

Properties of Highly Filled Polypropylene Derivative Composites Containing Calcite and Zeolite

Jagannath Biswas, Hyun Kim, Soonja Choe

Department of Chemical Engineering, Inha University, 253, Yonghyundong, Incheon 402-751, South Korea

Received 12 April 2005; accepted 5 June 2005

DOI 10.1002/app.22802

Published online 19 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This work aims to study the effects of high loading (total 50 wt %) of inorganic calcite, zeolite particulates, and calcite/zeolite mixture with structurally different copolymer [CoPP; poly(propylene-*co*-ethylene)] and terpolymer [TerPP; poly(propylene-*co*-ethylene-*co*-1-butene)] systems. Melt processing is the sole mode of mixing particulates with polymer for making master batch sample throughout this work. Mechanical properties, like the modulus and yield stress, continuously increase up to a critical zeolite ratio in calcite/zeolite mix and then decrease after exceeding the critical concentration. The impact strength of the composites is not improved by replacing the calcite

portion from the mix with zeolite. Morphological study was carried out for matrix-filler dispersion observation. The complex melt viscosity, increased for both systems with increasing zeolite content, indicates extra processing difficulties because of high filler volume. Burning properties and thermal stability of CoPP and TerPP composites with 50 wt % filler systems were also studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2627–2639, 2006

Key words: zeolite; poly(propylene-*co*-ethylene) (CoPP); poly(propylene-*co*-ethylene-*co*-1-butene) (TerPP); hybrid; thermal stability

INTRODUCTION

Polymer products are rarely “pure” materials, but are mixtures or compounds containing additives to modify or improve their properties, and thereby make them useful for their intended application. Polymeric materials have become ubiquitous in the modern society because they are comparatively easy to process.

The effects of individual fillers on the properties of compounds are relatively well studied, as it has been practiced for long time. The property enhancement reports for using single fillers with thermoplastic polymer^{1–3} have been numerous, but only a few works have been reported using mixed fillers with thermoplastics.^{4–10} Multicomponent compounding is also an effective way to reduce the amount of an individual component in a composite. For this reason, recent investigations on thermoplastics and thermosets composites are mainly focused on multicomponent filler systems.

There have also been publications on hybrid composites, with a couple of different reinforcements in the form of natural fibers, glass fibers, carbon fibers, talc, mica, and glass beads.^{11–14} Gan et al. reported about 30 wt % glass fibers/mica-filled poly(ether ether ketone) ternary composites. They suggested that the replacement of glass fibers with mica brings in im-

proved frictional and wear resistance properties in the composites.¹¹ Jarvela et al.¹⁵ reported that multicomponent compounding of polypropylene with several mineral fillers, glass beads (spherical), mica (sheet-like), and wollastonite (fibrous) gave better results than could be obtained with single component compounding.

Rheological properties of stearic acid-coated talc, calcite, and talc/calcite-filled polypropylene were studied.¹⁶ Several authors studied the effect of replacement of spherical fly ash with sand¹⁷ and by mica¹⁸ in unsaturated polyester. Their reports revealed that the substitution of fly ash by platelet mica in a mixed filler reduced the composite melt viscosity and thereby was easier to process.

Often, highly filled inorganic filler acts as a fire retardants and serves as an alternative way of replacing conventionally used organic flame retardants.^{19,20} Numerous publications report the use of 60 wt % magnesium hydroxide or aluminum trihydrate (ATH) as a flame retardant along with thermoplastic polymers.^{21,22}

Our present study is attributing on two different polypropylene derivative resins as a matrix component filled with 50 wt % inorganic calcite and zeolite individually or in their various combinations by the melt-extrusion process. One of the matrix (CoPP; poly(propylene-*co*-ethylene)) consists of two components, where 2% ethylene as a comonomer with propylene, and the other (TerPP; poly(propylene-*co*-ethylene-*co*-1-butene)) consists of three components,

Correspondence to: S. Choe (sjchoe@inha.ac.kr).

TABLE I
Resins Used in This Study

| Materials (grade name) | Code (comment) | Density (g/cm ³) | MI (g/10min) | 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.

where 2% ethylene and 5% 1-butylene as comonomers with propylene. We name these CoPP and TerPP composites as “hybrid material” as they are made from two different fillers (calcite/zeolite). Mechanical, thermal, and rheological properties of the CoPP and TerPP composites were thoroughly compared in terms of modulus, yield stress, impact strength, and flammability. The ultimate purpose of this study was to discover the processability and the extent of thermal stability of highly filled CoPP and TerPP composites by varying the zeolite ratio in the composites.

EXPERIMENTAL

Materials

The two polymers used in this study (CoPP and TerPP) are supplied by SK Corp. (Ulsan, Korea). The physical properties of the two selected resins are summarized in Table I, which also includes the physical properties.

Inorganic zeolite powder is procured from Zeobuilder Co. Ltd. (Chungnam, Korea) and stearic acid-coated calcite was procured from Dowa Co. (Japan). The properties of these materials are also tabulated in Table II.

Zeolite and calcite premixing and compounding

The zeolite and calcite were oven dried for 3 h at 110°C before mixing, and the resins were used as received from the supplier. Calcite and zeolite were thoroughly mixed before they were further mixed with resins for making the hybrid sample. Calcite (50 wt %) and zeolite (50 wt %) samples were also compounded with CoPP and TerPP, using identical con-

ditions. To obtain better mixing between these mixed fillers and matrices, the resin/calcite/zeolite batch was prepared by premixing them thoroughly before feeding them into the hopper. The laboratory Brabender twin-screw extruder (PL 2000) with L/D of 16 as a screw dimension was used for both the pelletized and calendered sample, and operated at a rotation speed of 60 rpm. 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 using a pelletizer. The 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 were 180°C, 190°C, 200°C, and 210°C, respectively, for the TerPP system.

Compression molding

The postcompounded CoPP and TerPP composites from the twin-screw extruder were kept in the oven at 105°C for 3 h for moisture removal. All dried pellets were then placed on a Carver laboratory hot press at a pressure of 5×10^4 Pa and a temperature of 200°C for preparing the impact bars at a dimension of $62.0 \times 12.7 \times 3.17$ mm³, according to ASTM D 256. The 2-mm thick disc shape specimen was also molded for rheological measurement. The hot mold was then allowed to cool at room temperature.

Film preparation

Film specimens were prepared by fixing a slit die in 100×0.5 mm² at the end of the extruder to measure

TABLE II
Properties of Zeolite and Calcite Used in This Study

| Form and chemical composition | Density (g/cm ³) | Particle size (μm) | pH | LOD (at 105 °C/hr) | BET area (m ² /g) | Supplier |
|--|------------------------------|--------------------|-------|--------------------|------------------------------|-------------------|
| Fine white powder, Na ₁₂ [(AlO ₂) ₁₂ (SiO ₂) ₁₂] · xH ₂ O | 1.9 | 2–5 | 10–12 | 4–6 | 250–350 | Zeobuilder, Korea |
| Fine white powder, CaCO ₃ | 2.9 | 1.1 | - | - | 4.8 | Dowa Co., Japan |

LOD, loss on drying.

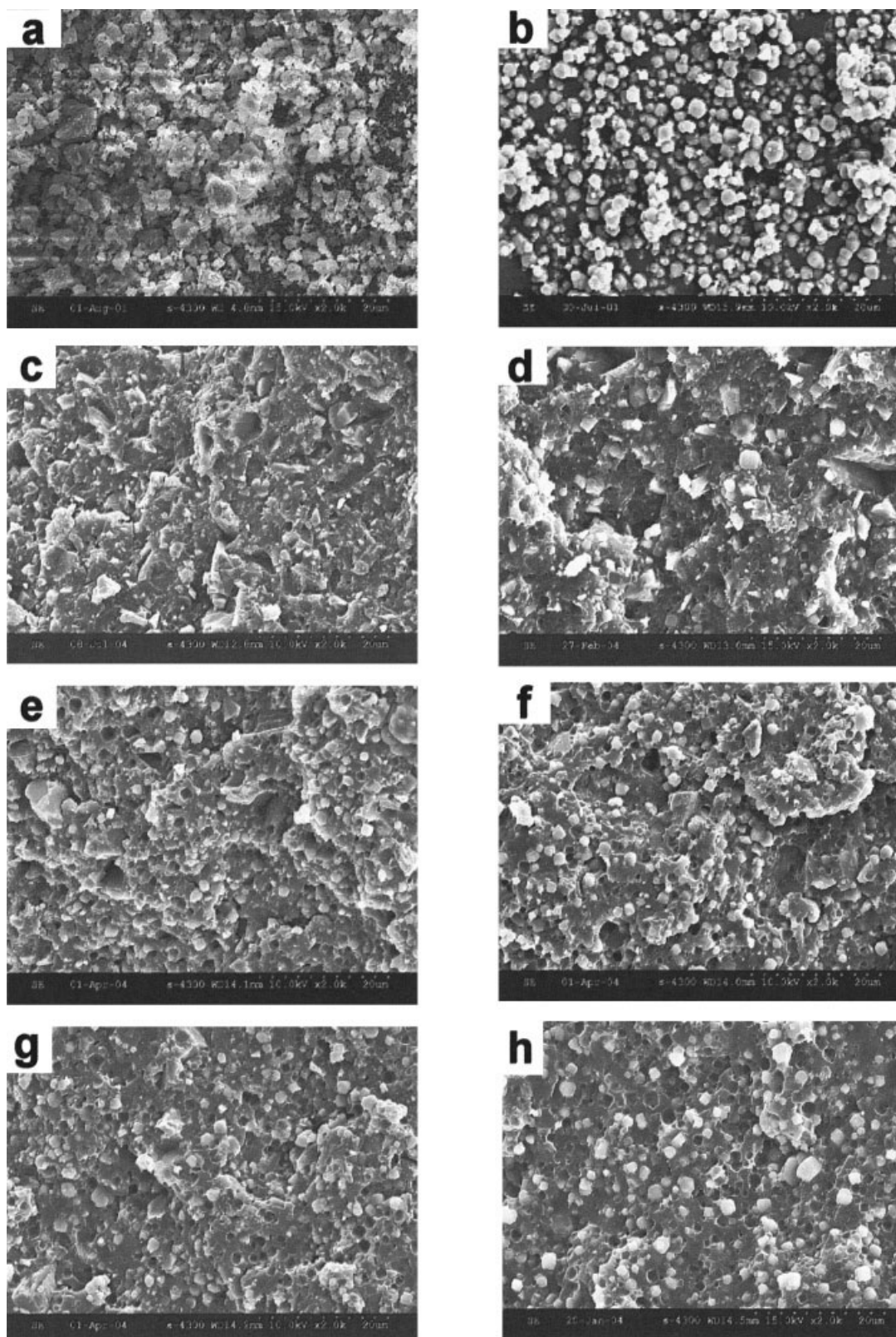


Figure 1 SEM photographs ($\times 2000$) of calcite-, zeolite-, and calcite/zeolite-filled CoPP composites surfaces fractured in liquid nitrogen. (CoPP/calcite/zeolite; (a) calcite only, (b) zeolite only, (c) 50/50/0, (d) 50/40/10, (e) 50/30/20, (f) 50/20/30, (g) 50/10/40, and (h) 50/0/50).

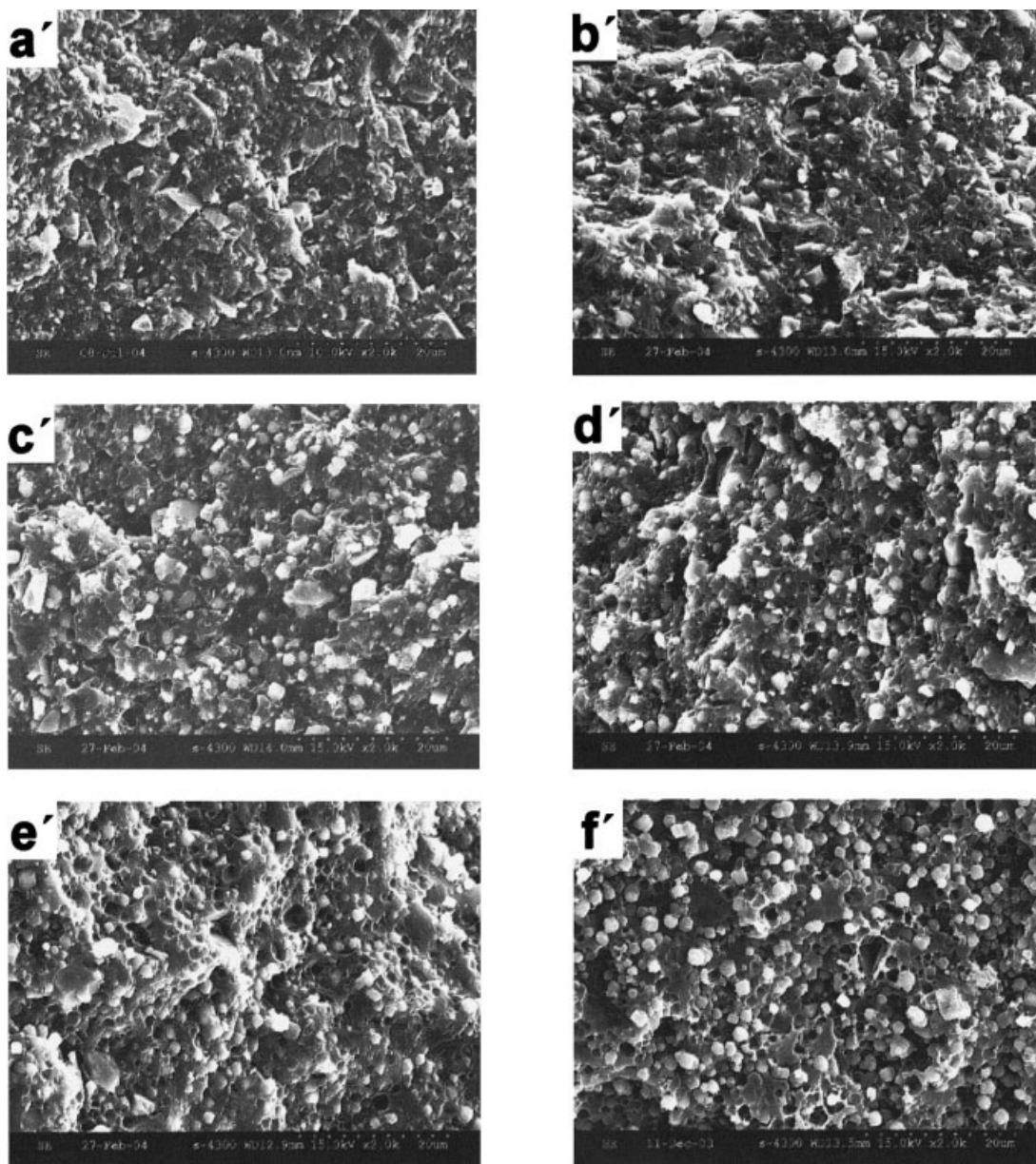


Figure 2 SEM photographs ($\times 2000$) of calcite/zeolite-filled TerPP composites surfaces fractured in liquid nitrogen (TerPP/calcite/zeolite; (a) 50/50/0, (b) 50/40/10, (c) 50/30/20, (d) 50/20/30, (e) 50/10/40, and (f) 50/0/50).

the mechanical properties. Extruded film was uniaxially drawn using a take-up device maintaining the film thickness of about $400\ \mu\text{m}$. The dimension of the film was $15 \times 0.4 \times 165\ \text{mm}^3$, according to the ASTM D882-97, for a tensile testing.

Characterizations

The morphological investigation of the calcite/zeolite hybrid-filled CoPP and TerPP was performed to observe the matrix/filler interface status. The dispersion of the calcite and zeolite in the matrices and the particle agglomeration were visualized from the cryogenically fractured surface. The cryogenically fractured

surface of the composites was 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 the SEM analysis.

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. The initial grip distance was maintained at 50 mm and the deformation rate was 50 mm/min.

The complex melt viscosity of CoPP and TerPP composites was measured using a Torsion Rheometer Mk

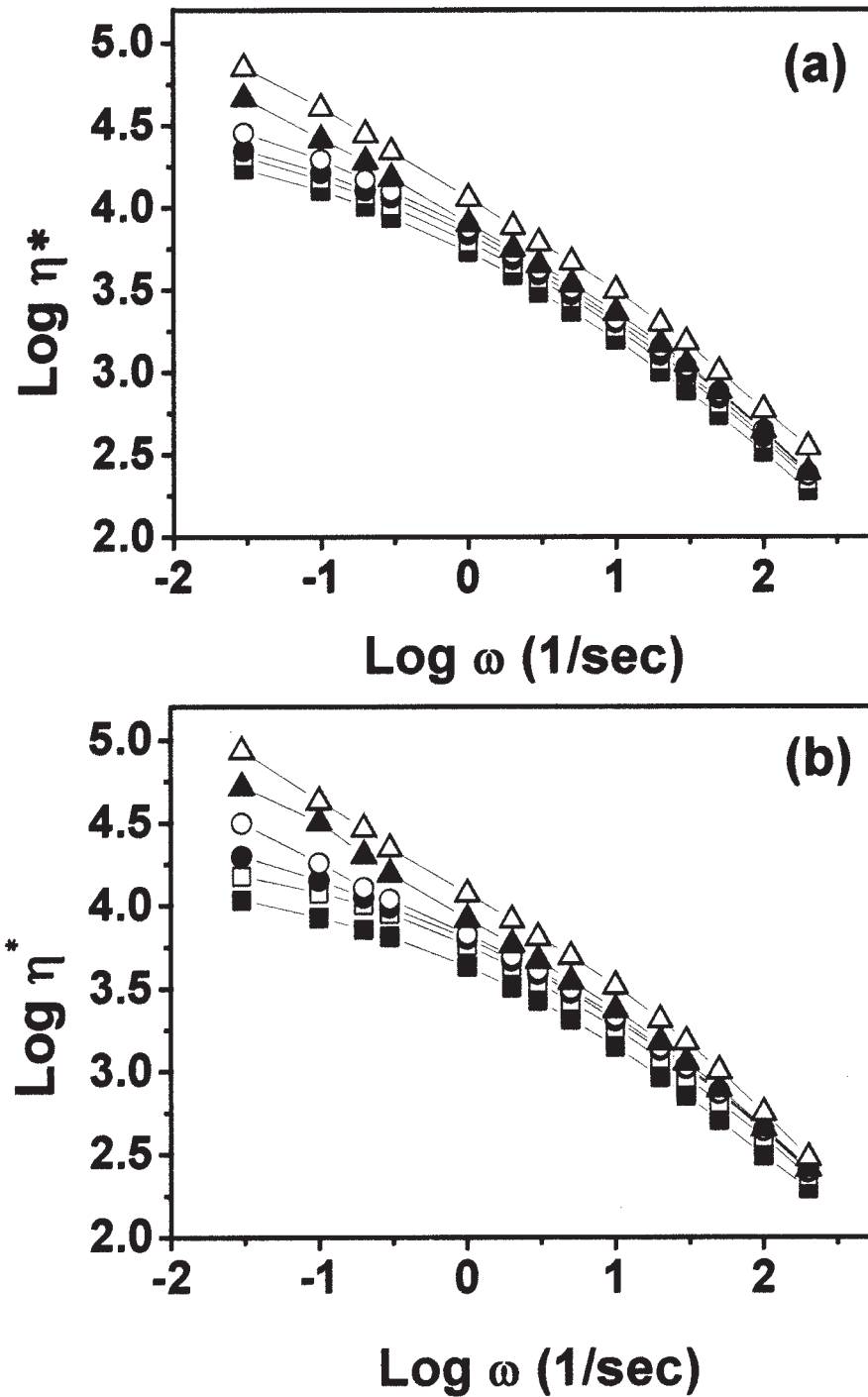


Figure 3 (a) Complex melt viscosities of calcite/zeolite-filled CoPP composites at 240°C. (CoPP/calcite/zeolite; (■): 50/50/0, (□): 50/40/10, (●): 50/30/20, (○): 50/20/30, (▲): 50/10/40, (△): 50/0/50). (b) Complex melt viscosities of calcite/zeolite-filled TerPP composites at 240°C (TerPP/calcite/zeolite; the symbols are the same as in a).

III (Polymer Laboratory, Great Britain). The complex 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%. The 2-mm thick disc shape specimens were compression molded from a hot press at 200°C. The pelletized samples were kept in a vacuum oven at 110°C for 6 h to prevent moisture absorption prior to molding.

Izod impact strength values were obtained 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 all samples containing a single or hybrid filler, at least 10 specimens were tested and the average values were collected. All tests were carried out at ambient temperature and the hammer impact velocity was the same 3.46 m/s for all specimens.

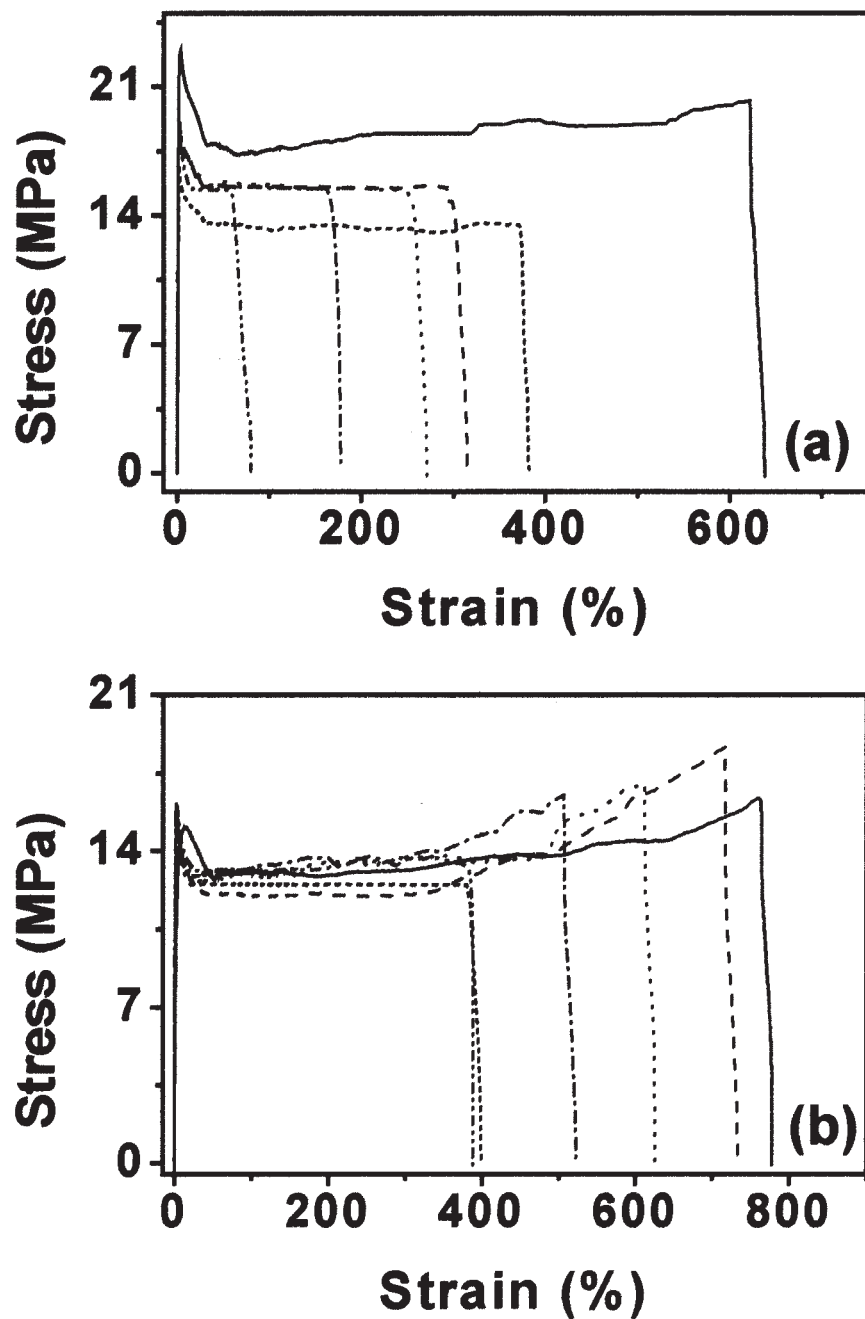


Figure 4 Stress-strain curves of film specimens for calcite/zeolite-filled CoPP and TerPP composites at crosshead speed of 50 mm/min: (a) CoPP system and (b) TerPP system (CoPP/calcite/zeolite; (—): 50/50/0, (---): 50/40/10, (· · · · ·): 50/30/20, (- · - · -): 50/20/30, (- -): 50/10/40, (---): 50/0/50).

Burning properties of the composite were tested according to ASTM D 635-98 in a horizontal position. The dimension of the specimens was 125 ± 5 mm in length, 13 ± 0.5 mm in width, and 3 ± 0.2 mm in thickness. A laboratory burner was constructed according to ASTM D 5025 and equipped with a technical grade methane gas. The specimen was marked with two lines perpendicular to the longitudinal axis of the bar, 25 ± 1 and 100 ± 1 mm from the end that was to be ignited. The horizon-

tally clamped specimen was then ignited with a burner inclined to approximately 45° . The flame height was maintained at 20 ± 2 mm during the flaming of the specimen end.

The degradation behavior of calcite, zeolite, neat resins, and composites were analyzed using a thermogravimetric analyzer (TGA Q50, TA instruments). The experimental conditions included a heating program from 30°C to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$ in N_2 purging environment.

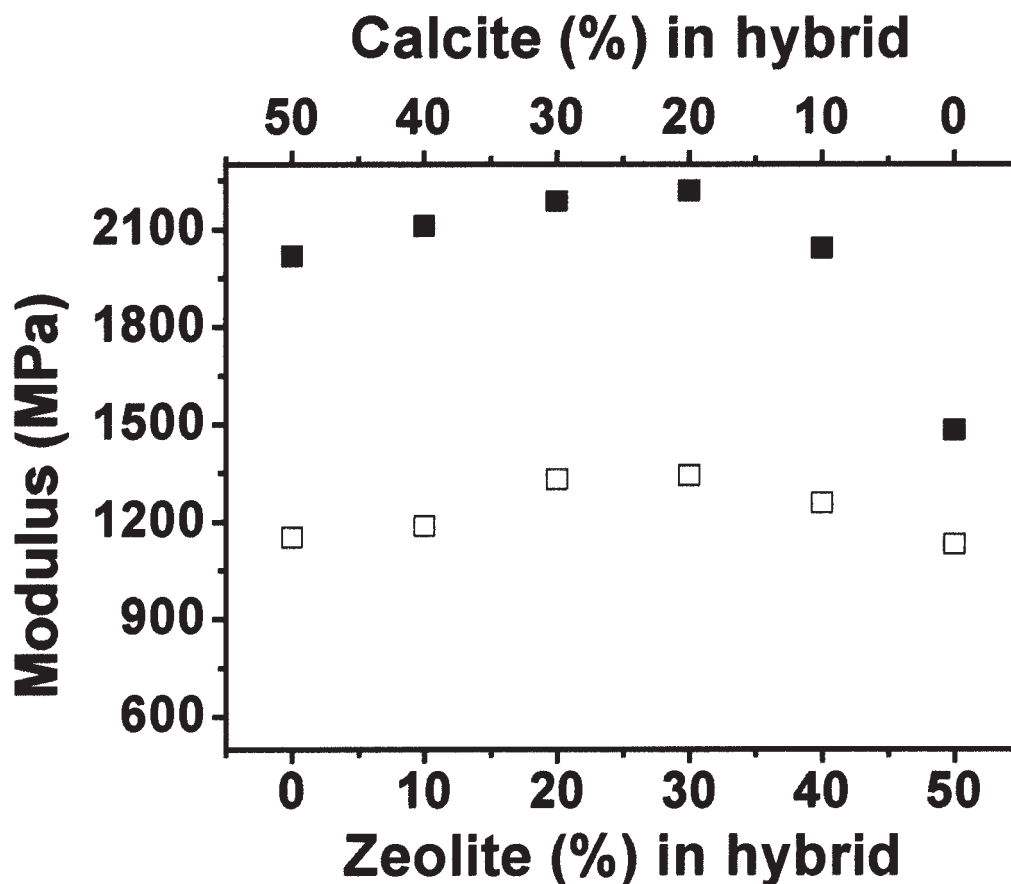


Figure 5 The Young's modulus of calcite/zeolite-filled CoPP and TerPP films with various composition at 50 mm/min: (■) CoPP and (□): TerPP.

RESULTS AND DISCUSSION

Dispersion state of calcite and zeolite in both matrices

Figure 1(a,b) represents the SEM microphotographs of coated calcite and zeolite particles at 2000 \times magnification, respectively. The two fillers have different geometrical shapes; calcite particles are anisotropic and agglomerated randomly, whereas zeolites are almost uniform in shape. It is seen that NaA-type zeolite used in this study has a polydispersed cubic-like shape with an approximate particle size range of 2–5 μm .

Figure 1(c–h) shows the dispersion of calcite and zeolite particles or their combinations in CoPP matrix taken using a cryogenically fractured surface. Figure 1(c–h) shows the sole 50 wt % calcite- and zeolite-filled fractured surface of CoPP composites, respectively. Figure 1(d,e) are showing mainly calcite dispersion morphology, and Figure 1(f,g) shows the gradually predominating zeolite morphology in hybrid systems. Zeolite particles are better dispersed without agglomeration than calcite, since a good distributive mixing was achieved during the compounding by means of a twin-screw extruder. At higher zeolite compositions, one can see a good dispersion and uni-

form population density of the zeolite particles than the calcite particles.

Figure 2 shows the dispersion of calcite and zeolite particles or their various combinations in the TerPP matrix taken from the cryofractured surface. The fracture surface morphology of the TerPP system has a similar result to the CoPP system. The differences in wetting behavior between the fillers and matrices are not discernible.

Rheology

Figure 3(a,b) represents the complex melt viscosity of the hybrid- (calcite/zeolite) or monofiller-filled CoPP and TerPP systems. As shown in these figures, the 50% calcite-filled CoPP and TerPP composites have the lowest complex melt viscosity, and conversely, the value is highest for 50% zeolite filled, which is true for both systems. It appears that the complex melt viscosity gradually decreases with increasing frequency, showing the typical non-Newtonian behavior.²³ The complex melt viscosities for both CoPP- and TerPP-hybrid-filled composites increased with increasing zeolite content.

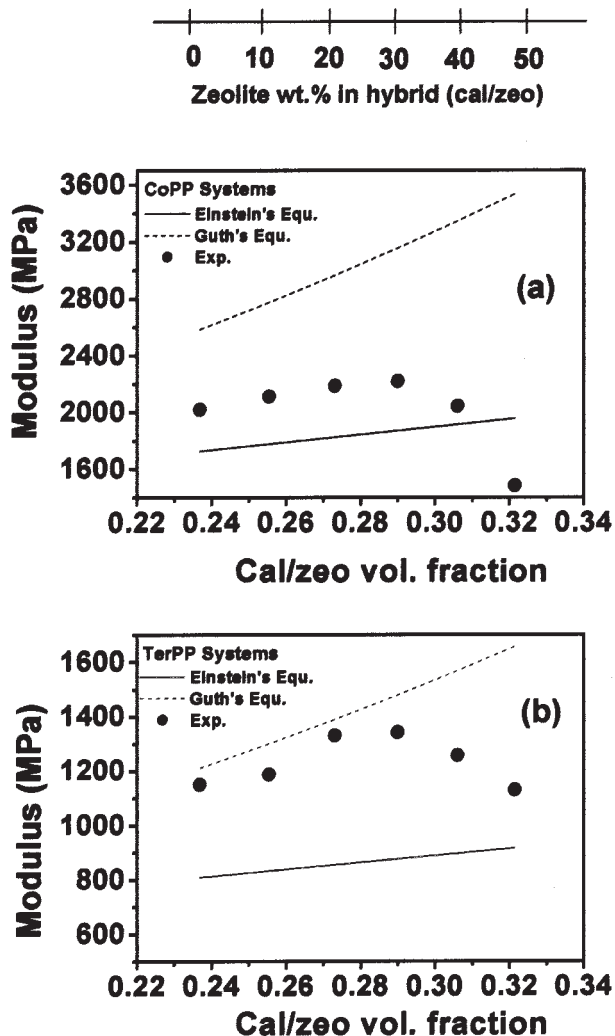


Figure 6 Verification of experimental and theoretical modulus of 50 wt % calcite-, zeolite-, and calcite/zeolite-filled systems: (a) CoPP and (b) TerPP (—: Einstein's equation, - - -: Guth's equation, ●: experimental).

Sen et al. also found similar results when the fly ash content was gradually increased in 40 wt % mica/fly-ash-filled polyester composites.²⁴ High volumes of zeolite filler may be responsible for this increasing melt viscosity of the composites. Zeolite acts as a sharp viscosity builder in the composites and may have indirect influence in commercial polymer processing industries.

Tensile properties

Figure 4(a,b) exhibits the stress-strain curves of film for CoPP and TerPP composites filled with 50 wt % calcite, zeolite, or calcite/zeolite mixed fillers at deformation rate of 50 mm/min. The typical results of modulus, yield stress, and elongation at break from these (S-S) curves were obtained for the CoPP and

TerPP composites. Elaborate explanations will appear later in Figures 5-7.

The Young's modulus, which is a characteristic of material rigidity, is calculated using the stress-strain (S-S) curve represented in Figures 5 and 6, for the CoPP and TerPP composite systems. As shown in Figure 5, the modulus of CoPP composite gradually increased from 2020 to 2220 MPa until 30 wt % zeolite in the combined fillers. The moduli decreased from these peak values to 1482 MPa by further replacement of calcite with zeolite portions. On the contrary, the moduli of 50 wt % calcite- and zeolite-filled TerPP film composite are 1150 and 1130 MPa, respectively. After all, the modulus increment trend is almost similar to that of CoPP up to a certain zeolite concentration. The moduli decrement of CoPP and TerPP composites decreased after a critical zeolite concentration, indicating weak adhesion for high volumes of filler in the composites. The presence of the rubbery component in TerPP is the reason for this unusual softness and lower modulus than all CoPP composites.

Few theoretical models explain the volume-dependent modulus^{25,26} of composites. Modulus of the composites increased with increasing amount of filler volume. Among these models, the simplest one introduced by Einstein has the following form.²⁵

$$M_c = M_p(1 + 2.5\phi) \quad (1)$$

where M_c , M_p , and ϕ are the modulus of the elasticity of the composite, the modulus of the elasticity of the unfilled polymer, and the volume fraction of the filler, respectively. This equation is valid for low filler loading and assumes perfect adhesion between filler and polymer matrix.

An extended form of Einstein's equation was derived by Guth and Smallwood²⁶ and has been expressed as follows:

$$M_c = M_p(1 + 2.5\phi + 14.1\phi^2) \quad (2)$$

(all notations are the same as the previous equation).

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

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

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

Figure 6 represents the theoretical model comparison of 50 wt % calcite, zeolite, or calcite/zeolite mixed

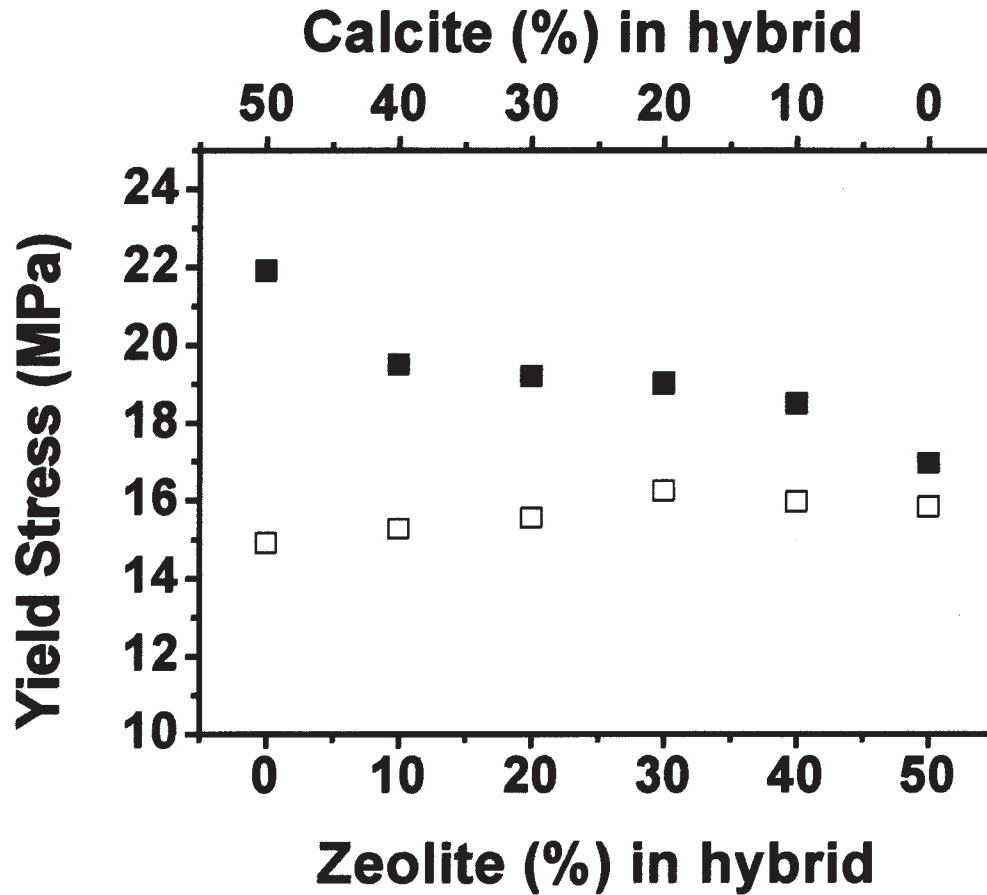


Figure 7 Yield stress of calcite/zeolite-filled CoPP and TerPP films with various composition (■: CoPP; □: TerPP).

CoPP and TerPP composites. Two marginal points on both graphs (a and b) are 50 wt % calcite and zeolite filled, whereas the values that lie between these rep-

resent the moduli of the calcite/zeolite-filled CoPP and TerPP composites. One can easily visualize from these figures that successive increments of volume

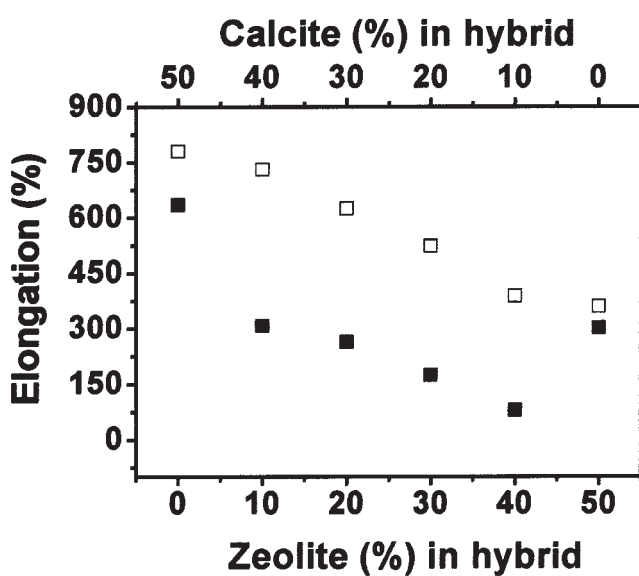


Figure 8 Elongation of calcite/zeolite-filled CoPP and TerPP films with various composition (■: CoPP; □: TerPP).

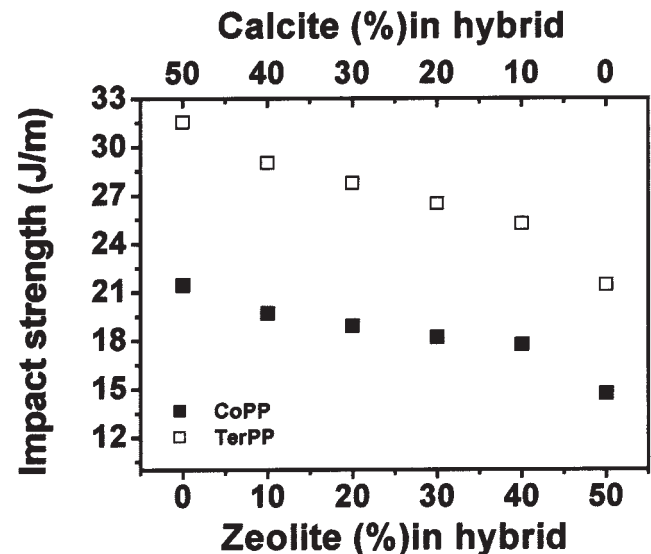


Figure 9 Impact behavior of calcite/zeolite-filled CoPP and TerPP systems with various composition at room temperature (■: CoPP, □: TerPP).

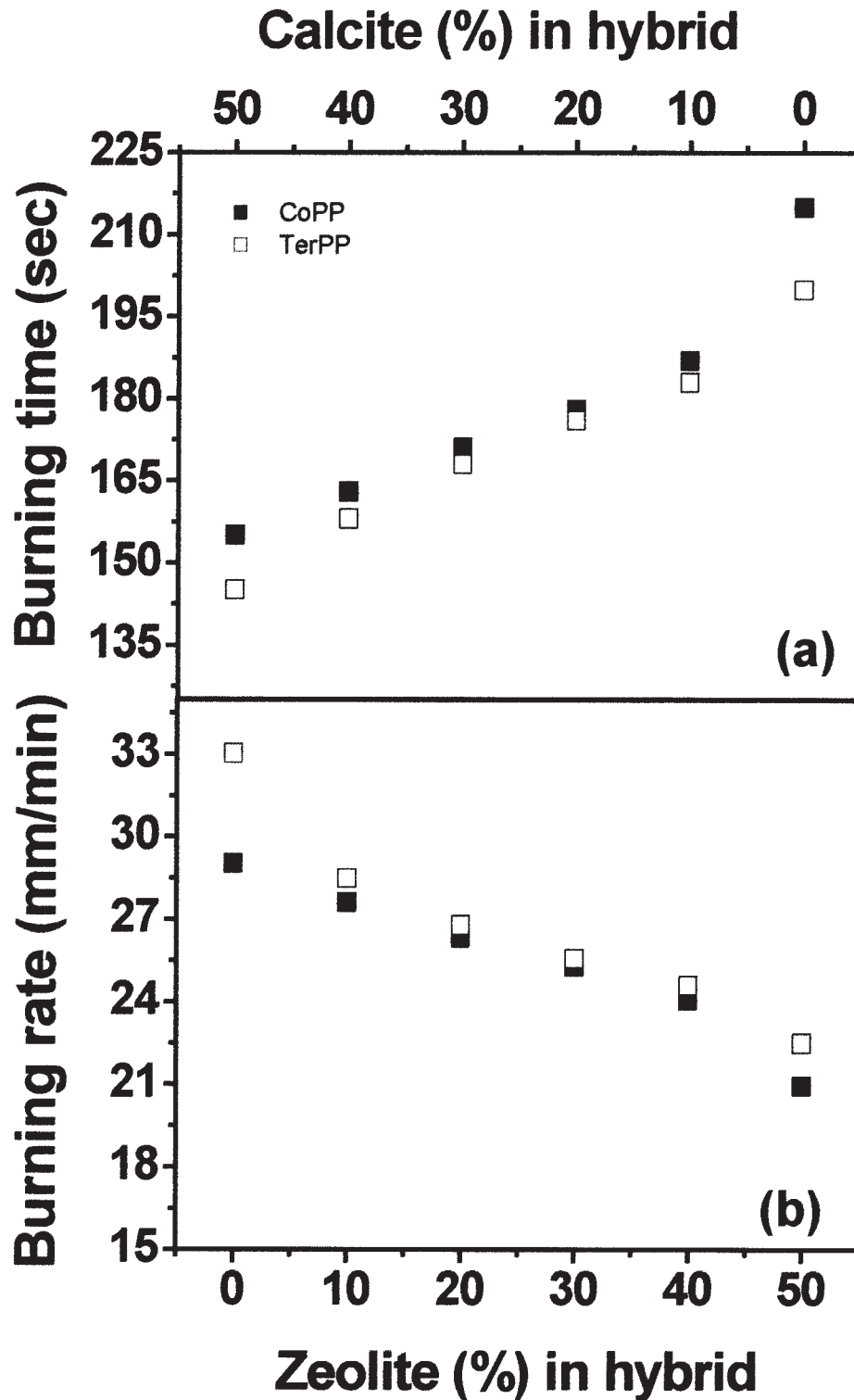


Figure 10 Burning characteristics of calcite/zeolite-filled CoPP and TerPP composites: (a) burning time and (b) burning rate (solid symbol for CoPP and open symbol for TerPP).

and the modulus should increase like those models. On the contrary, experimental values passed between these theoretical values and deviated from the linearity of Einstein's and Guth's equations. We mentioned earlier that those equations are applicable for low

filling levels with perfect adhesion but as our loading is very high, this anomalous behavior has been observed. Moreover, the values fall markedly after 30 wt % zeolite content in hybrid for both CoPP and TerPP composites. Decrease of modulus at very high zeolite

TABLE III
Residual Mass and Degradation Temperature Obtained Using TGA

| Sample | Residual mass (%) | Onset of degradation (°C) | Max. Degrad. Temp. (°C) |
|-----------------------|-------------------|---------------------------|-------------------------|
| Neat CoPP | - | 330 | 460 |
| CoPP:calcite:zeolite | | | |
| 50/50/0 | 45.9 | 400 | 469 |
| 50/40/10 | 47.9 | 403 | 465 |
| 50/30/20 | 46.0 | 406 | 466 |
| 50/20/30 | 44.1 | 406 | 467 |
| 50/10/40 | 41.7 | 410 | 469 |
| 50/0/50 | 37.5 | 410 | 468 |
| Neat TerPP | - | 323 | 460 |
| TerPP:calcite:zeolite | | | |
| 50/50/0 | 49.6 | 378 | 467 |
| 50/40/10 | 48.4 | 395 | 465 |
| 50/30/20 | 46.4 | 399 | 465 |
| 50/20/30 | 43.3 | 405 | 466 |
| 50/10/40 | 42.6 | 406 | 466 |
| 50/0/50 | 37.6 | 407 | 466 |

content may arise from apparent high filler/resin ratio. The high surface area of filler do not make possible complete coverage of resin and thereby uniform stress transfer is not possible.

In Figure 7, the yield stress of both systems was plotted against 50 wt % filler loading for film. The yield stress of 50 wt % calcite-filled CoPP films is a little higher than any other composition containing zeolite. The yield stress fluctuates between 21.9 and 17.0 MPa for film. But the yield stress of 50 wt % calcite-filled TerPP films is a little lower than any other 50 wt % filler compositions. The yield stress started increasing from 14.9 to 16.2 MPa for film specimens up to 30 wt % zeolite ratio. Further increasing the zeolite portion in the composites reduces the value to 15.8 MPa.

The elongation at break at a deformation rate of 50 mm/min is shown in Figure 8 for film specimens of CoPP and TerPP composites. Increasing the amount of zeolite portions in the hybrid filler gradually decreased the elongation of the composites. It is shown in the same figure that the elongation of the 50 wt % calcite-filled CoPP and TerPP film shows 635% and 750% and it becomes 300% and 360%, respectively, for 50% zeolite-filled composite. In the case of film specimen, they also show brittle nature by gradual increasing the zeolite concentration in filler composition. The structural variation of the terpolymer, which has an additional rubbery microstructure (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 at higher filler loading. The elongation at break decreases markedly with the increas-

ing zeolite content in hybrid-filler system because of the larger surface area of the zeolite.

Impact properties

Figure 9 is the graphical representation of the Izod impact strength of both CoPP and TerPP systems containing 50 wt % single or mixed filler. The impact strength is also very sensitive to zeolite content. Only 50 wt % calcite-filled CoPP and TerPP show the highest impact energy and the value falls markedly by increasing the zeolite content. The value is lowest for 50 wt % only zeolite-loaded CoPP and TerPP systems. In addition, the impact strength of the TerPP system is higher than that of the CoPP system, which implies that the presence of 1-butene is responsible for this behavior and is consistent with the mechanical properties. The impact property and yield stress of TerPP over CoPP due to the presence of 1-butene brings a characteristic property that is opposite in trend. In general, impact property has no positive effect when part of the rubbery phase is substituted from matrices by a rigid inert filler or inclusions. Liauw et al. also reported that the impact property is very poor for flame retardant PP filled with 60–70 wt % aluminum hydroxide.²⁷

Burning properties

Figure 10 shows the burning characteristics of CoPP and TerPP composites with respect to calcite and zeolite contents. The linear burning rate was calculated from the following simple equation:

$$R = 60S/t \quad (4)$$

where R is the burning rate (mm/min), S is the burned length (mm), t is the time (s) required to burn up to the marked length.

In Figure 10(a), we observed two extreme values for burning time. The composite that contained 50 wt % filled calcite burned faster than the 50 wt % zeolite-filled composite. By increasing the ratio of zeolite in the composites, the burning time gradually increased and it was at its maximum for 50% zeolite-filled composites. Therefore, zeolite has little influence on combustion and is responsible for slowing down the composite burning character. Another noticeable thing is that TerPP composites burned faster than all CoPP composites, and the reason may be the same as we mentioned earlier.

Figure 10(b) represents the burning rate, which was calculated according to eq. (4). From the figure, one can see that 50 wt % calcite-filled TerPP composite burned more than 33 mm/min compared with ~29 mm/min shown by the CoPP composites, whereas 50 wt % zeolite-filled TerPP and CoPP composites

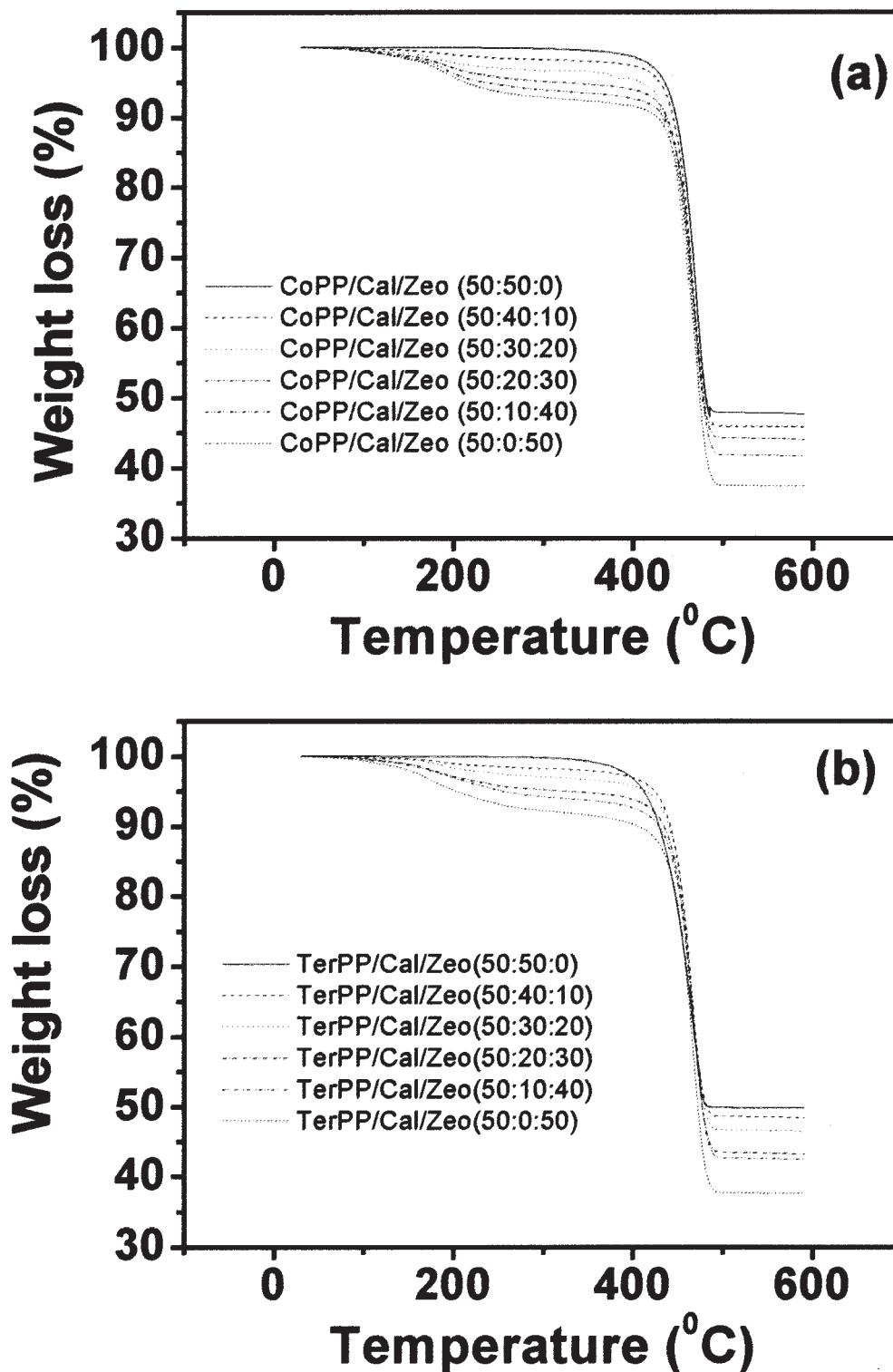


Figure 11 (a) TGA data for calcite/zeolite-filled CoPP composites in the temperature range 30–600°C at 20°C/min (CoPP/calcite/zeolite; (—): 50/50/0, (– –): 50/40/10, (· · · · ·): 50/30/20, (– · – · –): 50/20/30, (– · – · –): 50/10/40, (– – –): 50/0/50). (b) TGA data for calcite/zeolite-filled TerPP composites in the temperature range 30–600°C at 20°C/min (TerPP/calcite/zeolite; symbols are same as in a).

burned 22.5 and 21 mm, respectively. Some authors reported that polymeric materials filled with 60 wt % ATH show flame retardant character.²² In industry, it

is sometimes very informative to know a material's flammability and burning characteristics. Porter et al. reported in one review that silicate containing mate-

rial can be used for fire suppressants.²⁸ As zeolite inherently contains hydrate-type molecule, Al₂O₃ and SiO₂ in structure, it may have an indirect influence on the burning property of the composites.

Thermogravimetric analysis

Table III shows degradation behavior of neat CoPP, TerPP, and all other composites in identical conditions. Neat CoPP and TerPP initiate degradation around 330°C and 323°C, and the degradation rate is high at around 460°C. At the end of degradation they do not form measurable residue. Calcite lost weight by only 1.2% and zeolite by 20%, up to the experimental temperature of 600°C. Around 450°C temperature, the calcite decomposition rate is higher, which may result from CO₂ release.



Zeolite lost water in two stages: first at around 160°C and second at around 360°C. In first stage it lost almost 17 wt % water and weight became steady after losing little moisture in second stage.

Figure 11(a,b) is TGA data for calcite/zeolite-filled CoPP and TerPP systems. Details of the degradation state are tabulated in Table III. Both CoPP and TerPP, loaded with monofiller or difiller, attained thermal stability better than the neat resin. But the temperature, where the degradation rate is higher, is almost similar for both CoPP and TerPP systems, lie between 465°C and 469°C. Initial deviation of the TGA curve is due to the presence of higher moisture content in zeolite, which was around 190–200°C. We observed that the composites containing zeolite is more stable than calcite-filled systems, which can be seen from Table IV. Patra et al. observed similar behavior of nylon-6/zeolite composites during thermal degradation and reported that zeolite can improve char formation in nylon-6.²⁹ The onset temperature of degradation for 50 wt % calcite-filled TerPP is 378°C, and this temperature increases with zeolite content in hybrid. CoPP composites also showed a little higher onset temperature by increasing zeolite ratio in calcite/zeolite mix. The residue after degradation is higher for 50% calcite-filled CoPP and TerPP and lowest for 50 wt % zeolite-filled CoPP and TerPP composites because of the higher moisture content in zeolite structure.

CONCLUSIONS

Our observations provide some optimistic results on CoPP and TerPP composites containing inorganic calcite, zeolite, and calcite/zeolite hybrid, which are made from a conventional compounding procedure, with a laboratory twin-screw extruder. The mechanical properties of the composites made by 50 wt % single filler or calcite/zeolite mix are thoroughly analyzed using film

specimens. The improved the Young's modulus was observed by a successive increment of zeolite portion in the hybrid up to a certain limit. The yield stress of the CoPP film decreased with increasing zeolite portion but increased only a little for the TerPP film case. The elongation at break for 50 wt % calcite is higher than any other compositions. The impact strength of the composites also do not show any synergistic effects by increasing zeolite proportion in hybrid and 50 wt % calcite-filled composites showed the highest impact strength. The complex melt viscosity, which increased for both systems with increasing zeolite portion, indicates processing difficulties for high loaded fillers. Lower burning rates and thermal stability of CoPP and TerPP composites with higher filler content may be used for flame suppressant material. TGA results showed higher stability of zeolite-filled composites than composites filled by sole calcium carbonate.

This work was financially supported by Inha University from 2004–2005.

References

- Zuiderduin, W. C. J.; Westzaan, C.; Huétink, J.; Gaymans, R. J. *Polymer* 2003, 44, 261.
- Mamunya, Y. *Macromol Symp* 2001, 170, 257.
- Kim, K. J.; White, J. L. *Fluid Mech* 1996, 66, 257.
- Leong, Y. W.; Ishak, Z. A. M.; Ariffin, A. *J Appl Polym Sci* 2004, 91, 3327.
- Unal, H.; Mimaroglu, A.; Alkan, M. *Polym Int* 2004, 53, 56.
- Unal, H.; Findik, F.; Mimaroglu, A. *J Appl Polym Sci* 2003, 88, 1694.
- Nugay, N.; Erman, B. *J Appl Polym Sci* 2001, 79, 366.
- Fu, S. Y.; Lauke, B. *Composites A* 1998, 29, 575.
- Fiske, T. J.; Gokturk, H.; Kalyon, D. M. *J Appl Polym Sci* 1997, 65, 1371.
- Kim, K. J.; White, J. L. *J Appl Polym Sci* 2003, 90, 1716.
- Gan, D.; Cao, W.; Song, C.; Wang, Z. *Mater Lett* 2001, 51, 120.
- Cheng, K. B.; Lee, K. C.; Ueng, T. H.; Mou, K. J. *Composites A* 2002, 33, 1219.
- Stricker, F.; Bruch, M.; Mulhaupt, R. *Polymer* 1997, 38, 5347.
- Fu, S.; Mai, Y.; Lauke, B.; Yue, C. *Mater Sci Eng A* 2002, 323, 326.
- Jarvela, P. A.; Jarvela, P. K. *J Mater Sci* 1996, 31, 3583.
- Kim, K. J.; White, J. C.; Shim, S. E.; Choe, S. *J Appl Polym Sci* 2004, 94, 2105.
- Rebeiz, K. S.; Rosett, J. W.; Nesbit, S. M.; Craft, A. P. *J Mater Sci Lett* 1996, 15, 1273.
- Sen, S.; Nugay, N. *Eur Polym Mater* 2047 2001, 37.
- Pinto, U. A.; Visconte, L. L. Y.; Nunes, R. C. R. *Eur Polym Mater* 1935 2001, 37.
- Tai, C. M.; Li, R. K. Y. *Mater Des* 2001, 22, 15.
- Zhang, J.; Wang, X.; Zhang, F.; Horrocks, A. R. *Polym Test* 2004, 23, 225.
- Hippi, U.; Mattila, J.; Korhonen, M.; Seppälä, J. *Polymer* 2003, 44, 1193.
- Han, C. D. *J Appl Polym Sci* 1974, 18, 821.
- Sen, S.; Nugay, N. *Macromol Symp* 2001, 175, 421.
- Tavman, I. H. *J Appl Polym Sci* 1996, 62, 2161.
- Tavman, I. H. *Powder Technol* 1997, 91, 63.
- Liauw, C. M.; Lees, G. C.; Hurst, S. J.; Rotheron, R. N.; Dobson, D. C. *Plast Rubber Process Appl* 1995, 24, 249.
- Porter, D.; Metcalfe, E.; Thomas, M. J. K. *Fire Mater* 2000, 24, 45.
- Patra, P. K.; Warner, S. B.; Kim, Y. K.; Fan, Q.; Adanur, S. *National Textile Center Annual Report*, November 2002.