Effect of Ultrasound on the Morphology and Properties of Polypropylene/Inorganic Filler Composites

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ABSTRACT: The effects of ultrasonic irradiation on the rheology, structure, and properties of PP/inorganic filler composites were studied. Scanning electron microscopy showed that ultrasound increased the orientation degrees of acicular fillers to the flow direction. WAXD indicated that ultrasound vibration induced sheet fillers orient with its surface perpendicular to the direction of the ultrasound vibration. The orderly rearrangements of fillers in the polymer melt induced by ultrasound vibration can reduce the steric hindrances in the flow field and increase the flowability of the PP/inorganic filler composites. The effect of ultrasound on reducing the apparent viscosities is very prominent, especially at lower shear rate. Ultrasound has an even more marked effect on reducing the apparent viscosities of composites containing fillers of larger size. With ultrasound vibration, the mechanical properties of the composites are also improved because of the orientation and uniform dispersion of fillers in the matrix. J Appl Polym Sci 97: 1553–1560, 2005

Key words: polypropylene; ultrasound vibration; extrusion

INTRODUCTION

Ultrasound is the term used for sound waves in the frequency range 16 KHz to 10 MHz, i.e., the frequency range just above the human threshold of audibility. Ultrasound energy enters the system by cavitations, depending on the sonic frequency, or to a large extent by dissipation.

In a liquid, upon irradiation of ultrasound, molecules are exposed to alternate compression and expansion modes. Compression cycles exert a positive pressure on the liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another. In this process small bubbles are formed in liquids at mechanically weak points, usually at phase boundaries. These bubbles increase in size due to resonance in areas of underpressure.[1] Above a certain size the bubbles become unstable and collapse. Tiny zones of excess heat are formed, where a temperature of 5000 K and pressure of 50 MPa can occur temporarily. If the bubble forms near a solid surface, the implosion is asymmetric, expelling a jet of liquid at roughly 400 km/h. The jet, as well as the shock waves from the bubble implosion, erodes solid surfaces, removes nonreactive coating, and fragments brittle powders.[2]

Ultrasound is being applied in polymer processing more and more extensively. Compared to the low-frequency mechanical oscillation, ultraound can influence the viscoelasticity and rheology of polymer melt in a micrometer dimension. Isayev and co-workers[3–5] reported that during extrusion high-intensity ultrasonic waves affect the die characteristics, by reducing the pressure and extrudate swelling, and postpone melt fracture. Keishiro[6] applied 20- to 100-kHz ultrasound waves in a direction vertical to the rubber discharging direction through an extrusion and obtained rubber sheets with low extrudate swelling occurrence and good dimension accuracy. It is also found that ultrasonic vibration has a good effect on the structure and performance of polymer composites. Khamad et al.[7] reported that application of ultrasound on HDPE melts containing a small amount of butyl rubber resulted in an increase in crystallinity, reduction in structural defects, and enhancement of mechanical properties. Peshkovskii et al.[8] discovered that the average size of fillers was smaller and the size distribution was more homogeneous with ultrasonic treatment than without ultrasonic treatment in kaolin clay filled HDPE.

In the present study, we intended to investigate the effect of ultrasound on inorganic fillers with different sizes and different shapes when they are

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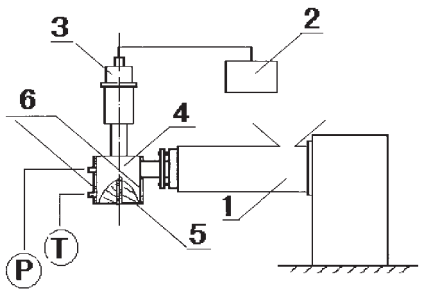


Figure 1 Scheme of the ultrasonic wave extrusion system. 1, extruder; 2, ultrasonic generator; 3, piezoelectric transducer; 4, die; 5, melt; 6, electric heaters; P, pressure transducer; T, thermocouple.

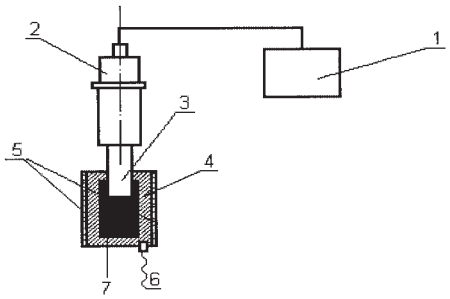


Figure 2 Scheme of the static ultrasonic wave system. 1, uUltrasonic generator; 2, piezoelectric transducer; 3, horn; 4, mold; 5, electric heaters; 6, thermocouple; 7, melt.

compounded with a polymer. Glass fiber and whisker were selected as two sizes of acicular fillers, and two sizes of mica were used as sheet fillers. The influence of ultrasonic vibration on the rheology, structure, and properties of the polypropylene composites was studied.

EXPERIMENTAL

Materials

Polypropylene powder, melt index 2.8 g/10 min, an unstabilized material, was supplied by Xinfeng Chemical Ltd. (Wulumuqi, China) and used in this study as matrix polymer. Glass fiber (average diameter: 13 μm, average length: 4.5 mm; Tianjing Glassfiber Factory, Tianjing, China) and mica (325 and 1000 mesh, Guangxian mineral Processing Factory, Xinjiang, China) were used, respectively, as minor components to mix with PP.

$MgAl(SiO_3)_2$ whisker was supplied by Qiwei New Materials Co. Ltd. (Sichuan, China) and extrudated with copolymeric PP (T30S, Yanshan Petrochemical Co. Ltd., Beijing, China) to make a premixed compound, in which the content of whisker was 30% by mass.

The coupling agent was KH-550, which is a product of Nanjing Shuguang Chemical Ltd. (China).

Processing equipment

The ultrasound-extrusion experimental setup consists of a single-screw extruder (d = 20 mm, L/D = 25), having a high-temperature pressure transducer and ultrasonic generator (Fig. 1). The ultrasonic frequency was 20 kHz and power ranged from 0 to 300 W. The direction of ultrasonic vibration coincides with that of the melt flow through the die. Two dies are ready for use. One is a variable cross section capillary (d = 3 mm, L/D = 7), and the other is a slit die with width (W) = 11.5 mm, height (H) = 0.92 mm, and length (L) = 17.5 mm.

The static ultrasound experimental equipment consists of a mold and ultrasonic generator (Fig. 2). The ultrasonic frequency was 20 kHz and power ranged from 0 to 300 W. The diameter of the horn was 15 mm.

Sample preparation

Original glass fibers (GF) and mica were surface treated with silane coupling agent KH-550 and then mixed with PP powder and antioxidant, respectively, by a mixer to get PP/GF and PP/mica mixtures, in which the ratios of the inorganic fillers was 10% by mass and that of the antioxidant was 0.1% by mass of PP. The mixtures and the $MgAl(SiO_3)_2$ whisker filled PP were extruded by single-screw extruder, respectively, with rotation speed of 15 rpm through the slit die. The die temperature was 200°C and ultrasonic intensity varied from 0 to 200 W. The strip extrudates were cut into sections of isolength and orderly ranged (Fig. 3) into the molds and then compression molded into 4-mm plates. Compression molding was carried out using the following conditions: preheating for 10 min at low pressure, compression for 5 min at 10 MPa at 190°C, and then cooling in the mold at 10 MPa. Specimens parallel to and perpendicular to the axis of the extrudate strips, i.e., parallel to the extrusion direction and perpendicular to the extrusion direction,

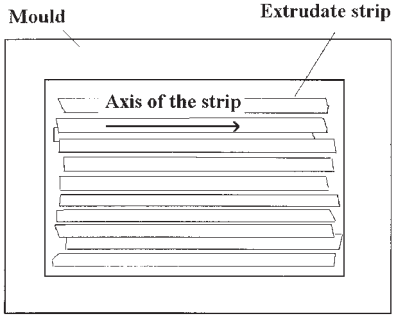


Figure 3 Scheme of compression molding.

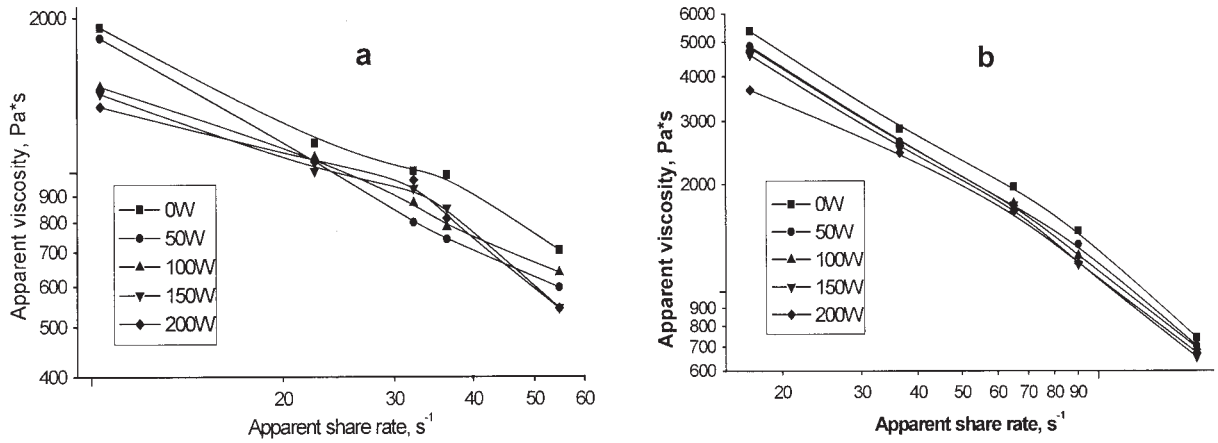


Figure 4 Apparent viscosity curves of PP/acicular fillers with various ultrasound intensities: (a) PP/GF; (b) PP/whisker.

were cut, respectively, from the plates for mechanical tests.

A static ultrasound experiment was also conducted for PP/mica. The PP/mica mixtures were melted in the static ultrasonic mold at 200°C for 10 min and then irradiated by ultrasonic wave for 5 min. After that the mixture was cooled to room temperature.

Mechanical testing

Three-point flexural strength was tested with an Instron 4302 universal testing instrument at a crosshead speed of 2 mm/min according toGB-9341–88.

Morphological analysis

A Japan JSM-5900LV scanning electron microscope (SEM) was used to observe blend morphology. The strip extrudates from the slit die were cut at the exit of the die, immerged into liquid nitrogen immediately, and then fractured longitudinally and transversely to get a longitudinal surface and a traversal surface. Fracture surfaces were plated with gold before examination.

X-ray diffraction

The WAXD patterns of PP were taken on a Philip X'pert PRD diffractometer with Ni-filtered CuKα radiation at room temperature.

Melt flow rate (mfr)

MFR was measured at 230°C under load of 2.16 kg with an American CS-127 MFR instrument.

RESULTS AND DISCUSSION

Rheological property

Treating the extruding die (d = 3 mm, L/D = 7) as a dynamic capillary rheometer, as shown in Figures 4

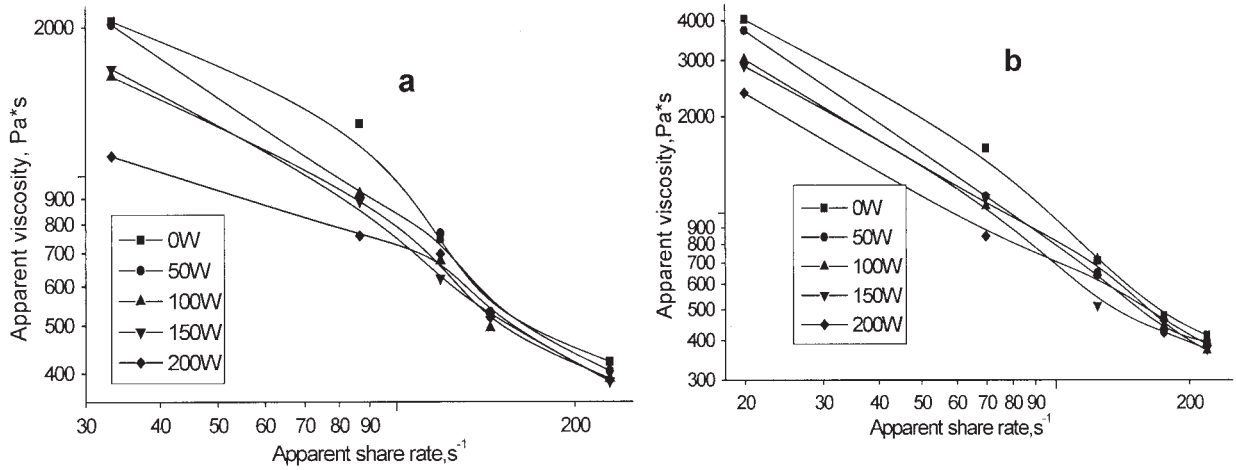
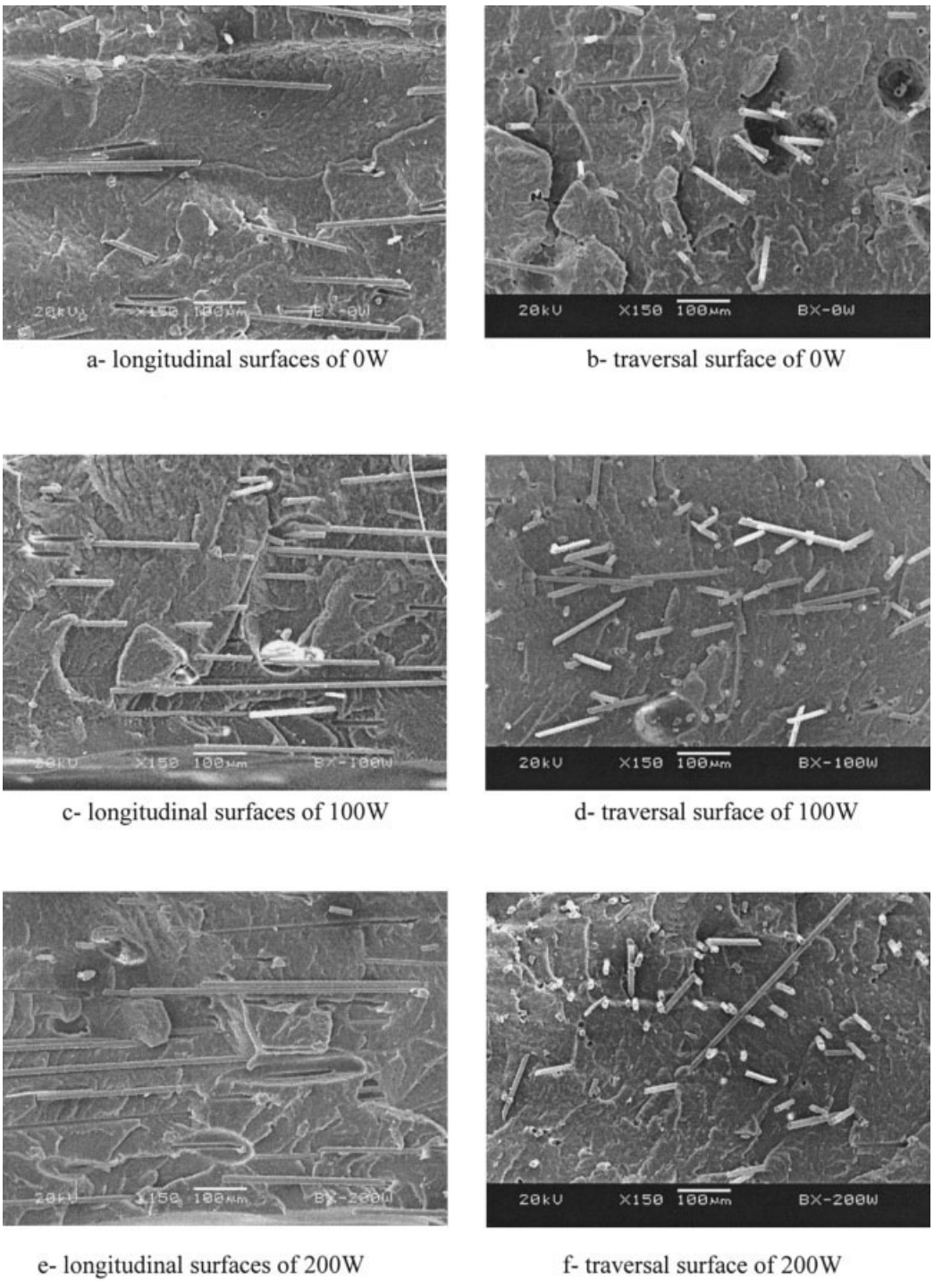


Figure 5 Apparent viscosity curves of PP/sheet fillers with various ultrasound intensities: (a) PP/mica-325; (b) PP/mica-1000.



a- longitudinal surfaces of 0W

b- traversal surface of 0W

c- longitudinal surfaces of 100W

d- traversal surface of 100W

e- longitudinal surfaces of 200W

f- traversal surface of 200W

Figure 6 SEM micrographs of brittle fractured surfaces of PP/GF extrudate strips.

and 5, gives rheological curves of the composites at various ultrasonic intensities,

$$\tau_w = \frac{PD}{4L} \tag{1}$$

$$\dot{\gamma}_w = \frac{32Q}{\pi\rho D^3} \tag{2}$$

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w}, \tag{3}$$

where τ_w is the shear stress on the capillary wall; $\dot{\gamma}_w$ is the apparent shear rate; η_a is the apparent viscosity; ρ is melt density; D and L are the diameter and length of the capillary, respectively; P is the pressure drop along the capillary, obtained from the pressure transducer at the entrance of the capillary;

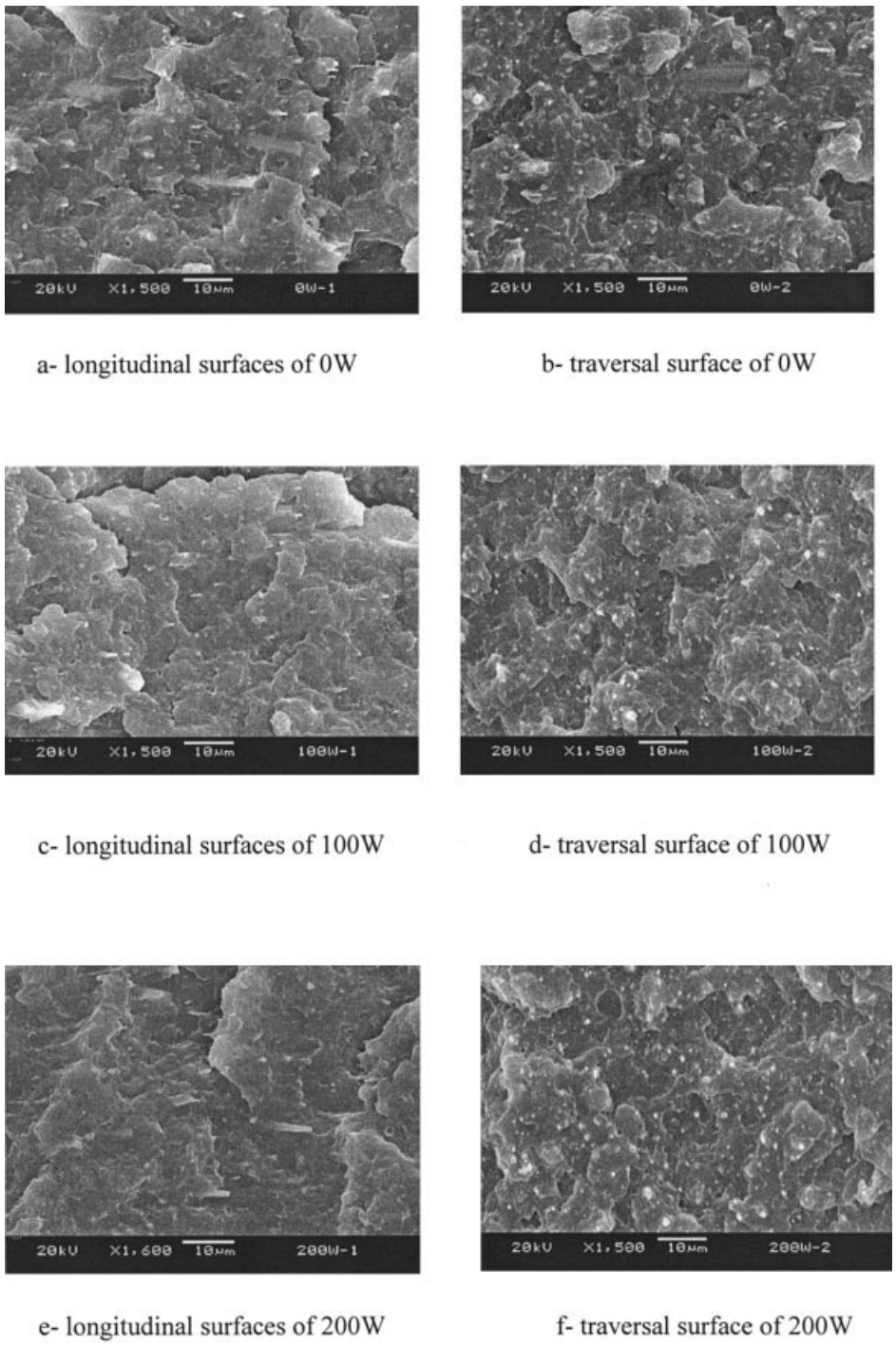


Figure 7 SEM micrographs of brittle fractured surfaces of PP/whisker extrudate strips.

Q is the flow rate, obtained by measuring the extrudate weight per second.

As shown in Figure 4, when ultrasonic vibration is applied, apparent viscosities of both composites decrease compared to that without ultrasonic vibration. For PP/whisker composite (Fig. 4b), the apparent viscosity falls smoothly with the increase in apparent shear rate. Since low share rate means long duration ultrasonic treatment of the melt, the apparent reduced viscosity caused by ultrasound vibration is more marked at lower shear rate than that at higher shear rate. For the PP/GF composite, the apparent viscosity curves are not very smooth, and the effect of ultrasound on the apparent viscosity is stronger compared to that of the PP/whisker composite. As shown in Figure 4a, at the reference shear rate 36.38 $s^{-1,}$ the apparent viscosity of PP/GF changes from 988.28 Pa · s without ultrasound irra-

diation to 813.55 Pa · s at 200 W ultrasound irradiation, i.e., a reduction of 17.7%. While for PP/whisker (Fig. 4b), at shear rate 36.50 s^{-1}, the apparent viscosity of PP/whisker changes from 2858.86 Pa · s without ultrasound irradiation to 2446.5 Pa · s at 200W ultrasound irradiation. The reduction is only 14.4%.

The glass fibers are much bigger in size than the whisker and can cause more steric hindrances in the flow field when the composite melt flows through the capillarity die. Ultrasound vibration causes the fillers to be distributed more orderly and more homogeneously in the melt, which reduces the steric hindrances in the flow field.

Figure 5 depicts the rheological curves of PP/mica composites. For PP/sheet filler composites, the effect of ultrasound on reducing the apparent viscosities is very prominent at lower shear rate, but very poor at higher shear rate. The critical value of shear rate is about 100 s^{-1}.

In PP/acicular filler composites ultrasound vibration also has a more marked effect on reducing the apparent viscosities of composites containing fillers with bigger size. As shown in Figure 5a, at the reference shear rate 33.18 s^{-1}, the apparent viscosity of PP/mica-325 changes from 2059.4 Pa · s without ultrasound irradiation to 1096.46 Pa · s at 200 W ultrasound irradiation. The reduction is 46.8%. For PP/mica-1000 (Fig. 5b), at the shear rate 19.91 s^{-1}, the apparent viscosity of PP/mica-1000 changes from 4034.39 without ultrasound irradiation to 2372.46 Pa · s at 200 W ultrasound irradiation. The reduction is only 41.2%.

Fracture surface morphology observation for PP/acicular-filler composites

Figures 6 and 7 show the micrographs of brittle fractured surfaces of PP/acicular filler composites in liquid nitrogen. As shown in Figures 6a and b and 7a and b, velocity gradient in the flow field caused some of the acicular fillers to orient to the flow direction when the composite melt flows through the capillary die. The micrographs of the longitudinal surfaces are obviously different from those of transversal surfaces. When ultrasound is applied, the direction of ultrasonic vibration coincides with that of the melt flow through the die, and more acicular fillers were oriented. The difference between the longitudinal surfaces and transversal surfaces are more notable, as seen in Figures 6c–f and 7c–f.

Figures 6 and 7 also show that ultrasound vibration promotes the interaction between the PP matrix and the coupling agent treated fillers. The dispersion of the fillers in the PP matrix becomes more uniform and the interface of fillers and PP becomes less clear as the ultrasound intensity increases from 0 to 100 W and then further to 200 W. That means that ultrasound vibration can improve the compatibility of inorganic fillers and the PP matrix.

WAXD analysis of PP/mica composites

For PP/sheet filler composites, it is hard to show the morphology of the disperse phase using micrographs. In this study, WAXD was used to analyze the PP/mica composites. Figure 8a shows the WAXD patterns for extrudates without and with 200-W ultrasonic irradiation at a screw rotation speed of 10 rpm. In this case, the diffraction planes are the surfaces of the extrudate strips, which are parallel to the ultrasound vibration direction. As labeled in Figure 8, the peaks located at 8.9, 17.8, 26.8, and 45.5° correspond to the (001), (002), (003), and (005) crystalline planes of mica, respectively. With 200-W ultrasound irradiation, the diffraction intensities of these planes become weaker than those of the samples without ultrasound irradiation. This implies that the ultrasonic wave results in the orientation of the (001), (002), (003), and (005) planes. Since the (001) crystalline plane of mica is actually the surface of mica crystal, and (002), (003), and (005) planes are parallel to the (001) plane, it is

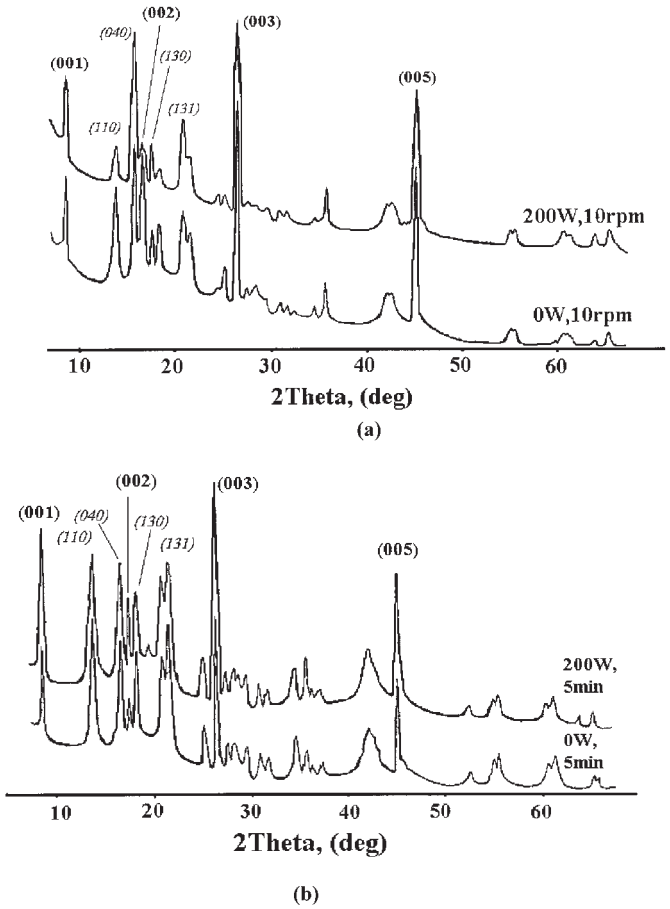


Figure 8 (a) WAXD patterns of PP/mica-325 for extrudate strips. (b) WAXD patterns of PP/mica-325 for static ultrasound irradiated specimens.

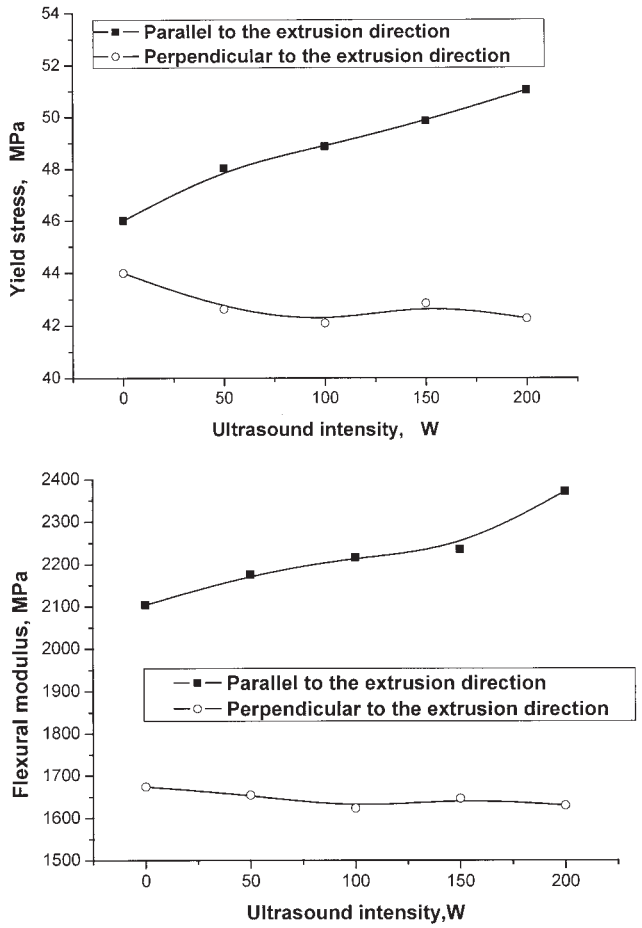


Figure 9 (a) Flexural yield stress of PP/whisker versus ultrasound intensity. (b) Flexural modulus of PP/whisker versus ultrasound intensity.

inferred that ultrasound vibration reduces the orientation of mica toward the surface of the extrudate strips. To verify this point, a further WAXD experiment was conducted. Figure 8b shows the WAXD patterns for specimens from the static ultrasound experiment without and with 200-W ultrasonic irradiation. In this case, the diffraction planes are the surfaces that are perpendicular to the ultrasound vibration direction. With 200-W ultrasound irradiation for 5 min, the diffraction intensities of the (001), (002), (003), and (005) crystalline planes become much stronger than those of the samples without ultrasound irradiation. That means that more mica flakes are oriented with its surface perpendicular to the ultrasound vibration direction. So, it can be concluded that ultrasound vibration can make mica flakes rotate in the polymer melt until the *c* crystallographic axis of mica is parallel to the direction of the ultrasound vibration.

Mechanical properties

Figures 9 and 10 depict the flexural yield stress and flexural modulus of PP/acicular filler composites. Since the orientation degrees of acicular fillers to the flow direction are increased by ultrasound vibration, as discussed above, the specimens for three-point bending were obtained by the method described under Experimental and illuminated in Figure 3 to preserve the ultrasound effect on the orientation degrees of acicular fillers. For the specimens parallel to the extrusion direction, the flexural yield stress and flexural modulus increase markedly when ultrasound intensity is varied from 0 to 200 W. For the specimens that are perpendicular to the extrusion direction, the flexural yield stress and flexural modulus increase a little for the PP/GF composite (Fig. 10) and even decrease a little in the PP/whisker composites. This corresponds well with the morphology shown in Figures 6 and 7.

Figure 11a and b shows the flexural yield stress and flexural modulus of PP/mica composites. Since ultrasound vibration makes mica flakes orient with their surface perpendicular to the direction of the ultrasound vibration, i.e., perpendicular to the extrusion direction, the method to obtain the three-point bending specimens does not help to preserve the ultrasound effect. But as seen in Figure 11, the flexural yield stress and flexural modulus for both PP/mica-325 and PP/mica-1000 increase sharply with increas-

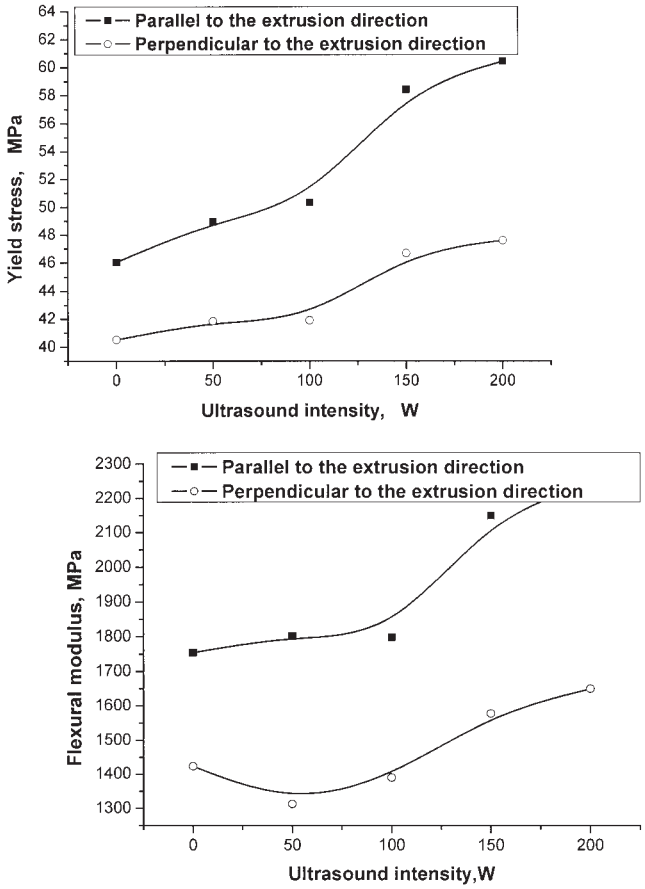


Figure 10 (a) Flexural yield stress of PP/GF versus ultrasound intensity. (b) Flexural modulus of PP/GF versus ultrasound intensity.

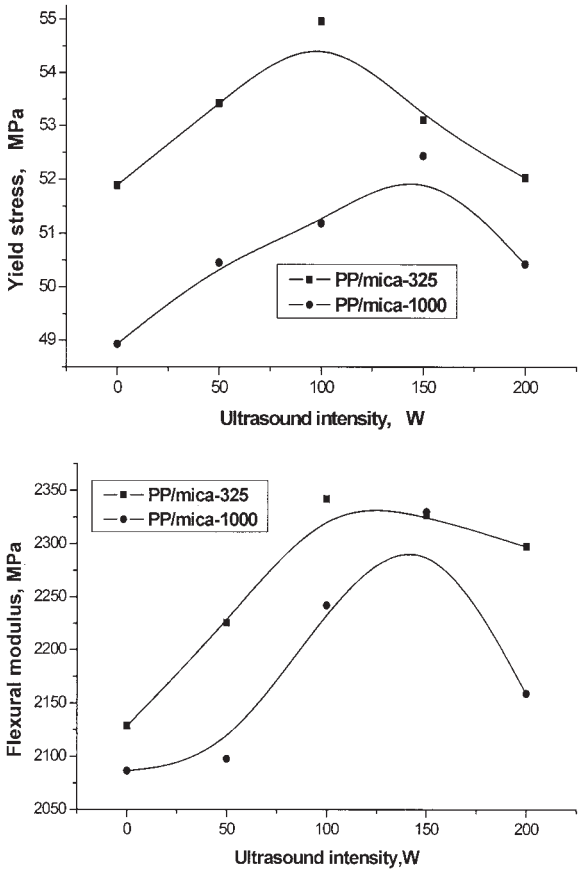


Figure 11 (a) Flexural yield stress of PP/mica ultrasound intensity. (b) Flexural modulus of PP/mica ultrasound intensity.

ing ultrasound intensity and reach a maximum at 100- or 150-W ultrasound intensity. This may be attributed to the ultrasound effect on promoting dispersion of the fillers in the PP matrix and improving the compatibility of inorganic fillers and the PP matrix.

CONCLUSIONS

When ultrasound vibration is applied during the extrusion of PP/inorganic filler composites, the cavitations are easily formed near the solid surface of the particles. The jet, as well as the shock waves from the bubble implosion, helps to disperse, rearrange, and orient the fillers. For PP/acicular filler composites, orientation degrees of acicular fillers to the flow direction are increased by ultrasound vibration. For PP/sheet filler composites, ultrasound vibration makes mica flakes orient with their surface perpendicular to the direction of the ultrasound vibration. The orderly rearrangements of filler in the polymer melt induced by ultrasound vibration can reduce the steric hindrances in the flow field and increase the flowability of the PP/inorganic filler composites. With ultrasound vibration,the mechanical properties of the composites are also improved because of the orientation and uniform dispersion of fillers in the matrix.

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