Effect of Ultrasound on Extrusion of Polypropylene/ Ethylene–Propylene–Diene Terpolymer Blend: Processing and Mechanical Properties

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ABSTRACT: The effects of ultrasonic irradiation on extrusion processing and mechanical properties of polypropylene (PP)/ ethylene–propylene–diene terpolymer (EPDM) blends are examined. Results show that appropriate irradiation intensity can prominently decrease die pressure and apparent viscosity of the melt, increase output, as well as increase toughness of PP/EPDM blends without harming rigidity. In case the blends are extruded with ultrasonic irradiation twice, the impact strength of the blend rises sharply at 50–100 W ultrasonic intensity, and amounts to more than 900 J/m, 1.5 times as high as that of blend without ultrasonic irradiation. Scanning electron microscopy observation shows that with ultrasonic irradiation, morphology of uniform dispersed EPDM phase and good adhesion between EPDM and PP matrix was formed in PP/EPDM blend. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3519–3525, 2003

Key words: extrusion; polypropylene; elastomers

INTRODUCTION

In polymer processing, to solve some problems that conventional means cannot, or to improve processability of some polymer materials, the aid of melt vibration technology has attracted extensive attention. Ultrasound is one sort of elastic mechanic wave of frequency 10^4–10^8 Hz. Isayev and coworkers studied the processing procedure of polymers that utilizes high-power ultrasound. It was shown that during extrusion high-intensity ultrasonic waves affect the die characteristics by reducing the pressure and extrudate swelling and postpone melt fracture.[1–3] By introducing ultrasonic vibration to an extruder, they accomplished recycling of rubber waste.[4,5] Ivanov et al.[6] disclosed that with ultrasonic treatment, SKEP-50 rubber increased its volume by 16%, and the flow of the rubber was a nonlinear function of ultrasonic intensity and ultrasonic treatment time. Keishiro[7] applied 20–100 kHz ultrasound wave in a direction vertical to the rubber discharging direction through an extrusion and got rubber sheets with low extrudate swelling occurrence and good dimension accuracy. Peshkovskii et al.[8] described a method for eliminating unstable flow of polybutene melt by application of ultrasonic irradiation, and ultrasound-initiating cavitations was confirmed by recording and taking pictures. Moreover, they discovered the average size of fillers was smaller and size distribution was more homogeneous with ultrasonic treatment than that without ultrasonic treatment in kaolin clay filled HDPE. Khamad et al.[9] reported that imposition of ultrasound on HDPE melts containing a small amount of butyl rubber resulted in increase of crystallinity, reduction of structural defects, and enhancement of mechanical properties.

To toughen polypropylene, intuitively one would select ethylene–propylene–diene terpolymer (EPDM) as an impact resistance additive, because the similarity in chemical composition would help interphase bonding (due to the low interaction parameter) and the material is readily available at a very acceptable price. The toughness of polypropylene (PP) is enhanced through the incorporation of elastomer, but the rigidity (i.e., the modulus and the tensile strength) is decreased. With the incorporating of elastomer into PP, melt viscosity of the blend system increases greatly, and processing become comparatively difficult. According to the reports, the dominant way to settle this problem is using special sorts of PP or elastomer. By copolymerizing ethylene and high-grade α-alkene, Exxon Chemical Co. prepared a sort of elastomer with some crystallinity, good stiffness, and low Moony viscosity, then blended it with PP,[10,11] and Nomurat used

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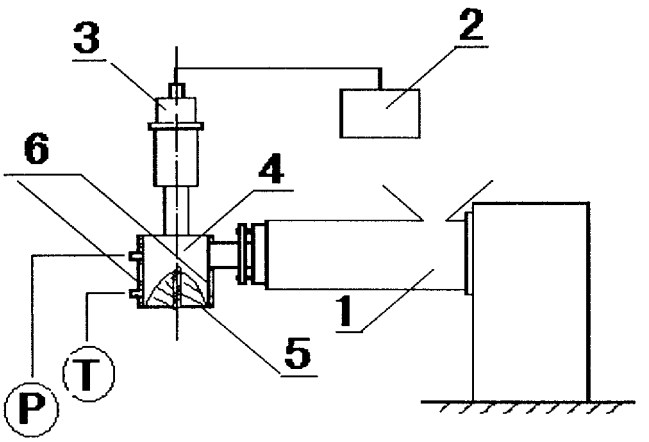

Figure 1 Scheme of ultrasonic wave–extrusion system. (1) Extruder, (2) ultrasonic generator, (3) piezoelectric transducer, (4) die, (5) melt, (6) electric heaters; P: pressure transducer; T: thermocouple.

high-crystallinity PP (low viscosity of melt and high rigidity of solid) to blend with EPDM,[12,13]—they both got polyolefin material of good toughness and fluidity.

In this study we introduce ultrasound vibration to PP/EPDM extrusion by applying ultrasound–extrusion equipment, and investigate the viscosity drop and toughening effect of ultrasonic irradiation.

EXPERIMENTAL

Materials

PP: F401 (Lanzhou Chemical Co., Lanzhou, China), Melt Index (MI) 2.0 g/10 min.
EPDM: Nordel 3745P (Dupont Dow Elastomers L.L.C., Wilmington, DE, U.S.A.).

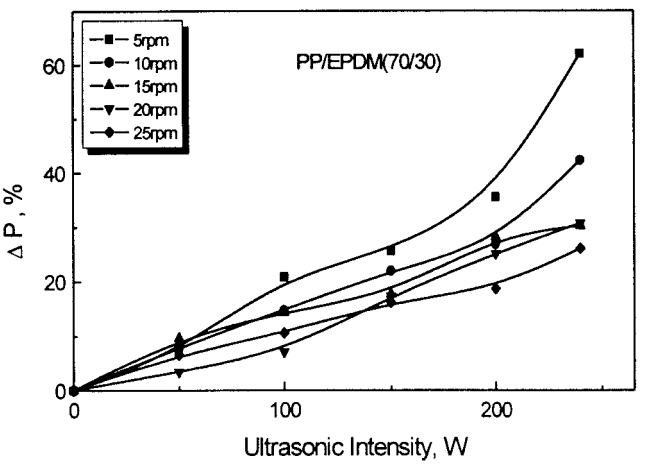

Figure 2 Relative die pressure reduction of PP/EPDM blends.

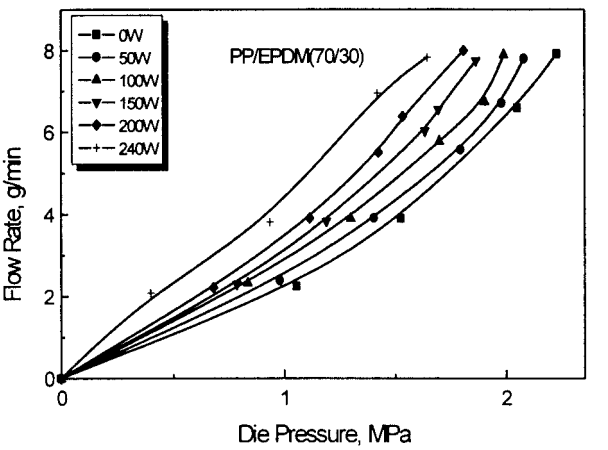

Figure 3 Flow-pressure characteristics of PP/EPDM blends.

Processing equipment

The ultrasound–extrusion experimental setup consists of a single-screw extruder (d=20 mm, L/D=25), with a variable cross-section capillary (d=3mm, L/D=7) having high-temperature pressure transducer and ultrasonic generator (Fig. 1). The ultrasonic frequency is 20 kHz and power ranges from 0 to 300 W. The direction of ultrasonic vibration coincides with that of the melt flow during extrusion.

Preparation of blends

Blends were prepared by two processing procedures as follows (die temperature of extruder was always 200°C):

1. 70 wt % PP +30 wt % EPDM was extruded by single-screw extruder with rotation speed of 20

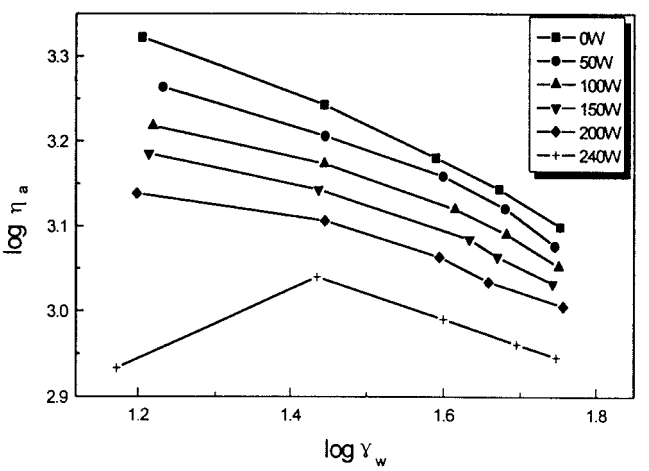

Figure 4 Apparent flow curves of PP/EPDM blends.

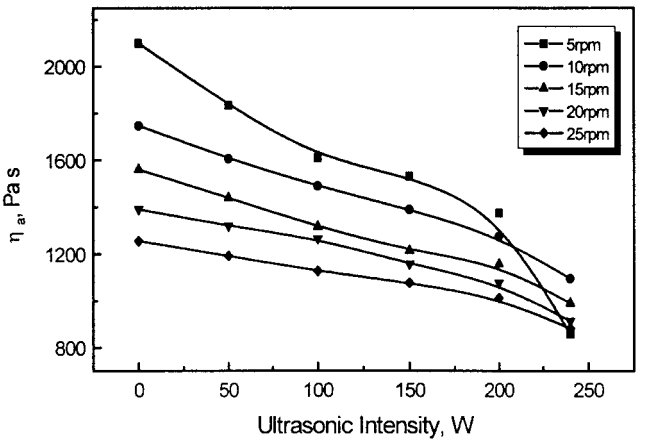

Figure 5 Apparent viscosity η_a vs ultrasonic intensity at various screw rotation speeds.

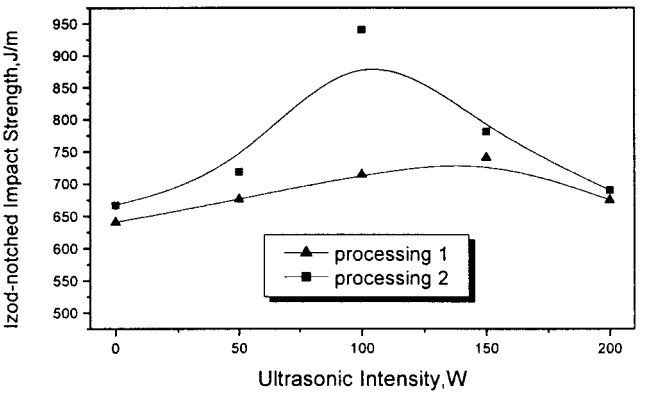

Figure 6 Impact properties of PP/EPDM blends vs ultrasonic intensity for various processing projects.

rpm, then made into pellets and extruded again with ultrasonic irradiation of various intensity.

2. 70 wt % PP +30 wt % EPDM was extruded by single-screw extruder with rotation speed of 20 rpm and ultrasonic intensity of 150 W, then made into pellets and extruded again with ultrasonic irradiation of various intensity.

The extrudates were then made into pellets and compression molded into 1 and 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 10MPa. Specimens for mechanical tests were cut from the plates.

Mechanical testing and characterization

Tensile strength was measured with an Instron 4302 universal testing instrument (U.K.) at tension speed of 100 mm/min according to GB1040-79. Izod-notched impact strengths were measured according to GB1843-80 with XJ-40 (China) impact tester. Melt flow rate (MFR) was measured at 230° C under load of 21.17N with a American CS-127 MFR instrument. A Japan JSM-5900LV scanning electron microscope (SEM) was used to observe blend morphology. Specimens were prepared by brittle fracturing under liquid nitrogen, then dissolving the rubber phase in xylene. Fracture surfaces were plated with gold before examination.

For each blend, different micrographs were made and were analyzed by an image analyzer to determine the diameter of each particle. A number average diameter (D_n) and a weight average diameter (D_w) were calculated according to the following formula:

$$D_n = \frac{\Sigma N_i D_i}{\Sigma N} \tag{1}$$

$$D_w = \frac{\Sigma N_i D_i^2}{\Sigma N_i D_i} \tag{2}$$

where N_i and D_i are the number and the diameter of the ith particle, respectively. The interfacial area (A_{3D}) per volume unit of the dispersed phase (V_{3D}) was denoted by A_i and calculated from the total perimeter of the particles (P_{2D}) divided by the total area of the particles (A_{2D}), as obtained from the micrographs[14]:

$$A_i(\mu m^2 / \mu m^3) = \frac{P_{2D}(\mu m)}{A_{2D}(\mu m^2)} = \frac{A_{3D}(\mu m^2)}{V_{3D}(\mu m^3)} \tag{3}$$

TABLE I
Mechanic Properties of PP/EPDM (73/30) at Various Ultrasonic Intensities by Different Blending Processings

	Processing 1		Processing 2	
Ultrasonic intensity (W)	Yield stress (MPa)	Young's modulus (MPa)	Yield stress (MPa)	Young's modulus (MPa)
0	20.05	1028.9	19.12	989.1
50	20.49	998.7	19.39	973.2
100	20.69	1031	19.12	910.0
150	20.77	1067.6	18.81	948.5
200	19.99	952.8	19.10	922.1

RESULTS AND DISCUSSION

Processing property and rheology

The dependence of die pressure on ultrasonic intensity at different screw speed was examined. Figure 2 shows that higher ultrasonic intensity contributes to larger reduction of die pressure. Lower rotation speed, which means longer duration ultrasonic treatment of the melt, also leads to larger pressure drop. In the case

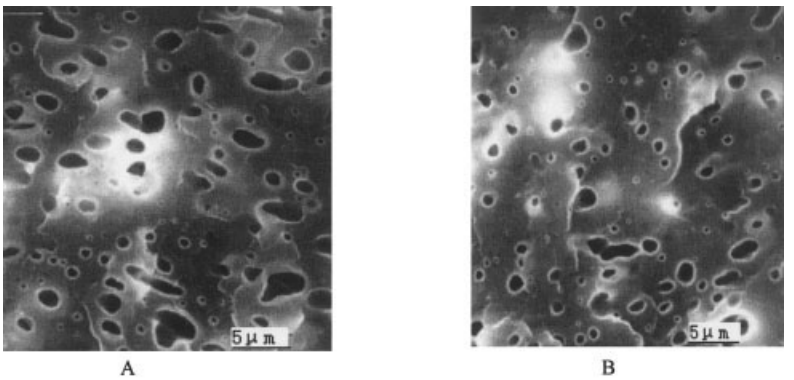

Figure 7 SEM of brittle fractured surfaces of PP/EPDM blends (A: 0 W; B: 150 W).

of 15 rpm of screw rotation speed and 240 W of ultrasonic intensity, the pressure drop is 30.2%. Furthermore, ultrasonic vibration during extrusion affects the throughput of extrudate. The flow rate increases as the ultrasonic intensity increases, as shown in Figure 3. All these characteristics demonstrate that ultrasonic treatment will significantly improve the extrusion efficiency.

Treating the extruding die as a dynamic capillary rheometer, as shown in Figure 4, gets a rheological curve of PP/EPDM blends at various ultrasonic intensities.

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

$$\dot{\gamma}_w = \frac{32Q}{\pi\rho D^3} \tag{5}$$

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \tag{6}$$

where τ_w is 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, got from the pressure transducer at the entrance of the capillary; Q is the flow rate, got by measuring the extrudate weight per second.

When ultrasonic vibration is applied, apparent viscosity of blend falls markedly compared to that without ultrasonic vibration. Without ultrasonic vibration, the blend shows linearly thinning with increasing of shear rate. The apparent viscosity vs apparent shear rate curve gradually deviates from linearity with ultrasonic intensity increasing. When ultrasonic intensity is 240 W, the apparent viscosity curve deviates from linearity dramatically. It may be attributed to the degradation of PP as a result of overmuch ultrasonic vibration.

Figure 5 shows the dependence of apparent viscosity on ultrasonic intensity at various rotation speeds. Since low rotation speed means long duration ultrasonic treatment of the melt, the apparent viscosity of the blends reduces more at lower rotation speed with ultrasonic irradiation. The decrease of apparent viscosity of PP/EPDM blends melt is also a function of ultrasonic intensity and irradiation time just like the pressure drop.

Mechanical testing

Data listed in Table I present the yield strength and Young's modulus as a function of ultrasonic intensity of PP/EPDM blends prepared by processing 1and 2. No obvious reduction of yield stress is observed as ultrasonic intensity increases, though Young's modulus reduces a little.

Figure 6 shows that impact strength of the PP/EPDM blend prepared with ultrasonic irradiation increases and is quite sensitive to a certain ultrasonic intensity. The maximum impact strength, 939.97J/m, is achieved when the ultrasonic intensity is 100 W in processing 2. It is 1.5 times as high as that of the blend without ultrasonic irradiation. All of the characteristics mentioned above demonstrate that introduction of ultrasonic vibration into extrusion is capable of toughening PP/EPDM blends without harming rigidity excessively.

TABLE II
Morphological Parameters of PP/EPDM Blends

Ultrasonic intensity (W)	D_n (μm)	D_w (μm)	Dispersion parameter (D_n/D_w)	A_i ($\mu m^2/\mu m^3$)
0	1.353	2.124	1.570	0.471
50	0.997	1.322	1.326	0.756
100	0.693	0.801	1.155	1.250
150	0.710	0.845	1.189	1.184
200	1.094	1.340	1.225	0.746

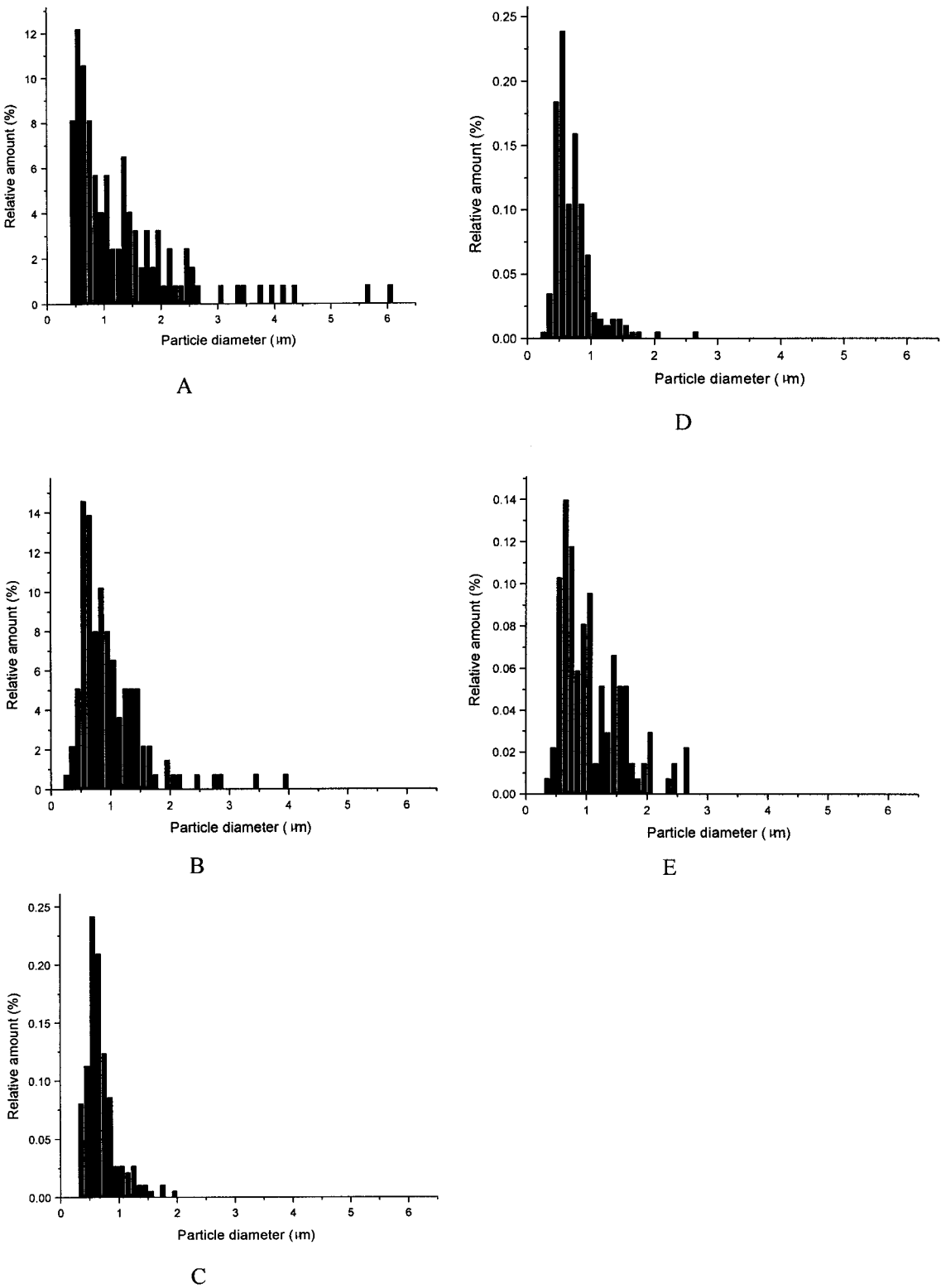

Figure 8 The particle size distribution of PP/EPDM blends: (A) 0 W, (B) 50 W, (C) 100 W, (D) 150 W, and (E) 200 W.

Fracture surface morphology observation

It is well known that toughness depended on the morphology of polymer blends; therefore, compatibility that controls morphology should be the dominant factor. Figure 7 is the micrographs of brittle fractured surfaces of PP/EPDM blends in liquid nitrogen. EPDM particles are much smaller in PP/EPDM blends with ultrasonic irradiation [Fig. 7(B)] than in that with-

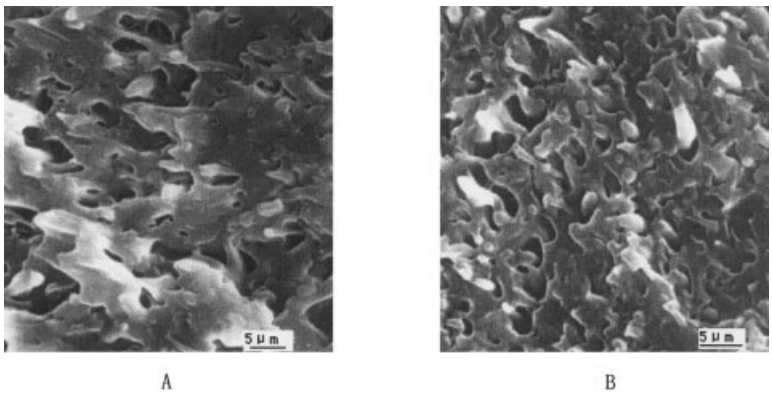

Figure 9 SEM of impact-fractured surfaces of PP/EPDM blends taken at the zone near the notch tip (A: 0 W; B: 150 W).

out ultrasonic irradiation [Fig. 7(A)]. It indicates a good dispersed EPDM phase is obtained through ultrasonic irradiation.

The morphological parameters in terms of the number average particle size (D_n), weight average particle size (D_w), Dispersion parameter (D_n/D_w), interfacial area per unit volume of dispersed phase (A_i) obtained from the SEM analysis, are listed in Table II. The EPDM particle size distributions in the blends of PP/EPDM at different intensities of ultrasonic vibration are presented in Figure 8. It is found that the number average particle size (D_n), weight average particle size (D_w), and dispersion parameter (D_n/D_w) all decrease then increase with ultrasonic intensity, and the values of the PP/EPDM blends with ultrasonic vibration are all smaller than those without ultrasonic vibration. Figure 8 shows the particle size distributions for PP/EPDM blends with ultrasonic vibration are much narrower than that without ultrasonic vibration and decrease then increase with ultrasonic intensity. The largest size of EPDM particle varied from 6.06 μm at 0 W to1.91 μm at 100 W of ultrasonic irradiation, since smaller particle size and narrower particle size distribution denote more homogeneous dispersion of EPDM in PP matrix. This leads to good impact resistance properties. All the phenomena demonstrated above correspond well to the Izod-notch impact property of PP/EPDM blends, which increases then decreases with ultrasonic intensity.

It has been reported that the interfacial area per unit volume of dispersed phase (A_i) is a measure of interfacial thickness in the multiphase polymer systems.[15] The values of A_i were found to increase significantly in the case of PP/EPDM blends with optimum ultrasonic vibration intensity. This indicates that ultrasonic vibration allows interfacial interaction of EPDM and PP matrix to become stronger. It also leads to good toughness of PP/EPDM blends.

When ultrasound is applied, its powerful vibration, shatter, and cavitations help to shear, cut, and disperse EPDM in PP matrix. When blend melt goes into the ultrasound effect zone (i.e., die of the extruder), ultrasonic vibration leads to disentanglement of molecular chains and interpenetration of the two phases by dynamics controlling process. Once the melt flows out of the zone, the thermodynamics process become dominant, and the chains get entangled again. This gives a chance to PP and EPDM molecules near the interface to entangle with each other. Therefore, interfacial thickness of PP/EPDM blend is improved by applying

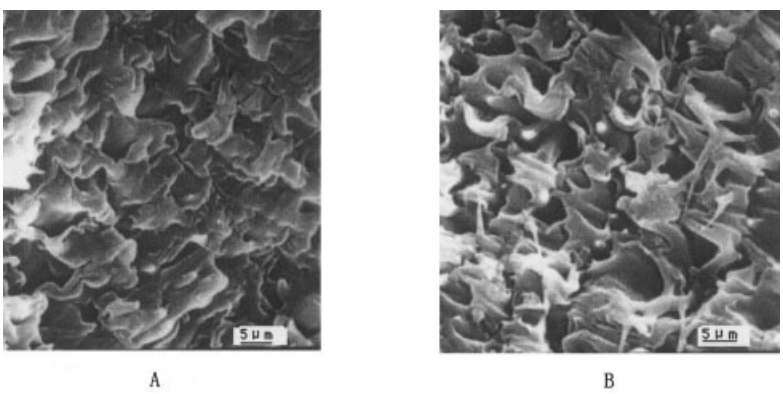

Figure 10 SEM of impact-fractured surfaces of PP/EPDM blends taken at the middle of the fracture surface (A: 0 W; B: 150 W).

ultrasonic vibration, which means compatibility of EPDM and PP matrix is improved.

During impact fracture at room temperature, plastic deformation occurs, as shown in Figure 9 taken at the crack growth zone. Some cavitation is seen, which becomes more intense in the samples with ultrasonic irradiation. Figure 10 was taken at the stress-whitening zone of the fracture surface of the PP/EPDM blend. In the ultrasound-applied PP/EPDM blend, some cavitation voids show evidence of coalescence and others are highly stretched and elongated, as the specimen deforms [Fig. 10(B)]. All these indicate that ultrasonic vibration enhances the toughness of PP/EPDM blends.

CONCLUSION

PP/EPDM blends were prepared by an ultrasound–extrusion experimental setup. It is shown that ultrasonic irradiation is very efficient in improving processability of the blends. The die pressure and apparent viscosity of the melt reduction and throughput of extrudate increase. The ultrasonic vibration has a significant effect on the impact strength of PP/EPDM blend, and this is attributed to the morphology of small particles of EPDM phase, and good adhesion between EPDM and PP matrix.

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