Structural Effects on the Tensile and Morphological Properties of Zeolite-filled Polypropylene Derivative Composites

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Abstract: We have studied the effects that inorganic zeolite powder have on structurally different copolymer [poly(propylene-*co*-ethylene)] and terpolymer [poly(propylene-*co*-ethylene-*co*-1-butene)] systems and the possibility of preparing suitable porous composite films. The impact strength and yield stress of the composites did not improve upon any further loading of zeolite, but the modulus increased gradually with respect to the filler loading. The experimental modulus of each of the two systems was compared with theoretical models. We performed a morphological study of the filler mixing efficiency and image analysis. The number-, weight-, and z-average air hole diameters were compared with respect to the draw ratio as well as the zeolite loading. The experimental results suggest that these two matrices can provide a new choice for preparing future multiphase polymeric porous films by stretching them unidirectionally. In particular, we suggest that a 40 wt% zeolite loading at a draw ratio of 4 is useful for porous film applications.

Keywords: zeolite, poly(propylene-*co*-ethylene), poly(propylene-*co*-ethylene-*co*-1-butene), multiphase composite, porous film.

Introduction

Various properties of polymeric systems can often be improved with the addition of organic or inorganic fillers.[1] These systems, termed as multicomponent systems,[2] can under go substantial property improvements that can include mechanical strength, viscoelastic response, chemical resistance, gas and chemical barrier properties.[3-6] The use of particulate materials for enhancement of polymer properties dates back to the earliest years of the polymer industry. Initially used as extending agents to reduce the cost of polymer-based products, fillers were soon recognized to be an integral component in many applications involving polymers, particularly in reinforcement.[7-10] In spite of the wide spread use of polymer composites throughout the polymer industry, a satisfactory understanding of the fundamental mechanism of the properties of these materials has eluded researchers.

The mechanism of reinforcement in filled polymer composites depends on various factors, including the properties of the polymer and filler, size and shape of the filler (particulate, fibrous, fabric, etc), phase state of the polymer (crystalline, rubbery, etc.), process by which the filled polymer composite is manufactured, and the nature of the interphase between the polymer matrix and the filler. While all these factors, and more, have an effect on the final product and the stress of matrix is partially transferred to the fille. Since, improved strength and stiffness are typically the properties of interest in the final composite, this effort has usually centered around a search for improved adhesion between the filler and polymer matrix. Generally, this search is for a coupling agent,[11] or compatibilizer[12] that bridges between the matrix and filler phases by providing improved adhesion. The quest for improved compatibilizers[12] has attracted the talents of many researchers. However, many of the fillers used, such as inorganic clays or layered silicates are immiscible with the polymer matrix. This leads to aggregation of the filler particles that can seriously hinder the property improvements of the composite. Often, surface modification[13] of the filler particles is carried out to decrease the disfavorable interactions between the filler and the polymer matrix, thusly creating a finer and more homogenous dispersion within the composite material that leads to greater enhancement of the target properties. Though modified filler is suitable for property enhancement, still commercially many fillers used in its original form.
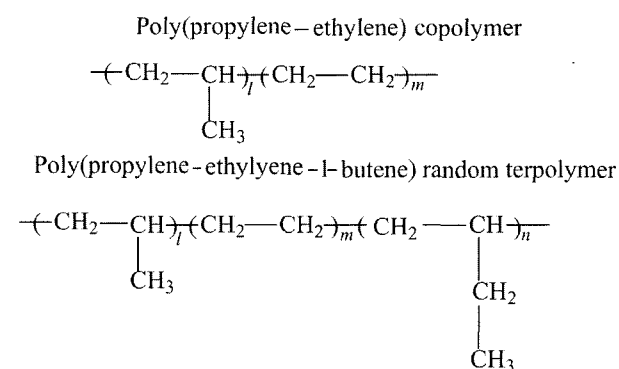
Nago *et al.* described about biaxially stretched calcite filled microporous polypropylene sheet structure.[14] They clearly specified about rigid nonporous filler melt processed with polyolefin matrix. Kundu & Choe recently reported elaborately in their exclusive review about porous polyolefin film making procedure for moist air transmission.[15] Zeolite is a spectrum of inorganic materials known in diverse applications such as molecular sieves, catalysis, and ion exchange materials.[16] But they are also known as a filler in thermoplastic matrices.[17-20] Crystalline zeolite is a framework of alumino-silicates based on infinitely extending three-dimensional networks of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of all oxygens.[21] Recently, a novel technique for the preparation of porous polyolefin films using polyethylene and polypropylene copolymer blends is developed throughout a wide range of strain 50-700%.[22]

In the field, HDPE/calcite film stretched up to 100% is often used for diapers for baby and adults. However lamination of this PE film with PP derived adhesives is not easy due to a lack of compatibility between PE and PP. Based on this phenomenon, CoPP and TerPP are proposed as main matrices to investigate the characteristics of pores, because these two materials contain ethylene and/or butylene repeating unit with propylene.

Our present study focused on two different polymer systems along with propylene derivative polymers as matrix component filled with zeolite by melt extrusion process. One of the matrix is two components, CoPP, where 2% ethylene as a comonomer with propylene and the other one consists of three components, TerPP, where 2% ethylene and 5% 1-butylene as comonomers with propylene. The special attention is also paid on the nature of porous structure that is formed due to stretching and filler loading for these different matrices. Suitable porous film could be a good application area where ventilation is prerequisite.

Experimental

Materials. Two polymers used in this study are poly(propylene-*co*-ethylene), which is called CoPP and poly(propylene-*co*-ethylene-*co*-1-butene), which is called TerPP supplied by SK Corporation, Ulsan, Korea. The physical properties of the two selected resins are summarized in Table I, which also includes the physical data of these two resins used in this work. The chemical representation of CoPP and TerPP microstructure is the following;

Poly(propylene−ethylene) copolymer

$$-\!\!\left(CH_2\!-\!\!CH\right)_{\!l}\!\!\left(CH_2\!-\!\!CH_2\right)_{\!m}\!\!-$$
$$\quad\quad\quad | $$
$$\quad\quad\quad CH_3$$

Poly(propylene-ethylyene-1-butene) random terpolymer

$$-\!\!\left(CH_2\!-\!\!CH\right)_{\!l}\!\!\left(CH_2\!-\!\!CH_2\right)_{\!m}\!\!\left(CH_2\!-\!\!CH\right)_{\!n}\!\!-$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad CH_3 \quad\quad\quad\quad\quad\quad CH_2$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$$

Here, the subscript l, m, and n denote the relative ratio of the repeating unit.

Inorganic zeolite powder is procured from Zeobuilder Co. Ltd., Chungnam, Korea. Chemical structure and properties of the zeolite used in this study is also tabulated in Table II.

Zeolite Premixing and Compounding. The zeolite was oven dried before mixing for 3 hrs at 110°C and the resin used as received by kindly provided by the supplier. In order to apply better mixing between the zeolite and matrices of CoPP or TerPP, the resin/zeolite batch was prepared by premixing them thoroughly before feeding into the hopper of a laboratory Brabender twin-screw extruder (PL 2000) with L/D of 16 as a screw dimension. The mixed compounds,

Table I. Resins Used in This Study

Materials (grade name)	Code (comment)	Density (g/cm³)	MI (g/10 min)	HDT (°C)	Supplier
Copolypropylene (R930Y)	CoPP PP:Ethylene (98:2 wt%)	0.90	4.5	90	SK Corporation, Korea
Ternary polypropylene (T131N)	TerPP PP:Ethylene:Butylene (93:2:5 wt%)	0.90	5.0-5.5	60	SK Corporation Korea

MI: melt index; HDT: heat distortion temperature.

Table II. Properties of Zeolite Used in This Study

Form and Chemical Composition	Density (g/cm³)	Particle Size (μm)	pH	LOD (at 105°C/hr)	BET Area (m²/g)	Supplier
Fine white powder, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$	1.9	2~5	10~12	4~6	250~350	Zeobuilder, Korea

LOD: loss on drying.

extruded through a round die, were immediately passed through cold water-bath, then the solidified long strands of composite were pelletized using a pelletizer. A temperature gradient, maintained in the twin-screw extruder, was 190 °C in a feeding zone, 200 °C in a compression zone, 210 °C in a metering zone and 220 °C in the die zone for the CoPP system and these variables were 180, 190, 200, and 210 °C, respectively, for the TerPP system. The rotation speed of the screw was maintained between 60 and 70 rpm.

Compression Molding. The post-compounded CoPP and TerPP pellets and their composites from twin-screw extruder were kept in oven for moisture removal at 105 °C for 3 hrs. All dried pellets were then placed on a Carver laboratory hot press at a pressure of 5×10^4 Pa and the temperature at 200 °C for preparing the impact bars at a dimension of $3.64 \times 12.7 \times 3.17$ mm according to ASTM D 256. The hot mold was allowed to cool then under room temperature.

Film Preparation. Film specimens were prepared by fixing a slit die in 100×0.5 mm at the end of the extruder in order to measure the mechanical and morphological properties. The dimension of the film was $15 \times 0.4 \times 165$ mm according to the ASTM D882-97 for a tensile testing. Extruded film was uniaxially drawn using a take-up device maintaining the film thickness about 400 micrometers.

Characterizations. The morphology study of the zeolite filled CoPP and TerPP was done for two purposes. One is for viewing fractured surface and the other for drawn film morphology study. The dispersion of the zeolite in the matrix and the particle agglomeration were visualized from the cryogenically fractured surface. Cryogenically fractured surface 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 test using SEM.

Tensile properties of the film specimens were measured using Instron 4465 at 25 °C and 30% humidity. The Young's modulus, yield stress, elongation at break, and maximum stress were enumerated from a stress-strain curve. In particular, the Young's modulus, which is a measure of the stiffness, was compared with the theoretical model. The initial grip distance of the film was maintained 50 mm and the deformation rate was fixed at 50 mm/min.

Izod impact strength values were evaluated on V-shape notched samples on a CEAST instrument (Italy) according to ASTM D 256 with a notch depth of 2.5 mm and a notch angle of 45 °. For pure CoPP, TerPP as well as their composites, at least ten specimens were tested and the average values were collected. All the tests were carried out at ambient temperature.

For mechanical and morphological characterizations, at least ten specimens were used and the most probable results were averaged. The SEM images were used for quantitative analysis of the air-hole area and the aspect ratio using the special image analyzer (IA) soft ware.

Results and Discussion

Zeolite Particles and Its Dispersion in Both Matrices. Figure 1(a) represents the SEM microphotographs of zeolite particles at 2,000 magnification. Zeolites are crystalline inorganic materials possessing an infinitely extended three-dimensional network of AlO_4 and SiO_4 linked to each other. It is seen that Na-A type zeolite used in this study has a polydispersed cubic-like shape with an approximate particle size range of $2{\sim}5\ \mu m$.

In order to confirm the uniform dispersion and wetting behavior of the zeolite particles in all compositions, SEM microphotographs of zeolite containing CoPP and TerPP systems were taken using a cryogenically fractured surface. Figures 1(b) through 1(d) are the representations of the cryogenically fractured surface of 10, 30 and 50% filled CoPP composites. Zeolite particles are well dispersed with-
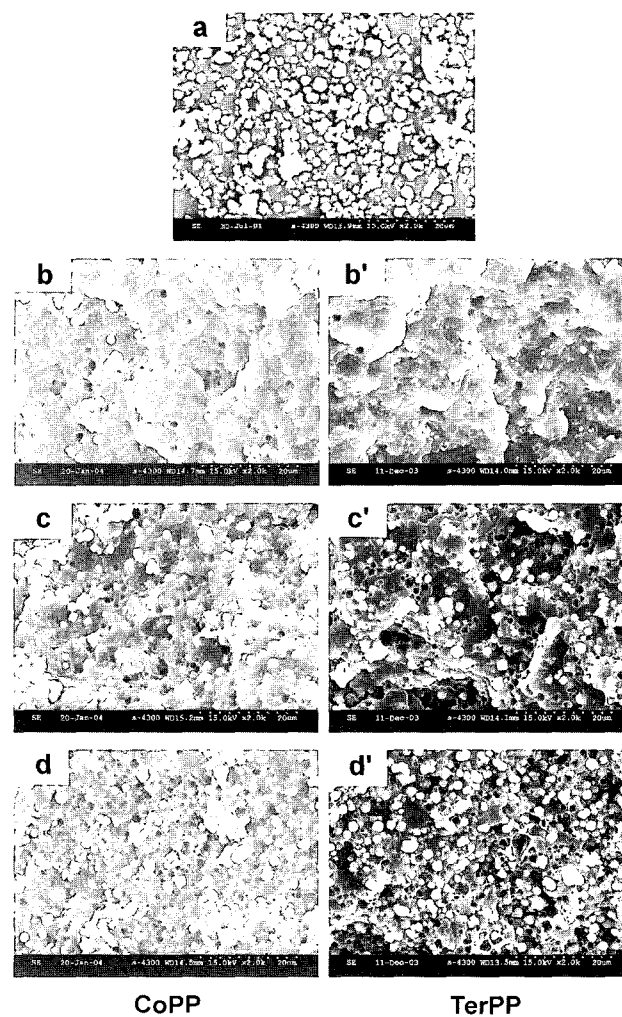

CoPP   TerPP

Figure 1. SEM microphotographs ($\times$ 2,000) of zeolite and cryogenically fractured surface of zeolite filled composites. (a): zeolite (b-d): 10, 30, and 50% zeolite filled CoPP (b'-d'): 10, 30 and 50% zeolite filled TerPP system.

out agglomeration since a good distributive mixing was achieved during the compounding by means of a twin-screw extruder. One can see a good dispersion of the zeolite and uniform population density of the zeolite particles at higher filler loading. It is also true that the zeolite particles in TerPP matrix seem to show a fair adhesion and a good wetting without a filler agglomeration as seen in Figure 1(b) to 1(d). The dispersion of the filler looks better than the calcite filled systems with HDPE and LLDPE, where the fracture morphology of 50 wt% calcite loaded CoPP, TerPP induced noticeable particle agglomeration.[7, 8]

Tensile Properties. Figure 2 exhibits the stress-strain curves of the film for the pure CoPP and various compositions of zeolite filled CoPP at deformation rate of 50 mm/min (Figure 2(a)). The tensile stress increases with the zeolite content and this may be due to a reinforcement effect of the zeolite. The yielding behavior was observed for pure and all zeolite filled CoPP specimens. In addition, pure and 5~10 wt% zeolite filled composites showed that the elongation at break exceeds 1,000% (due to the machine limit which

was fixed to stretch the specimen for a span of 20 min) at 50 mm/min, then declines upon zeolite loading.

Figure 2(b) also represents the stress-strain curves of the TerPP composites film measured at a crosshead speed at 50 mm/min. As shown in this figure, the tensile stress and yield stress decreased gradually with zeolite loading. As mentioned earlier in the investigation of dispersion, the higher loading of zeolite may induce a large number of air holes upon stretching and reduced stress in zeolite filled CoPP and TerPP system. Similar results have been reported using PP/zeolite composite by Upadhyay,[19] where, synthetic zeolite was added up to 40 wt% in PP matrix, and the tensile strength and the elongation at break decreased with the zeolite content.

The Young's modulus, which is a characteristic of materials rigidity, is calculated using the stress-strain (S-S) curve represented in Figures 3(a) and 3(b) for the CoPP and TerPP system, respectively. As the zeolite loading increased from 5 to 50 wt% in the CoPP system, a correspondingly increment of modulus from 1181 to 1482 MPa was observed. Whereas, the Young's modulus of the TerPP system increased from 535 to 1210 MPa for the same loading of zeolite. It is
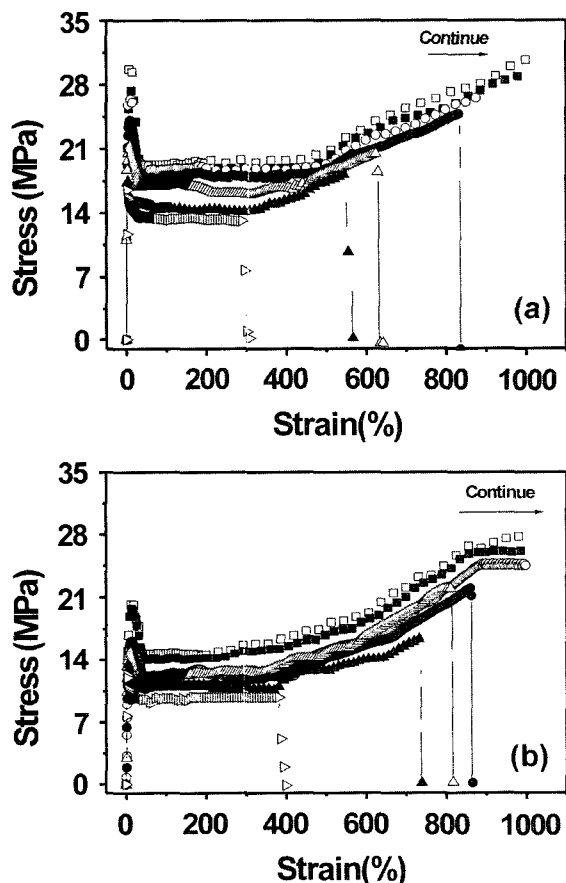

Figure 2. Stress-strain curves of film specimens for pure and zeolite filled CoPP and TerPP composites at crosshead speeds of 50 mm/min (a): CoPP systems, (b): TerPP systems (□ : Pure; ■: 5% zeolite; ○: 10% zeolite; ●: 20% zeolite; △: 30% zeolite; ▲ : 40% zeolite; ▷ : 50% zeolite).
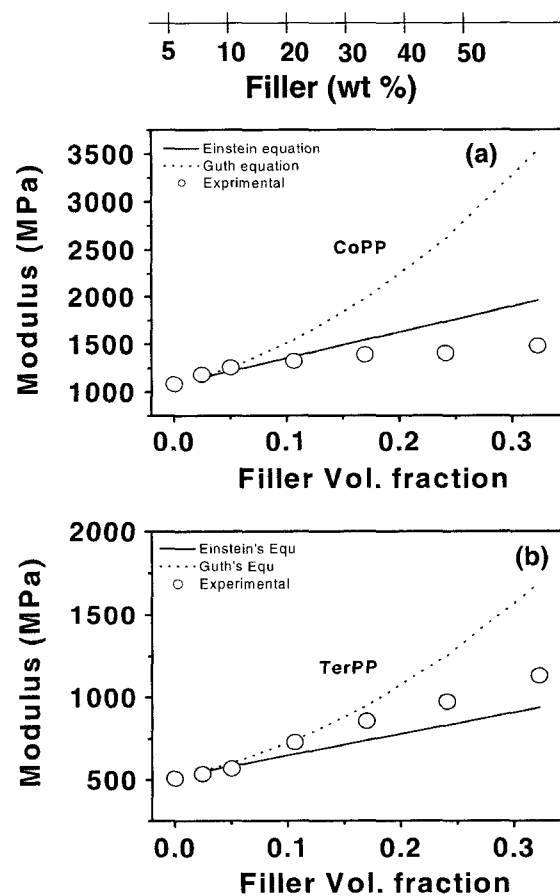

Figure 3. Verification of experimental and theoretical modulus of pure and zeolite filled systems (a): CoPP, (b): TerPP (— : Einstein's Equation, ··· : Guths Equation, ○: Experimental).

well known that inclusion of rigid particulate fillers induces an increase in stiffness and the Young's modulus of the composites.[8] Theoretically there are several approaches for modulus calculations of the particulate filled composites. Among these equations, the simplest one introduced by Einstein has the following form.[25]

$$M_c = M_p(1 + 2.5\phi) \tag{1}$$

Where M_c, M_p, and ϕ are the modulus of the elasticity of the composite, unfilled polymer and the volume fraction of filler, respectively. This equation is valid for low filler loading and assumes perfect adhesion between filler and polymer matrix. Einstein's equation implies that the stiffening action of filler is independent of the size of the filler particles. Another noticeable aspect of the equation is that it followed the volume occupied by the filler only and neglected filler weight.

The modulus of the composite followed the Einstein's theory was derived by Guth & Smallwood.[26]

$$M_c = M_p(1 + 2.5\phi + 14.1\phi^2) \tag{2}$$

where, all notations are the same as the previous equation.

The calculation of volumetric filler and resin concentration is based on solid densities of the constituents. The relationship between the volume fraction (ϕ) and weight fraction (φ) of filler in the composite is represented by:

$$\phi = \frac{\varphi}{\varphi + (1 - \varphi) \cdot \dfrac{\eta_f}{\eta_p}} \tag{3}$$

where η_f, η_p are the densities of filler and pure polymer, respectively.

We calculated the modulus values using these two equations and plotted in Figure 3. In Figure 3(a) representing the CoPP/zeolite system, the experimental data up to 5 vol% of zeolite loading fairly well followed the theoretical value of Einstein and Guth equations, but lowered with increased volume fraction than the theoretical values calculated using both equations. The predicted values using the Guth equation were much higher than the experimental one. On the contrary, for TerPP/zeolite (Figure 3(b)) system, the experimental data run between the calculated values obtained from these two equations. The equation was coincided at low filler loading and the deviation becomes large at high filler loading for both CoPP and TerPP composites. It is not easy to directly measure the bond energy between zeolite and polymer at this moment. Adhesion promoter and filler surface modification may also have influence on it. However, among these systems TerPP might be adhered strongly with filler than CoPP because experimental values passed between these two theories. Tjong et al. also found anomalous result when they verified the modulus of whisker reinforced

polypropylene composites by theoretical model.[27]

In Figure 4(a), the yield stress of both systems was plotted against filler loading. The yield stress reduced from 31 to 17 MPa for the CoPP and from 21.5 to 15.5 MPa for TerPP systems upon zeolite loading; the yield stress of CoPP system was higher than TerPP system. This behavior may arise from 1-butene in CoPP system, which lowers the stress upon incorporation of rubber type component. This behavior is totally opposite to that of the zeolite filled LLDPE system,[21] but similar trend is observed with the calcite filled HDPE[7] and zeolite filled HDPE composite.[20] This reduced yield stress may arise from the fact that the matrix is weakening due to the increased area of air holes upon stretching. Thus the yield stress variation between the systems clearly results in due to the structural dissimilarity of the matrices upon addition of comonomer.

The elongation at break drawn in Figure 4(b) is more than 1000% for up to 10% zeolite loading and 836, 640, 565, and 302% for 20, 30, 40, and 50% zeolite filled CoPP system, respectively. In addition, they are more than 1,000% for up to 10% zeolite and 863, 820, 737 and 400% for 20, 30, 40 and 50% zeolite loading TerPP system, respectively. The elongation values are similar up to 20 wt% zeolite loading,
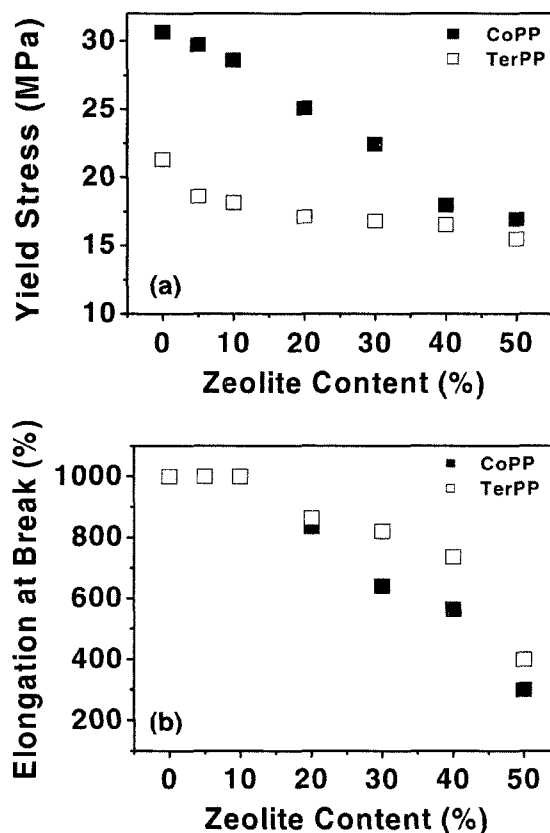

Figure 4. The yield stress and elongation at break of pure and zeolite filled CoPP and TerPP: (a) Yield Stress and (b) Elongation at break (■ : CoPP, □ : TerPP).

but beyond this, that of the TerPP system showed slightly higher elongation. The structural variation of the terpolymer, which is an addition of rubbery microstructure of 1-butene plays a vital role in ultimate elongation of the film. The discontinuity and stress concentration due to rigid inclusions in the matrices is generally responsible for the reduced elongation phenomenon at higher filler loading. The elongation at break falls very fast after 30 wt% of zeolite loading due to immense surface area of the zeolite filler.

Impact Properties. The graphical representation of the impact strength of both CoPP and TerPP systems, respectively, decreases with zeolite loading as usual (Figure 5). In addition, the impact strength of TerPP system is higher than the CoPP system, which implies that incorporation of 1-butene is responsible for this behavior and this is consistent with the mechanical properties. The impact property of TerPP over CoPP due to the presence of 1-butene, brings a characteristic property that has absolutely opposite trend compared to the yield stress. In general, impact property has no positive effect when part of the rubbery phase is substituted from matrices by rigid inert filler or inclusions. This result is similar to that of HDPE/zeolite syetems,[20] but opposite to that of LLDPE/Zeolite systems.[21]

The comparative drawn morphology of 30 wt% zeolite filled CoPP with the draw ratio of 0.5, 2.0, 3.0 and 4.0 are shown in Figures 6(a), 6(b), 6(c), and 6(d), respectively, and in Figures from 6(a') to 6(d') with the same draw ratio for the TerPP system. Between the two systems, one can observe that the wetting nature of zeolite in both CoPP and TerPP matrices is almost same. At the draw ratio of 0.5 the dewetting is initiated between the zeolite particles and the matrices (Figure 6(a), 6(a')), however as the applied draw ratio increases, the size of the previously formed air holes continue to grow towards machine direction (MD) irrespective of the systems. In addition, the initially formed air holes are continuously enlarged along the MD upon uniaxial stretch-
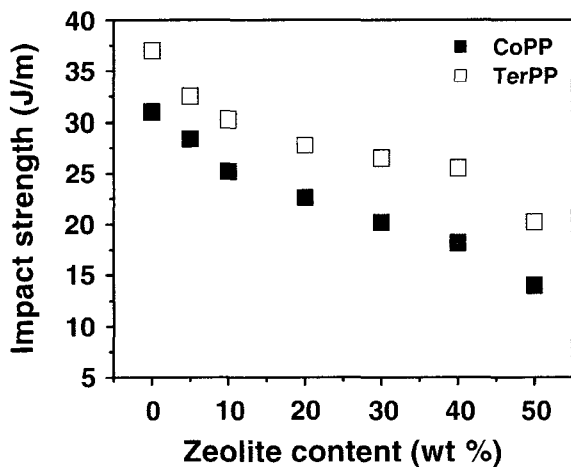

Draw ratio 0.5

Draw ratio 2.0

Draw ratio 3.0

Draw ratio 4.0
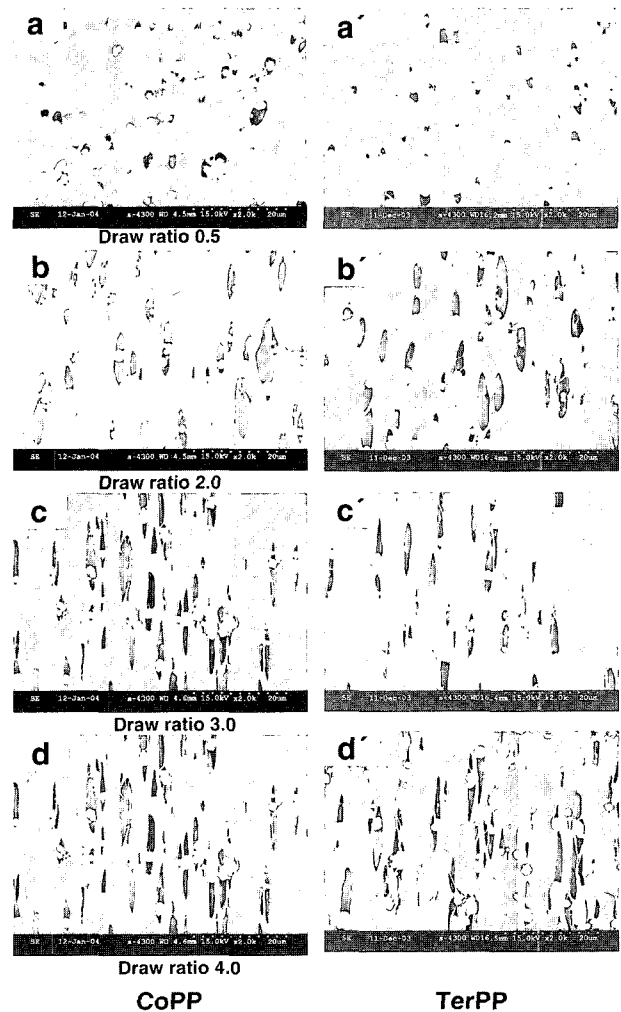
CoPP   TerPP

Figure 6. The comparison of SEM photographs on 30% zeolite filled CoPP (a-d) and TerPP (a'-d') composites stretched film at different draw ratios (0.5, 2, 3, 4, respectively).

ing. Significant fibril structure in zeolite filled CoPP and TerPP systems was not observed, whereas it was observed in HDPE/zeolite[20] composite film.

Quantitative Analysis of Air Hole by Image Analysis. The image analyzer software was utilized for quantitative measurement on the scanning electron microscopic image. The average air hole aspect ratio, total area of air hole and diameter of air holes upon stretching were calculated at 30 wt% of fixed zeolite content with varying draw ratio.

To analyze the morphological properties between CoPP and TerPP composite, the comparative values of the aspect ratio and total area of air-holes are plotted in Figures 7(a) and 7(b), respectively, for 30 wt% zeolite filled systems upon various draw ratios. In Figure 7(a) the values of the aspect ratio l/d (the ratio of the major axis to the minor axis of air hole) of the air holes linearly increase with the draw ratio. The observed average aspect ratio increases from 1.51 to 6.06 for the CoPP system and from 1.48 to 5.5 for the
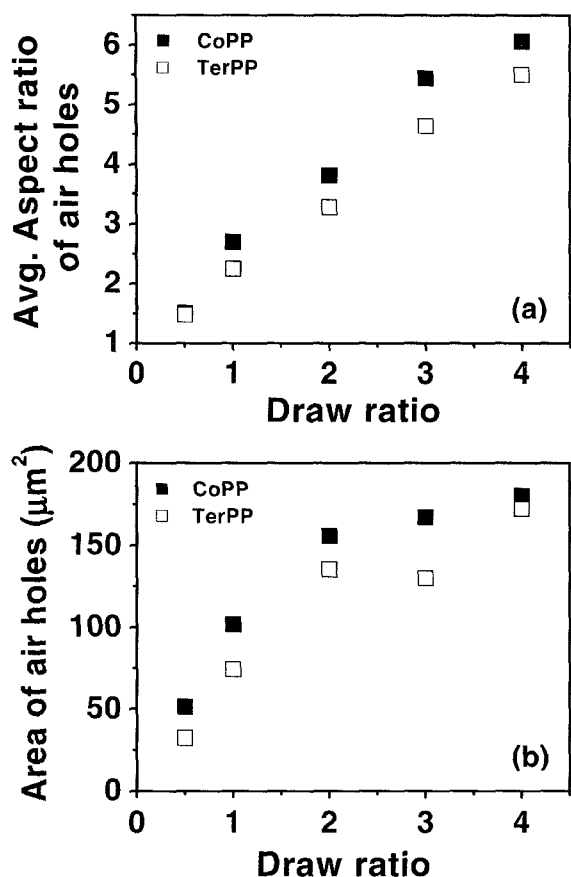

Figure 5. Impact properties of pure and zeolite filled systems at room temperature (■ : CoPP, □ : TerPP).

Figure 7. (a) The aspect ratio and (b) total area of air holes of CoPP and TerPP composite film as a function of draw ratio (■ : CoPP, □ : TerPP).

Figure 8. (a) The aspect ratio and (b) total area of air holes of CoPP and TerPP composite film as a function filler content at fixed draw ratio 4.0 (■ : CoPP, □ : TerPP).

TerPP system. The result was analogous to that of our previous report of zeolite filled LLDPE and HDPE systems.[20,21] The lower aspect ratio of TerPP than CoPP systems can be explained from their microstructural differences, of which the rubbery and glassy behavior of the polymer matrix may be influencing on the aspect ratio of air hole. At equal drawing, the elastomeric film will create more circular air hole shape than do in glassy film, which results in lower aspect ratio. On the other hand, the glassy film will produce sharp elliptical air hole that causes higher aspect ratio. It seems that the higher the stiffness in matrix, the more will be the aspect ratio of air hole when interacted with rigid filler.

In Figure 7(b), the total area of air holes in both CoPP and TerPP system according to the draw ratio showed successive increment up to the maximum draw ratio of 4. The air hole area of CoPP system is slightly larger than that of TerPP system.

The aspect ratio and total area of air holes are also plotted in Figures 8(a) and 8(b), respectively, with respect to zeolite content up to 40% at fixed draw ratio of 4.0. The air hole aspect ratio lies between 4.7 and 6.5 for all compositions and the zeolite content doesn't remarkably influence on the
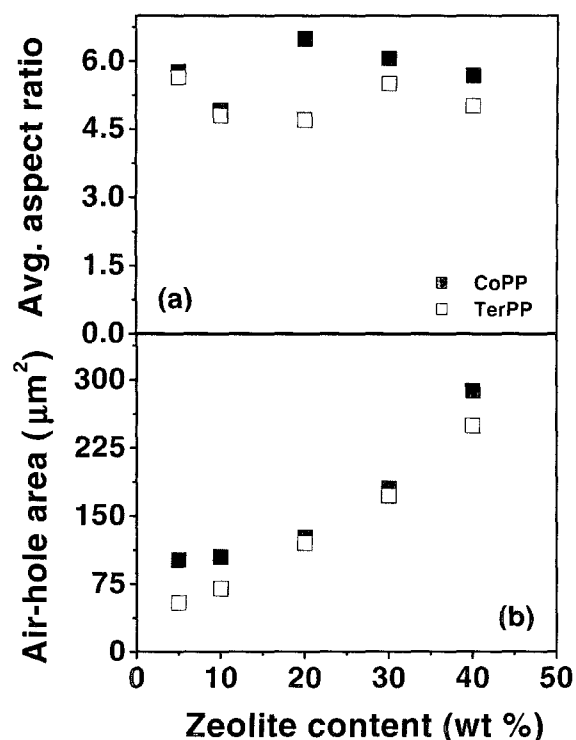
aspect ratio. In Figure 8(b), the total area of air holes in both CoPP and TerPP system is plotted with zeolite content at fixed draw ratio of 4.0. The area of air hole of both CoPP and TerPP system gradually increased with zeolite loading and maximized at 40 wt% of zeolite loading.

Conclusions

We have attempted to develop the CoPP and TerPP composites using an inorganic filler, zeolite, by using a conventional compounding procedure with a twin-screw extruder. Mechanical properties of the unfilled CoPP, TerPP and their composites having various amounts of zeolite are thoroughly analyzed using film specimens. The improved Young's modulus was observed by a successive increment of the filler in both systems. The yield stress of the CoPP and TerPP films gradually decreased, which indicates a weak adhesion between matrices and filler. The elongation at break is almost constant up to a certain draw ratio, but reduced at higher draw ratio in both systems. The impact strength of the composites also does not show any synergistic effect. The wide variation of mechanical properties was obviously a result from the structural differences of CoPP and TerPP. The aspect ratio and the area of air holes increased almost linearly with draw ratio. Number-, weight- and z-average quantitative air hole diameter was calculated

with respect to the stretching ratio and filler content of the film. The air hole structure and shape of the zeolite filled drawn film in CoPP and TerPP matrices looks smooth than the calcite filled polyolefin matrices. The present study suggests that these two matrices could be new choice for making future multiphase polymeric porous film by stretching it unidirectionally and controlling the zeolite inclusions.

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