Mechanical Property and Morphology Comparison between the Two Blends Poly(propylene)/Ethylene-Propylene-Diene Monomer Elastomer and Poly(propylene)/Maleic Anhydride-*g*-Ethylene-Propylene-Diene Monomer

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ABSTRACT: The comparison of the mechanical properties between poly(propylene)/ethylene-propylene-diene monomer elastomer (PP/EPDM) and poly(propylene)/maleic anhydride-*g*-ethylene-propylene-diene monomer [PP/MEPDM (MAH-*g*-EPDM)] showed that the latter blend has noticeably higher Izod impact strength but lower Young's modulus than the former one. Phase morphology of the two blends was examined by dynamic mechanical thermal analysis, indicating that the miscibility of PP/MEPDM was inferior to PP/EPDM. The poor miscibility of PP/MEPDM degrades the nucleation effectiveness of the elastomer on PP. The observations of the impact fracture mode of the two blends and the dispersion state of the elastomers, determined by scanning electron microscopy, showed that PP/EPDM fractured in a brittle mode, whereas PP/MEPDM in a ductile one, and that a finer dispersion of MEPDM was found in the blend PP/MEPDM. These observations indicate that the difference in the dispersion state of elastomer between PP/EPDM and PP/MEPDM results in different fracture modes, and thereby affects the toughness of the two blends. The finer dispersion of MEPDM in the blend of PP/MEPDM was attributed to the part cross-linking of MEPDM resulting from the grafting reaction of EPDM with maleic anhydride (MAH) in the presence of dicumyl peroxide (DCP). © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2486–2491, 2002

Key words: poly(propylene) (PP); ethylene-propylene-diene monomer (EPDM); maleic anhydride; mechanical properties; miscibility; dispersion state

INTRODUCTION

In poly(propylene) (PP) impact modification, ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer elastomer (EPDM) are the two most widely used types of elastomer. PP blends containing EPR or EPDM have been extensively investigated, centering on the factors determining the effectiveness of the elastomers on impact enhancement.[1–13] To date, it is well known that the miscibility between PP and elastomer as well as phase morphology of the PP blends play the dominant role in determining the effectiveness of the elastomers on impact enhancement.

The blends investigated in our study are the toughened versions of PP with a small percentage of elastomer. A dispersion phase is usually developed for minor elastomer component in PP blend. To achieve effective impact enhancement, good adhesion between the dispersed elastomer particle and PP matrix is essential. In spite of similar molecular structures, the interfacial adhesion is poor because of the apolar nature of both PP and elastomer. Effort has been devoted to improving the interfacial adhesion, such as the addition of compatibilizer and chemical modification of PP and the elastomer.[9–12] As far as phase morphology is concerned, the elastomer particle size and size distribution are the crucial parameters in governing the impact modification effectiveness.[1–4,13] It has been proposed that there is an optimum particle size for a particular polymer pair, and it has been proved that the optimum value is ~0.4 μm for PP/EPR.[3] The size and size distribution of the dispersed elastomer phase depend strongly on the composition and melt properties, in addition to the compounding process.[1,14–16]

The introduction of maleic anhydride (MAH) into the blend of PP/EPR or PP/EPDM was employed to improve the interfacial adhesion and morphology of the blends. Jancar et al. investigated a blend of maleated PP with EPR and maleated EPR with PP.[8] The results indicated that the relative Charpy impact strength for maleated PP/EPR is higher than that for PP/EPR; however, MAH grafting on EPR hardly affects the impact modification effectiveness of the elastomer. The *in situ* grafting and dynamic vulcanization were performed simultaneously from PP and EPDM with MAH in the presence of DCP by Ha et al.[12] The morphology of the blend was optimized by this method.

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In this work, the grafting and simultaneous cross-linking of EPDM were performed with MAH in the presence of dicumyl peroxide (DCP) using a twin-screw extruder. In this way, MEPDM (MAH-g-EPDM) was obtained. The mechanical properties and morphology were compared between the two blends, PP/EPDM and PP/MEPDM, and the effect of the grafting and cross-linking of EPDM on the miscibility, crystalline behavior, dispersion state, and rheological behavior of the PP blends was investigated.

EXPERIMENTAL

Homopolymer poly(propylene) (T300, the Plastices of Shanghai Petrochemical Company, China) was used as matrix. T300 has a melt flow index of 3 g/10 min. EPDM, (Keltan512, DSM, the Netherlands) containing 55 wt % ethylene was used to toughen PP and to prepare MAH-g-EPDM. The Mooney viscosity [ML (1+4) 125°C] and density of Keltan512 were 46 and 0.86 g/cm^3, respectively. Maleic anhydride (MAH) obtained from LeHua Special Chemical Reagent Company (China) and dicumyl peroxide (DCP) obtained from Shanghai Chemical Reagent Company (China) were used as received without further purification.

EPDM was preblended with 10 phr MAH and 0.3 phr DCP in a roller mixer at room temperature. The EPDM grafting reaction was carried out in a twin-screw extruder (MAPRE, GE2.8.30-41) at temperatures from 170 to 200°C. A nitrogen atmosphere was maintained over the reaction mixture. The residence time was controlled at 5 min by monitoring the throughput. The amount of MAH grafted on PP was determined as 1.5 wt % by the KOH titration method.[18] The cross-linking extent in MEPDM was determined using cyclohexane as solvent at room temperature. The determining procedure was the same as that reported in the literature.[19] The gel content of MEPDM was 37 wt %.

PP with EPDM or MEPDM was blended in the twin-screw extruder at temperatures from 180 to 200°C. Pelletized blends were injection-molded in a mechanical test specimen. The Young's modulus of the injection-molded dog-bone specimens were measured using a CMT 4204 universal testing machine (China) and an extensometer at a cross-head speed of 1 mm/min. The test method was consistent with the ASTM D638 standard. The notched Izod impact strength of the injection-molded specimens with a V notch was determined according to the ASTM D256 standard. Both the mechanical tests were performed at 23°C.

Dynamic mechanical thermal measurements were carried out with a thermal dynamic analyzer Netzsch DMA 242 at a frequency of 1 Hz and at a heating rate of 3°C/min from −100 to 150°C. The crystalline curves of the PP blends were obtained with a 2910 Modulated differential scanning calorimeter (DSC) at a heating

TABLE I
Parameters Used for the Model Calculations of the Young's Modulus of the PP/EPDM Blend

Component	Density, ρ (g/cm^3)	Young's modulus, E (MPa)	Poisson ratio, ν	Maximum packing fraction, $\varphi_e{}^{max}$
PP	0.91	1150	0.34	—
EPDM	0.86	1	0.49	0.79

rate of 10°C/min. The cross-sections of the injection-molded bars, which were etched with n-heptane for 1 min to remove the elastomer, were observed by scanning electron microscopy (SEM), and the dispersion state of the elastomer was analyzed. The fracture surfaces produced during the Izod impact test were also examined by SEM to analyze the fracture mode of the PP blends. Rheological properties of the components and the PP blends were determined at 200°C by a XLY-II capillary rheometer (China).

RESULTS AND DISCUSSION

Mechanical properties

It has been proposed that the Young's modulus of PP/elastomer blends is primarily determined by composition and modulus of constituent components; thus it can be predicated by theoretical models.[20,21] The Lewis–Nielsen model (eq. 1), which has been corroborated to be accurate in the Young's modulus prediction for PP/EPDM,[7] was employed in this study:

$$G = G_m \frac{(1 - B_e \Psi \varphi_e)}{1 + A_e B_e \varphi_e} \tag{1}$$

$$A_e = \frac{8 - 10\nu_m}{7 - 5\nu_m} \qquad B_e = \frac{G_m - G_e}{G_m - A_e} \tag{2}$$

$$\Psi = 1 + \left(\frac{1 - \varphi_e^{max}}{\varphi_e^{max2}} \right) \tag{3}$$

$$E = 2G(\nu + 1) \tag{4}$$

where the subscripts m and e refer to the matrix PP and the elastomer, respectively; G is the shear modulus; ϕ_e is the volume fraction of the elastomer; ϕ_e^{max} is the maximum packing fraction of the elastomer in PP; ν is the Poisson ratio (the blend Poisson ratio was calculated by the rule of mixture, $\nu = \nu_m(1 - \phi_e) + \nu_e \phi_e$); and E is the Young's modulus of the blend. The values of the parameters used for the calculation are presented in Table I.

The Young's modulus for the two PP blends decreases with increasing elastomer content, as shown in Figure 1, and the blend of PP/EPDM has higher mod-
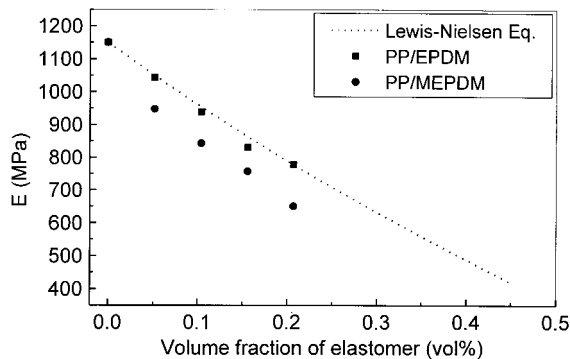
Figure 1 Young's modulus of PP blends as a function of elastomer content.

Figure 3 Dynamic mechanical spectra for the two blends PP/EPDM and PP/MEPDM with 20 vol % elastomer content.

ulus than PP/MEPDM. It can also be seen that good agreement exists between the theoretical prediction and the experiment for the blend of PP/EPDM. However, the blend of PP/MEPDM shows negative deviation from the theoretical prediction. The elastomer content dependence of the Izod impact strength for PP/EPDM and PP/MEPDM is shown in Figure 2. It is obvious that impact strength of PP is significant increased by MEPDM, whereas EPDM is less effective in toughening PP. The difference in the mechanical properties between the two blends PP/EPDM and PP/MEPDM should be related to the difference in morphology between the two blends, which will be interpreted in the later sections.

Dynamic mechanical properties and crystalline behavior

The storage modulus and the loss tangent as a function of temperature for the blend PP/EPDM and PP/MEPDM are shown in Figure 3. Two relaxation regions around −40 and 30°C are observed, which correspond to the glass transitions of the incorporated elastomer and PP, respectively. The differences in dynamic mechanical properties between the two blends are revealed: (i) PP/MEPDM exhibits lower storage
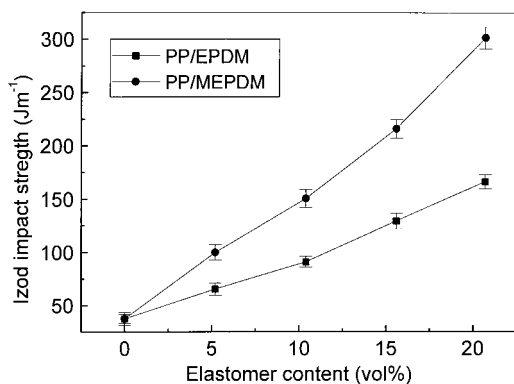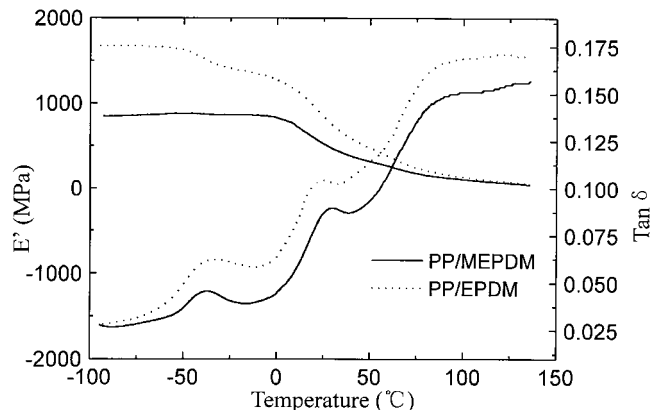
modulus than that of PP/EPDM within the whole temperature range; (ii) the damping capacity of PP/MEPDM is lower than that of PP/EPDM, reflected by the lower values of tan δ of PP/MEPDM; (iii) the two loss tangent peaks of PP/EPDM (−34 and 25°C) is closer compared to those of PP/MEPDM (−38 and 30°C).

The third difference between the two blends indicates that the miscibility between MEPDM and PP is inferior to PP/EPDM. The presence of the polar groups of MAH on MEPDM leads to incompatibility between PP and the elastomer, which contributes to the miscibility deterioration to the large extent. It is also believed that the cross-linking of MEPDM is in part responsible for the poor adhesion between PP and MEPDM, because the cross-linking can prevent the chains of MEPDM from diffusing into the matrix of PP and therefore reduces the physical interaction between PP and MEPDM. The lower damping capacity of PP/MEPDM probably results from the cross-linking of MEPDM. The damping or energy dissipation of a polymer material arises from the internal friction caused by the viscous slipping of the chains. If the chains are partly cross-linked, the viscous slipping of the chains will be constrained to some extent, thereby reducing the internal friction and hence the damping capacity.

It is well known that EPDM or EPR has a significant nucleating effect on PP.[1,2,22] The crystallization behavior of the two blends PP/EPDM and PP/MEPDM was investigated in this work. The nonisothermal crystallization curves are shown in Figure 4, and the DSC results are presented in Table II. It can be seen the crystallinity of PP is hardly changed by the blending with either EPDM or MEPDM. However, the temperature of the crystallization peak maximum of PP is remarkably increased in the case of PP/EPDM, indicating a strong nucleating effect of EPDM. In the case of PP/MEPDM, the temperature of the crystallization
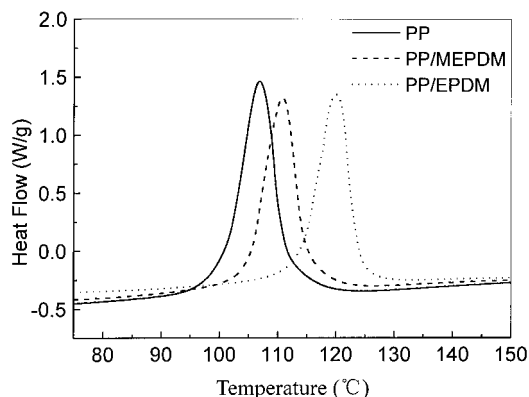

Figure 2 Izod impact strength of PP blends as a function of elastomer content.

Figure 4 DSC curves of PP, PP/EPDM, and PP/MEPDM with 20 vol % elastomer content.

peak maximum of PP is only slightly increased. It is believed that the nucleating efficiency of the elastomer is related to the miscibility between the elastomer and PP. It can be expected that the poor interfacial adhesion between PP and MEPDM corroborated by the DMTA analysis may reduce the nucleating effect of MEPDM. In return, the DSC results support the conclusion obtained by DMTA that the interfacial adhesion between PP and MEPDM is poor.

Morphology observation and rheological behavior

The SEM micrographs of the fracture surfaces resulting from the Izod impact test for the blend of PP/EPDM and PP/MEPDM are shown in Figure 5. It is evident that the morphologies of the fracture surfaces for the two blends are quite different. In the case of the blend containing EPDM, a large number of holes is clearly observed, formed by the dewetting of the EPDM particles. This result indicates that the interfacial adhesion between PP and EPDM is so poor that it cannot prevent the dewetting of the elastomer particles. Moreover, it can be seen that the fracture surface is smooth, indicating that the matrix PP fractures in a brittle manner during impact. In the case of the blend containing MEPDM, holes can also be observed, but the size of the holes is smaller compared with those for PP/EPDM, and the outline of the holes is indistinct. In contrast to PP/EPDM, the fracture surface of PP/MEPDM is rough, showing noticeable plastic defor-
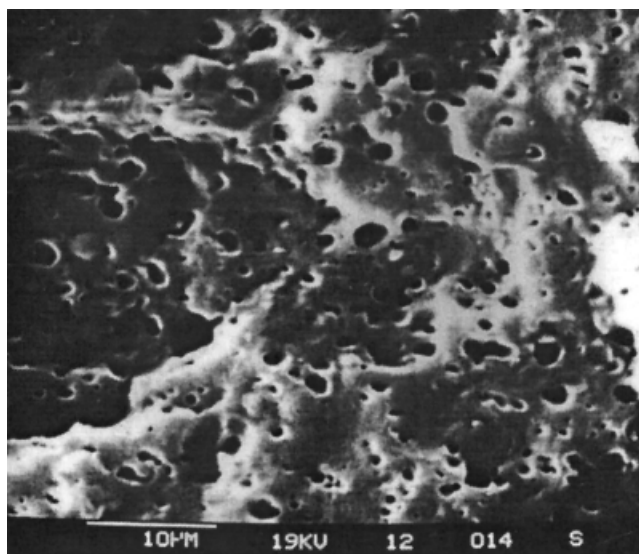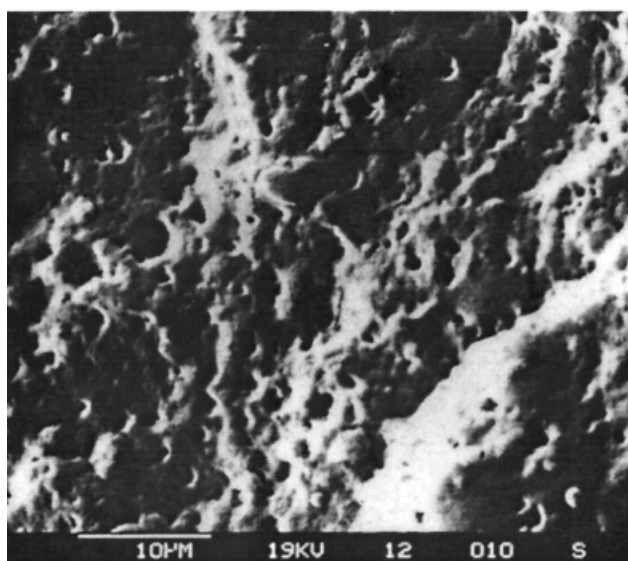
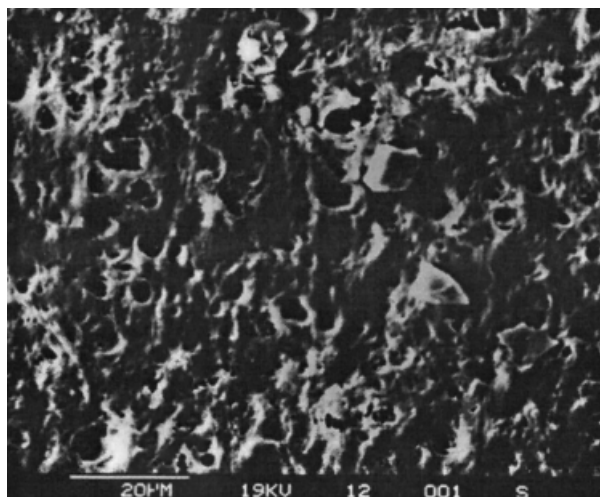**Figure 5** SEM micrographs of the impact fracture surfaces of the blends with 20 vol %; elastomer content: (a) PP/EPDM; (b) PP/MEPDM.

mation of the matrix and a ductile fracture mode. The significant difference in impact resistance between PP/EPDM and PP/MEPDM can be ascribed to the fact that the former blend fractures in a brittle mode, whereas the latter one fractures in a ductile mode.
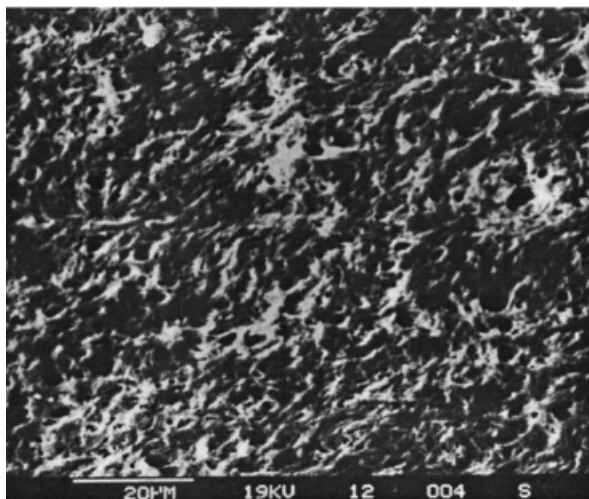
To determine the elastomer particle size and the size distribution, cross-sections of the injection-molded bars were etched for 1 min in boiling *n*-heptane to remove the elastomer. The SEM micrographs of the etched surfaces of the two samples PP/EPDM and PP/MEPDM are shown in Figure 6. The particle size of EPDM is in the range 0.1–5 μm for the blend of

TABLE II
Crystallization Peak Maximum Temperature and Crystallinity of PP for PP, PP/EPDM, and PP/MEPDM

Sample	Crystallization peak maximum temperature, T_c (°C)	Crystallinity (wt %)
PP	107.0	54.0
PP/EPDM	119.9	55.4
PP/MEPDM	110.7	54.9

Figure 6 SEM micrographs of the cut and etched surfaces of the blends with 20 vol %; elastomer content: (a) PP/EPDM; (b) PP/MEPDM.

PP/EPDM. The blend of PP/MEPDM shows a finer and more even dispersion of the elastomer particles in the range 0.1–2 μm. Determined by measuring 100 particles randomly, the number average particle sizes of the elastomer for PP/EPDM and PP/MEPDM are 2 and 0.5 μm, respectively. The difference in dispersion state between PP/EPDM and PP/MEPDM is most likely responsible for the difference in fracture mode.

The elastomer-toughening mechanism of PP has been proposed as the elastomer particles acting as stress concentrators that may promote crazing and/or shear yielding of the matrix, which determine the extent of plastic deformation prior to fracture.[23,24] A proper particle size and its distribution of the elas-

tomer are essential to effective matrix crazing, as well as to effective shear yielding. In addition, good interfacial adhesion between matrix and elastomer particles is indispensable to effective matrix crazing. Though the interfacial adhesion for PP/EPDM is superior to that for PP/MEPDM, it is weak as reflected by the dewetting of the elastomer particles. Furthermore, the particle size and its distribution are too large. It can therefore be expected that the elastomer particles would not promote matrix crazing or shear yielding effectively. With respect to the PP/MEPDM blend, significant plastic deformation is observed, which is likely attributed to the matrix shear yielding. It is known that the interfacial adhesion for PP/MEPDM is weaker than that for PP/EPDM, but the elastomer particle size is smaller for PP/MEPDM. It seems that the smaller elastomer particle size can promote matrix shear yielding effectively, which is responsible for the higher impact resistance of PP/MEPDM.

It can also be observed from Figure 6(b) that some particles are so close to each other that almost agglomerate and some matrix is isolated by the surrounding of the elastomer particles. As a result, the effective volume loading level for MEPDM is higher, thereby resulting in the lower Young's modulus of the blend PP/MEPDM relative to PP/EPDM. Naturally, it is also favorable to the impact modification effectiveness for MEPDM.

The rheological properties of the single components and blends were determined by a capillary rheometer. The differences in viscosity for the single components and blends are shown in Figure 7. It is clear that MEPDM has a much higher viscosity compared with EPDM, which is attributed to the part cross-linking of MEPDM. As a consequence, the viscosity of PP/MEPDM is higher than that of PP/EPDM. With increasing shear rate, the difference in viscosity between MEPDM and EPDM and the two blends is reduced, especially to the blends.
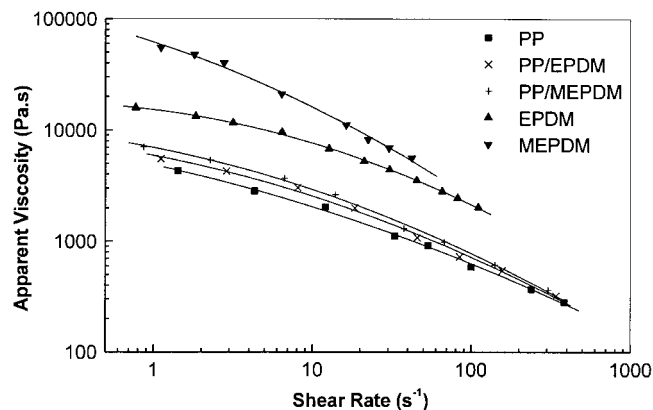

Figure 7 Apparent viscosity of components and PP blends with 20 vol % elastomer content as a function of shear rate.

It has been proposed that the phase viscosity ratio ($\eta_r = \eta_{dispersed}/\eta_{matrix}$) is a crucial factor in determining the elastomer particle size and size distribution, and that both the average particle size and the size distribution coarseness increase with increasing viscosity ratio.[1,2] This theory is established on the basis that the elastomer phase is broken up by the shear stress transferred by the PP matrix during blending. With increasing viscosity ratio, the ability of PP to transfer shear stress to the elastomer phase decreases. Referring to Figure 7, it can be expected that the blend PP/MEPDM should have a higher viscosity ratio than that of PP/EPDM. During processing with the breakup of the elastomer phase, the elastomer particles can recombine by collision to form large particles. The final elastomer particle size is also affected by the elastomer particle recombination.[1] Taking into account this fact, a tentative explanation of the difference in the elastomer particle size and size distribution between PP/EPDM and PP/MEPDM is proposed, assuming that though MEPDM is not easily broken up due to its high viscosity, once it is broken up, the trend of the particles to recombine is reduced by its part cross-linking nature. So, it is suggested that part cross-linking of the elastomer is beneficial to promote the dispersion of the elastomer, and therefore improve its effectiveness on impact modification of PP, but this is unfavorable to the modulus of its blend with PP.

CONCLUSIONS

The grafting and cross-linking of EPDM with MAH in the presence of DCP were performed. MEPDM (MAH-*g*-EPDM) with part cross-linking was prepared. A comparison of mechanical properties and morphology between PP/EPDM and PP/MEPDM was reported. The differences in mechanical properties between the two blends correlated well with the differences in morphology.

MEPDM is much more effective in impact modification of PP than EPDM. However, the blend containing MEPDM has lower Young's modulus, which could arise from the particle agglomeration. The interfacial adhesion between elastomer particles and PP is weak for PP/EPDM and it is further degraded for PP/MEPDM, which is responsible for the degradation of the nucleating effectiveness of MEPDM on PP. The blend PP/MEPDM shows a much finer dispersion of elastomer particles than PP/EPDM. This result was attributed to the part cross-linking nature of MEPDM, which may prevent the broken elastomer particles from recombining during processing. In the case of PP/MEPDM, the finer elastomer particles promoted plastic deformation of the matrix during fracture, thereby leading to higher impact strength than in the case of PP/EPDM.

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