Study on the Thermoplastic Vulcanizate Using Ultrasonically Treated Rubber Powder

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ABSTRACT: Nowadays, waste EPDM (ethylene propylene diene monomer) increasingly has been causing significant environmental problems with increasing numbers of vehicles. From the perspective of the environment and economics, recycling is the best method to treat waste materials. This study investigated waste EPDM/PP (polypropylene) blends with waste EPDM. Waste EPDM powders were treated ultrasonically, which physically modifies the rubber particles to confer good mechanical properties. Also investigated were the relevance of the mass percentage of the dispersed phase, the influence of the geometry and rotation speeds of the screw used in extrusion, and the melting temperature of PP materials on the morphology and mechanical properties of the blend. The purpose of this study was to develop a valuable thermoplastic elastomer from waste EPDM. This study concentrated on determining the optimum conditions for producing a blend by extrusion, including parameters of screw geometry, screw rotational speed, and operating temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2503–2507, 2003

Key words: screw configurations; waste EPDM/PP blend; modification; thermoplastics; waste

INTRODUCTION

Development of several kinds of recycling of waste ethylene propylene diene monomer (EPDM), including microwave,[1] bioreactor,[2] milling,[3] and other devulcanization techniques,[4,5] has been the focus of over two decades of research. Because the application of waste EPDM powder treatment is mostly confined to commercial uses, we studied how to make a highly valuable product by using rubber powder in this research work.

We applied an ultrasonic reactor to modify waste rubber powder using a continuous system. The effect of ultrasonic treatment of polymers has been widely studied. Ultrasonic waves of certain levels in the presence of pressure and heat rapidly break up the three-dimensional network in crosslinking rubbers, although the mechanism of degradable crosslinked elastomers is still in debate. However, it is believed that most of the physical effects caused by ultrasonic treatment are usually attributed to cavitation, rapid growth, and contraction of microbubbles as high-intensity sound waves are propagated through the rubber.[6–8]

Effects of ultrasonic treatment allow the combination of favorable properties of known polymers as well as the development of new quality characteristics.[9] In general, the development of a new polyblend is more cost-effective than that of a new polymer.[10] During the processing of polyblends and depending on material combination, the mostly single-phase starting materials form different microstructures inside the solid. Blends of polypropylene (PP) with EPDM have been widely used as engineering polymeric materials. Many studies[11–14] reported that the dynamic vulcanization of EPDM during melt mixing with PP could improve some properties of high-impact PP.[15–17]

During processing, the barrel and screw configurations as well as the processing conditions such as screw speeds and temperature strongly affect the phase morphology and mechanical properties of the blends. In this work these dependencies were investigated by use of various screw configurations of the extruder during processing. A substantial reduction in the particle size of waste EPDM in the PP matrix can be observed in the melting zone of the extruder. The final morphology and mechanical properties of the blend are determined by the design of the geometry loads to the flow and mixing conditions as well as the screw speeds.

EXPERIMENTAL

Materials

Characteristics of the polymers used in this study are summarized in Table I. The PP was the commercial extrusion grade of SK Chemical Co. (R930Y, RE520Y; Korea). Waste EPDM powder was obtained by an

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TABLE I
Characteristics of the Polymers Used in This Work

Material	Proper[a]	Source
Random Co-PP	MFI = 4.5 g/10 min Density = 0.9 g/cm^3 Melting point = 152°C	Grade R930Y (SK Chemical Co., Korea)
PP-*graft*-MAH	MFI = 2.8 g/10 min Density = 0.9 g/cm^3 Melting point = 152°C	Grade RE520R (SK Chemical Co., Korea)
Waste EPDM powder	Size = 5–20 μm Density = 1.057 g/cm^3 Component C = 90.09% H = 8.42% N = 0.122% S = 0.066%	Cooling crush method (Dong-a Hwasung Co., Korea)

[a] MFI, melt flow index.

TABLE II
Formulation and Blend Conditions of Waste EPDM/PP Blend

Waste EPDM/PP blend ratio			
Waste EPDM	PP	Barrel temperature	Screw rpm
75	25	200–235°C	100
70	30		

ambient grinding crush method from the vulcanized EPDM compound.

Blending

Waste EPDM/PP samples were prepared at ratios of 25/75 and 30/70, as shown in Table II. We used a corotating intermeshing twin-screw extruder (D = 19 mm, L/D = 40) and five different screw configurations, which are shown in Figure 1. Such configurations involve different combinations of right-handed and left-handed screw and neutral kneading disc elements. The geometrical parameters and dimension data of the kneading block of the extruder are given in Table III. The radial clearance, the distance between the cylinder's inner wall and the tip of the kneading block, was 0.6 mm. Screw speeds were kept at 100 rpm in a corotating twin-screw extruder. The cylinder temperature was maintained at 200, 220, 230, and 235°C from the hopper to the die.

TABLE III
Geometry and Dimension Data of the Kneading Block

Item	First kneading block set		Second kneading block set		Third kneading block set	
	L[a]	S[b]	L	S	L	S
Number of kneading disc	5	5	3	4	—	7
Paddle orientation	30°	30°	90°	30°	—	30°

[a] L: 9.55-mm kneading disc.
[b] S: 4.75-mm kneading disc.

Ultrasonic treatment

After grinding, the waste EPDM powder (particles of 5 to 20 μm) was then fed into an extruder (L/D = 30) with an ultrasonic die attachment. A 1.5-kW ultrasonic power supply, converter, and booster were used to provide the longitudinal vibration of the horn with a frequency of 16 kHz. A die, whose gap varied between 1 and 3 mm, with radial length of 30 mm was used in these experiments (Fig. 2).

Testing methods

Morphology

The morphology was investigated by using a scanning electron microscope (SEM; Philips XL 30S, The Neth-

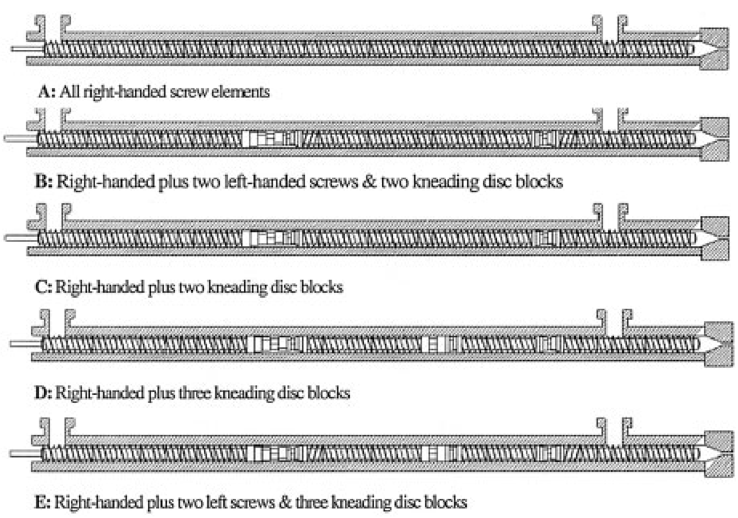


Figure 1 Screw configurations used in the blending experiment.

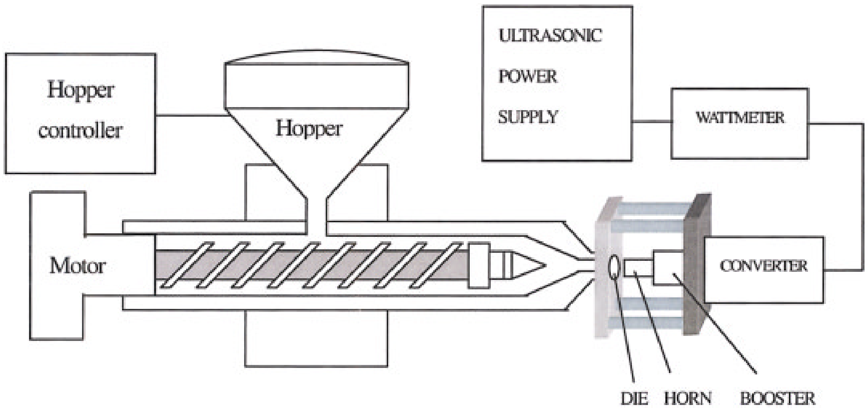


Figure 2 Ultrasonic extrusion reactor built in our laboratory.

erlands) after sputtering the samples with a fine coat of gold (JEOL JFC-1100E; Tokyo, Japan). Surface analysis was performed by using cryogenically fractured etched samples in *p*-xylene.

Mechanical properties

The extrudates were pelletized and then injection molded. Specimens were tested according to ASTM standards [dumbbell-shape samples for tensile test (ASTM D412)]. The temperature of the injection-molding cylinder was kept at 235°C and the mold temperature was 35–40°C with the injection pressure at 2000–2400 psi. The mechanical properties (tensile strength and elongation at break) were determined by using a Lloyd LR10K tensile-testing machine (Fareham Hampshire, UK). The crosshead speed was 500 mm/min for tensile measurements and a load cell of 10 kN capacity was used.

RESULTS AND DISCUSSION

Morphology

We investigated the effect of the screw configuration on the morphology of the blend. As expected, different screw configurations produced different morphologies. Figure 3 shows SEM micrographs with different screw configurations of the untreated waste EPDM/Random Co-PP (70/30) blend. The results indicated that the better morphology of blends occurs in screw configurations B and E because of the kneading disc block and left-handed screw element in their screw configurations. The kneading disc or left-handed screw induced a complicated flow, which leads to good dispersion.

The SEM micrographs showing morphologies of untreated and ultrasonically treated waste EPDM/Random Co-PP and waste EPDM/PP-*graft*-maleic anhydride (MAH) with etching are presented in Figure 4. Figure 5 shows the morphology at different blend ratios of ultrasonically treated waste EPDM/PP-*graft*-MAH. As may be seen, for all blends the rubber constitutes the dispersed phase. Also, before etching there is no major difference in morphology between the plastic and rubber phases in untreated and treated blends. After etching, however, the interface adhesion of ultrasonically treated waste EPDM is superior to that of untreated waste EPDM using PP-*graft*-MAH in the blend. It is believed that during residence time the reaction of PP-*graft*-MAH in the treated waste EPDM

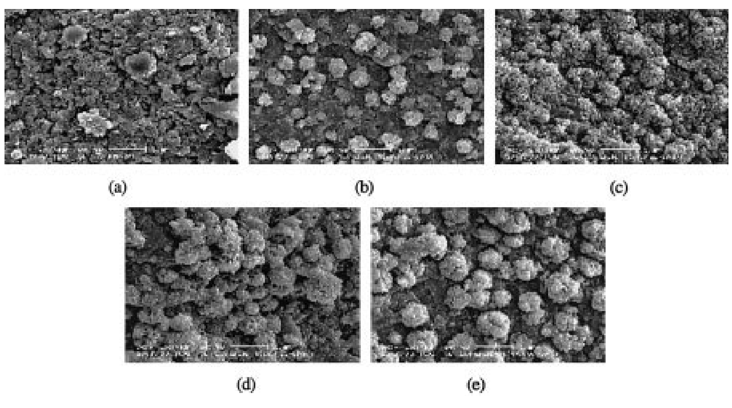


Figure 3 SEM micrographs of composite formed by dynamic vulcanization in extruder: (a) screw configuration A; (b) screw configuration B; (c) screw configuration C; (d) screw configuration D; (e) screw configuration E.

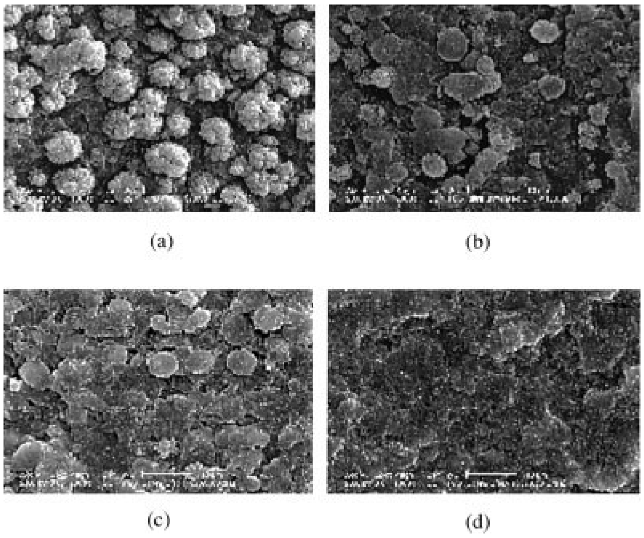


Figure 4 SEM micrographs of composite formed using ultrasonically treated and untreated waste EPDM in screw configuration E: (a) untreated waste EPDM/Random Co-PP; (b) untreated waste EPDM/PP-*graft*-MAH; (c) treated waste EPDM/Random Co-PP; (d) treated waste EPDM/PP-*graft*-MAH.

occurs and its morphology becomes more stable than that of the untreated waste EPDM because of the reactive functional group created by the ultrasonic treatment.

Mechanical properties

Tensile strength, elongation at break, and 50% modulus with different screw configurations are shown in

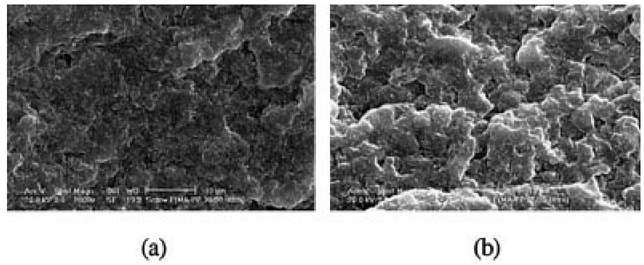


Figure 5 SEM micrographs of samples prepared at different blend ratios using treated waste EPDM and PP-*graft*-MAH: (a) 70/30; (b) 75/25.

Figure 6. Configurations B and E show better mechanical properties than those of other screw configurations. These results indicated that the mechanical properties were affected by an applied shear stress and a residence time during processing.

Figure 7 shows the mechanical properties of the untreated and the ultrasonically treated waste EPDM/Random Co-PP and the waste EPDM/PP-*graft*-MAH in screw configuration E. Table IV shows the mechanical properties of ultrasonically treated waste EPDM/PP-*graft*-MAH blends of different blend ratios. The blends containing ultrasonically treated waste EPDM with PP-*graft*-MAH showed better mechanical properties compared to those of other samples that were compounded with untreated waste EPDM. It is believed that during residence time the reaction of PP-*graft*-MAH in the treated waste EPDM occurs and its interfacial energy becomes stronger than that of the untreated waste EPDM because of the reactive func-

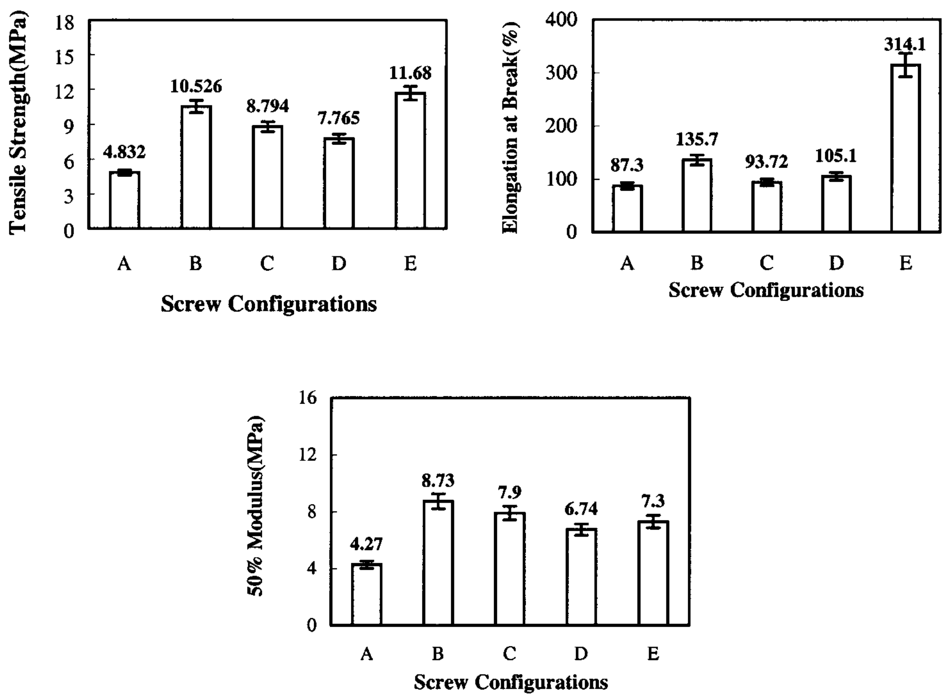
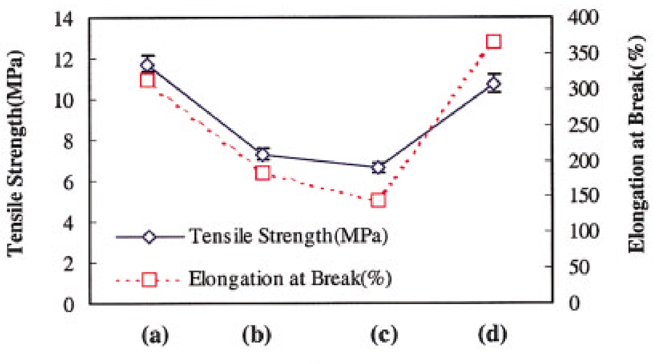


Figure 6 Mechanical properties of the composite as a function of screw configurations.

tional group created by the ultrasonic treatment. Therefore, the reason for the enhanced mechanical properties in the ultrasonically treated blends is the presence of the *in situ*–created copolymers leading to enhanced chemical interaction at the interface and improved adhesion between treated waste EPDM and PP-*graft*-MAH.

CONCLUSIONS

The purpose of this study was to recycle waste EPDM powder by blending it with PP. Therefore, we set out to determine the optimum conditions of extrusion relative to screw configurations and PP grade. We investigated the morphology and mechanical properties (tensile strength, elongation at break, and 50% modulus) of the ultrasonically treated waste EPDM/PP blends to ascertain the optimum conditions. From experimental results, the best conditions among them are shown in screw configuration E and PP-*graft*-MAH, which contain two left-handed screws and three kneading disc blocks for the best conditions for dynamic vulcanization. In screw configuration E, the optimum screw speed is at 100 rpm for the best blend. These results indicate that the properties strongly depend on the dynamic vulcanization during blending. This study shows the potential for producing thermoplastic elastomers from waste rubber.



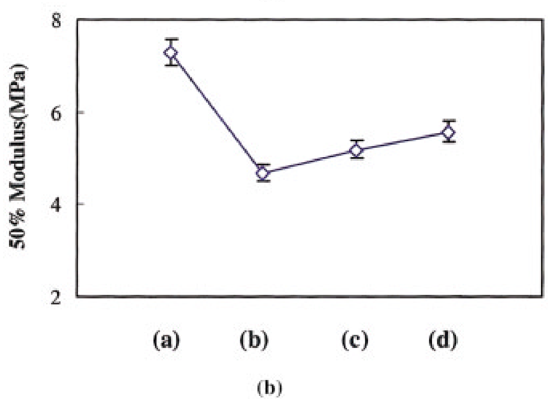


Figure 7 Mechanical properties of samples prepared using ultrasonically treated and untreated waste EPDM in screw configuration E: (a) untreated waste EPDM/Random Co-PP; (b) untreated waste EPDM/PP-*graft*-MAH; (c) treated waste EPDM/Random Co-PP; (d) treated waste EPDM/PP-*graft*-MAH.

TABLE IV
Mechanical Properties of Ultrasonically Treated Waste EPDM/PP-*graft*-MAH Blends of Different Blend Ratios

Blend ratio	Tensile strength (MPa)	Elongation at break (%)	50% modulus (Mpa)
75/25	10.44	362.2	5.13
70/30	10.74	365.8	5.58

References

1. Fix, S. R. Elastomerics 1980, 112, 38.
2. Siutu, B. Scrap Tire News 1997, 12, 14.
3. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. Rubber Chem Technol 1983, 56, 726.
4. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
5. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 92.
6. Isayev, A. I.; Yushanov, S. P.; Chen, J. J Appl Polym Sci 1996, 59, 803.
7. Yashin, V. V.; Isayev, A. I. Rubber Chem Technol 1999, 72, 741.
8. Yashin, V. V.; Isayev, A. I. Rubber Chem Technol 2000, 73, 325.
9. Anon. Aufbereiten von Polymerblends; VDI: Dusseldorf, Germany, 1982.
10. Utracki, L. A. Polymer Alloys and Blends: Thermodynamics and Rheology; Hanser Munchen: Vienna/New York, 1989.
11. Dao, K. C. Polymer 1984, 25, 1527.
12. Kresge, E. N.; Lohse, D. J.; Datta, S. Makromol Chem Macromol Symp 1992, 53, 173.
13. Krulis, Z.; Fortenlny, I.; Kovar, J. Collect Czech Chem Commun 1993, 58, 2642.
14. Inouse, T. J Appl Polym Sci 1994, 54, 723.
15. Kim, J. K.; Park, J. Y.; Lee, K. K.; Bae, C. H.; Kim, S. J. Rubber Technol 2000, 1, 87.
16. Kim, J. K.; Lee, S. H.; Hwang, S. H. J Appl Polym Sci 2002, 85, 2276.
17. Kim, J. K.; Lee, S. H. Rubber World 2002, 225, 26.