An Application of Powerful Ultrasound to Rubber Processing : in-situ Compatibilization of Rubber Blends

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ABSTRACT

Plastic/rubber blends are ultrasonically treated during continuous extrusion in order to investigate the *in-situ* compatibilization of the blends without any chemicals. The mechanical properties of each blend were significantly improved by ultrasonic treatment. It is believed that ultrasonic treatment of the blends enhances intermolecular interaction, improves adhesion at the interface and creates copolymers during very short time. The created copolymers are believed to be a major reason for enhancing mechanical properties of the blends by *in-situ* compatibilization during extrusion. This process can be applied for preparing plastic/rubber blends to make thermoplastic elastomers or plastic/plastic and rubber/rubber blends, and for making novel copolymers from practically any pairs of existing polymers to achieve desirable chemical and physical properties.

1. INTRODUCTION

Polymer blending is a useful approach for the preparation of new materials with specially tailored or improved properties that are often absent in the single component polymers. However, many polymer pairs are incompatible or immiscible with each other and exhibit either very low or no interfacial adhesion and phase separate on blending.[1] In most cases, melt mixing of two dissimilar polymers results in blends that are weak and brittle. The mechanical properties of polymer blends are strongly influenced by the strength of the interfaces between the different phases, as well as the dispersion and interaction or adhesion between them.

Compatibilization of polymer blend has been studied for decades.[2] It is commonly known that compatibilization is achieved by addition of a third component, typically a block copolymer, to the system, or by inducing chemical reaction using chemicals, leading to modification of the polymer interfaces in two-phase blends, and thereby to tailoring of the phase structure, and hence properties. The addition of pre-made block copolymers can lead to a reduction of interfacial tension.[3-6] However, these methods are likely to be restricted to the use of available polymers and the synthesis of block copolymers is not available for most polymer pairs of interest. Reactive blending relies on the *in-situ* formation of interacting polymers using specifically selected or tailored chemicals.[1,7] The blend com-

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ponents themselves are chosen so that reaction at the interface occurs during melt blending leading to a reduction in particle size of the dispersed phase.[8] Although some polymers naturally contain functional groups at chain end, most must be functionalized prior to reactive compatibilization and the reaction rates are very slow thus, this method is impractical for use. Also, existing technologies for making plastic/rubber blends use simple mixing of components with aid of chemicals or dynamic vulcanization of rubber phase with aid of curatives.[9] Notably, the ability to make polymer blends at low cost from practically any pairs of existing polymers is very desirable.

It is known that by high intensity ultrasonic waves long-chain polymer molecules can be ruptured during extrusion.[10,11] The particular interest of ultrasonic degradation is the fact that, contrary to all chemical or thermal decomposition reactions, ultrasonic depolymerization in solutions is a nonrandom process that produces fragments of definite molecular size.[12-14] The mechanical rupture of polymer chains leads to the formation of macro-radicals.[15,16] The breakage of the C-C bond by the action of ultrasound usually leads to the formation of long-chain radicals.[12] Obviously, in the absence of scavengers the macro-radicals are free to combine. In polymer blends, both polymers can be ruptured by the high intensity ultrasonic waves. Besides the recombination of single type radicals, radicals from the two polymers may combine with the formation of block copolymers.[17] It will obviously be more important when the chains of the polymers do not have vulnerable sites easily accessible to the free macro-radicals.

In this study, plastic/rubber are ultrasonically treated during continuous extrusion in order to investigate *in-situ* compatibilization of the blends by making copolymers in the dissimilar polymer blends.

2. EXPERIMENTAL

2.1 Materials

The polymers used in these experiments were High Density Polyethylene (HDPE, Marlex HMN4550-3, Phillips Chemical Company), Polypropylene (PP, Pro-fax 6523, Himont Inc.), natural rubber (NR, SMR CV60, Akrochem Co.), styrene-butadiene rubber (SBR, Duradene 706, Firestone Co.), and ethylene-propylene-diene rubber (EPDM, Keltan EPDM 2506, DSM).

2.2 Preparation of Ultrasonically Treated Plastic/Rubber Blends

Polyolefins (HDPE or PP) and uncured rubbers (NR, SBR or EPDM) were first mixed using a twin screw extruder (JSW Labotex30) before ultrasonic treatment. The composition of each of these polymer blends, based on weight percent, was 50:50. The feed rate was 60 g/min. Screw speed was set at 150 rpm and zone temperatures of 140℃/140℃/145℃/150℃/150℃/155℃/160℃/160℃ for HDPE/rubber blends and 165℃/165℃/175℃/180℃/180℃/185℃/190℃/190℃ for PP/rubber blends were used. After the mixtures were extruded from the twin screw extruder, the extrudates were cooled and dried in a vacuum oven for 24 hours at a temperature of 60℃.

After drying, the blends were ultrasonically treated using a 1.5-inch single screw extruder with ultrasonic attachment (shown in Fig. 1) developed in our

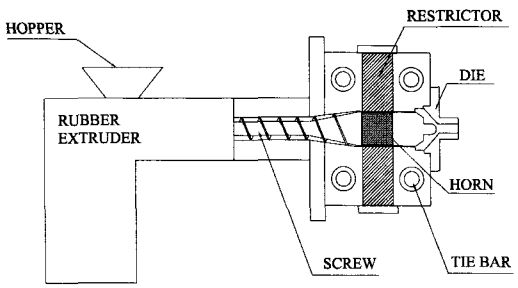


Figure 1. Schematics of barrel ultrasonic reactor.

laboratory. A 3 KW ultrasonic power supply was used. Two ultrasonic horns inserted to the barrel vibrate longitudinally. A frequency of 20 kHz and two amplitudes 6 and 10 μm were utilized. The temperature of the extruder barrel was 150℃ for HDPE/rubber blends and 190℃ for PP/rubber blends with tap water-cooling of the horns. The feed rate was 0.63 g/sec. Screw speed was 20 rpm. The gap between the horn and screw was set at 2 mm. The average residence time in treatment zone was 11.2 seconds.

2.3 Compressing Molding

The compressing molding of sheets (127 x 127 x 2 mm^3, for tensile test) and disks (diameter of 76.2 mm and thickness of 3 mm, for dart impact test) for the blends was performed using an electrically heated compression molding press (Wabash). The mold was at a temperature of 160℃ for HDPE/rubber blends and 180℃ for PP/rubber blends and under a pressure of 13.8 MPa for 5 minutes. The samples were kept under compression and cooled in water to maintain the overall dimensional stability and flatness of the sheets and disks.

2.4 Characterization

The rheological behavior of the blends was investigated using a Monsanto Processability Tester (MPT). Three capillary dies (diameter of 1.506 mm and length/diameter (L/D) ratios of 5, 10 and 20) were used. End corrections were applied for the calculations of the shear viscosity.

A Hitachi S-2150 Scanning Electron Microscope (SEM) was used to characterize the morphology of the blends. The compression-molded blends were used. Also, the blends were annealed to investigate the change of morphology. The annealing was performed at a temperature of 160℃ for HDPE/rubber blends and 190℃ for PP/rubber blends and the annealing time was 10 minutes. The prepared samples with and without annealing were fractured in liquid nitrogen and the rubber phase was extracted in benzene at 50℃ for 24hours. After etching, the samples were dried in a vacuum oven at 60℃ for 12 hours and were coated with silver using sputter coater.

Extraction experiment was carried out by the soxhlet extraction methods using benzene in order to measure the non-extracted fraction of untreated and ultrasonically treated PP/NR blends. Each sample was pre-weighted and then placed in a soxhlet with solvent for 72 hours. After extraction, the samples were put in a vacuum oven at 50℃ for 24 hours. The dried samples were weighed again and the non-extracted fractions were obtained.

An Instron tensile tester (model 5567) was used for the mechanical property measurements. All tests were performed at room temperature with a crosshead speed of 500 mm/min. Young's modulus was measured at 3% strain.

Impact testing was performed using a dart impact tester (Dynatup 8250) with velocity of 4.17 m/s and a dart weight of 5.08 kg. The diameter of a hemispherical probe was 12.7 mm and samples were held in place on an annular ring with an internal diameter of 38.1 mm. All samples were totally penetrated. All tests were performed at room temperature.

3. RESULTS AND DISCUSSION

The flow curves of untreated and ultrasonically treated HDPE/NR, HDPE/EPDM and HDPE/SBR blends at different ultrasonic amplitudes are presented in Figure 2. It is seen that the viscosity of the ultrasonically treated blends is lower than that of untreated blend for all blends. Also, the viscosity of ultrasonically treated blends decreases with an increase in ultrasonic amplitude. The decreased viscosity is an indication that the breakup of main chains occurs during extrusion with the imposition

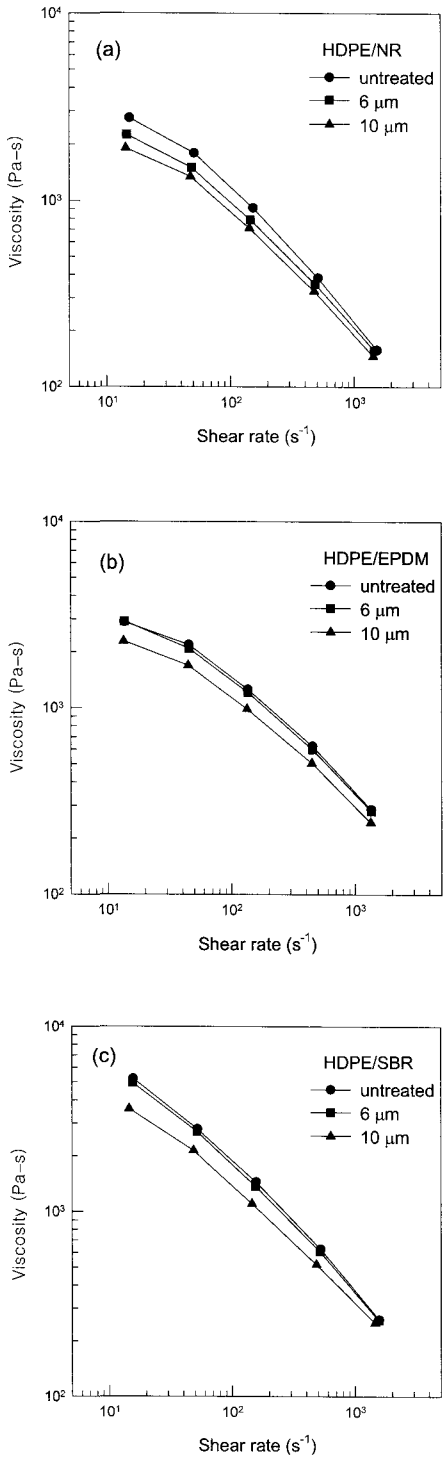


Figure 2. Flow curves of untreated and ultrasonically treated HDPE/NR (a), HDPE/EPDM (b) and HDPE/SBR (c) blends at 180℃.

of ultrasonic waves. This observation is in accord with the ultrasonic power consumption.

The stress-strain behaviors of untreated and ultrasonically treated PP/NR, PP/EPDM, HDPE/NR, HDPE/EPDM and HDPE/SBR blends are given in Figure 3. It is seen that ultrasonic treatment of the blends during extrusion significantly increased tensile stress, elongation at break, Young's modulus and toughness of each blend as compared to the untreated blend. It is believed that ultrasonic treatment of the blends enhances intermolecular interaction and possibly makes chemical bonds between dissimilar polymers creating copolymer without use of any chemicals. The breakage of the C-C bond during ultrasonic treatment can lead to the formation of long-chain radicals. Possibly, the macro-radicals from the two polymers in the blends may recombine with the formation of copolymers during ultrasonic treatment. It was reported earlier[18,19] that, in aqueous solution of heterogeneous systems, the block copolymerization could be initiated by free radicals produced by ultrasonic waves after prolonged treatment. Also, the improved mechanical properties are believed to result from *in-situ* compatibilization by copolymers created at the interface between dissimilar polymers and the vicinity during a very short time (in the order of seconds) of ultrasonic treatment under high pressure and temperatures. It is believed that these copolymers led to the improved adhesion between two dissimilar polymers and also better dispersion of polymers in the blends. These effects are believed to be a major reason for enhancing mechanical properties of ultrasonically treated polymer blends.

Figure 4 shows the plots of the impact behavior of untreated and ultrasonically treated PP/NR, PP/EPDM, HDPE/NR, HDPE/EPDM and HDPE/SBR blends. This figure represents the impact force felt at the probe of the falling dart plotted against

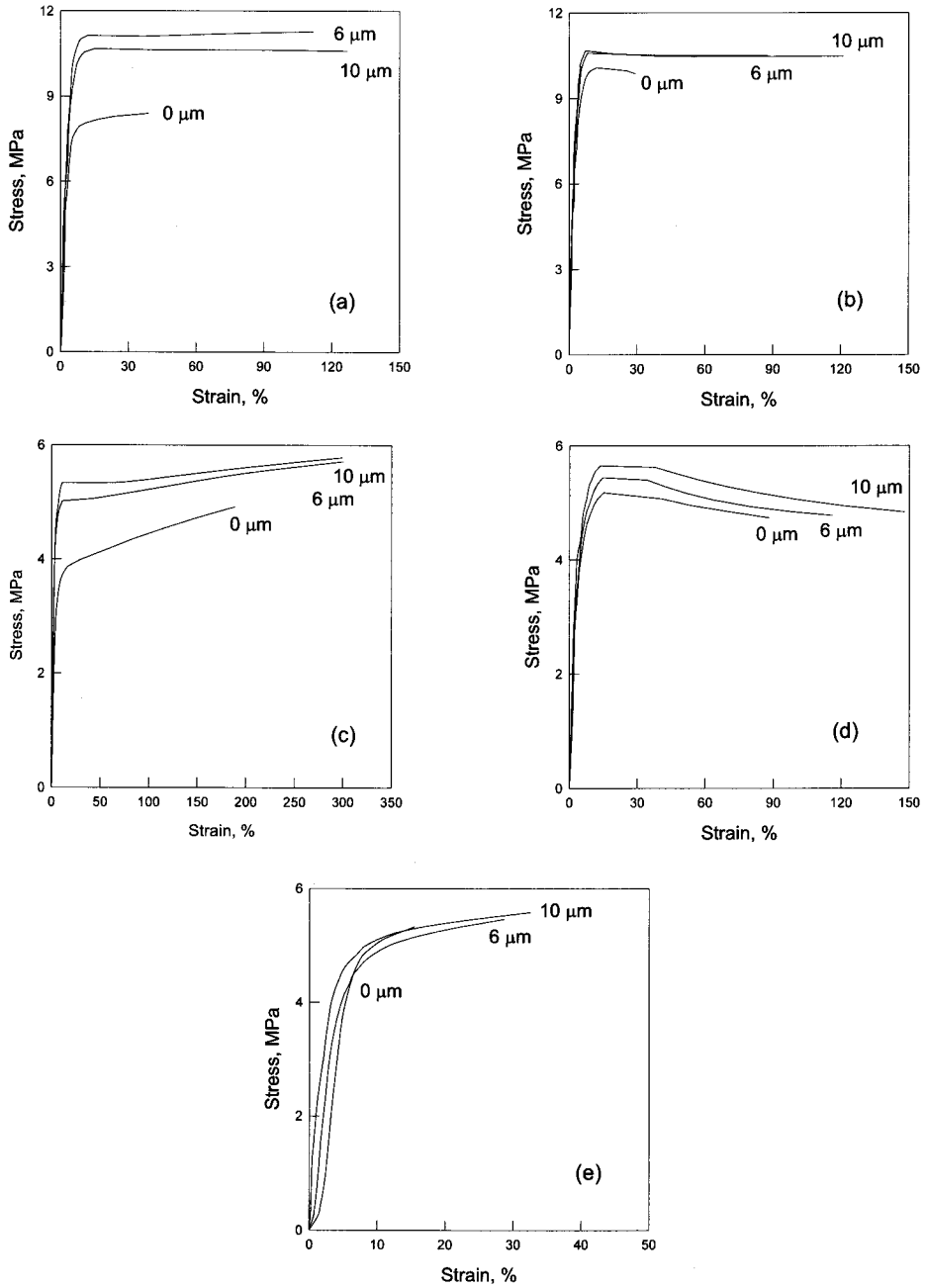


Figure 3. The stress-strain curves of PP/NR (a), PP/EPDM (b), HDPE/NR (c), HDPE/EPDM (d) and HDPE/SBR (e) blends.

its displacement through the sample. It is seen that the impact properties are increased by ultrasonic treatment. The impact energy, given by the area under the force-displacement curve, of ultrasonically treated blend is considerably higher than that of untreated blend. Impact properties are improved due to *in-situ* compatibilization by copolymers created during ultrasonic treatment.

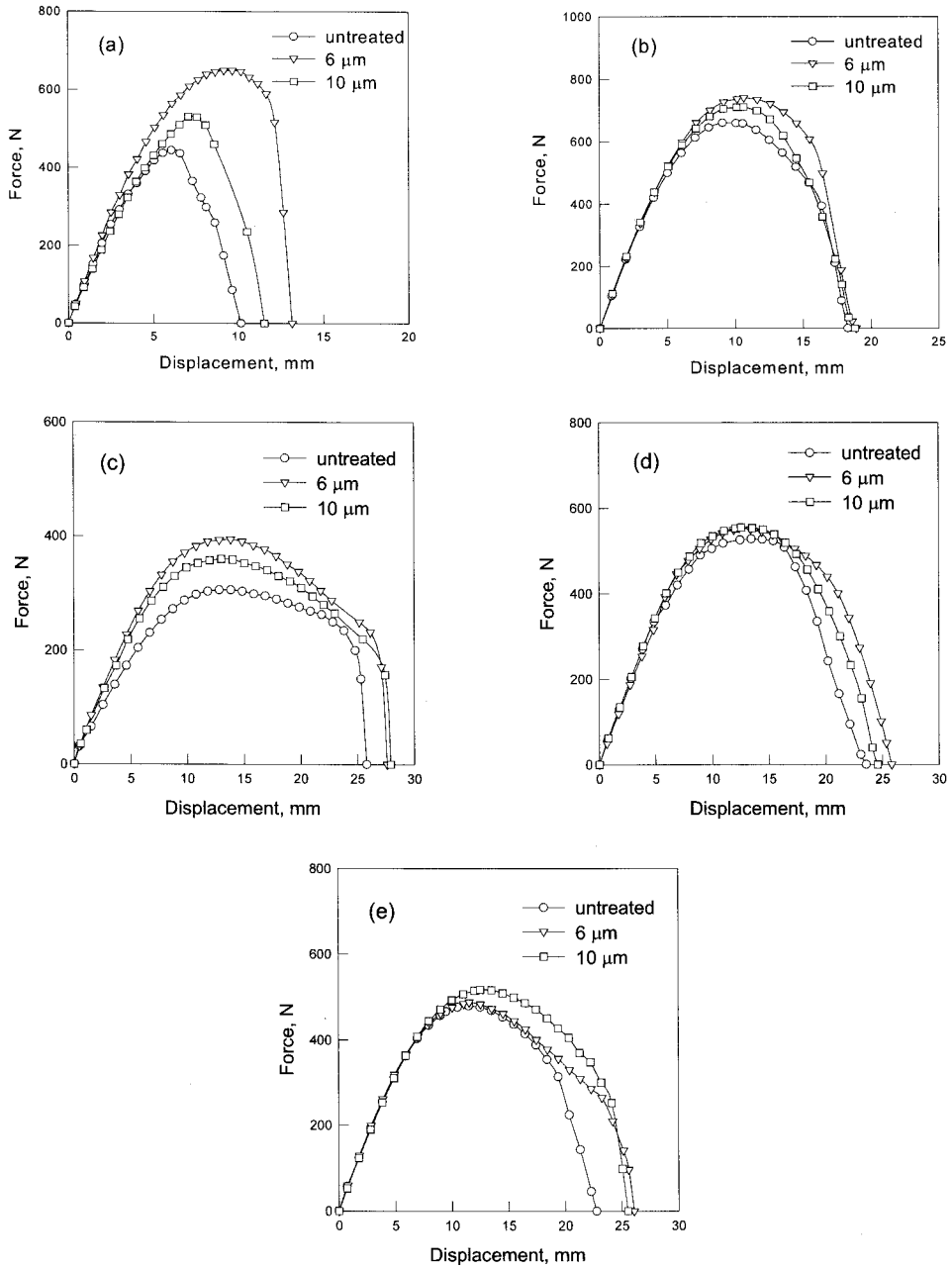
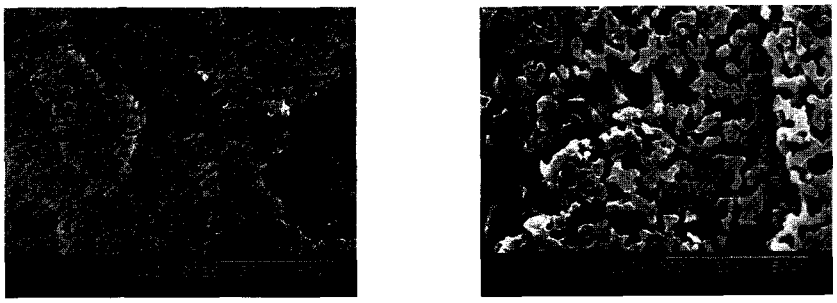


Figure 4. Impact force vs. displacement for PP/NR (a), PP/EPDM (b), HDPE/NR (c), HDPE/EPDM (d) and HDPE/SBR (e) blends.

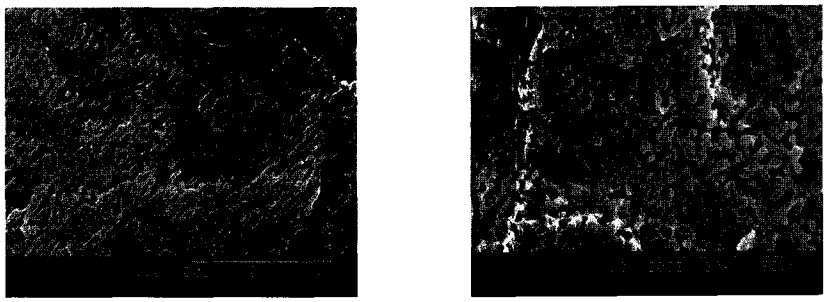
Experimental results support the belief that copolymers are created through ultrasonic treatment of the blends. Table 1 shows the results of an extraction experiment of untreated and ultrasonically treated PP/NR (50/50wt. %) blends at different

Table 1. The results of extraction experiment for PP/NR blends.

	Untreated	6 μm	10 μm
Unextrcted fraction, %	49.8	56.1	54.1

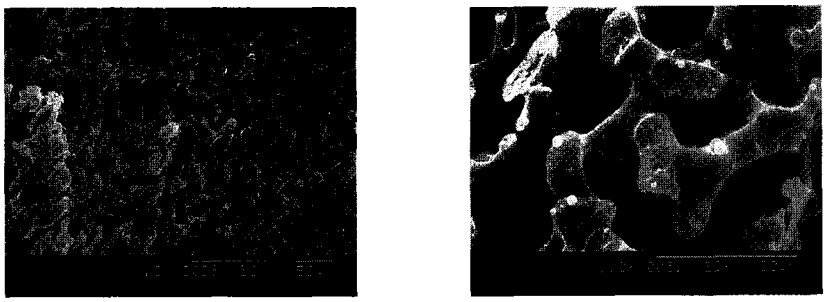


untreated　　untreated, after annealing

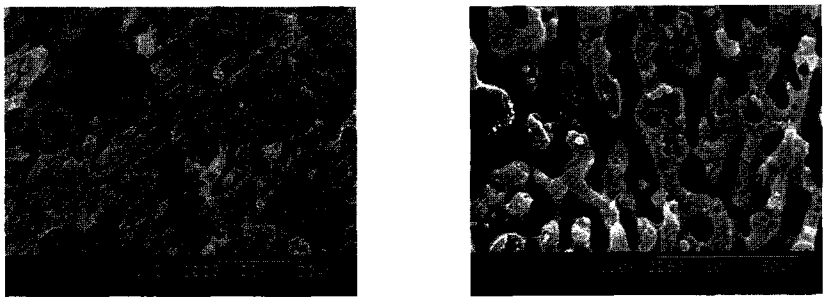


6 μm　　6 μm, after annealing

(a) PP/EPDM blends



untreated　　untreated, after annealing



10 μm　　10 μm, after annealing

(b) PP/NR blends

Figure 5. SEM photomicrographs of untreated and ultrasonically treated blends

ultrasonic amplitudes. In this experiment, benzene was used as a solvent to dissolve NR portion in the blends. As shown, 49.8% of untreated blend was not extracted indicating that initial NR content (50%) was dissolved in benzene. In contrast, 56.1% of ultrasonically treated blend at 6 μm and 54.1% of treated blend at 10 μm were not extracted. It can be thought that PP-NR copolymer was created during ultrasonic treatment and could not be dissolved or extracted by benzene. Accordingly, it is believed that this copolymer created during ultrasonic treatment led to compatibilization and the improved mechanical properties of the blend. The amount of copolymer is higher at lower amplitude. Possibly, at higher amplitude, due to the more degradation the non-extracted fraction and therefore the amount of copolymer was lower.

The SEM photomicrographs showing morphologies of untreated and ultrasonically treated PP/NR and PP/EPDM blends with and without annealing are given in Figure 5. As seen, for all blends the rubber is dispersed phase. Also, before annealing there is no major change in morphology between plastic and rubber phase in untreated and treated blends. However, after annealing the domain size in the morphology of ultrasonically treated blend is much smaller than that of untreated blends. It is believed that during annealing the retardation of phase growth in the treated blend takes place and the morphology of treated blend is more stable than that of untreated blend due to copolymer created during ultrasonic treatment. Therefore, the reason for the enhanced mechanical properties in the ultrasonically treated blends is copolymers leading to enhanced chemical interaction at the interface and improved adhesion between dissimilar polymers in the blend.

4. CONCLUSIONS

In this study, plastic/rubber blends are prepared by ultrasonic treatment during continuous extrusion in order to investigate the *in-situ* compatibilization of the blends without any chemicals. The tensile strength, elongation at break, Young's modulus and toughness and impact properties of each blend were significantly improved by ultrasonic treatment as compared to the untreated blend. After annealing, the domain size in the morphology of ultrasonically treated blend is much smaller than that of untreated blends. It is believed that ultrasonic treatment of the blends enhances intermolecular interaction, improves adhesion and possibly makes chemical bonds between dissimilar polymers without use of any chemicals. Also, the results of extraction experiment supported the belief that copolymers are created during ultrasonic treatment of the blends. This process can be applied for preparing plastic/rubber blends to make thermoplastic elastomers or plastic/plastic and rubber/rubber blends, and for making novel copolymers from practically any pairs of existing polymers to achieve desirable chemical and physical properties.

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