Relationship Between the Morphology and Interfacial Tension of Polypropylene and Ethylene Propylene Diene Monomer Blends: The Effect of Repetitive Extrusion

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ABSTRACT: In this study, the effects of repeated extrusion on the mechanical properties, morphology, and interfacial tension of polypropylene (PP)/ethylene propylene diene monomer (EPDM) (80/20) blends were investigated. For the PP/EPDM (80/20) blends, the impact strength of the blends increased with repeated extrusion, which could be attributed to the interaction between the PP and the EPDM. The interfacial tension of the PP/EPDM (80/20) blends, which was determined using the Palierne and Choi–Schowalter models, decreased with an increase in the number of repeated extrusion. Based on the results of the mechanical properties and morphology, the interaction between the PP and the EPDM with repeated extrusion contributed to the reduction of interfacial tension between the PP and the EPDM, which consequently improved the impact strength of the PP/EPDM (80/20) blends. The results for the nuclear magnetic resonance studies supported the increase in impact strength of the PP/EPDM (80/20) blends with repeated extrusion. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The use of plastics has increased dramatically over the last 30 years and this trend has resulted in the generation of a vast waste stream, which must be properly managed to avoid environmental damage. Currently, most inactivated plastics are placed in land-fills or incinerated and only a small fraction of plastics is recycled. If plastics are not treated prior to disposal, they will not decompose rapidly, which can cause serious environmental problems.[1] Landfills will soon no longer be an option for waste disposal as they are getting filled to capacity in many countries. Incineration of plastics is also not ideal for disposal of plastics because of issues associated with dioxin release.[2] In addition, the recycling ratio of plastic is not high enough to reduce the pollution problems it causes. Because of this trend, there is an urgent need to increase the level of recycling and develop novel recycling techniques.[3]

To increase the rate of recycling polymers, there is a need to better understand the factors that affect polymers as this knowledge will prove valuable in determining what parameters are important to the recycling process such as the number of process cycles that a polymer can undergo.[4–7] In the plastics industry, most recycled plastic consist of simple polymers, like homo-

polymers. However, processed and inactivated materials often contain a complex mixture of different polymers. Therefore, there is a need to develop techniques to recycle multicomponent polymers.

Blending with rubber is a well-known method to reinforce the properties of polymers. The addition of rubber reinforces its notch sensitivity and impact toughness. In this regard, the morphological, mechanical, and thermal properties of polypropylene (PP) blends with various polymers or fillers have been studied, including ethylene propylene diene monomer (EPDM) rubber,[8–11] polyurethane elastomer,[12] natural rubber,[13] styrene-butadiene rubber,[14] poly(acrylonitrile-butadiene-styrene),[15–17] polyethylene,[18–22] and organoclay.[22–26]

In this study, the effect of repeated extrusion using a twin screw extruder on the mechanical, morphological, and rheological properties of PP/EPDM (80/20 wt %) blends was investigated. Possible changes in chemical structure, physical structure, and morphology were studied by nuclear magnetic resonance (NMR) spectrometry, differential scanning calorimetry (DSC), and scanning electron microscopy, respectively. The effects of structural changes in the PP/EPDM (80/20) blends on the mechanical properties were studied using tensile and impact

Table I. Characteristics of the PP and EPDM Rubber Used in This Study

Sample	T_m (°C)	MFI (g/10 min)	Tensile strength (kg$_f$/cm^2)	Impact strength (kg$_f$ cm/cm)
PP[a]	169	10.0	302.2	6.4
EPDM[b]	–	0.5	–	–

[a]Supplied by Samsung Total, Korea.
[b]Supplied by Kumho Petrochemical, Korea.

tests. The interfacial tension of the PP/EPDM (80/20) blends was calculated from the particle size of the dispersed phase (EPDM), storage modulus, and loss modulus of the PP/EPDM (80/20) blends. Also, the interfacial tension of the PP/EPDM blends was shown to be correlated with the degree of compatibility of the PP/EPDM (80/20) blends.

EXPERIMENTAL

Materials

The polymers used in this study were PP and EPDM rubber. PP (grade BJ 500) was supplied by Samsung Total Petrochemicals, Korea and EPDM (grade KEP-570P) rubber was supplied by Kumho Petrochemicals, Korea. The characteristics and sources of the PP and EPDM are summarized in Table I.

Blend Preparation

PP and EPDM were blended at a weight ratio of 80/20 using a 27-mm diameter twin screw extruder (Leistritz, Allendale, New Jersey) at 120 rpm. To measure the thermal aging effect, samples were extruded up to seven repeat cycles. Before extrusion, PP and EPDM were dried in a vacuum oven at 70°C for 24 h. The temperature of the extruder was set at 260°C for the PP/EPDM (80/20) blends. When pure PP and pure EPDM were blended with the extruder the first time, the blend sample was designated as PP/EPDM (80/20) R1.

Crystallinity and Morphology

The crystallinity of the PP/EPDM (80/20) blends was analyzed using DSC (Perkin-Elmer DSC-7). Temperature calibration was performed using indium ($T_m = 156.6$°C, $\Delta H_f = 28.5$ J/g). The morphology of the PP/EPDM (80/20) blends was determined by scanning electron microscopy (SEM) (Hitachi S-4300) after Pt coating. The samples were fractured under cryogenic conditions and etched in cyclohexane for 24 h. A solid-state carbon NMR (Varian Unity Inova 200 MHz) spectrometer was used to investigate the structure of the PP after repeated extrusion.

Mechanical Properties

The impact strength of the PP and PP/EPDM (80/20 wt %) blends with repeated extrusion was determined at room temperature and −30°C using a notched Izod impact tester (Toyoseiki DG-IB2). The impact test was conducted according to the ASTM D-256 and five specimens were measured and averaged. The samples for the mechanical tests were prepared using injection molding machine (BOY, model BOY 12A, Germany). The tensile strength of the PP/EPDM (80/20) blends was studied under ambient conditions using a universal testing machine (Instron 4467). The elongation speed was 5 mm/min. Tensile

tests were conducted according to the ASTM D-638 and five specimens were measured and averaged.

Rheology

The rheological properties of the PP/EPDM (80/20) blends were measured using an advanced rheometric expansion system (ARES) in oscillatory shear at 8% strain under a dry nitrogen atmosphere. A parallel-plate arrangement with a 25-mm plate was used to measure the rheological properties. In these experiments, the samples were fabricated in a disk that was 2 mm thick. Frequency sweeps from 0.1 to 100 rad/s were carried out at 260°C for the PP/EPDM blends. The rheological test took about 15 min when the frequency range was between 0.1 and 100 rad/s. Therefore, it is believed that the blend morphology is stable. In the rheological measurements of the blends, samples were tested in the linear viscoelastic strain range.

RESULTS AND DISCUSSION

Crystallinity

The crystallinity of the pure PP and PP in the PP/EPDM (80/20) blends as a function of the number of extrusions as shown in Figure 1. As shown in Figure 1, the crystallinity of the pure PP slightly increased with the number of extrusion. This may have occurred owing to PP chain scission during the extrusion process. Therefore, a low-molecular-weight chain should increase chain's mobility and allow crystallization to occur in a more ordered way.[5,6] In contrast, the crystallinity of the PP in the PP/EPDM (80/20) blends remained almost constant with the number of extrusion. This result suggests that the EPDM particles interrupted the mobility of the PP particles.

Mechanical Properties

Figure 2 shows the tensile strength of the PP and PP/EPDM (80/20) blends as a function of the number of repeated extrusions. For PP, the tensile strength did not change appreciably up to five repeated extrusions (302.5 kg$_f$/cm^2) when compared to PP that had not been repeatedly extruded (304.2 kg$_f$/cm^2). After seven repeated extrusions, the tensile strength decreased slightly (279.7 kg$_f$/cm^2). This decrease in tensile strength was most likely owing to a decrease in the molecular weight as a result of the
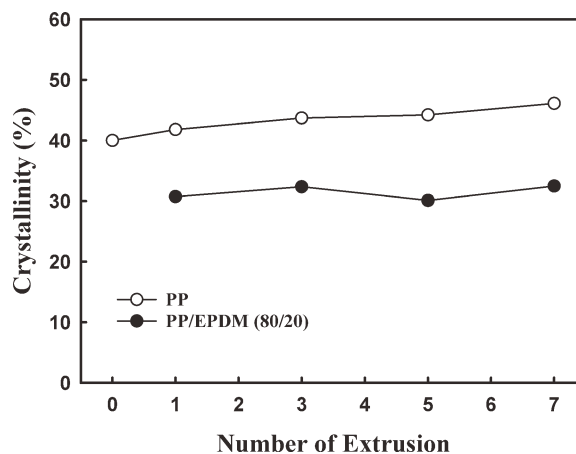

Figure 1. Crystallinity of the PP and PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP; (●) PP/EPDM.
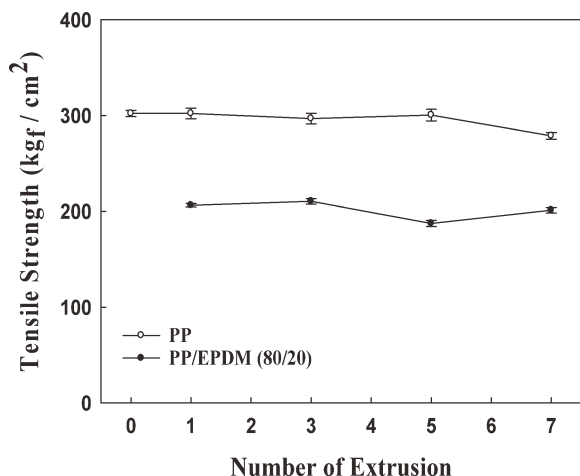
Figure 2. Tensile strength of the PP and PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP; (●) PP/EPDM.

repeated extrusion steps. For the PP with five repeated extrusions, the standard deviation of tensile strength was observed to be 6.1 kg_f/cm^2. For the PP/EPDM (80/20) blends, the tensile strength decreased slightly with repeated extrusions. After five repeated extrusions of the PP/EPDM (80/20) blends, the tensile strength (187.5 kg_f/cm^2, standard deviation: 3.1 kg_f/cm^2) decreased slightly compared that of the blends after one repeated extrusion (206.3 kg_f/cm^2, standard deviation: 2.2 kg_f/cm^2). This may have also been owing to a decrease in molecular weight during the repeated extrusion steps and the low tensile property of the EPDM particles in the blends.[10]

Figures 3 and 4 show the impact strengths at room temperature and low temperature (−30°C) of the PP/EPDM (80/20) blends, respectively. As shown in Figure 3, the impact strength of the PP/EPDM (80/20) blends increased from 39.6 to 46.5 kg_f cm/cm when the number of repeated extrusion was 3. The impact strength then remained relatively constant up to seven repeated extrusions (45.9 kg_f cm/cm). The increase in impact strength may have been owing to the interaction between the PP and the EPDM with the repeated extrusion of the PP/EPDM (80/20)
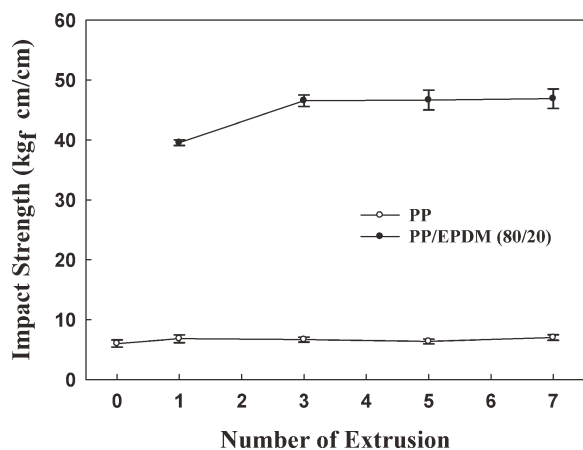
blends which will be explained in the **NMR Spectrum** section. Also, decreased EPDM particles acted as an impact modifier of the PP/EPDM (80/20) blends.

As shown in Figure 4, the impact strengths of the multiextruded PP and PP/EPDM (80/20) blends at low temperature (−30°C) remained almost constant. This was most likely owing to the mobility restriction of the PP, which were interrupted by the low temperature. As shown in Figures 3 and 4, a significant reduction of the impact strengths at low temperature (−30°C) of the PP and PP/EPDM (80/20) blends was observed compared to that of the PP and blends at room temperature. The T_gs of the PP and EPDM are about −15 and −35°C, respectively. Therefore, the mobility of the PP and EPDM would be decreased at low temperature (−30°C).

Morphology
The morphology of the PP/EPDM (80/20) blends with repeated extrusion was examined by SEM. Figure 5(a–d) shows SEM images of the cryogenically fractured surfaces of the PP/EPDM (80/20) blends with one, three, five, and seven repeated extrusions, respectively. EPDM was etched out from the broken surface of the specimens using cyclohexane and the etched sites looked like crater holes in the micrographs. As shown in Figure 5(a–d), the droplet size of the PP/EPDM (80/20) blends decreased slightly with an increase in the number of extrusion cycles and the average size of the droplet was 2.73, 2.51, 2.40, and 2.33 μm, respectively.

Rheology and Interfacial Tension
Figure 6 shows the complex viscosity of the PP/EPDM (80/20) blends as a function of the number of extrusions. As shown in Figure 6, the complex viscosity of the blends did not change significantly with the number of repeated extrusion cycles especially when the frequency is high. This was most likely owing to the presence of stabilizers in the PP.

The complex viscosity of the PP/EPDM (80/20) blends was 1.323, 1.193, 1.189, and 1.090 Pa s at 10^1 frequency when the number of repeated extrusions was 1, 3, 5, and 7, respectively.

Figure 3. Impact strength of the PP and PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP; (●) PP/EPDM.
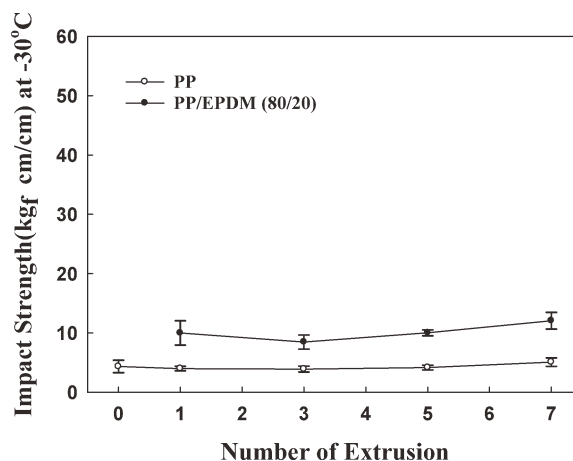

Figure 4. Low temperature (−30°C) impact strength of the PP and PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP; (●) PP/EPDM.
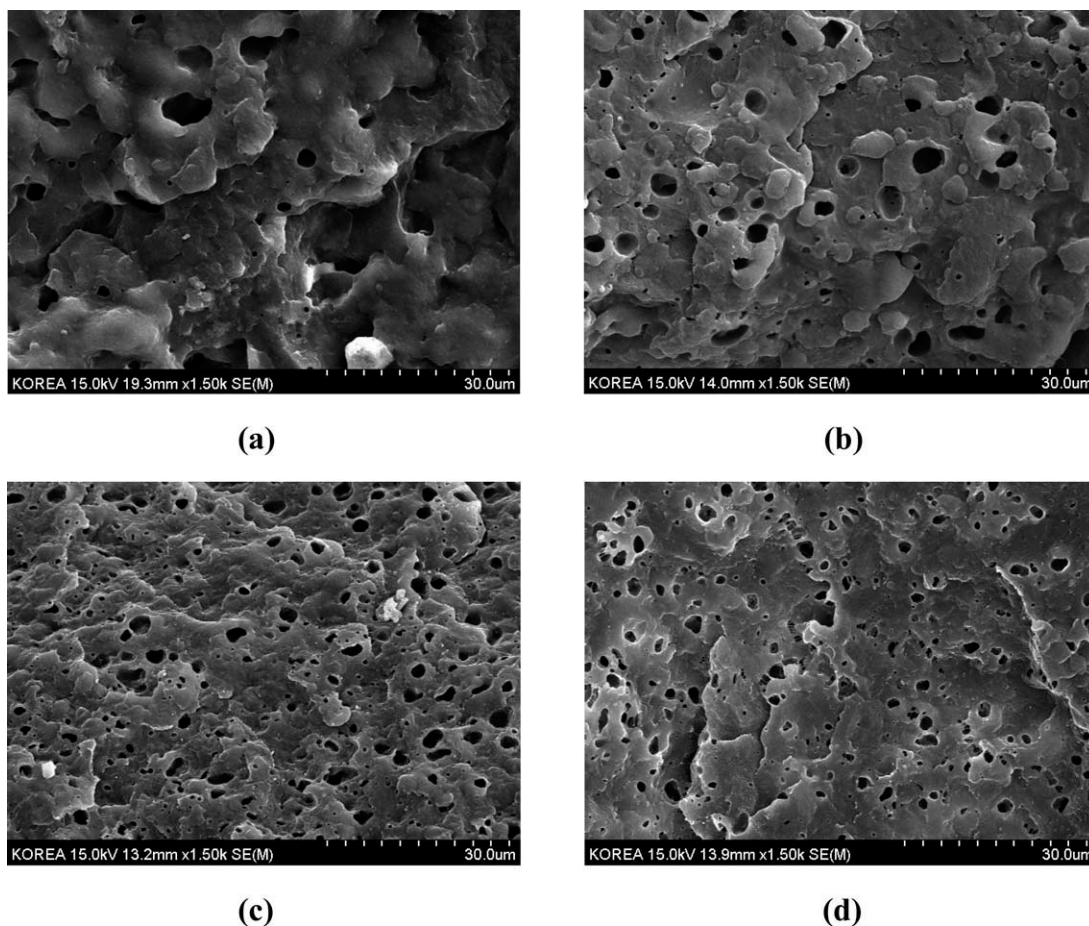
(a)

(b)

(c)

(d)

Figure 5. Scanning electron micrographs of the PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (a) 1, (b) 3, (c) 5, and (d) 7.

As changes in the complex viscosity of the blends with the number of extrusions were not significant, it was not surprising that the tensile and impact strength of the blends did not change appreciably with the number of extrusions (Figures 2 and 3).

Figure 7(a, b) shows the storage modulus (G') and loss modulus (G'') of the PP/EPDM (80/20) blends with the number of repeated extrusions. As shown in Figure 7(a), the storage moduli of the blends with one and seven repeated extrusions are 228.6 and 27.8 Pa at 10^{-2} frequency, respectively. As shown in Figure 7, the difference in storage modulus of the blends with the number of repeated extrusions shows somewhat significant, especially when the frequency is low.

One of the most striking properties of emulsions is that particles change shape under a shear stress. The balance between the two types of forces exerted on the particles, viscous forces, and Laplace pressure, which originates from the interfacial tension, dictates their equilibrium form. The process during which a deformed particle regains its spherical form is called the form relaxation process. This process has a characteristic relaxation time (τ_1), which is the form relaxation time. Gramespacher and Meissner[27] observed that the relaxation spectrum of the blend was the combination of three peaks. Two of the peaks are related to the relaxation time of each of the blend components.

The remaining peak is related to the form relaxation time (τ_1) owing to the relaxation of the interface between the two components.
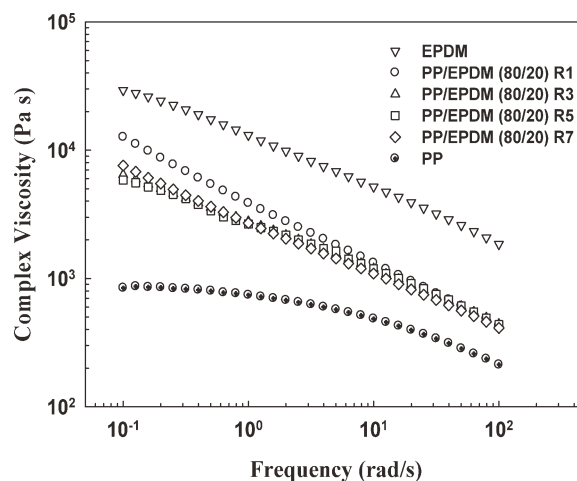

Figure 6. Complex viscosity of the PP, EPDM, and PP/EPDM (80/20) blends as a function of the number of repeated extrusions: ($\odot$) PP; ($\bigcirc$) PP/EPDM (R1); ($\triangle$) PP/EPDM (R3); ($\square$) PP/EPDM (R5); ($\diamond$) PP/EPDM (R7); ($\triangledown$) EPDM.
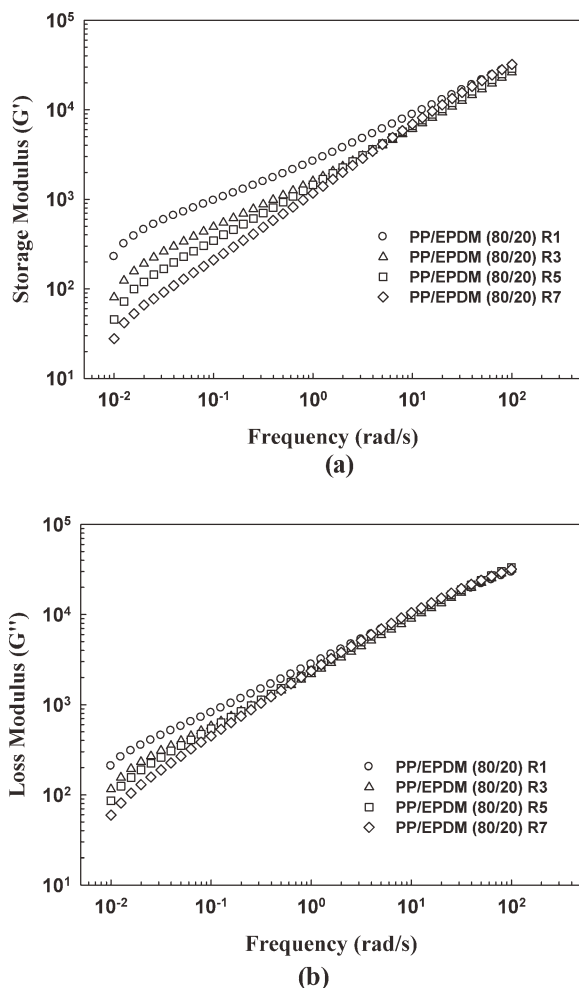
Figure 7. (a) Storage modulus (G') and (b) loss modulus (G'') of the PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP/EPDM (R1); (△) PP/EPDM (R3); (□) PP/EPDM (R5); (◇) PP/EPDM (R7).

The compatibility of polymer blends can be determined by measuring the interfacial tension of the blends. Interfacial tension can be calculated from the Palierne emulsion model[28] and Choi–Schowalter model[29] using the relaxation time, which is shown in eqs. (1) and (2), respectively.[30–34]

$$\tau_1 = \frac{R_v \eta m}{4\alpha} \frac{(19K+16)(2K+3-2\emptyset)(K-1))}{10(K+1)-2\emptyset(5K+2)} \tag{1}$$

$$\tau_1 = \frac{R_v \eta m}{4\alpha} \frac{(19K+16)(2K+3)}{40(K+1)} \times \left[1 + \emptyset \frac{5(19K+16)}{4(K+1)(2K+3)}\right] \tag{2}$$

where τ_1 is the form relaxation time owing to the relaxation of the interface of the polymers, η_m is the viscosity of the matrix, α is the interfacial tension of the blend, ø is the volume fraction of the dispersed phase, and $K = \eta_i/\eta_m$ is the zero shear viscosity ratio of the matrix and droplet. The form relaxation time was calculated from the weighted relaxation spectrum ($\tau H(\tau)$) using

eqs. (3) and (4). The storage modulus (G') and loss modulus (G'') were measured by ARES.[34–36]

$$G'(\omega) = \int_{-\infty}^{\infty} \left[\frac{H(\tau)\omega^2\tau^2}{1+\omega^2\tau^2}\right] d(\ln\tau) \tag{3}$$

$$G''(\omega) = \int_{-\infty}^{\infty} \left[\frac{H(\tau)\omega\tau}{1+\omega^2\tau^2}\right] d(\ln\tau) \tag{4}$$

where τ is the relaxation time and ω is the frequency.

The weighted relaxation spectrum ($\tau H(\tau)$) was calculated using RSIOrche600 software, and the weighted relaxation spectrums of the neat PP and the PP/EPDM (80/20) blends fabricated using different numbers of repeated extrusion are shown in Figures 8 and 9, respectively. As shown in the relaxation spectrum of the PP in Figure 8, the form relaxation time of the PP was about 0.2 s. In the relaxation spectrum of the PP and PP/EPDM (80/20) blend shown in Figures 8 and 9, three relaxation spectrum peaks were observed at about the 10^{-1}, 10^1, and 10^2 s regions, respectively. The first peak (about 10^{-1} s) was related to the continuous phase (PP), the second peak (about 10^1 s) was related to the dispersed phase (EPDM), and the third peak (about 10^2 s) was related to the long relaxation time, which was associated with the interface between the PP and the EPDM blend.

Figure 9(a, b) shows the weighted relaxation spectrum of the PP/EPDM (80/20) blends fabricated with 1 and 3, and 5 and 7 repeated extrusion steps, respectively. As shown in Figure 9, the third peak, which represents the form relaxation time of the interface between the PP and the EPDM blend, increased from 37.0 to 72.4 s as the number of repeated extrusions was increased up to 7. When the third relaxation time of the blend increased, the degree of compatibility of the blend increased. This result might be related to the interaction between the PP and the EPDM at a higher number of repeated extrusions for the PP/EPDM (80/20) blends.

Table II summarized the interfacial tension of the PP/EPDM (80/20) blend calculated using the Palierne and Choi–Schowalter models. The interfacial tension of the blend can be obtained
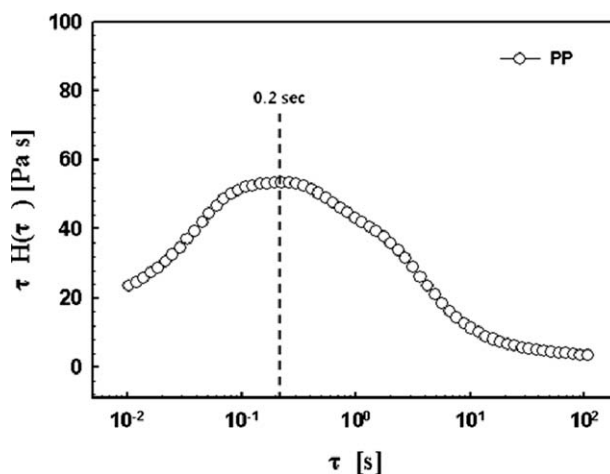

Figure 8. Weighted relaxation spectrum of the PP.

Figure 10. NMR spectrum of the PP and PP subject to three repeated extrusion steps (R3).
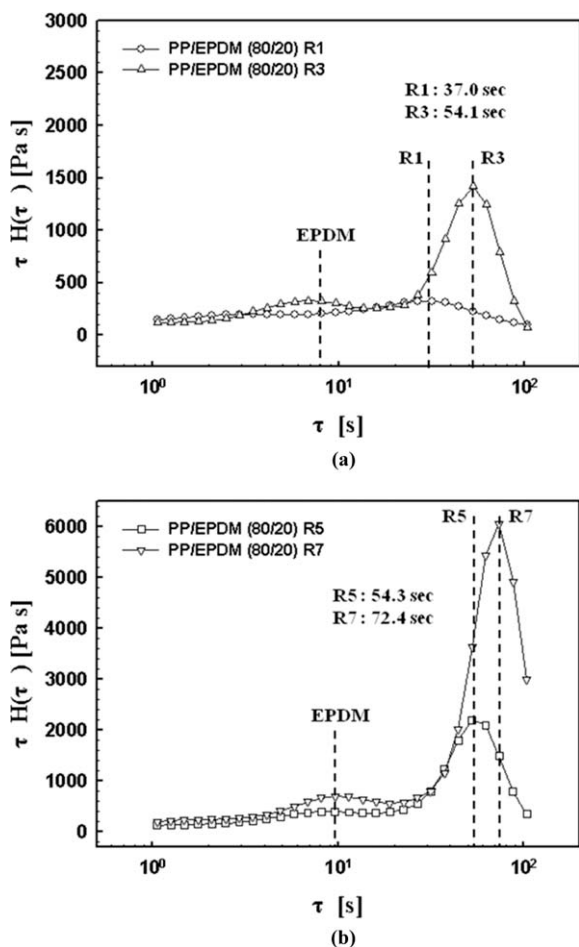
Figure 9. Weighted relaxation spectrum of the PP/EPDM (80/20) blends as a function of the number of repeated extrusions: (○) PP/EPDM (R1); (△) PP/EPDM (R3); (□) PP/EPDM (R5); (▽) PP/EPDM (R7).

from the third relaxation time by using the relaxation of the interphase of the PP and EPDM blend and particle size of the EPDM in the PP/EPDM (80/20) blends. Based on the Palierne model, the interfacial tension of the PP/EPDM (80/20) blends was shown to decrease from 8.35 to 4.68 mN/m as the number of repeated extrusions increased up to 7, which suggests that the compatibility increased with the number of repeated extrusions. A similar trend was also observed for the interfacial

tension of the PP/EPDM blends when the Choi–Schowalter model was used. The repeated extrusion of the PP/EPDM (80/20) blends resulted in a increase in the interaction between the PP and the EPDM, which ultimately reduced the interfacial tension between the PP and the EPDM blends.

NMR Spectrum
The NMR spectra of the PP and PP (R3) are shown in Figure 10. When comparing the PP and PP (R3) characteristic signals, the PP (R3) had a higher signal at 33 ppm, which was associated with the unsaturated ethylenic, probably vinyl terminal groups, and/or vinylene units at the middle of the chain.[18] This result supports the previous findings; the compatibility of the PP/EPDM (80/20) blends improved with the number of repeated extrusion steps. Figure 11 shows the NMR spectra of the PP/EPDM (80/20) blend (R3). As shown in Figure 11, it is suggested that after interaction between the unsaturated ethylenic groups associated with PP and ethylenic group of EPDM, the signal at 33

Table II. Form Relaxation Time (τ_1) and Interfacial Tension (α) of the PP/EPDM (80/20) Blends as a Function of the Number of Repeated Extrusion

Blend	Repeated extrusion	τ_1 (s)	Droplet Size (μm)	$\alpha_1{}^a$ (mN/m)	$\alpha_2{}^b$ (mN/m)
PP/EPDM	1	37.0	2.73	8.35	8.65
	3	54.1	2.51	6.73	6.95
	5	54.3	2.40	6.41	6.64
	7	72.4	2.33	4.68	4.84

[a] α_1 was calculated from the Palierne model.
[b] α_2 was calculated from the Choi–Schowalter model.
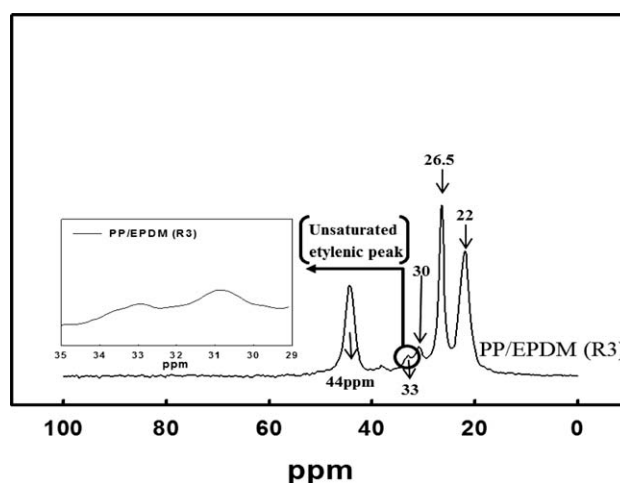

Figure 11. NMR spectrum of the PP/EPDM (80/20) blend subject to three repeated extrusion steps (R3).

ppm showed slightly lower than that of the PP (R3). Repeated extrusion increased the number of unsaturated ethylenic groups, which may have increased the reaction between the PP and the ethylenic group of EPDM. This may be one of the reasons for the improved compatibility of the PP/EPDM (80/20) blends.

CONCLUSIONS

In this study, the effects of repeated extrusion on the tensile and impact strengths, morphology, and interfacial tension of the PP/EPDM (80/20) blends were investigated. The tensile strength of the blends did not change appreciably with the number of extrusions; however, the impact strength of the blends increased with the number of repeated extrusions, which suggests that the increase in the impact strength of the PP/EPDM (80/20) blends was attributed to the interaction between PP and EPDM with repeated extrusion. Also, smaller EPDM particles acted as an impact modifier of the PP/EPDM (80/20) blends. The interfacial tension of the blend was determined from the form relaxation time of the interphase between the PP and the EPDM blend and particle size of the EPDM using Palierne and Choi–Schowalter models. The interfacial tension of the PP/EPDM (80/20) blends decreased with an increase in the number of repeated extrusions. Based on the above results, it can be concluded that repeated extrusion of the PP/EPDM (80/20) blends improved the compatibility between the PP and the EPDM because of the interaction between the PP and the EPDM. NMR studies support these findings; the impact strength of the PP/EPDM (80/20) blends increased with repeated extrusion.

ACKNOWLEDGMENTS

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