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In situ compatibilization of PP/EPDM blends during ultrasound aided extrusion

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Abstract

Blends of isotactic polypropylene (iPP) and uncured ethylene–propylene diene rubber (EPDM) of various concentrations were treated by high power ultrasonic waves during extrusion. Die pressure and power consumption were measured. The effects of different gap sizes, blend ratios and number of ultrasonic horns were investigated. The rheological properties, morphology and mechanical properties of the blends with and without ultrasonic treatment were studied. In situ compatibilization of the blends was observed as evident by their more stable morphology after annealing, improved mechanical properties and IR spectra. The obtained results indicated that ultrasonic treatment induced the thermo-mechanical degradations and led to the possibility of enhanced molecular transport and chemical reactions at the interfaces. Processing conditions were established for enhanced in situ compatibilization of the PP/EPDM blends.

Keywords: Ultrasound; In situ compatibilization; Polypropylene/ethylene–propylene diene rubber

1. Introduction

Preparation of novel polymer blends is a research area of considerable interests. Most polymer pairs in blends are thermodynamically incompatible; the incompatible blends often give poor mechanical properties due to the lack of physical or chemical interactions between different phases and poor interfacial adhesion [1]. Compatibilization of polymer blends has been studied for decades [2]. There are several ways to improve the compatibility among different polymers, like addition of compatibilizer, typically block or grafted copolymer [3–6], or inducing chemical reaction between polymers [7,8], leading to a modification of interfaces in two phase blends, and thereby tailoring of phase structure and properties.

The effects of ultrasound on polymer solutions have been widely studied. Early in the 1930s the reduction of the viscosity of solution of natural polymers by ultrasound was noted [9]. Over the past several decades, a number of studies in this area have been performed and reported. It was observed when polymer solutions are subjected to exposure of high intensity ultrasound waves, stresses induced by cavitation led to homolytic cleavage of polymer chains, and consequently causing the molecular weight decrease [9,10]. The breakage of the C–C bond by ultrasound usually leads to the formation of long-chain radicals in polymer solutions, which can cause the formation of copolymer by coupling of those long-chain radicals from different polymers [11,12]. The free radicals formed by the irradiation of polymer solution can also start polymerization reactions [11,13].

High power ultrasound is also applied to the polymer melts during processing. Isayev and his coworkers use high power ultrasound to devulcanize ground tire rubber (GRT) and many other rubbers [14–19] as a promising recycling method for waste rubbers. It is also known that long-chain polymer molecules can be ruptured by high power ultrasound during melt extrusion [20]. Recently, ultrasonic compatibilization of PE/PS [21], PP/PS [22], PC/PS, PMMA/PS [23] in batch mixing processes and PP/PA 6 [24], PP or PE/rubber blends [25–29] in continuous process were reported. It was found that for immiscible polymers, ultrasonic treatment during prolonged batch mixing (tens of minutes) or extrusion at a residence time of seconds can improve interfacial adhesion and compatibilization between different phases, which is also attributed to the formation of copolymers at the interface by the long-chain radicals from different polymers generated by an ultrasonic treatment.

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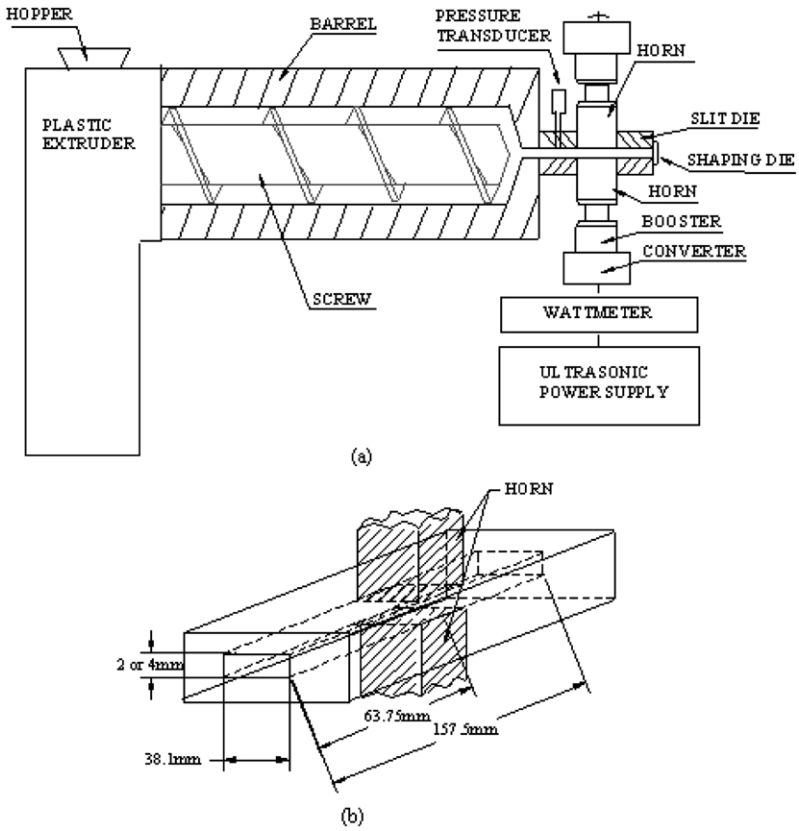

Fig. 1. Schematic drawing of the ultrasonic reactor with a slit and shaping die (a) and the slit die dimensions with positions of horns (b).

Blends of isotactic polypropylene (iPP) with ethylene–propylene diene rubber (EPDM) are well studied and widely used industrial materials. Typically, blends with a low content of EPDM are utilized as a high-impact polypropylene, while blends with a high content of EPDM are used as thermoplastic elastomers. Therefore, a possibility of further improvement of the properties of these blends is a challenging problem.

With this in mind, the present study describes the effects of ultrasonic treatment on the rheological and mechanical properties of PP/EPDM blends. Also, the morphological development of treated and untreated PP/EPDM blends is characterized.

2. Experimental

2.1. Materials

Isotactic polypropylene (iPP) made by Basell under trade name Pro-fax 6523 was used. The iPP had melt flow index of 4.0 g/10 min at 230 °C and density of 0.9 g cm^{-3}. Ethylene propylene diene terpolymer (EPDM) with 5-ethylidene-2-norbornene (ENB) as a termonomer containing 70% ethylene with 4.5% ENB unsaturation was used. Its density was 0.86 g cm^{-3}. It was generously supplied by DSM Elastomers Americas under the trade name Keltan® 5508. Benzene from Aldrich was used as solvent to extract EPDM phase in PP/EPDM blends.

2.2. Preparation of blends

The blending of PP and EPDM was carried out on a co-rotating twin-screw extruder FTX-80 of Farrell Company. PP and EPDM pellets were premixed and then were fed into extruder. Blending was performed using temperature settings in eight zones and nozzle of 165/165/175/185/185/190/195/195/200 °C, screw speed of 100 rpm and feed rate of 120 g/min. The extrudates were pelletized after quenching by cooled water.

2.3. Ultrasonic reactor and blends treatment

The pellets of PP and EPDM blends were fed into a Killion single screw extruder with an ultrasonic die attachment. Schematic drawing of the ultrasonic reactor is shown in Fig. 1. Two water-cooled ultrasonic horns of rectangular cross sections (38.1 × 38.1 mm^2) were inserted into the extrusion slit die. A pair of 3.3 kW ultrasonic power supply, converter and 1:1 booster were connected to the horns. Horns vibrating in a direction perpendicular to the flow direction impose longitudinal ultrasonic waves to the polymer melt. Two pressure transducers (Dynisco) were placed in the slit die before and after the treatment zone.

The temperature of the extruder barrel and ultrasonic attachment were set at 180 °C. The ultrasonic treatment was carried out at a frequency of 20 kHz and various amplitudes ranging from 5 to 10 μm. The flow rate and the gap between the two horns were varied. Extrudates were pelletized for molding and AFM study.

2.4. Molding

Treated and untreated blends were molded into slabs with dimensions of $127 \times 127 \times 2\ mm^3$ at 190 °C by the compression molding press (Wabash) at a pressure of 17.2 MPa for 8 min.

2.5. Characterization

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spectrometer with parallel plate geometry. Tests were carried out in a strain controlled dynamic frequency mode at 200 °C. The rheological properties were determined as a function of frequency from 0.1 to $100\ s^{-1}$. The strain amplitude was kept constant at 4%.

Tensile measurements were performed according ASTM D-412-97 (type C) at room temperature on an Instron testing machine, Model 5567. The tests were carried out at a crosshead speed of 50 mm/min with a 1 kN load cell. All the results were the average of five measurements.

In order to study the morphology of the extrudates and compression molded blends, scanning electron microscope (SEM) and atomic force microscope (AFM) were used. For SEM, the compression-molded specimens were fractured in liquid nitrogen; rubber phase was etched by benzene at 50 °C for one day. Etched samples were then coated with

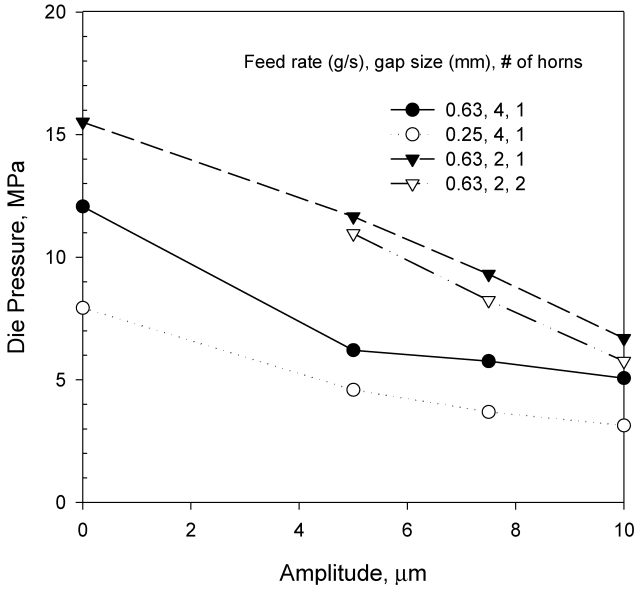

Fig. 2. Die pressure vs. amplitude of ultrasound during treatment of PP/EPDM 50/50 blend.

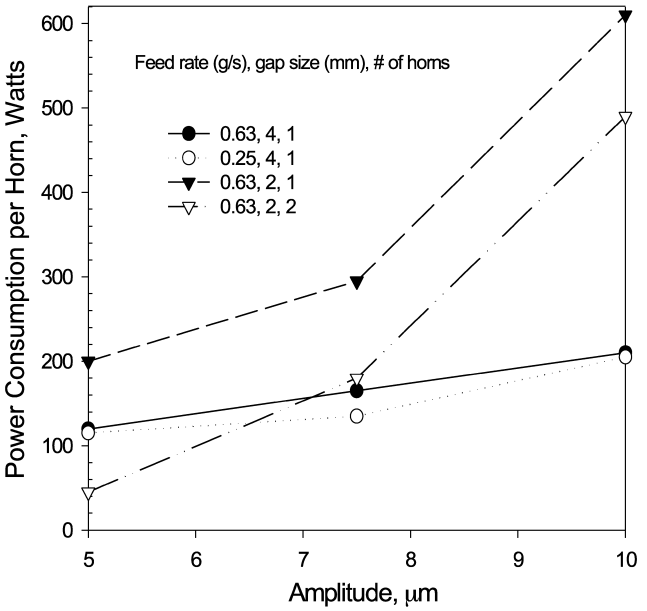

Fig. 3. Power consumption vs. amplitude of ultrasound during treatment of PP/EPDM 50/50 blend.

silver and the morphology was observed using a SEM (Hitachi S-2156). For AFM, studies of samples cryomicrotomed at −80 °C were done in air at ambient conditions using Dimension 3000 IIIa AFM (Digital Instruments). The tapping mode was used using Si probes (TAP 300, Nano Metrology Devices) with a spring constant of $40\ N\ m^{-1}$, resonance frequencies 300 kHz, and the tip radius less than 10 nm. The AFM topographic (height) and the elastic (phase) images were simultaneously obtained under tapping conditions on the cryomicrotomed surface of PP/EPDM blends. Phase images revealed hard regions in dark (the PP phase) and soft regions in bright (the EPDM phase). Root-mean-square (RMS) surface roughness, which is typically used to quantify variations in surface elevation, was determined directly from the height data as

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{n} (Z_i - Z_{\mathrm{ave}})^2}{n}} \tag{1}$$

where RMS is the RMS roughness, Z_i the ith height sample out of N the total samples, and Z_{ave} the mean height.

The chemical structure of the untreated and ultrasonically treated PP/EPDM blends was identified by Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, 16PC) with 16 scan per sample at a resolution of $2\ cm^{-1}$. In order to carry out the FT-IR spectroscopy, films of the blends were pressed at 190 °C using an electrically heated compression molding press (Wabash) and placed in a Soxhlet with benzene as solvent for 48 h to extract EPDM phase. After drying in a vacuum oven for 24 h, the films were prepared by compression molding again. These films were used in FT-IR experiments.

3. Results and discussion

3.1. Process characteristics

Figs. 2 and 3 show die pressure at the entrance to ultrasonic treatment zone and ultrasonic power consumption vs. amplitude during ultrasonic treatment of PP/EPDM 50/50 blends. Pressure at the treatment zone was substantially reduced as the amplitude of ultrasound was increased. Ultrasound facilitates the flow of polymer melt due to heat-up effect by the energy dissipated from ultrasound, shear-thinning effect by ultrasound wave propagation in polymer melt, reduction of friction at horn surfaces due to ultrasound vibrations and degradation of polymers. At the same amplitude the pressure decreases as gap size increases and flow rate decreases during ultrasonic treatment. The pressure is lower when two horns are in operation, which is caused by the same reason as stated above, and in addition, due to interaction of two ultrasound waves.

The power consumption measured is the total energy used during the treatment. The power consumption of horns working without load, zero power consumption, was subtracted from the total power consumption. Power consumption increased with amplitude of ultrasound (Fig. 3). This indicated that more energy was transmitted from horn or horns into the polymer melt with an increase of the amplitude. Also the decrease of the gap size led to higher power consumption. When two horns were used, the power consumption per horn decreased. In fact, the sum of power consumption of two horns was more than that in case of using only one horn, but less than two times of the energy consumption of one horn. Clearly there is an interaction between two horns, which makes the power output per horn to decrease.

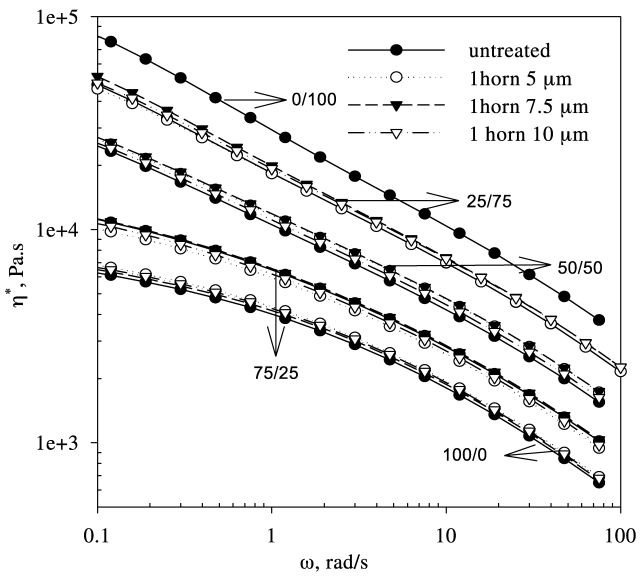

Fig. 4. Complex viscosity vs. frequency of PP/EPDM blends untreated and treated by one horn at a gap size of 4 mm, a flow rate of 0.63 g/min and various amplitudes.

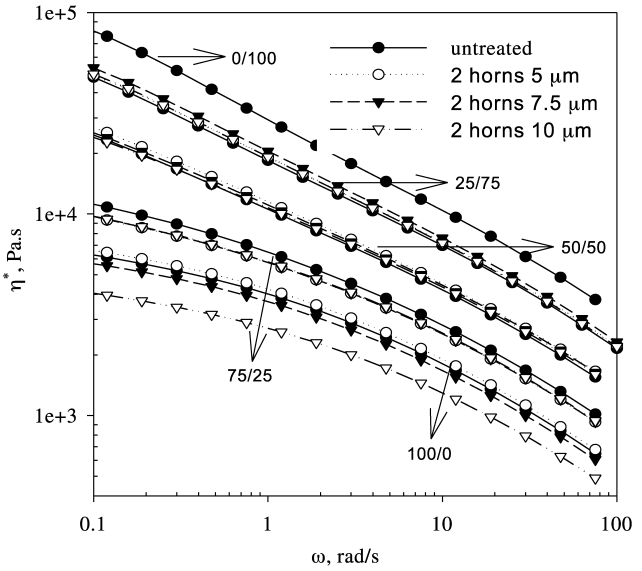

Fig. 5. Complex viscosity vs. frequency of PP/EPDM blends untreated and treated by two horns at a gap size of 4 mm, a flow rate of 0.63 g/min and various amplitudes.

3.2. Rheology

Figs. 4 and 5 show the complex viscosity of untreated and treated 75/25, 50/50 25/75 PP/EPDM blends. It is clearly seen that the viscosities of PP/EPDM blends increases with the increasing of rubber content and viscosity of the treated blends were only slightly changed compared to that of untreated blend with the same blend ratio when treated by only one horn (Fig. 4). The viscosity of PP treated by two horns with amplitudes of 7.5 and 10 μm were decreased (Fig. 5). The viscosity of PP/EPDM 75/25 blends also decreased when treated by two horns with 10 μm amplitude. The decrease of viscosity was due to the thermo-mechanical degradation that occurred during ultrasonic treatment. In polymer solutions, it is known that polymer chains undergo degradation during ultrasonic irradiation. The effect is ascribed to acoustic cavitation, initiated in polymer solutions [10]. In case of ultrasonic treatment of polymer melts, the mechanism is not as well understood as that in polymer solutions, though it was also believed due to the ultrasonic cavitation effects [20,25–28].

It is also seen from Figs. 4 and 5 that the effects of ultrasound irradiation on the viscosity of blends were greatly influenced by the blends ratio. The viscosities of PP/EPDM 50/50 and 25/75 blends remained almost unchanged when treated by either one or two horns and different amplitudes, while PP and PP/EPDM 75/25 blend show a decrease of viscosities at some conditions. However, it does not mean that there is no degradation at all in the former blend system, since the viscosity data may not be detected if other molecular transformation simultaneously occurred during treatment, because compatibilization may lead to an increase of viscosity [30].

Fig. 6, shows the complex viscosities of PP/EPDM 75/25

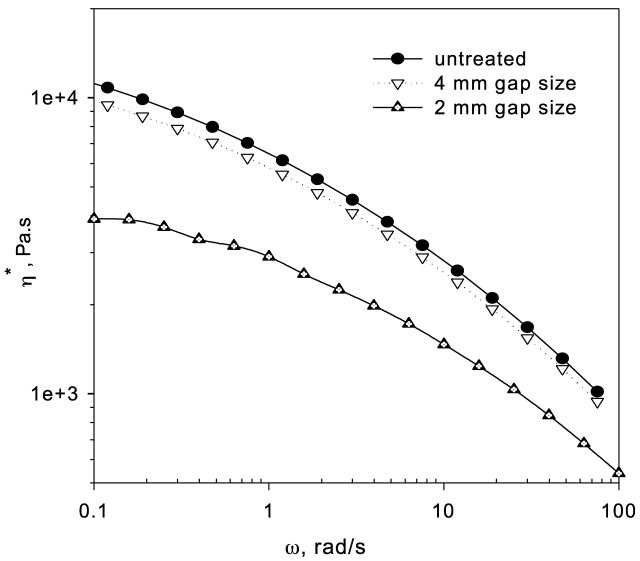

Fig. 6. Complex viscosity vs. frequency of PP/EPDM 75/25 blends untreated and treated by two horns at an amplitude of 10 μm, a flow rate of 0.63 g/min and various gap size.

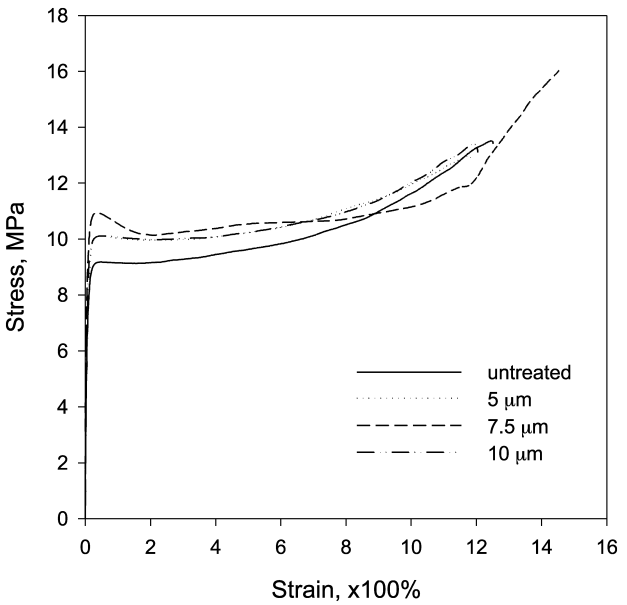

Fig. 7. Stress–strain curves for compression molded samples of PP/EPDM 50/50 blends untreated and treated at a gap size of 4 mm, a flow rate of 0.63 g/s, and with one ultrasound horn.

blends treated by two horns at an amplitude of 10 μm at different gap sizes. As the gap size decreased to 2 mm, viscosity of PP/EPDM 75/25 blend decreased much more. Since the mean residence time (t_r) is different in dies of 2 ($t_r = 4$ s) and 4 mm ($t_r = 8$ s) gap size at the same flow rate (0.63 g/s), it is obvious that when gap size decreases, the polymer melt was subjected to irradiation for a shorter time. However, since at the same ultrasonic amplitude, the strain amplitude imposed by ultrasound and the power consumption was much higher in case of 2 mm gap size, therefore more degradation was observed.

3.3. Mechanical properties

Fig. 7 shows the typical stress–strain curves for PP/EPDM 50/50 blends untreated and treated at a gap of 4 mm, a flow rate of 0.63 g/s, and with one ultrasound horn. Clearly, we can see that the yield strength, elongation at break and tensile strength are highest for the sample treated at an ultrasound amplitude of 7.5 μm. Evidently, during ultrasonic treatment, long chain radicals are formed [11]. Those radicals can combine and generate copolymers which improve the compatibility and interfacial tension between immiscible polymers at the interfaces, which lead to the better mechanical properties.

Table 1 shows the mechanical properties of PP/EPDM blends, including the modulus, yield stress, elongation at break, tensile strength and toughness with different blend compositions and treatment conditions. Depending on the composition and treatment conditions, the modulus at 5% strain was unchanged, slightly or significantly increased in the treated samples. However, under most conditions other properties are improved in all compositions subjected to ultrasonic treatment as compared to those of untreated blends. The increase of properties is more significant at lower flow rate, 0.25 g/s ($t_r = 20$ s), evidently due to longer residence time. In fact, for PP/EPDM 50/50 blends at 2 mm gap size, the increase of properties is more than that at 4 mm gap size since power consumption at 2 mm gap is more than double of that at 4 mm gap, though residence time is only half of that at 4 mm gap.

Ultrasonic treatment of blends with two horns at higher amplitudes induce more degradation of polymer blends, that overcomes the positive effect of compatibilization and diminishes the mechanical properties of PP/EPDM 50/50 blend treated by two horns with 10 μm amplitude, 0.63 g/s flow rate.

3.4. Morphology

The AFM phase images of compression moldings of untreated and treated PP/EPDM 25/75, 50/50, 75/25 blends are shown in Fig. 8. EPDM is continuous phase in PP/EPDM 25/75 blends and dispersed phase in PP/EPDM 75/25 blends. Clearly, as rubber content increases, the morphology of PP/EPDM blends goes through phase inversion [31,32]. The morphology of PP/EPDM 50/50 blends is close to a co-continuous morphology, but EPDM is still a dispersed phase. The morphology of immiscible blends depends highly on the processing conditions, the blends composition and rheology. It is generally observed that a dispersed morphology is formed if the concentration of one component in blend composition is dominant and a co-continuous morphology is formed if the blend composition is about equal [2,33]. On the other hand, there are significant differences in domain size between untreated and

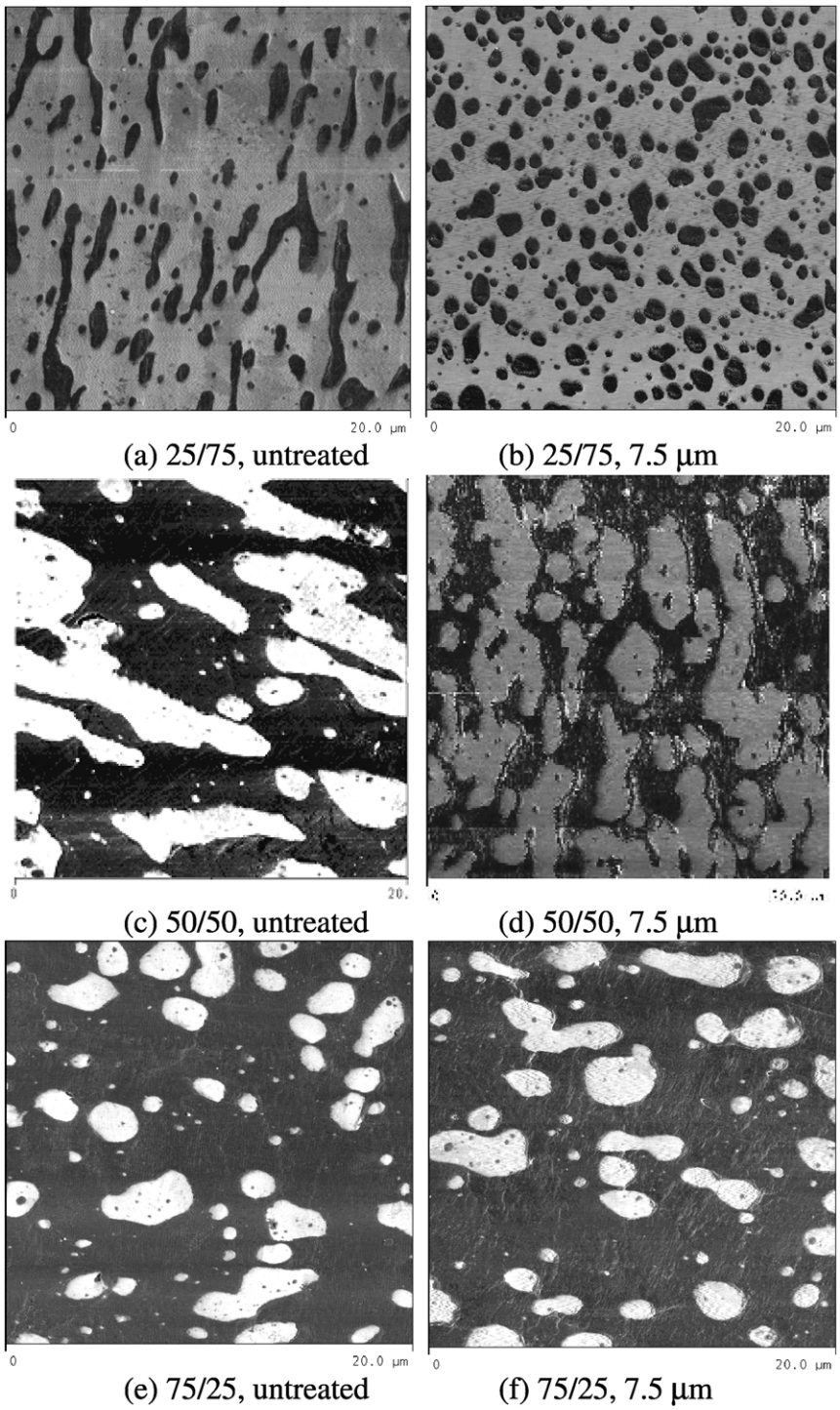

Fig. 8. AFM phase image of compression molded samples of PP/EPDM blends untreated and treated by one horn at a gap size of 2 mm and a flow rate of 0.63 g/s.

ultrasonically treated PP/EPDM 25/75, 50/50 blends. In particular the domain sizes of untreated blends are much larger than those of treated blends. However, domain sizes of untreated and treated PP/EPDM 75/25 blends are similar.

Fig. 9 shows the root mean square (RMS) roughness of untreated and treated PP/EPDM blends at different blend ratios. It is seen from Fig. 9 that the RMS roughness also has the same trend as the domain size with different blend ratios. The RMS roughness of the surface of untreated blends is much higher than that of the treated PP/EPDM 25/75 and 50/50 blends, while for PP/EPDM 75/25 blends, RMS roughness is similar for both untreated and treated blends. It is also interesting to see that as rubber content decreases, the effect of ultrasound compatibilization is less significant or

Table 1
Mechanical properties of PP/EPDM blends

Sample				Modulus at 5% strain (MPa)	Yield stress (MPa)	Elongation at break (%)	Tensile strength (MPa)	Toughness (MPa)
PP/EPDM	Gap size (mm)	Flow rate (g/s)	# of horns/amplitude (μm)					
75/25	2	0.63	Untreated	232	16.2	1340	28.2	236
			1/5	234	16.2	1360	28.2	238
			1/7.5	241	16.6	1390	28.8	253
			1/10	246	16.7	1310	27.9	230
50/50	4	0.25	Untreated	94.9	7.74	1140	20.6	126
			1/5	101	8.02	1250	23.2	151
			1/7.5	105	8.45	1300	24.4	163
			1/10	103	8.31	1370	25.8	180
50/50	4	0.63	Untreated	131	9.27	1300	13.9	138
			1/5	127	9.96	1200	13.3	129
			1/7.5	154	10.7	1440	16.0	169
			1/10	144	10.0	1210	13.7	135
50/50	2	0.63	Untreated	103	7.96	1340	20.4	164
			1/5	108	8.27	1300	19.9	157
			1/7.5	101	7.75	1270	19.8	151
			1/10	125	9.17	1420	24.1	196
			2/5	103	7.87	1250	19.5	149
			2/7.5	114	8.56	1220	19.3	146
			2/10	102	7.87	818	12.3	75.7
25/75	2	0.63	Untreated	12.8	–	1480	10.7	91.9
			1/5	18.9	–	1540	12.3	111
			1/7.5	19.0	–	1540	12.5	107
			1/10	20.2	–	1440	12.1	97.7

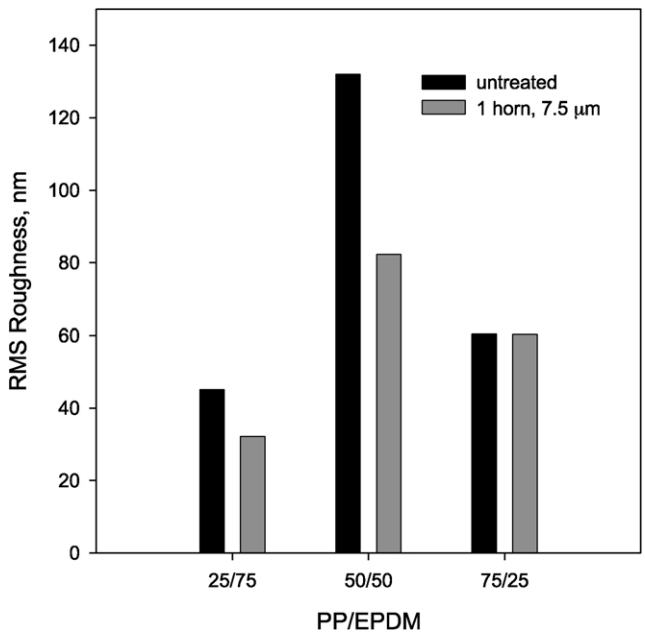

Fig. 9. RMS roughness vs. blend composition of compression molded samples of PP/EPDM blends untreated and treated by one horn at a gap size of 2 mm and a flow rate of 0.63 g/s.

absent. The treated PP/EPDM 25/75, 50/50 blends have better mechanical properties (Table 1) and more stable morphology as experiments of annealing indicated as shown below. PP and EPDM have different thermal expansion coefficients, so, after cryomicrotoming, they will expand according with the temperature difference between the temperature of cryomicrotoming and room temperature. Apparently, the copolymers formed at the interface during ultrasonic treatment of blends improve the interfacial adhesion, which will restrict the thermal expansion. So the treated blends have a smoother surface.

The annealing experiments were also carried out in order to see the morphology changes at high temperature. The AFM phase images of extrudates and compression moldings of untreated and ultrasonically treated PP/EPDM 25/75 blends before and after annealing at 200 °C for 10 min are shown in Fig. 10. The morphology of extrudates of untreated and treated blends are similar. Size of particles of dispersed phase is about 350 nm. After 8 min compression molding at 190 °C (Fig. 8a and b), the untreated blend shows more coarse morphology than the treated blend. While after 10 min annealing at 200 °C, the domain size of untreated blend is increased to about 2.1 μm which is even larger than that of treated blend with particle size of about 1.6 μm.

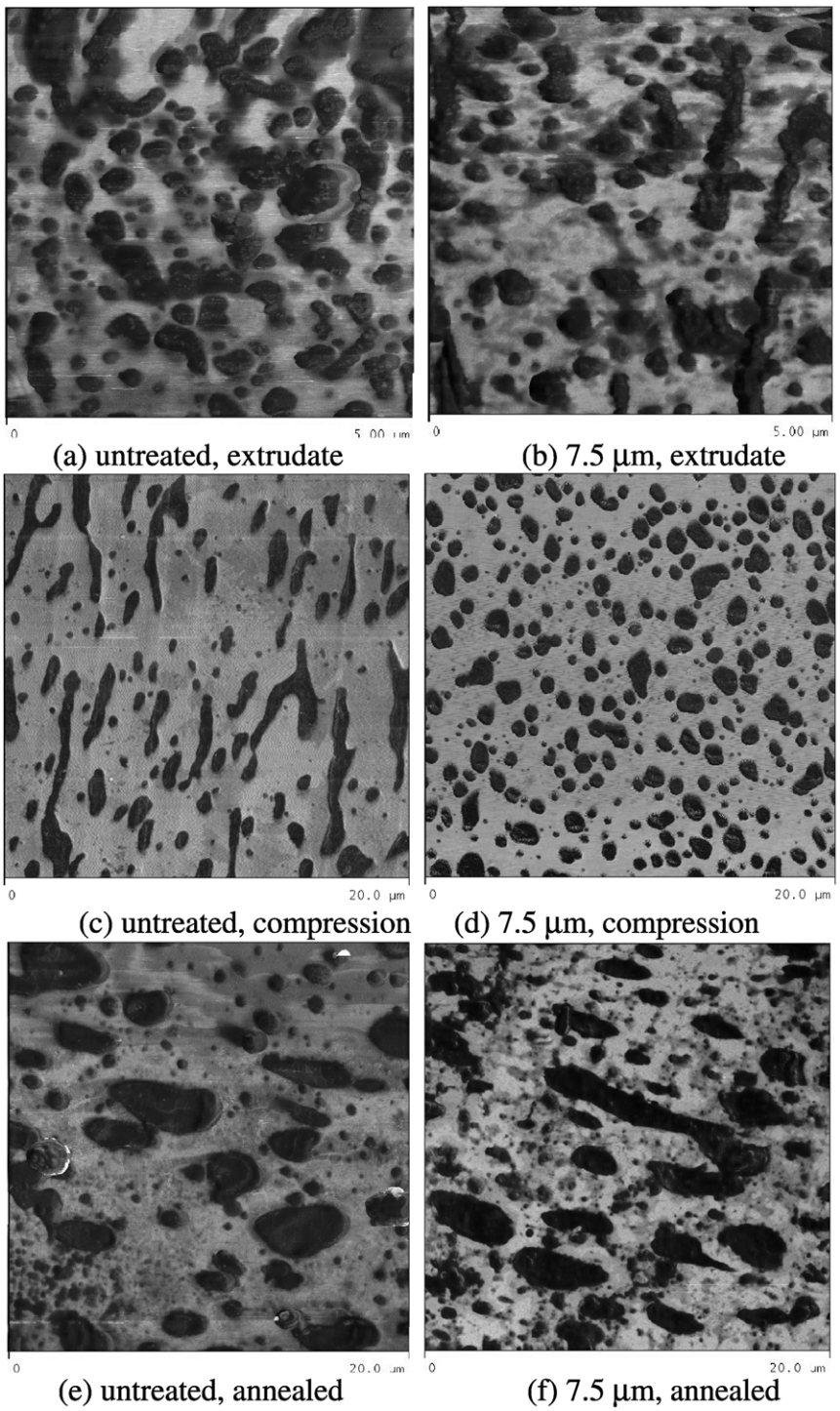

Fig. 10. AFM phase image of extrudates and compression moldings of PP/EPDM 25/75 blends untreated and treated by one horn at a gap size of 2 mm and a flow rate of 0.63 g/s, (a), (b) extrudates; (c), (d) compression moldings; (e), (f) compression moldings annealed at 200 °C for 10 min.

The SEM photographs of untreated and ultrasonically treated PP/EPDM 50/50 blends before and after annealing at 200 °C for 10 min are shown in Fig. 11. Before annealing, there is not much difference among treated and untreated blends. After annealing, there are still some small particles in the treated blends, and the domain size of annealed treated blends is smaller than that of the untreated one. It is believed that during annealing the phase growth in the treated blends is retarded to some extent. The morphology of treated blend is more stable than that of the untreated blend since the in situ compatibilization at the interface delays the phase growth [34,35].

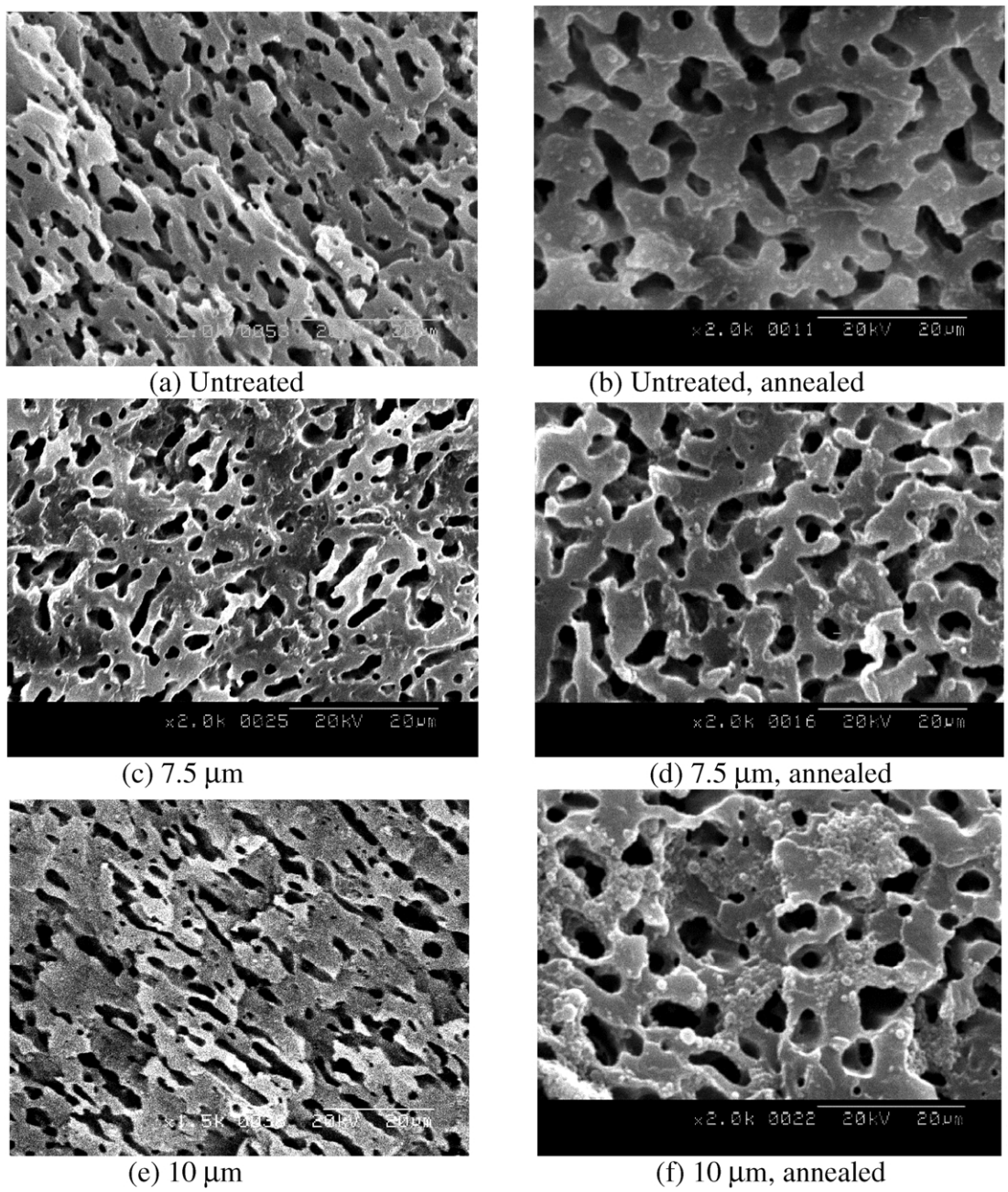

Fig. 11. SEM photographs of compression molded samples of PP/EPDM 50/50 blends untreated and treated by one horn at a gap size of 4 mm and a flow rate of 0.63 g/s.

3.5. IR spectrum

IR spectrums of the methylene rocking region of PP, EPDM, untreated and treated PP/EPDM 50/50 blends are shown in Fig. 12. For EPDM, the band at 720 cm^{-1} is associated with the $P(E-E)_{n\geqq 2}$ sequence [36,37]. After extraction, treated PP/EPDM 50/50 blend still shows the peak related to the ethylene sequence of EPDM, while there are no such peak in neat polypropylene and untreated PP/EPDM 50/50 blend after extraction. Those IR spectra confirm the existence of copolymer in the ultrasonically treated PP/EPDM 50/50 blend.

4. Conclusions

Ultrasonic treatment improved the processing behavior of PP/EPDM blends by reducing the die pressure. Ultrasound power consumption increased with the increase of ultrasound amplitude and the decrease of gap size. When two horns were used, the total power consumption was more than that in the case of one horn, but less than twice of the value of one horn.

PP/EPDM blends underwent degradation during ultrasonic treatment, the degradation of blends strongly depended on the blend ratio and ultrasonic treatment

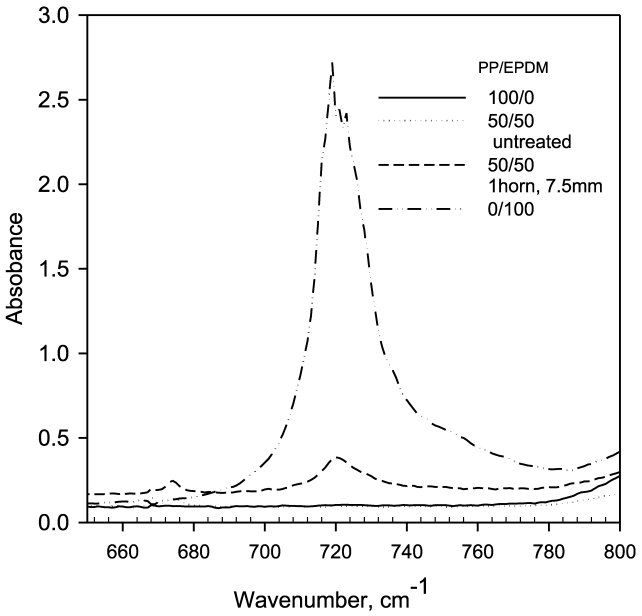

Fig. 12. IR spectrums of PP, EPDM, PP/EPDM 50/50 blends untreated and treated by one horn at a gap size of 4 mm and a flow rate of 0.63 g/s.

conditions, including number of horns used, amplitude, gap size and flow rate.

The yield strength, elongation at break, tensile strength, and toughness of ultrasonically treated PP/EPDM 50/50 blends were improved at certain conditions of ultrasonic treatment compared to those of untreated blends. The effect was dependent on the treatment conditions.

SEM pictures show that the domain size for the untreated and treated blends before annealing is about same; after annealing the domain size for the treated blends is smaller than that of untreated one. The morphology of treated PP/EPDM blends is more stable than the untreated one after annealing.

IR spectra of untreated and treated PP/EPDM 50/50 samples show that copolymer is formed in the treated sample. The ultrasonic treatment of blends enhanced the intermolecular diffusion and interaction, produced copolymer, and thereby improved interfacial adhesion and gave rise to the in situ compatibilization of blends.

Acknowledgements

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