their inability to respond with deformation as HDPE system behaves.

Dewetting and yield stress have a good correlation in terms of adhesion, molecular structure, and mechanical properties of the filled polymers. For instance, in most cases, highly dewetted systems yielded at lower stress [4]. Among our studied systems, we observed that the HDPE system yielded sharply at lower stress than the other LDPE and LLDPE. As mentioned previously, HDPE has numerous short chains than LDPE and LLDPE, which is responsible for its higher crystallinity by regular folding in main chains from melt.

In DSC measurements, the T_m of pure LDPE, LLDPE, and HDPE with the uncoated zeolite has almost no change, whereas that of the polyethylene derivative composites with the coated zeolite slightly (2–3 °C) shifts to lower temperature with successive addition of fillers. In general, the addition of inorganic filler not merely replaces polymer crystals and occupies the crystal lattice sites but also makes the amorphous regions increase [27]. On the other hand, the T_c of pure LDPE, LLDPE, and HDPE with the uncoated zeolite slightly increases, whereas that of the coated zeolite system slightly lowers. Lowering T_m or T_c in the coated filler system can be melting point depression or crystallization point depression due to a low molecular weight of stearic acid.

3.4. Air hole property

In order to study the formation and growth of air holes upon stretching, the representative film of 30 wt% uncoated and coated zeolite filled composites were used by stretching up to a certain level of strain. The comparative morphology of the film surfaces in Fig. 4(a) and (b), (a′)–(c′), and (a″)–(c″) for uncoated and in Fig. 5(a) and (b), (a′)–(c′), and (a″)–(c″) for coated zeolite filled LDPE, LLDPE, and HDPE film specimens with the same draw ratio of 50, 100, and 300% is shown, respectively. In the uncoated zeolite filled system shown in Fig. 4, it seems that particulate fillers are better wetted in the LDPE and LLDPE matrices than in the HDPE one. In addition, for the same elongation and strain rate, the HDPE composite provides a greater number of air holes due to the prominent dewetting behavior between the zeolite and HDPE matrix with high crystallinity. However, as the applied strain increases, the enlargement, number, and size of the formed air holes were greatly different from those observed in three matrices composites; the initially formed air holes are continuously enlarged along the machine direction (MD) upon stretching in LDPE and LLDPE composites. On the other hand, the above three variables increase dramatically in the HDPE composite. The fibril structure due to the merging effect, originated from the structural difference [28] between the nearest air holes, is more predominant in the HDPE composite.

In the case of the coated zeolite in Fig. 5, the more fibril structure is observed in both LLDPE and HDPE composites at a high draw ratio of 300%. However, this phenomenon is still superior in the HDPE composite. In addition, much larger air holes with higher aspect ratios are formed due to the improved flexibility of the matrix induced from the addition of a coupling agent, compared to the uncoated zeolite system. As a result, easier merging behaviors of air holes at high draw ratios lead to the reduced number of air holes as well as the augmented aspect ratio with respect to air holes.

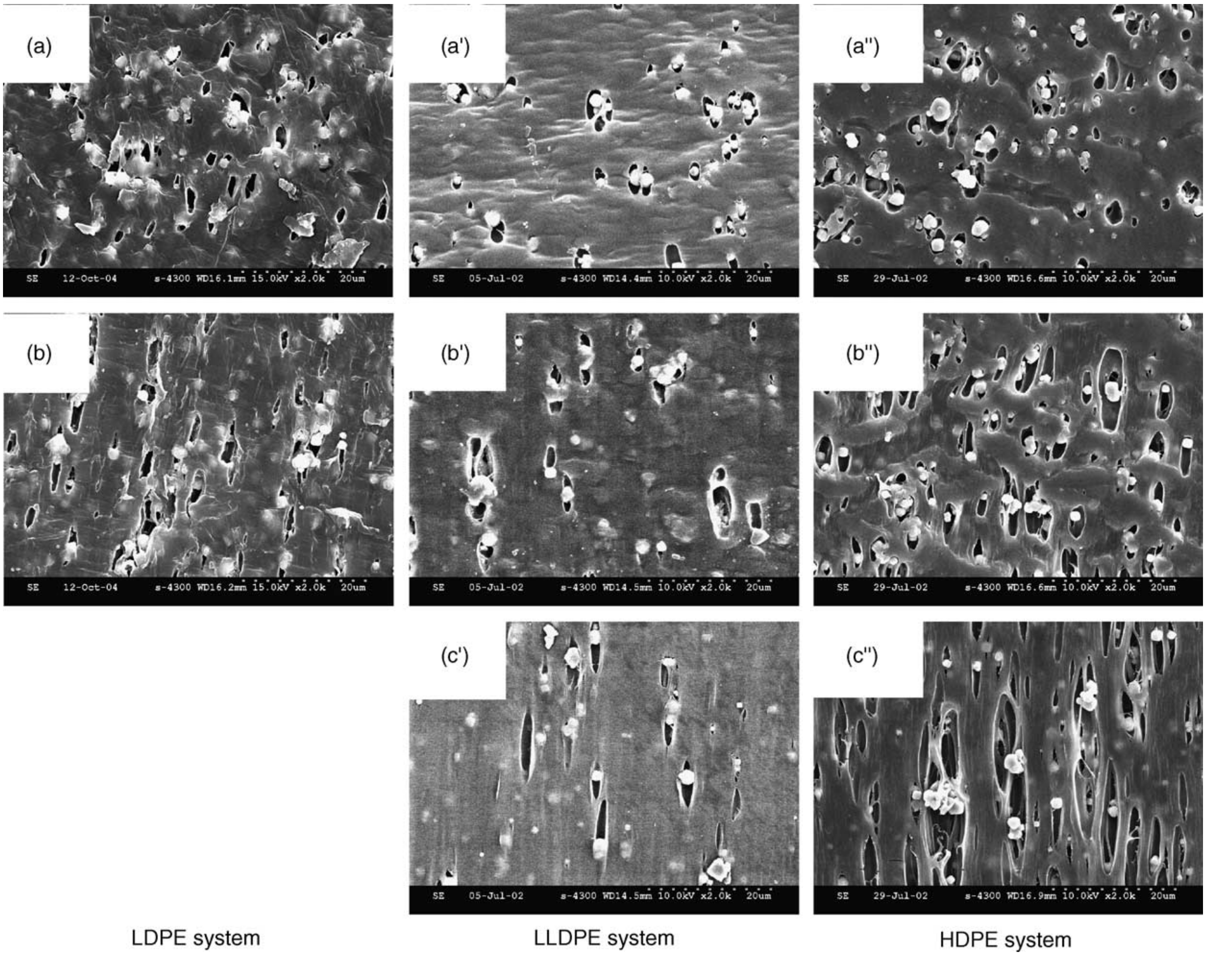

Fig. 4. The comparison of SEM microphotographs (×2000) on 30 wt% uncoated zeolite filled LDPE (a) and (b), LLDPE (a′–c′), and HDPE (a″–c″) composite films stretched to different draw ratios (50, 100, and 300%).

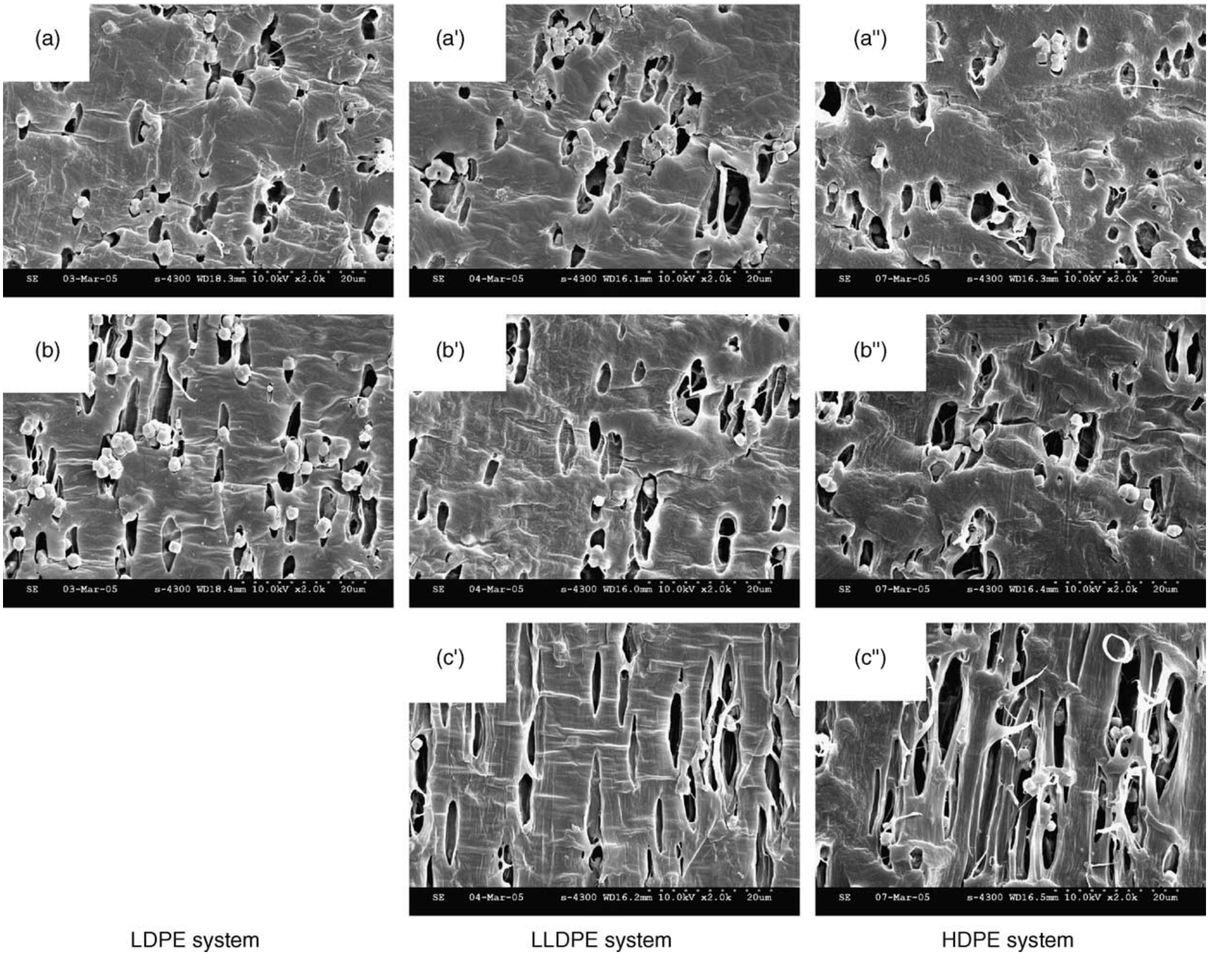

Fig. 5. The comparison of SEM microphotographs (×2000) on 30 wt% stearic acid coated zeolite filled LDPE (a–b), LLDPE (a′–c′), and HDPE (a″–c″) composites films stretched to different draw ratios (50, 100, and 300%).

The morphological properties of the LDPE, LLDPE, and HDPE composites were analyzed in terms of the aspect ratio, number of air holes, and area of air holes using the image analyzer calculated from the SEM photographs. Irrespective of the sorts of matrix, the average aspect ratio of air holes gradually increases with the draw ratio without any remarkable influence on filler content, as shown in Fig. 6(a)–(c) for the uncoated system and Fig. 6(a′)–(c′) for the coated one. In the LDPE system, the aspect ratio increased from 2 to 5.2 for the uncoated filler system, whereas it increased from 2 to 8 for the coated system during 300% of draw ratio. Whereas, for the LLDPE system, the aspect ratio augmented from 2 to 5.1 up to 400% draw ratio, whereas it rose from 2 to 6 up to 300% draw ratio. On the other hand, the aspect ratio of the HDPE system increased from 2 to 8 for 500% of draw ratio regardless of the uncoated or coated system. The result was analogous to that of our previous report of zeolite filled CoPP, TerPP systems [29]. In general, At equal drawing, the stiff matrix yielded a higher aspect ratio than the soft matrix.

This means that the coating of the zeolite surfaces enhances the aspect ratio of the matrix of LDPE and LLDPE, but do not affect at all that of HDPE. In our earlier investigation on LDPE, LLDPE, and HDPE composites filled with 50 wt% calcite coated with stearic acid, the similar behavior of the aspect ratio was observed with the draw ratio [21]. However, the degree of the increment of the aspect ratio in the stearic acid coated zeolite system was slightly higher than that of the stearic acid coated calcite filled system. This may be interpreted as a better size-distribution of zeolite particles in the matrix and more frequent merging behavior between neighboring air holes.

In comparison on the number of air holes plotted in Fig. 7(a)–(c) and (a′)–(c′) for the uncoated and coated systems, those in LDPE and LLDPE composites filled with coated zeolite decreased to 1/3 compared to the uncoated system and that in HDPE decreased to half of the uncoated system. This means that the neighboring air holes can be merged by means of enhanced flexibility induced by the addition of stearic acid. In particular, the merging effect is more visible in HDPE composites due to the fibril structure of HDPE.

On the other hand, the area of the air hole showed prominently dependent on the matrix filled with stearic acid coated zeolite as well as the draw ratio and the filler content. As seen in Fig. 8(a)–(c) and (a′)–(c′) for the stearic acid uncoated and coated zeolite filled composites, respectively, the area of the air holes for 50% draw ratio of LDPE increased from 20 to 220% for the uncoated zeolite system and from 50 to 650% for

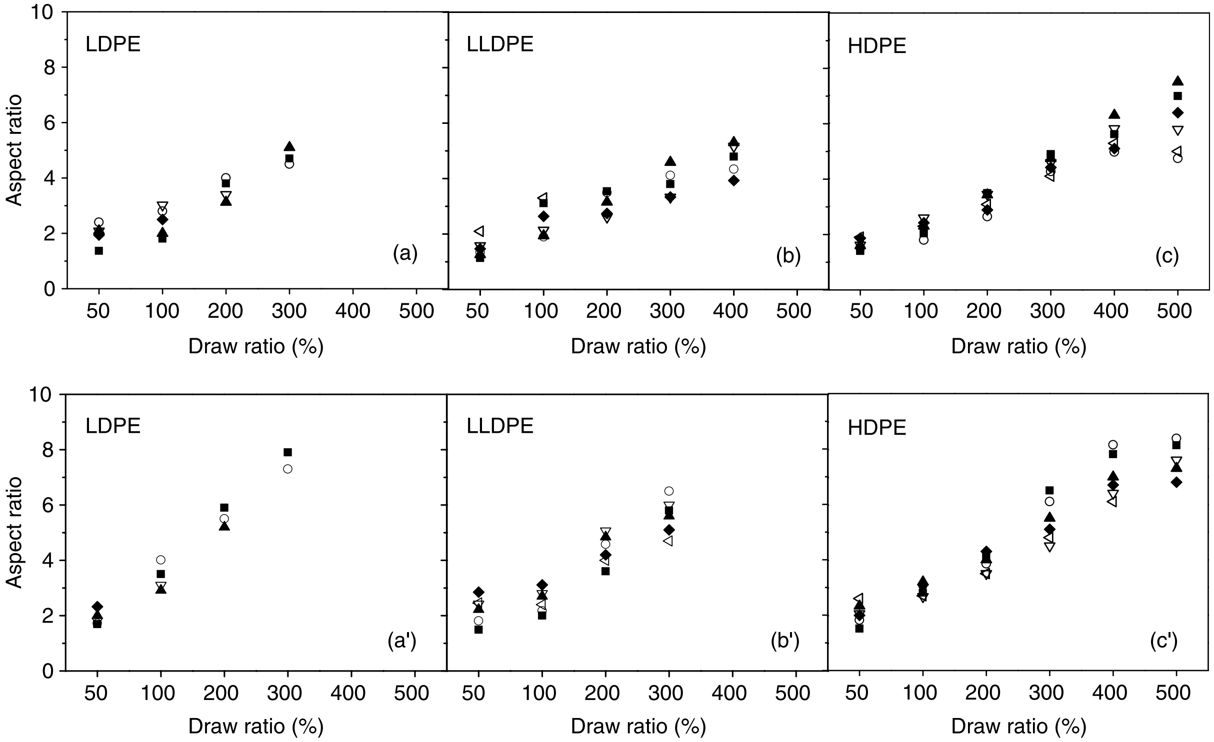

Fig. 6. The aspect ratio of air holes of uncoated (a–c) and coated (a′–c′) zeolite filled LDPE, LLDPE and HDPE composite films as a function of draw ratio (■: 5%; ○: 10%; ▲: 20%; ▽: 30%; ◆: 40%; ◁: 50% filler content).

the coated zeolite system. Whereas for 100% draw ratio, the area of the air hole of the stearic acid uncoated system increased from 50 to 450% and the coated system increased from 80 to 630%, respectively. However, for the further draw ratio, there was no significant improvement observed. For the LLDPE system, the enhancement in the area of the air hole is prominent upon both the filler content and draw ratio. For 50% draw ratio, the maximum area of the air hole between

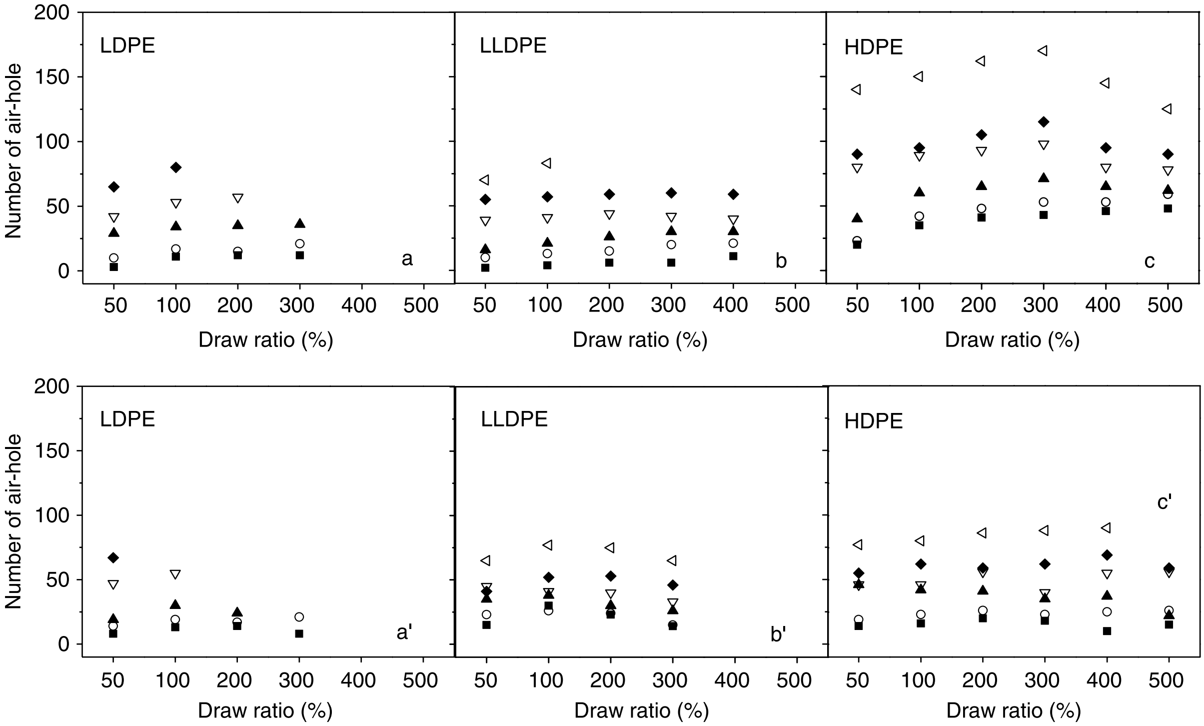

Fig. 7. The area of air holes of uncoated (a–c) and coated (a′–c′) zeolite filled LDPE, LLDPE and HDPE composite films as a function of draw ratio (■: 5%; ○: 10%; ▲: 20%; ▽: 30%; ◆: 40%; ◁: 50% filler content).

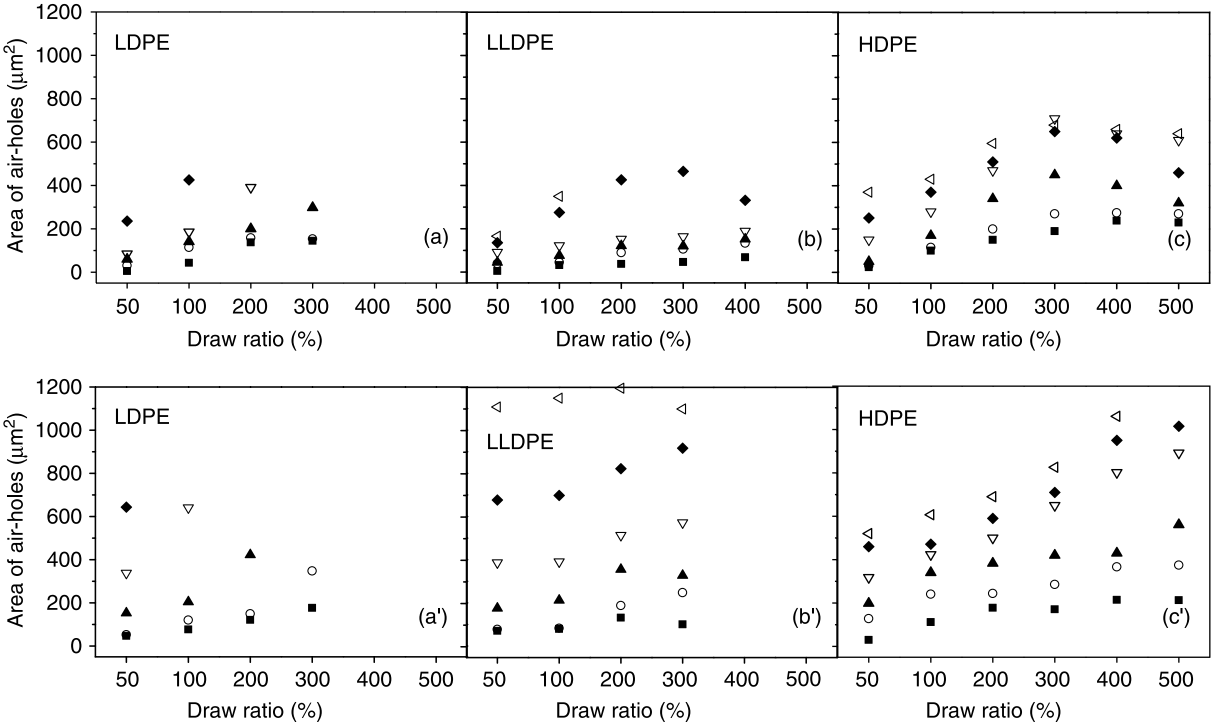

Fig. 8. The number of air holes of uncoated (a–c) and coated (a′–c′) zeolite filled LDPE, LLDPE and HDPE composite films as a function of draw ratio (■: 5%; ○: 10%; ▲: 20%; ▽: 30%; ◆: 40%; ◁: 50%).

the stearic acid uncoated and coated system dramatically increased from 180 to 1120 μm^2, respectively, while for the 300% draw ratio, it increased from 450 to 1100 μm^2 between the stearic acid uncoated and coated system. In the case of the HDPE system, the area of the air hole up to 300% draw ratio slightly increased with draw ratio and filler content has not much influence, but for 400 and 500% draw ratio, the area of the air hole for uncoated system was the maximum of 700 μm^2. For coated system, the increment area of 1000–1050 μm^2 was calculated as a function of both filler content and draw ratio of 400 and 500%. Thus, the increase in the area of the air hole is closely related to the aspect ratio and the number of air holes. In particular, for the LLDPE and HDPE systems, the area of the air holes with a high loading of filler dramatically increased due to the surface smoothness caused by the stearic acid coating and this is directly related with the reduced number of air holes and augmented aspect ratio caused by the merging effect of the fibril structure. In one article, Kwon et al. [22] also observed fibrillated air hole structure of HDPE, and its expansion along MD in dewetted region in the presence of stearic acid coated calcite unlike those of LDPE and LLDPE.

3.5. Rheological property

According to the basic principle of rheology, the flow behavior of a material can be expressed by the power of equation, as follows [30]:

$$\tau = K(\dot{\gamma})^n$$

where, τ and $\dot{\gamma}$ are the true shear stress and shear rate, K is the consistency index, and n is the flow behavior index. When n has the value below 1, it is called pseudoplastic in nature. Most of the polymeric systems are pseudoplastic character.

The complex melt viscosity (η^*) of pure LDPE, LLDPE and HDPE, and their composites filled with various contents of zeolite uncoated and coated with stearic acid is plotted against log frequency in Fig. 9(a)–(c) and (a′)–(c′), respectively. All the samples including pure LDPE, LLDPE and HDPE exhibit a power law behavior following a non-Newtonian in the frequency span operated. In addition, the shear-thinning or thixotropy phenomenon related to pseudoplastic behavior prominently is represented in all composites.

As the uncoated zeolite content increases, the complex melt viscosity smoothly increases up to around 30 wt% filler content, and then sharply increases. In particular, composites with 40 and 50 wt% zeolite show a significant leap compared to the other composites with LDPE, LLDPE, and HDPE.

In general, the complex melt viscosity increases with the addition of an inorganic particulate filler. On the contrary, in our coated system, the viscosity of 5 and 10 wt% zeolite filled LDPE and HDPE composites and 5, 10, and 20 wt% zeolite filled LLDPE system is lower than that of the corresponding pure resin at high frequency. In addition, the complex melt viscosity of the coated LDPE, LLDPE, and HDPE are all lower than the respective composites filled with the uncoated system. This may be due to the plasticizing or lubricating effect by an incorporation of stearic acid as a coupling agent, so that higher shear force must be imposed for uncoated zeolite filled composites.

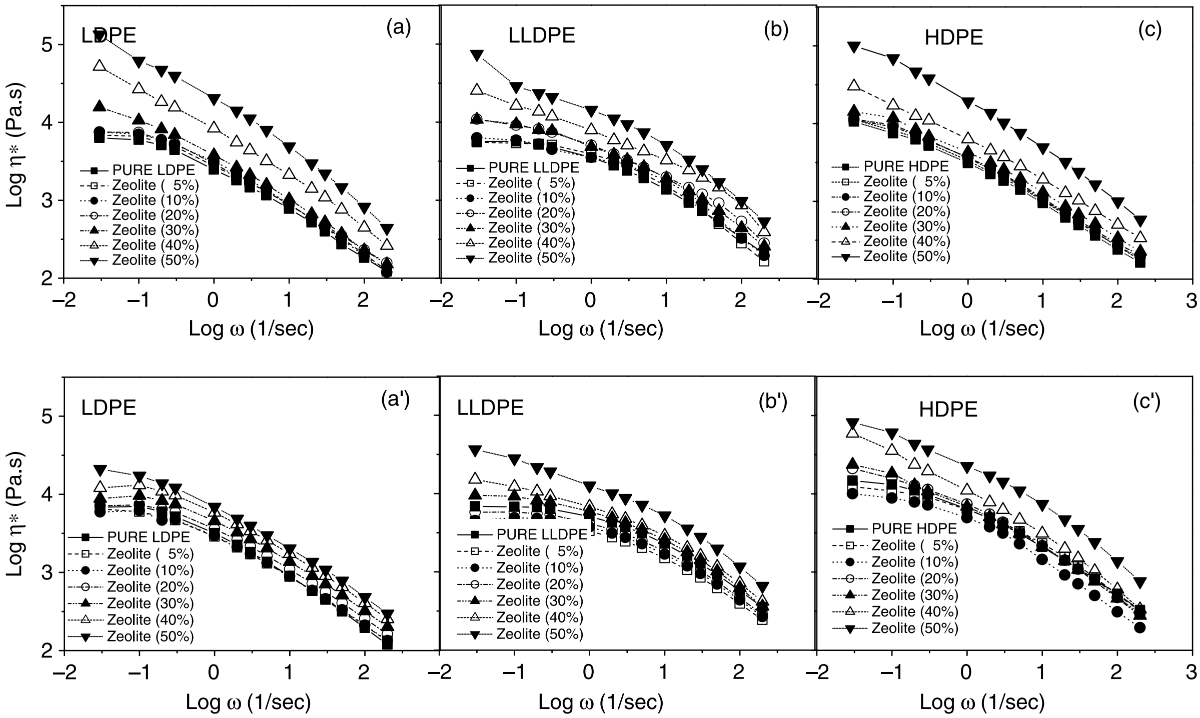

Fig. 9. The comparison of complex melt viscosity as a function of frequency for uncoated (a–c) and coated (a′–c′) zeolite filled LDPE, LLDPE and HDPE composites at 200 °C.

3.6. Impact strength

Fig. 10(a) and (a′) are graphical representations of the Izod impact strength of all respective uncoated and coated zeolite filled LDPE composites (error bar indicates the experimental deviation), respectively. As seen in Fig. 10(a) and (a′), there is seldom a difference on the impact strength between uncoated and coated zeolite filled composites under marginal experimental error and slight difference between 20 and 40 wt% of filler loading. In the LLDPE system seen in Fig. 10(b) and (b′), no significant enhancement up to 30 wt% of filler content was observed, but 40 and 50 wt% in the coated zeolite filled

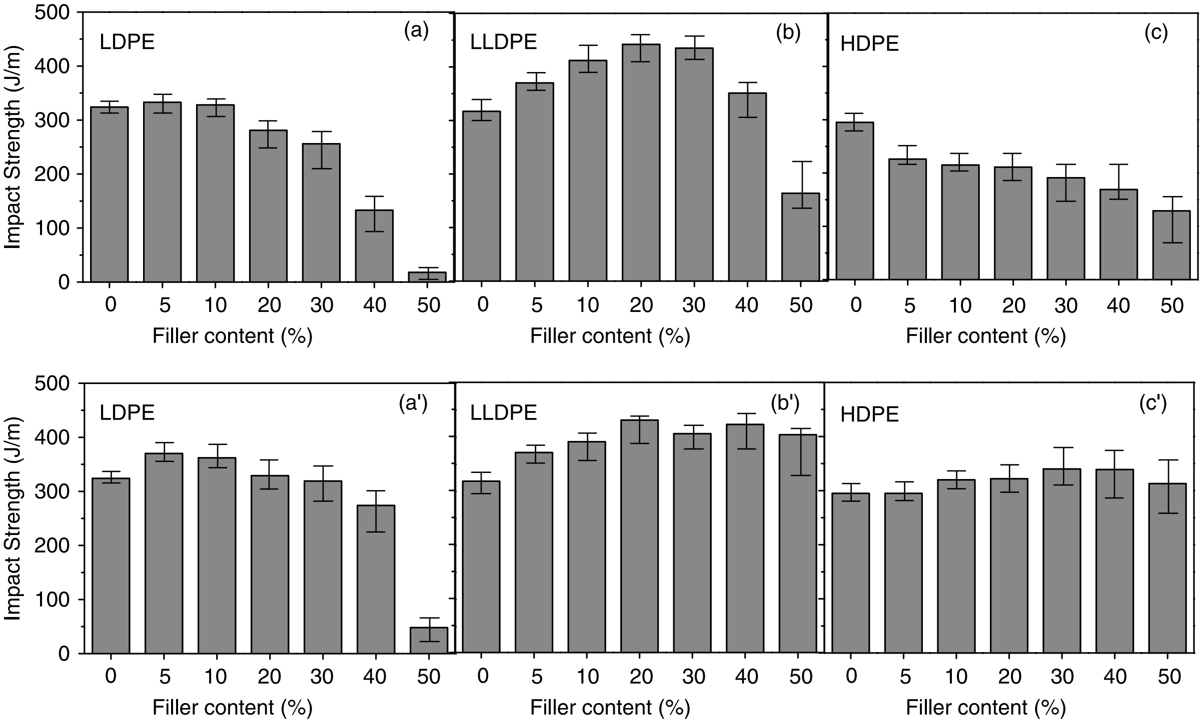

Fig. 10. Impact properties of uncoated (a–c) and coated (a′–c′) zeolite filled LDPE, LLDPE and HDPE composites at room temperature.

LLDPE composite showed improved impact strength compared to that in the uncoated system, in particular, highly improved impact property with 50% loading. On the other hand, the enhancement of the impact strength is remarkably observed in the HDPE composites, in particular between 5 and 50 wt% zeolite content, the improvement of the impact strength increased from 50 to 150 J/m as seen in Fig. 10(c) and (c′).

As a result, it is obviously shown that the stearic acid used as a coupling agent strongly influences the air hole and impact properties of LLDPE and HDPE composite systems, in particular with high loading (40–50 wt%)of zeolite.

Comparing to the impact strength of the LLDPE composite filled with 50 wt% calcite coated with stearic acid [27,30], the impact strength of virgin LLDPE resin was around 300 J/m and that of respective 50 wt% calcite and zeolite filled LLDPE composite was 386 and 403 J/m, respectively. Thus, the stearic acid coated zeolite in LDPE, LLDPE, and HDPE composite is more effective in air hole property and impact strength than in the calcite filled system [21,22,27,31] because of the reduced surface area. Since, zeolite is used for moisture absorber, it may be more valuable than calcite for the breathable application.

4. Conclusion

On the purpose of manufacturing the microporous polymeric films, LDPE, LLDPE, and HDPE/zeolite composites, filled with zeolite uncoated and coated with stearic acid were prepared. In this study, we have focused our attention on verifying how the stearic acid as a coupling agent influences the air hole properties measuring such as mechanical, thermal, morphological, and rheological measurements. The incorporation of stearic acid on zeolite surfaces enhances the flexibility of polymer matrices. As a result, coated zeolite filled composites had higher impact strength than that of uncoated ones. Both the aspect ratio and total area of air holes of coated systems increased upon filler loading and draw ratio, whereas reverse tendency was observed in the number of air holes. In particular, the increase of the area of the air holes in LLDPE and HDPE composites was prominent upon filler loading and draw ratio. On the other hand, the better adhesion between polymer matrices and inorganic fillers by modification of stearic acid led to the enhanced Young's modulus and elongation at break. Whereas, the declined values were observed in melting temperature (T_m), crystallization temperature (T_c), and complex melt viscosity. Our experimental results will be a good guideline of manufacturing breathable microporous films as well as selection of appropriate matrices.

Acknowledgements

This work is financially supported by Inha University in the year of 2004–2005.

References

[1] Torró-Palau AM, Fernández-García JC, Orgilès-Barceló AC, Martínez JM. Int J Adhes Adhes 2001;21:1.
[2] Yang J, Zhang Y, Zhang Y. J Appl Polym Sci 2002;85:1207.
[3] Verbeek CJR. Mater Lett 2002;52:453.
[4] Nielsen LE, Landel RF. Mechanical properties of polymers and composites. New York: Marcel Dekker; 1994.
[5] Wang G, Jiang P, Zhu Z, Yin J. J Appl Polym Sci 2002;85:2485.
[6] Bai SL, Chen JK, Huang ZP, Liu ZD. Polym Int 2001;50:222.
[7] Hale WR, Dohrer KK, Tant MR, Sand ID. Colloid Surf, A 2001;483:187.
[8] Kocsis-Karger J. Polypropylene structure, blends and composites. London: Chapman & Hall; 1995.
[9] Tavman IH. J Appl Polym Sci 1996;62:2161.
[10] Ghosh K, Maiti SN. J Appl Polym Sci 1996;60:323.
[11] Bekkum HV, Flanigen EM, Jacobs PA, Jansen JC. Introduction to zeolite science and practice. Elsevier: Amsterdam; 2001.
[12] Maiti SN, Singh G, Ibrahim MN. J Appl Polym Sci 2003;87:1511.
[13] Maiti SN, Mahapatro PK. J Appl Polym Sci 1991;42:3101.
[14] Mareri P, Bastide S, Binda N, Crespy A. Compos Sci Technol 1998;58:747.
[15] Rozman HZ, Lai CY, Ismail H, Ishakmohd ZA. Polym Int 2000;49:1273.
[16] Miles IS, Rostami S. Multicomponent polymer systems. 1st ed. New York: Longman Scientific & Technical; 1992.
[17] Metin D, Tihminlioğlu F, Balköse D, Ülkü S. Composites: Part A 2004;35:23.
[18] Kundu PP, Choe S. J Macromol Sci, Part C: Polymer Rev 2003;C43:143.
[19] Kundu PP, Biswas J, Kim H, Chung CW, Choe S. J Appl Polym Sci 2004;91:1427.
[20] Kim H, Kim KJ, Kwon S, Kundu PP, Jo BC, Lee BH, et al. J Appl Polym Sci 2002;86:2041.
[21] Kim KJ, Kwon S, Kim H, Kundu PP, Kim YW, Lee YK, Lee KJ, Lee BH, Choe S. J Appl Polym Sci 2003;87:311.
[22] Kwon S, Kim KJ, Kim H, Kundu PP, Kim TJ, Lee YK, et al. Polymer 2002;43:6901.
[23] Özmihci F, Balköse D, Ülkü S. J Appl Polym Sci 2001;82:2913.
[24] Tanaka Y, White JL. J Appl Polym Sci 1983;28:1481.
[25] Kim KJ. Dissertation. Rheology, processing, and characterization of isotropic, anisotropic, and mixed particle filled polymer system. USA: University of Akron; 1998.
[26] Wang Y, Lu J. G Wang. J Appl Polym Sci 1997;64:1275.
[27] Biswas J, Kim H, Shim SE, Kim GJ, Lee DS, Choe S. J Ind Eng Chem 2004;10:582.
[28] Kundu PP, Bhattacharya AK, Tripathy DK. J Appl Polym Sci 1997;66:1759.
[29] Biswas J, Kim H, Yim CS, Cho J, Kim GJ, Choe S. Macromol Res 2004;12:443.
[30] Martuscelli E, Palumbo R, Kryszewski M. Polymer blends. 1st ed. New York: Plenum; 1979.
[31] Kim H. Dissertation. Properties of the calcite and zeolite filled polyethylene composites. South Korea: Inha University; 2005.