Improved Interaction Effected by Maleic Anhydride-Grafted Polypropylene in PRP Triblock Polymer–EVA Blend

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SYNOPSIS

The role of anhydride-grafted polypropylene in the ethylene–propylene triblock polymer and ethylene–vinyl acetate copolymer blend has been studied. Maleic anhydride grafted onto polypropylene interacts with polymer components in the blend and also improves the dispersion of the rubber phase in the plastic matrix. Improved interaction is reflected in the ultimate properties of the blend. Blends with good impact resistance and low-temperature brittleness may be obtained by optimizing the modifier concentration. Composition with good low-temperature brittleness is achieved by lowering the glass transition temperature of the plastic phase by adding a low concentration of modifier. Impact strength of the studied blend does not depend only on the reactive maleic anhydride content but also on the type of modifier. Generally, an increase in interfacial surface area improves impact strength. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

The ethylene–propylene copolymer with low ethylene content is a good construction material. Such a copolymer combines the advantageous properties of polyethylene as well as of polypropylene. The ultimate properties of the ethylene–propylene copolymer, however, depend not only on comonomer content but also on the polymerization technique. In some cases, due to a limitation of polymerization techniques, it is difficult to prepare such copolymers with the exact properties desired. For this reason, it is often necessary to modify the properties of such copolymers by adding other polymer additives. Elastomers are widely used to modify such copolymers.[1,2]

Our earlier work[1] on ethylene–vinyl acetate (EVA) elastomer (42 wt % vinyl acetate content) modified propylene–ethylene copolymer (PRP triblock polymer, where the "P" indicates isotactic polypropylene, and the "R," random ethylene–propylene block) revealed that the addition of a small amount of EVA elastomer deteriorates mechanical properties, increases brittle temperature, and lowers the impact resistance at low temperature.[1] It is, however, found that deterioration of mechanical properties is minimal for the PRP triblock polymer—ethylene–vinyl acetate elastomer composition containing only 8 wt % EVA elastomer. From a morphological study, it was observed that the interfacial surface area, a measure of degree of dispersion, plays an important role in determining the ultimate properties of the compositions studied and a maximum interfacial surface per unit volume of the dispersed phase has been achieved with the PRP–EVA composition containing 8 wt % EVA elastomer. Thus, it is thought that poor compatibility between the PRP triblock polymer and the EVA elastomer is the cause for deterioration of properties.

Use of an interphase compatibilizer is known to improve some properties of certain dissimilar blends.[2] Past studies showed that compositions containing reactive maleic anhydride (MAH) as a functional polymer are very effective modifiers for blends prepared from mixtures of polar and nonpolar polymer components.[2,3] The efficiency of modification, however, depends on the nature of the blend

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components as well as on the method of modification. Attempts have been made in the past to qualitatively explain the function of MAH-grafted PP as a modifier, but understanding of the reactions occurring in the system was very difficult due to other complex side reactions.[2] Nevertheless, the versatile modification efficiency of reactive MAH-grafted PP as a modifier for several other blends[3] prompted us to seek to understand the chemistry and technology involved in the process of modification.

We report herein some of our findings in this line that might give a better understanding of the role of MAH-grafted PP modifiers for the PRP–EVA composition studied.

2. EXPERIMENTAL

In our experiments, three different types of maleic anhydride-grafted polypropylene (MAH–PP) modifiers were used. Each product differs in grafted MAH content. Powdered PP (TATREN HPD, Czechoslovakia) and laboratory reagent-grade MAH (BDH Chemicals, U.S.A.) were used for the grafting reaction. The grafted MAH contents for three samples were 0.98, 1.41, and 2.94 wt %, which were denoted as MAH–PP-I, MAH–PP-II, and MAH–PP-III, respectively, and each of them were separately prepared by chemical synthesis using two different catalyst systems. MAH–PP-I and MAH–PP-II were prepared by impregnating PP with MAH in a heterogeneous system at a temperature below the melting point of PP and the reaction was catalyzed by t-butyl perbenzoate.[4,5] On the other hand, MAH–PP-III was prepared in a Brabender mixer by kneading PP and MAH with dicumyl peroxide at 180–190°C and at a 100 rpm rotor speed. The detailed methods of grafting have been described elsewhere.[6,7] Each modifier was added to the PRP–EVA composition in different concentrations to investigate separately the effect of modifier concentrations on properties of the PRP–EVA blend. In all PRP–EVA compositions, the concentration of the EVA copolymer was 8 wt % of the final blend. The EVA copolymer used in the system (Levaprene 450, Bayer, Germany) contained 42 wt % vinyl acetate, had a density of 978 kg m^{-3}, and was used in the form of granulate. On the other hand, propylene–ethylene copolymer was a triblock polymer with isotactic PP blocks at both ends and an ethylene–propylene random copolymer block at the center, denoted as PRP triblock (trade name KD-703, Slov-naft, Czechoslovakia; ethylene content 14.4 wt %, density 903 kg m^{-3}).

The compositions were prepared in a Brabender mixer. The melt-mixing of the KD 703 PRP triblock polymer and Levaprene 450 EVA was done at 195°C. During the mixing process, a combination of calcium stearate and 2,2-t-butyl-methylphenol was added as a stabilizer. Mixing was carried out at a 30 rpm rotor speed for about 6 min time in total. After 1 min of mixing, the MAH–PP graft polymer was added and mixing was then continued for another 5 min. After the specified time of mixing, each composition was cooled by cold pressing to a thickness of about 3 mm and then cut into pieces for the subsequent compression-molding process. Molding was carried out at 200°C using the following molding cycle: preheating for 10 min at 200°C, hot pressing for 5 min at 200°C, and, finally, cooling for 15 min at 60°C. The thickness of the molded slabs that were used for testing mechanical properties was 2 and 3 mm.

3. TESTING

The mechanical properties of the PRP–EVA compositions studied were determined according to the procedure described in ASTM standard D638-64T. The stretching rate was 100 min^{-1}. The Charpy impact strength was obtained by ASTM standard test method D256-56. Similarly, low-temperature brittleness was measured according to ASTM test method D746-73. The detailed test procedures are described elsewhere.[1,8] The flow properties of the compositions were recorded as the amount of material in grams per 10 min for a load 2.16 kgf at 230°C according to ASTM standard test method D1238.[9]

The dynamic mechanical properties were measured with a torsion pendulum at 1 Hz for all the compositions studied. A Tesla BS-300 scanning electron microscope (SEM) was used to study morphology of PRP–EVA compositions. However, an SEM study was made only for a selected composition of the PRP–EVA blend containing 8 wt % EVA copolymer. An SEM study of an MAH–PP-II modified PRP–EVA blend was done for a composition containing 5 wt % MAH–PP-II and 8 wt % EVA copolymer on the final blend. Polymers were selectively etched with toluene and acidified KMnO$_4$. The fractured surface was studied by breaking the sample in liquid nitrogen. In all cases, the surfaces were coated with a thin-sputtered film of gold. The total
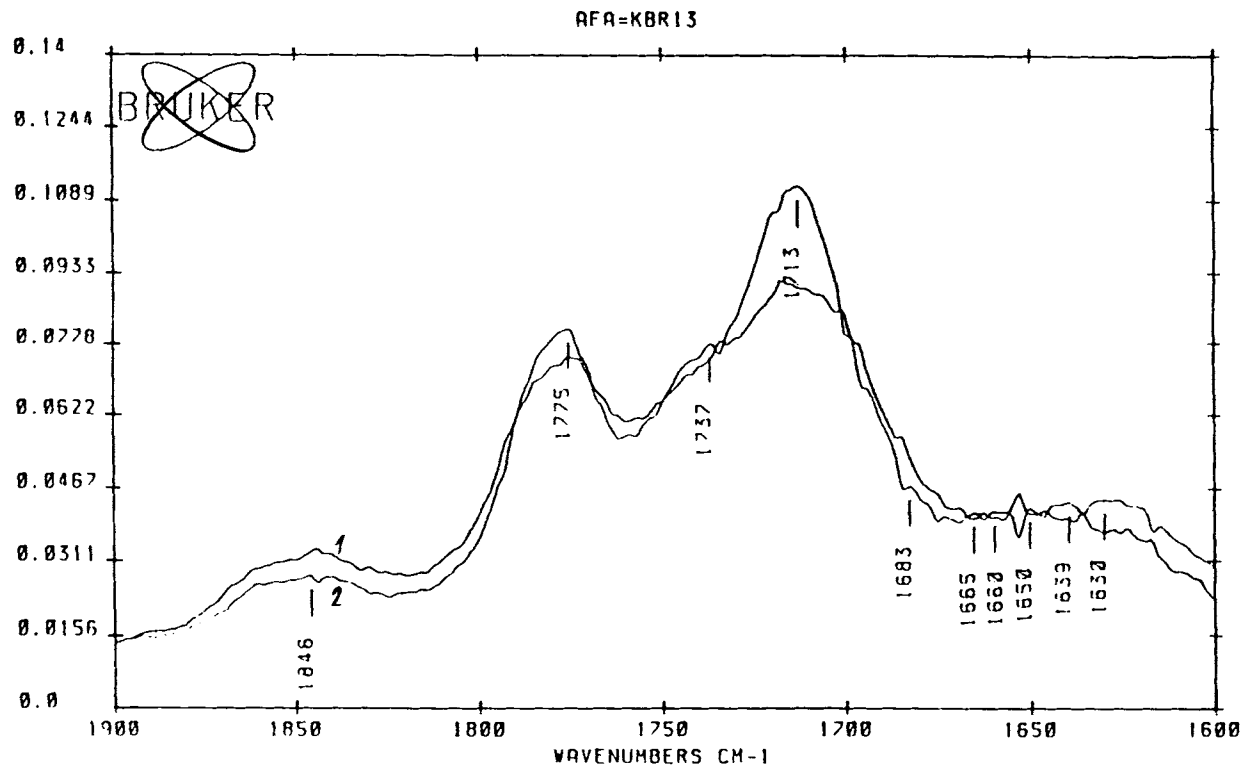
Figure 1   IR spectroscopy of MAH-PP-III: (1) before reprecipitation; (2) after reprecipitation.

4. RESULTS AND DISCUSSION

4.1. Reactivity of MAH-PP Graft Polymers

surface area (S_v) of the dispersed phase was measured using the Saltykov method.[10]

The amount of reactive MAH in all the three types of MAH-PP modifiers was estimated before mixing with the PRP-EVA compositions and after melt-mixing with the PRP-EVA compositions as well. The process of estimation was reprecipitation of samples from suitable solvents followed by dissolving a small quantity of reprecipitated sample in hot xylene and titrating it against 0.1 N KOH solution. The reactive grafted MAH was quantitively estimated using the following relationship:

$$\text{MAG}_g(\text{wt } \%) = \frac{100 \cdot V_i \cdot C \cdot M_w}{2m}$$

where MAH_g is the amount of grafted maleic anhydride; V_i, the volume of the KOH solution consumed during titration; C, the concentration of KOH; M_w, the molecular weight of MAH, 98.06 g/mol; and m, the weight of the sample in grams used for titration. Phenolphthalein was used as the indicator and the KOH solution was standardized by titrating against a standard 0.1N oxalic acid solution.

The MAH-grafted PP samples prepared with two different catalyst systems differ in their grafted MAH contents. Based on the assumption that modification of PRP-EVA composition can be affected only by the reactivity of the grafted MAH in PP chains and not by the free MAH present in modifiers, it was necessary to find out the amount of graft as well as free maleic anhydride contents, if any, in

Table I   Grafted Maleic Anhydride (MAH_g) Contents in Three Types of MAH-PP Modifiers

Modifier Type	MAH_g Content[a] (wt %)	Experimental Error[b]
MAH-PP-I	0.98	0.06
MAH-PP-II	1.41	0.07
MAH-PP-III	2.95	0.08

[a] All samples were reprecipitated from a suitable solvent to eliminate unreacted free MAH before estimation of MAH content.
[b] Experimental error in analysis of MAH_g estimated from five repeated experiments.

Table II Dependence on MAH–PP Modifiers Concentration of Grafted MAH Consumption in MAH–PP-modified PRP–EVA Compositions[a]

MAH–PP-I Modified PRP–EVA Mix			MAH–PP-II Modified PRP–EVA Mix			MAH–PP-III Modified PRP–EVA Mix		
Modifier Concn in Mix (wt %)	MAH_g Content in MAH-PP-I (wt %)	MAH_g Consumed in Mix (wt %)	Modifier Concn in Mix (wt %)	MAH_g Content in MAH-PP-II (wt %)	MAH_g Consumed in Mix (wt %)	Modifier Concn in Mix (wt %)	MAH_g Content in MAH-PP-III (wt %)	MAH_g Consumed in Mix (wt %)
6.0	0.059	54.0	2.0	0.028	76	1.0	0.029	70
8.0	0.078	31.0	3.0	0.042	68	2.0	0.059	51
12.0	0.117	27.0	4.0	0.056	53	3.0	0.088	30
15.0	0.147	26.5	5.0	0.070	34	4.0	0.118	24
			6.0	0.085	29	5.0	0.147	19
			8.0	0.113	26			

[a] MAH_g = grafted maleic anhydride in MAH–PP modifier.

all three types of MAH–PP modifiers studied. FTIR analysis of the samples in their original form and after their reprecipitation from a suitable solvent revealed that only the MAH–PP-III-type modifier contains free MAH. The IR spectra of the original MAH–PP-III, and after reprecipitation, are shown in Figure 1. A reduction in the peak height at 1775 cm^{-1} after reprecipitation is evident. Table I furnishes data on actually grafted MAH contents for all three tested modifiers. Evidently, modifiers differ in their degree of polarity. Whereas the sample containing 0.98 wt % grafted MAH is more hydrophobic in nature due to its relatively high aliphatic content, the sample containing 2.95 wt % MAH is more hydrophilic in nature.

To confirm the chemical reactivity of grafted MAH in MAH–PP modifiers with PRP–EVA composition during high-temperature mixing and subsequent molding operations, mechanical blends of the PRP triblock polymer with 8 wt % EVA elastomer have been prepared separately in the presence of all three types of MAH–PP graft polymers. The unreacted MAH contents in all such prepared compositions have been estimated by chemical analysis as described in the preceding part of this paper. Table II summarizes the results of the estimation of grafted MAH consumed due to interaction with PRP–EVA compositions for all types of MAH–PP modifiers. It is evident that all three tested MAH–PP modifiers interact with the PRP–EVA composition, resulting in the involvement of grafted MAH groups in the process of blend preparation. Moreover, it is found that the extent of consumption of MAH depends on the type of modifier used. Presumably, consumption of grafted MAH in the composition studied improves the chemical compatibility between the PRP triblock polymer and the EVA elastomer. This fact is partly reflected in the results of measurement of dynamic mechanical properties of modified PRP–EVA compositions. Figures 2 and 3 show the dependence of the loss tangent tan δ and storage modulus E' on temperature. For the PRP–EVA blend modified with MAH–PP-III, a sudden drop in storage modulus near the glass transition zone corresponding to the random ethylene–propylene block at $-50°C$[10] and a significant shift of the glass transition peak at $-50°C$ to a lower temperature, as shown in the tan δ vs. temperature plot, probably indicate a chemical interaction between the modifier and PRP–EVA composition.

4.2. Blend Properties and MAH–PP Modifiers

The physicomechanical properties of the PRP–EVA composition modified with three different types of
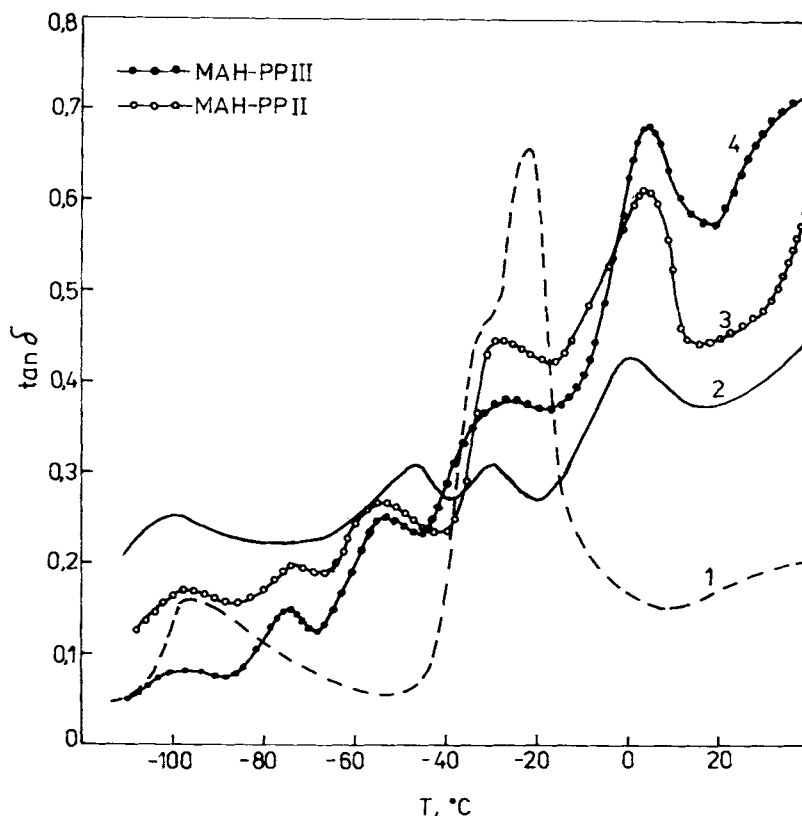
Figure 2 Variation of tan δ with temperature for (1) Levaprene 450, (2) PRP-EVA 92/8 blend, and (3, 4) PRP-EVA blend modified with MAH-PP.

MAH-PP modifiers are presented in Tables III-V. Most of the measured properties are found to be influenced by the type as well as concentration of MAH-PP modifiers. Compositions with better impact strength, as well as with improved brittleness, can be prepared by varying the type of modifiers and their concentrations. Tensile strength and elongation are not significantly influenced by the addition of a modifier. An increase in the modifier concentration is marked by an initial increase in low-temperature impact resistance and lowering of the brittle point of the studied composition. However, both

Table III   Effect of MAH–PP-I Modifier Concentration on Properties of PRP–EVA Blend[a]

MAH-PP-I Content in Blend (wt %)	MAH_g Content[b] (wt %)	T.S. (MPa)	E_b (%)	I_p (kJ m^{-2})	T_B (°C)	H_{ah} (ShA)	MFI (g 10 min^{-1})
0.0	0.000	15.9 (0.6)	85 (3)	13.4 (1.1)	−41 (2)	66 (2)	6.8 (0.3)
1.5	0.015	18.3 (0.4)	120 (3)	13.7 (1.2)	−48 (3)	62 (1)	6.2 (0.5)
3.0	0.029	16.2 (0.7)	135 (4)	16.7 (0.9)	−56 (3)	60 (2)	7.4 (0.3)
6.0	0.059	14.9 (0.6)	86 (3)	21.8 (1.4)	−57 (4)	63 (1)	10.1 (0.6)
7.0	0.069	16.0 (0.5)	96 (2)	24.4 (1.9)	−57 (4)	63 (2)	10.5 (0.4)
8.0	0.078	16.3 (0.5)	107 (3)	23.8 (1.3)	−51 (2)	63 (2)	10.8 (0.5)
15.0	0.147	16.3 (0.6)	105 (2)	20.1 (1.7)	−44 (4)	65 (1)	11.0 (0.4)

[a] Mean values. Values in parentheses are standard deviations. T.S., tensile strength; E_b, elongation at break; I_p, impact strength; T_B, brittle point; H_{ah}, shore A hardness; MFI, melt flow index. All property values are the mean of 10 specimens.
[b] Wt % of grafted MAH added in PRP-EVA composition in the form of modifier MAH-PP-I.
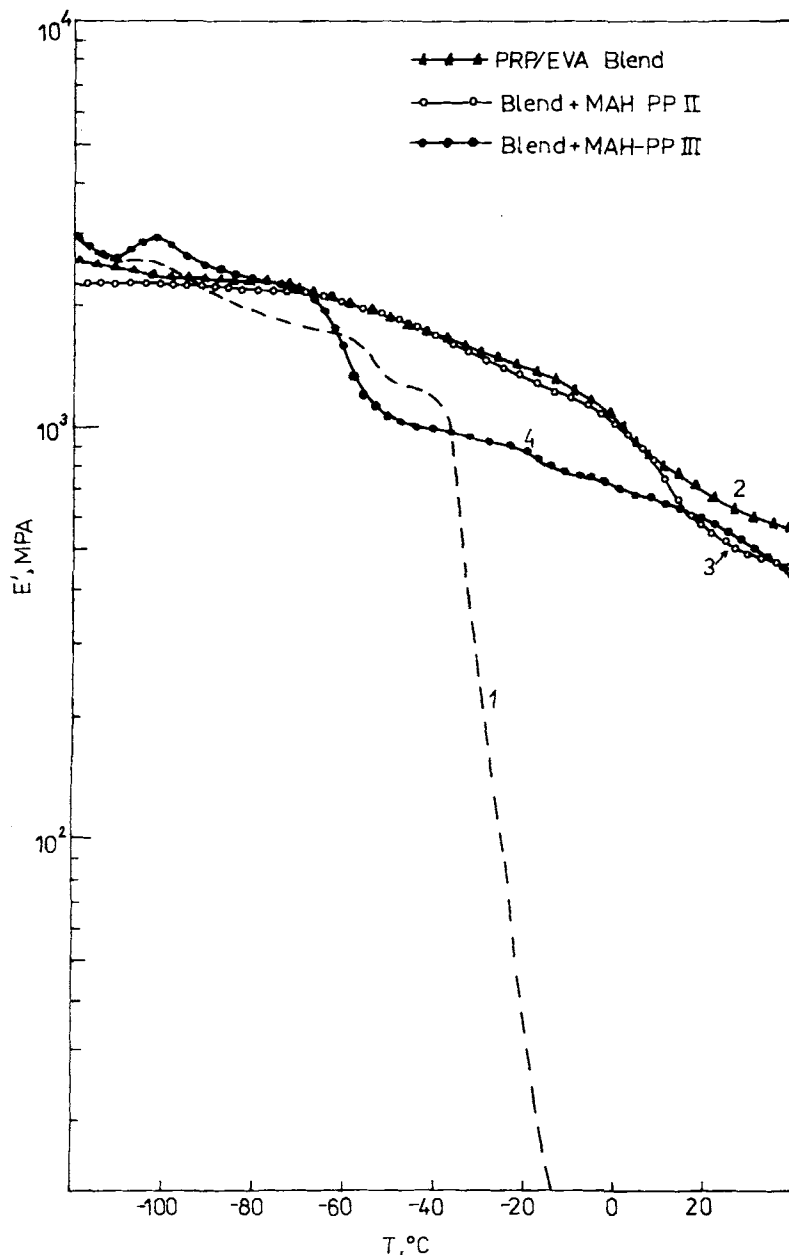
Figure 3   Variation of mechanical E with temperature; figures are assigned the same as in Figure 2.

impact strength and brittleness temperature, T_B, deteriorated when the PRP–EVA composition contained a relatively high level of modifiers.

To elucidate the cause of this complex dependence of low-temperature brittleness and impact strength on the modifier concentration of PRP–EVA compositions, we have studied the dynamic mechanical properties and morphology as well as the flowability of unmodified and modified compositions. The low-

ering of the glass transition temperature from -45 to $-55°C$ of the PRP triblock polymer in the PRP–EVA composition modified with MAH–PP does not give sufficient information about the nature of the interphase interaction between the two dissimilar phases of the PRP triblock polymer and the EVA elastomer. However, it should be possible to explain the effect of the modifier by studying the morphology using scanning electron micrography (SEM). Ad-

Table IV   Effect of MAH–PP-II Modifier Concentration on Properties of PRP–EVA Blend[a]

MAH–PP-II Content in Blend (wt %)	MAH$_g$ Content[b] (wt %)	T.S. (MPa)	E_b (%)	I_p (kJ m^{-2})	T_B (°C)	H_{ah} (Sh A)	MFI (g 10 min^{-1})
1.0	0.014	15.6 (0.5)	98 (2)	13.2 (1.2)	−43 (3)	63 (2)	7.0 (0.2)
1.5	0.021	16.4 (0.9)	96 (3)	15.3 (1.3)	−44 (4)	63 (1)	6.8 (0.8)
3.0	0.042	16.5 (0.7)	102 (2)	22.3 (2.0)	−46 (2)	63 (2)	7.0 (0.4)
6.0	0.085	13.3 (0.6)	73 (2)	29.9 (0.9)	−48 (3)	62 (1)	8.7 (0.2)
8.0	0.113	15.9 (0.8)	90 (4)	27.2 (2.4)	−38 (3)	60 (2)	10.0 (0.6)
10.0	0.141	16.4 (0.3)	68 (2)	25.3 (2.1)	−38 (2)	63 (3)	12.5 (0.6)

[a] See footnote a to Table III.
[b] Wt % of grafted MAH added in the PRP–EVA composition in the form of modifier MAH–PP-II.

Table V   Effect of MAH–PP-III Modifier Concentration on Properties of PRP–EVA Blend[a]

MAH–PP-III Content in Blend (wt %)	MAH$_g$ Content[b] (wt %)	T.S. (MPa)	E_b (%)	I_p (kJ m^{-2})	T_B (°C)	H_{ah} (Sh A)	MFI (g 10 min^{-1})
0.5	0.015	15.0 (0.3)	81 (3)	31.0 (2.8)	−36 (2)	64 (2)	7.7 (0.2)
1.0	0.029	15.7 (0.4)	79 (2)	51.0 (4.2)	−48 (4)	63 (1)	7.3 (0.3)
1.5	0.044	16.1 (0.5)	98 (4)	36.5 (3.1)	−46 (2)	62 (2)	7.5 (0.4)
2.0	0.050	15.8 (0.3)	95 (3)	30.1 (2.4)	−46 (3)	63 (3)	8.5 (0.5)
3.0	0.088	15.5 (0.5)	88 (2)	28.1 (2.6)	−45 (3)	60 (1)	8.8 (0.4)

[a] See footnote a to Table III.
[b] Wt % of grafted MAH added in the PRP–EVA composition in the form of modifier MAH–PP-III.

Table VI   Effect of Concentration and Type of MAH–PP on Morphological Properties of the PRP–EVA Blend[a]

MAH–PP Type	MAH–PP Content in Blend (wt %)	S_v (m^2 m^{-3})	S_v^p (m^2 m^{-3})	T.S. (MPa)	I_p (kJ m^{-2})	T_B (°C)	MFI (g 10 min^{-1})
MAH–PP-I	0.0	0.26	3.40	15.9	13.4	−41	6.8
	1.5	0.36	4.60	18.3	13.7	−48	6.2
	1.7	0.32	4.20	19.7 (0.5)	15.8 (1.0)	−52 (4)	6.8 (0.4)
	3.0	0.43	5.90	16.2	16.7	−56	7.4
MAH–PP-II	1.0	0.32	4.10	15.6	13.2	−43	7.0
	5.0	0.49	5.70	16.1 (0.6)	27.8 (2.1)	−51 (3)	7.2 (0.4)
	10.0	0.75	8.35	16.4	25.3	−38	12.5
MAH–PP-III	1.5	0.38	4.49	16.1	36.5	−46	7.5
	3.0	0.41	6.10	15.5	28.1	−45	8.8

[a] See footnote a to Table III; in a multiphase system PRP–EVA, we define total specific surface area, S_v, as total area of the circumferencial surface of the EVA phase in unit volume of the mixture and relative surface area, S_v^p, is given as the total surface area of EVA microparticles extrapolated to the unit volume of the EVA phase.
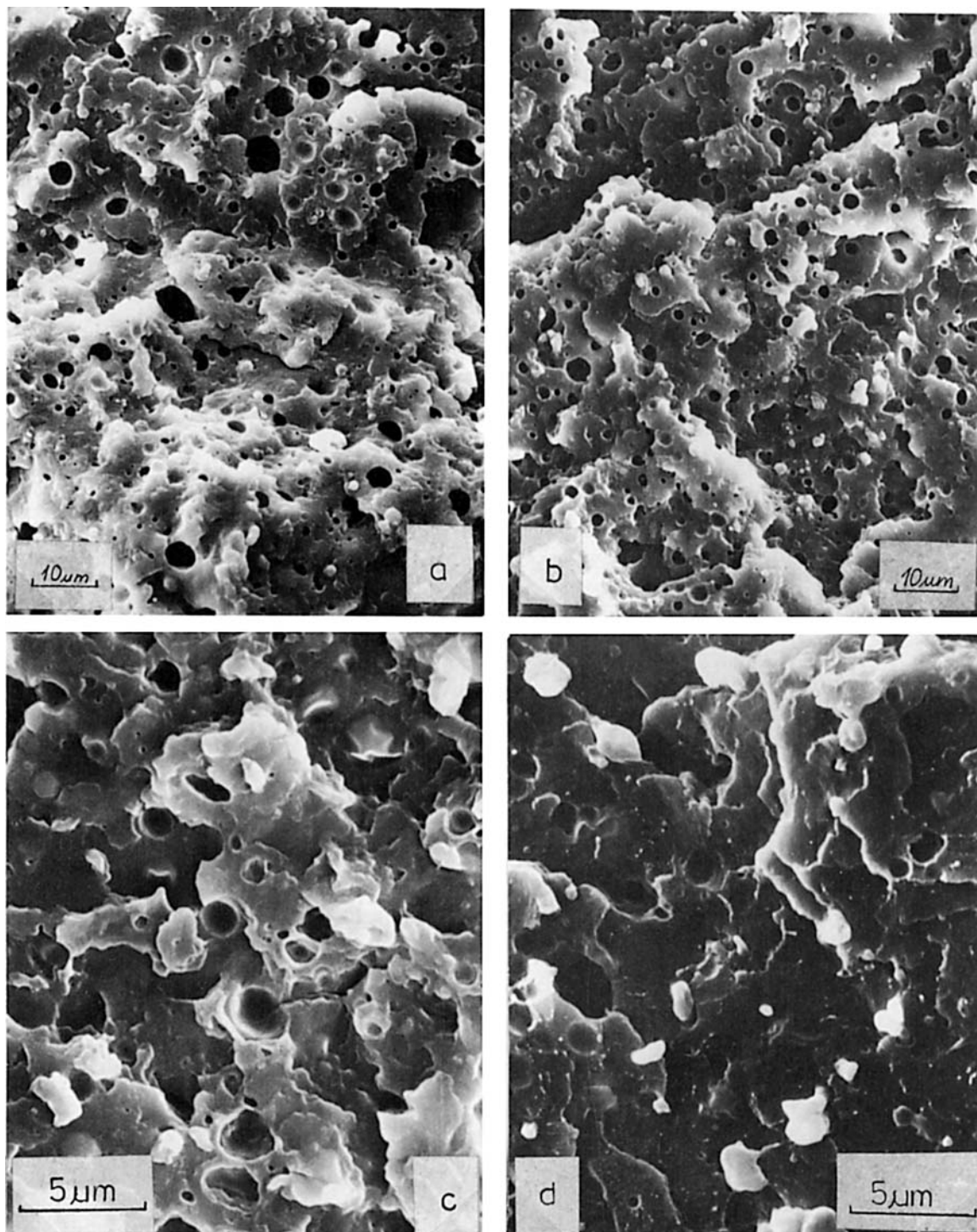
Figure 4   Microphotographs of PRP–EVA 92/8 blends: (a) unmodified and etched with toluene; (b) modified with 5 wt % MAH–PP-II and etched with toluene; (c) unmodified fractured surface; (d) fractured surface of 5 wt % MAH–PP-II modified composition.

dition of MAH–PP significantly increased the interfacial surface area (S_v) of the dispersed phase, as evident from Table VI, indicating a stronger physical interaction between the polymeric phases. Figure 4 shows SEM images of the etched unfractured (a, b) and fractured surfaces (c, d) from un-

modified and MAH–PP-modified PRP–EVA compositions. The EVA elastomer domains with a particle size of 0.5 to 3.0 μm are visible in the form of dark holes. It is apparent from the fracture surface of the unmodified composition in Figure 4(c) that fractures are brittle in nature with "dropping out" (dark holes) of elastomer particles. On the other hand, the modified composition resists phase separation by partly preventing "dropping out" of the elastomer phase. Dispersed elastomeric microparticles preferentially "break" (bright spots) with the development of crazes around the broken rubber domain, as evident in Figure 4(d). Thus, it is expected that in the modified PRP–EVA composition, probably due to interphase modification by a transesterification reaction between the pendant MAH groups in MAH–PP and acetate groups in the EVA elastomer, as predicted in reaction Scheme I, the dispersed rubber particles become more efficient in craze initiation:
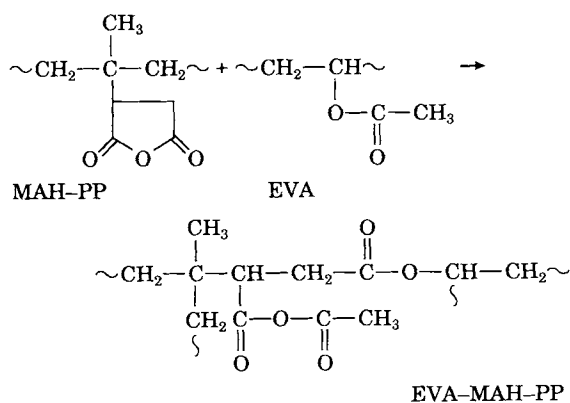
Scheme I

Although the reaction Scheme I predicts a possible increase in molecular weight of the modified composition compared to the unmodified one, results in Table VI indicate that the meltflow index practically remains unchanged in the low concentration range of MAH–PP additive and then progressively increases with increasing modifier concentration. This may be due to the efficiency of the modifier progressively decreasing, as evidenced by the comparatively low consumption rate of grafted MAH as given in Table II. Thus, high MAH–PP modifier concentration acts more like a "diluent" in the PRP–

EVA composition rather than as an effective chemically reactive phase compatibilizer.

5. CONCLUSION

The effect of MAH-grafted PP on PRP–EVA composition has been studied. The modifier studied improves physicomechanical properties of PRP–EVA composition not only by improving the degree of dispersion of the EVA elastomer in the plastic PRP triblock polymer matrix but also probably improves interfacial interaction by forming chemical bonds between the EVA elastomer and the modifier. Compositions with improved low-temperature brittleness as well as impact strength have been prepared by adding a small quantity of MAH–PP modifier. An increased concentration of modifier in the composition studied, however, is found to have a negative influence on mechanical properties.

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