

Solution Maleation of EPDM and Blending of Acetal Copolymer with Rubber Using Maleated EPDM as Compatibilizer

HONG-QUAN XIE, DING-SONG FENG, JUN-SHI GUO

Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

Received 20 February 1996; accepted 8 September 1996

ABSTRACT: Maleation of EPDM in xylene solution using dibenzoyl peroxide as initiator at the boiling point of solution was studied. Effects of amounts of dibenzoyl peroxide and maleic anhydride (MAH), reaction time and temperature, as well as the concentration of EPDM on the bond MAH content of the product were investigated. The results showed that by optimization of the maleation conditions, maleated product with high bond MAH content up to 20 wt % can be obtained without gelation. The maleated EPDM (MEPDM) was utilized in the blending of acetal copolymer and rubber such as EPDM or *cis*-1,4-polybutadiene. Both the impact strength and the tensile strength of the blends increased when a certain amount of MEPDM was added. Decrease of crystallinity of acetal copolymer in the blends determined by wide angle X-ray diffraction and morphology of the blends examined by scanning electron microscope demonstrated the action of MEPDM as compatibilizer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 329–335, 1997

Key words: EPDM; maleation; acetal copolymer; blend; compatibilizer

INTRODUCTION

Maleation of ethylene–propylene copolymer or ethylene–propylene–diene terpolymer (EPDM) in solution^{1,2} or in melt^{3–5} has been studied in several works. However, in the melt method the content of bond MAH in the products is quite low, usually below 1.6 wt %, due to the limited solubility of MAH in the rubber and the high volatility of MAH at high temperature, while in the solution method most works were concerned with the copolymer and the bond MAH content only reached 7 wt %, so as to avoid gel formation.³

The toughness of many engineering thermoplastics can be improved by incorporation of a low

modulus second component. When highly dispersed, the rubbery phase acts as an effective stress concentrator and enhances resistance to crack propagation in the matrix. Acetal copolymers (POM) are strong, hard, highly crystalline thermoplastics with a unique balance of mechanical, thermal, chemical, and electrical properties. But they fail in a brittle manner when impacted. In order to increase the toughness of POM, blending of POM with thermoplastic polyurethane has been reported by Flexman,⁶ Chiang and Lo,⁷ and Chiang and Huang.⁸ However, almost no work concerning the blending of POM with rubber for general purposes has been published.

This paper deals with both the solution maleation of EPDM and the blending of POM with EPDM or *cis*-1,4-polybutadiene (BR) using the maleated EPDM as compatibilizer, in order to increase the MAH content of the maleated EPDM

Correspondence to: H. Q. Xie

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/020329-07

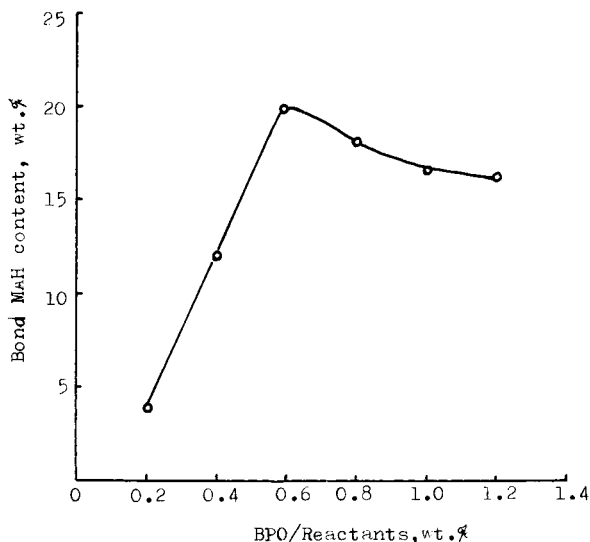


Figure 1 Effect of initiator concentration on the bond MAH content of the maleated EPDM obtained by maleation at 139°C for 1 h using MAH/EPDM = 40 wt %.

without gel content and to toughen POM, respectively.

EXPERIMENTAL

Materials

EPT 4045 with Mooney viscosity of 42 used as EPDM was made by Miyi Co. Acetal copolymer with MI 14 was produced by Shanghai Solvent Factory. All reagents and solvents used were chemically pure and used without purification except dibenzoyl peroxide (BPO), which was recrystallized from absolute ethanol. Antioxidant 618 was made by Borg-Warner Co.

Maleation of EPDM

Both EPDM and MAH were dissolved in xylene with stirring and the solution was purged with nitrogen. After slowly adding a xylene solution of BPO, the mixture was refluxed for 1 h. After cooling to about 80°C, acetone was added to precipitate the product. The precipitate was dissolved in hot xylene and precipitated with acetone again. The maleated product was dried in vacuum.

Determination of the Bond MAH Content in the Maleated EPDM (MEPDM)

The sample (0.1–0.2 g) was weighed out accurately and dissolved in 100 mL water-saturated

xylene. After neutralization with 10–15 mL 0.1M KOH in excess, the mixture was refluxed for 5 h and then titrated with 0.1M HCl in isopropyl alcohol solution while hot, using phenolphthalein as indicator.

The bond MAH content and the reaction efficiency of MAH (Eff.) can be calculated as follows:

Bond MAH content (wt %)

$$= \frac{M_{\text{KOH}} \cdot V_{\text{KOH}} - M_{\text{HCl}} \cdot V_{\text{HCl}}}{2000 \times \text{sample wt}} \times 98.06 \times 100$$

$$\text{Eff. (\%)} = \frac{\text{MAH content in MEPDM (\%)}}{\text{MAH used in the reactants (\%)}} \times 100$$

Blending of POM with Rubber

Variety of compositions of POM/EPDM/MEPDM or POM/BR/MEPDM at different wt ratios were compounded and blended with 0.5% dicyandiamide and 0.5% Antioxidant 618 on a hot mill at 170–175°C for 10 min. Test pieces were prepared by compression molding at 180 ± 5°C.

Characterization and Testing

IR spectrum of the MEPDM was taken with a Shimadzu IR 408 spectrophotometer. Crystallinity was determined by a Rigako 3015 wide angle

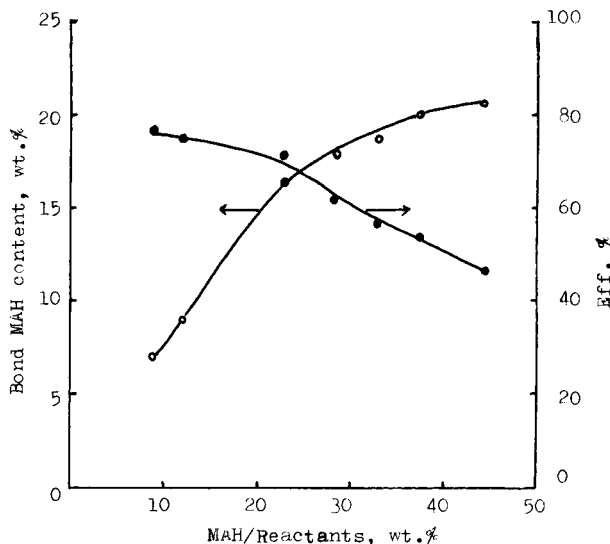


Figure 2 Effect of MAH concentration on the bond MAH content of the maleated EPDM obtained by maleation at 139°C for 1 h using BPO/EPDM = 0.6 wt % and on the reaction efficiency of MAH.

X-ray diffractometer. Morphology of fracture surfaces of the blend was observed with a JSM-35C scanning electron microscope with magnification of 300.

RESULTS AND DISCUSSION

Solution Maleation of EPDM

Figure 1 shows the effect of initiator concentration on the bond MAH content of the maleated product. When the amount of BPO is 0.2 wt % based on EPDM, the bond MAH content is only ~ 3 wt %. With increasing BPO amount, the bond MAH content increases and reaches a maximum value of 20 wt % at 0.6 wt % of BPO/EPDM, whereas the reaction efficiency of MAH reaches 70 %. BPO decomposes at high temperature to form radicals, which abstract hydrogen from the polymer chain. Then MAH molecules add to these macroradicals, thus forming MAH radicals covalently bound to the rubber. The initial marked increase in the bond MAH content most likely corresponds to increasing number of free radicals per EPDM macromolecules. Further increase of BPO lowers the bond MAH content. This trend should be ascribed to a combination of effects deriving from: (a) the rubber-grafted MAH radicals have a low tendency to homopolymerize and the radical site is transferred to an adjacent polymer chain;

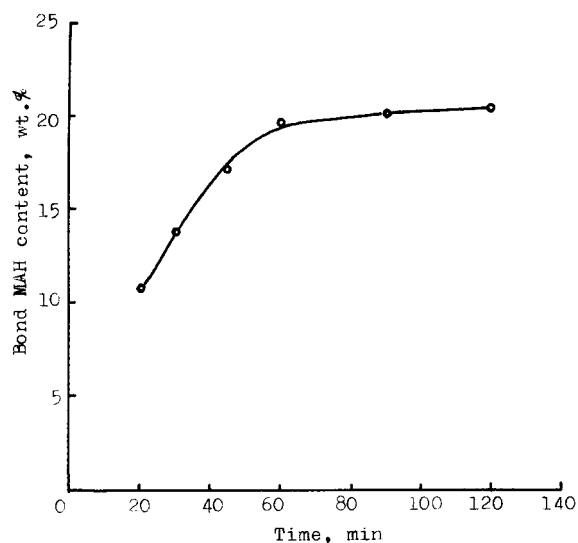


Figure 3 Effect of maleation time on the bond MAH content of the maleated EPDM.

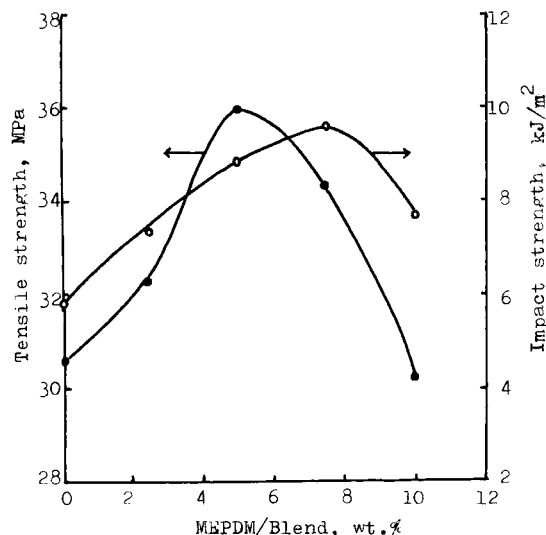


Figure 4 Effect of MEPDM added on the mechanical properties of POM/EPDM blends with wt ratio of POM/(EPDM + MEPDM) = 80 : 20.

(b) partial saturation of reactive sites on EPDM chains; (c) decreasing efficiency of the initiator due to the recombination reactions among primary radicals, and (d) increasing probability of secondary reaction of EPDM macroradicals. At BPO/EPDM = 1.2 wt %, part of the product forms gel and precipitates out, chiefly due to the combination of EPDM macroradicals. The optimum amount of BPO is 0.6–0.8 wt % based on EPDM.

Figure 2 indicates the effect of MAH amount used in the maleation on the bond MAH content of the MEPDM. With an increase of MAH used the bond MAH content increases up to 20 wt % and then levels off, while the reaction efficiency of MAH decreases slowly at first and quickly beyond 25 wt % MAH/EPDM. This phenomenon is probably due to the fact that a fixed amount of BPO can only initiate certain radical sites on the EPDM chain and MAH molecules; besides, maleation at the radical sites of EPDM cannot homopolymerize further, since MAH has the double bond associated with appreciable steric hindrance and shows a low tendency to homopolymerize. Thus no formation of a real graft copolymer should occur. Hence, excess MAH cannot be utilized to maleate or graft the EPDM chains, resulting in markedly decreasing reaction efficiency of MAH.

In the maleation process it is necessary to add slowly a concentrated solution of BPO into the xylene solution of MAH and EPDM within 20 min in order not to form a gel. Concentration of EPDM

in the reaction mixture is also very important. As the concentration of EPDM increases from 5 wt % to 6 wt %, the bond MAH content decreases slightly. When the concentration of EPDM reaches 7.5 wt %, gelation occurs rapidly.

When the reaction time increases from 20 min to 60 min at 139°C, the bond MAH content increases obviously, then it levels off with further increase of reaction time, as shown in Figure 3. The reaction temperature was chosen at above 100°C, since the viscosity of EPDM solution is higher at lower temperature, whereas higher temperature is favorable to the reaction rate. In the range from 100°C to 139°C, the bond MAH content of the maleated product only varied from 18.6 wt % to 19.1 wt % with no gel formation.

The IR spectrum of the MEPDM purified from MAH showed an obvious absorption peak at 1776 cm^{-1} for C=O group of the bond MAH and absorption peaks at 916, 1046, and 1246 cm^{-1} for C—O group of the bond MAH.

Toughening of POM by EPDM Using MEPDM as Compatibilizer

Tensile strength of POM is 54.6 MPa, whereas its notched impact strength is only 6.5 kJ/m^2 and its ultimate elongation 7%. If POM is simply blended with EPDM at a wt ratio of POM/EPDM = 80 : 20, the impact strength decreases to 5.9 kJ/m^2

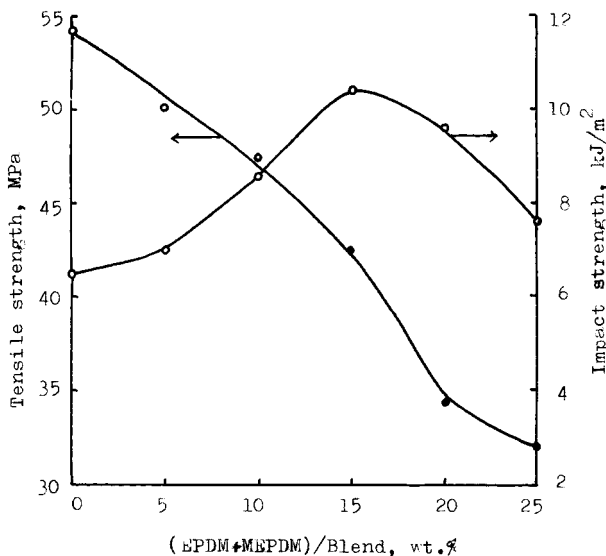


Figure 5 Mechanical properties of the POM/EPDM blend versus wt % of EPDM plus MEPDM at wt ratio of MEPDM/EPDM = 2 : 3.

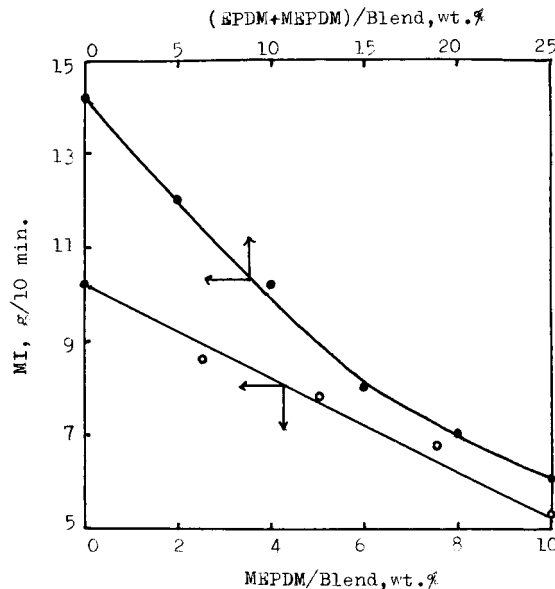


Figure 6 Change of melt index of the blend with MEPDM content at wt ratio of POM/(EPDM + MEPDM) = 80 : 20 and with wt % of (EPDM + MEPDM) at wt ratio of MEPDM/EPDM = 2 : 3.

and the tensile strength decreases to 30.6 MPa, since the two polymers are almost incompatible. But if MEPDM is added to the blend, both the two mechanical properties are improved, as shown in Figure 4. This phenomenon can be attributed to the compatibilizing effect of MEPDM on the blend. With increasing MEPDM content in the blend, the impact strength or the tensile strength of the blend each reaches a maximum value and then decreases. Hence excess MEPDM is not beneficial to the blend. The maximum impact strength occurs at 7.5 wt % MEPDM in the blend, whereas the maximum tensile strength occurs at 5 wt %.

Table I Crystallinity of POM Determined by WAXD in the POM/EPDM/MEPDM or POM/BR/MEPDM Blends

POM/EPDM/MEPDM (wt ratio)	POM/BR/MEPDM (wt ratio)	X_c (%)
100/0/0		74.7
80/20/0		72.9
80/15/5		69.1
80/12.5/7.5		65.8
	100/0/0	74.7
	80/20/0	73.6
	80/17.5/2.5	70.1

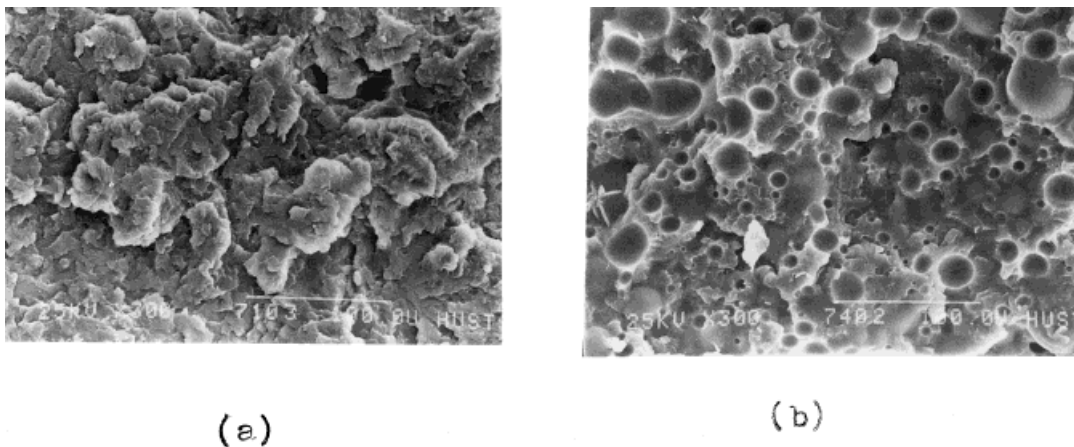


Figure 7 SEM microphotographs of the fracture surface of the POM/EPDM/MEPDM blends: (a) 80 : 20 : 0, (b) 80 : 12.5 : 7.5.

Figure 5 illustrates the change of mechanical properties of the blend versus the total amount of EPDM and MEPDM at the wt ratio of MEPDM/EPDM = 2 : 3. As the wt % of (EPDM + MEPDM)/blend increases, the tensile strength of the blend decreases almost linearly at first and then decreases slowly, while the impact strength reaches a maximum at 15 wt % of (EPDM + MEPDM)/blend. Since MEPDM containing 16–20 wt % bond MAH still looks like elastomeric material, it functions both as compatibilizer and also as toughener. The change of mechanical properties

of the blend with (EPDM + MEPDM)/blend is therefore similar to that of a partially compatible blend of plastics and rubber.

When the wt ratio of (EPDM + MEPDM)/POM is kept at 20 : 80, the melt index of the blend decreases with increasing amount of MEPDM, as shown in Figure 6. This is probably because MEPDM as a compatibilizer can increase the adhesion force between the rubber phase and POM phase, resulting in raising the melting viscosity of the blend. When the wt ratio of MEPDM/EPDM is kept at 2 : 3, the melt index of the blend decreases

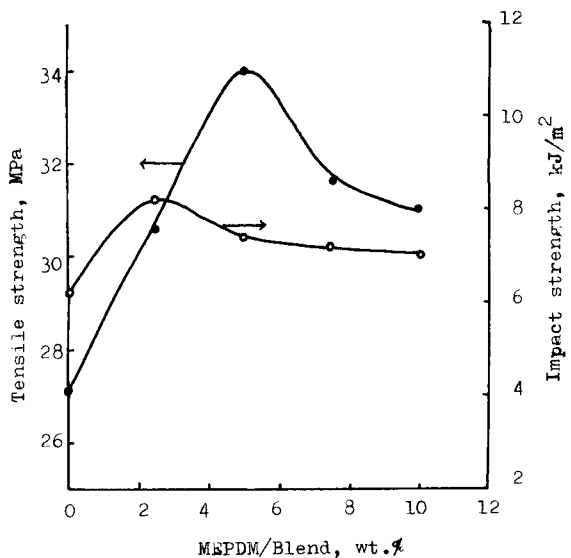


Figure 8 Mechanical properties of the POM/BR/MEPDM blends versus MEPDM content at wt ratio of POM/(BR + MEPDM) = 80 : 20.

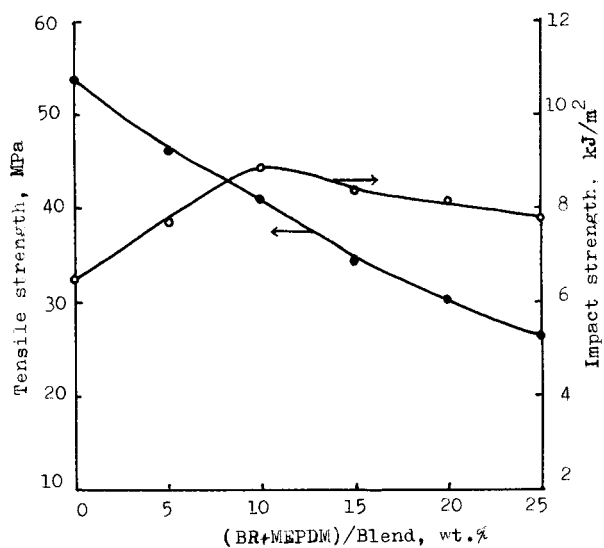


Figure 9 Mechanical properties of the POM/BR/MEPDM blends versus content of BR and MEPDM at wt ratio of MEPDM/BR = 1 : 7.

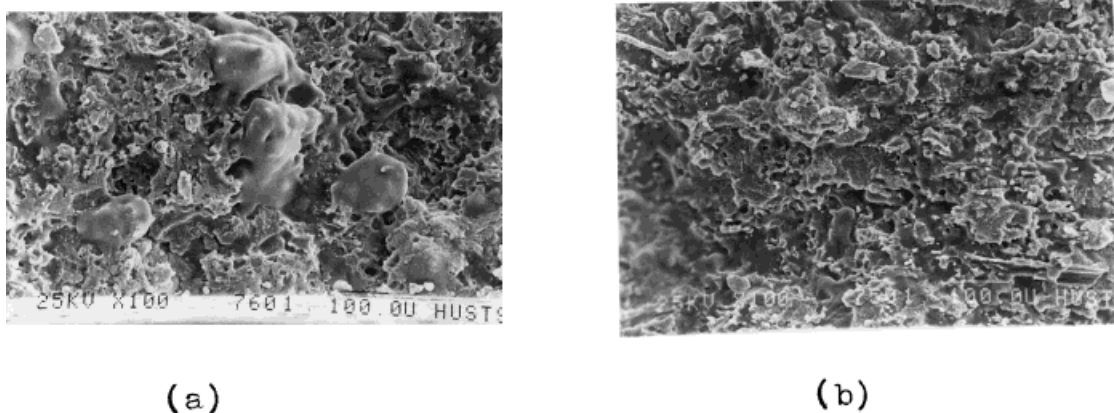


Figure 10 SEM microphotographs of the fracture surface of POM/BR/MEPDM blends: (a) 80 : 20 : 0, (b) 80 : 17.5 : 2.5.

with the increase of wt % of (EPDM + MEPDM)/blend, as illustrated in Figure 6. Since both EPDM and MEPDM behave like elastomer, addition of EPDM and MEPDM enhances the melt viscosity of the blend.

Table I showed that the crystallinity of POM determined by WAXD decreased as EPDM was blended with POM and diminished further when a part of EPDM was replaced by MEPDM. This fact also indicates that MEPDM can compatibilize the blend of EPDM and POM, increase the interfacial interaction between the two phases, and destroy part of the POM crystals.

SEM microphotographs of the broken sections of blends (Fig. 7) show that the dispersed phase becomes finer when a part of EPDM was replaced by MEPDM in the blend. This phenomenon may be attributed to the strong reduction of interfacial tension by MEPDM.

Toughening of POM by *cis*-1,4-Polybutadiene (BR) Using MEPDM as a Compatibilizer

When POM was blended with BR at the wt ratio of POM/BR = 80 : 20, the impact strength of the blend was not improved, but the tensile strength decreased to about half the value of POM. But in the case when MEPDM was added to the blend instead of part of BR, as the amount of MEPDM increases, both the impact strength and tensile strength of the blend increase to maximum value and then decrease, as shown in Figure 8. This implies that MEPDM can also compatibilize the blend of POM and BR. The maximum value of impact strength occurred at 2.5 wt % MEPDM or

wt ratio of MEPDM/BR = 1 : 7. If the wt ratio of MEPDM/BR is fixed at 1 : 7, the tensile strength of the blend decreases with increasing total amount of BR and MEPDM, while a maximum impact strength occurs at 10 wt % of (BR + MEPDM)/blend (Fig. 9). However, either the maximum impact strength of the POM/BR blend or its maximum tensile strength was mostly lower than those in the case of POM/EPDM blend. This is probably due to the similarity between MEPDM and EPDM rather than that between MEPDM and BR. The similarity between the compatibilizer and the two phases is favorable to the compatibility of the blend.

The crystallinity of POM determined by WAXD decreased as POM was blended with BR. If MEPDM is used instead of part of BR in the blend, the crystallinity decreases further, as shown in Table I. Figure 10 shows the SEM microphotographs of the fracture surfaces of the POM/BR blends. The dispersed phase of the blend without the compatibilizer, MEPDM, seems coarser than that of the blend containing MEPDM. Both WAXD and SEM results demonstrate that MEPDM acts as a compatibilizer for the POM/BR blend.

CONCLUSION

EPDM was successively maleated in solution to high bond MAH content (up to 20%) using 0.6 wt % BPO based on EPDM and 5–6% concentration of EPDM at 139°C for 1 h without gelation. The maleated EPDM can be used as an effective com-

patibilizer for the blending of POM with EPDM or BR. Both the impact strength and tensile strength of the blend can be improved by adding MEPDM in place of part of BR or EPDM. Both crystallinity and morphology demonstrate the compatibilizing effect of MEPDM.

REFERENCES

1. G. De Vito, N. Lanzetta, G. Maglio, M. Malinconico, P. Musto, and R. Palumbo, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1335 (1984).
2. S. Cimminio, L. D'Orazio, R. Greco, G. Maglio, M. Malinconico, E. Martuscelli, R. Palumbo, and G. Ragoista, *Polym. Eng. Sci.*, **24**, 48 (1984).
3. N. G. Gaylord, M. Metha, and R. Metha, *J. Appl. Polym. Sci.*, **33**, 2549 (1987).
4. N. G. Gaylord, R. Metha, V. Kumar, and M. Tazi, *Polym. Prepr.*, **27**, 105 (1986).
5. A. J. Oostenbrink and R. J. Gaymans, *Polymer*, **33**, 3086 (1992).
6. E. A. Flexman, *Mod. Plast.*, **62**, 72 (1985).
7. W. Y. Chiang and M. S. Lo, *J. Appl. Polym. Sci.*, **36**, 1685 (1988).
8. W. Y. Chiang and C. Y. Huang, *J. Appl. Polym. Sci.*, **38**, 951 (1989).