

Studies on Impact Modification of Polystyrene (PS) by Ethylene–Propylene–Diene (EPDM) Rubber and Its Graft Copolymers. III. PS/EPDM-*g*-(Styrene-co-Maleic Anhydride) Blends and Its Relative Performance

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Synopsis

The graft copolymer of ethylene–propylene–diene (5-ethylidene-2-norbornene) rubber with styrene and maleic anhydride is synthesized, characterized, and blended with polystyrene. The tensile and the impact behaviors of the blends were investigated. The relative performance of EPDM-*g*-(styrene-co-maleic anhydride) as impact modifier for polystyrene has been evaluated.

INTRODUCTION

The polymer industry has been challenged to produce new polymeric materials by blending two or more homopolymers or copolymers, which are chemically incompatible. To meet the challenge, several methods have been developed. One of the methods is based on synthesis of graft copolymers having segments identical or similar to the blend components which, when added to two incompatible polymers, can decrease the size of the dispersed domains and improve the interfacial properties and thus the desired mechanical and other physical properties. The grafting on rubber increases when maleic anhydride is added as comonomer with styrene.¹ At the same time the impact resistant and heat distortion temperature of EPDM graft copolymers based blends also improve.² In the present case, EPDM-*g*-(styrene-co-maleic anhydride) graft copolymer has been synthesized and it has been blended with PS. Its relative performance has been evaluated in comparison with other graft copolymers studied in the authors' laboratory.^{3,4}

EXPERIMENTAL

Materials

Maleic anhydride (supplied by Lobo Chemie Indo Austranol Co., India) was recrystallized from purified chloroform three times and then dried under reduced pressure. Benzene (Analar E. Merck, India) was purified by usual procedures. Tertiary dodecyl mercaptan (Fluka, Switzerland) was used directly as chain

TABLE I
Characteristics of Materials Used

System	Mol wt (MEK- soluble fraction)	η_c^b (dL/g)	η_g^c (dL/g)	Grafting efficiency (%)	Grafting percentage	Gel content (%)	Styrene comonomer in copolymers (wt %)
PS	1.5×10^5	0.66 (toluene)	—	—	—	—	—
EPDM- <i>g</i> -(styrene-co-maleic anhydride) (EPDM- <i>g</i> -SMAH)	7.34×10^3 ^a	0.15 (THF)	1.40	20.0	118.2	19.23	5
EPDM- <i>g</i> -styrene (EPDM- <i>g</i> -S)	2.7×10^6	0.75 (toluene)	1.20	39.57	338.4	13.0	—
EPDM- <i>g</i> -(styrene-co-methylmethacrylate) (EPDM- <i>g</i> -SMMA)	2.3×10^4	0.135 (MEK)	1.21	20.2	60.0	16.0	51

^a Molecular weight was determined by vapor pressure osmometry.

^b η_c = intrinsic viscosity of copolymers.

^c η_g = intrinsic viscosity of graft copolymers.

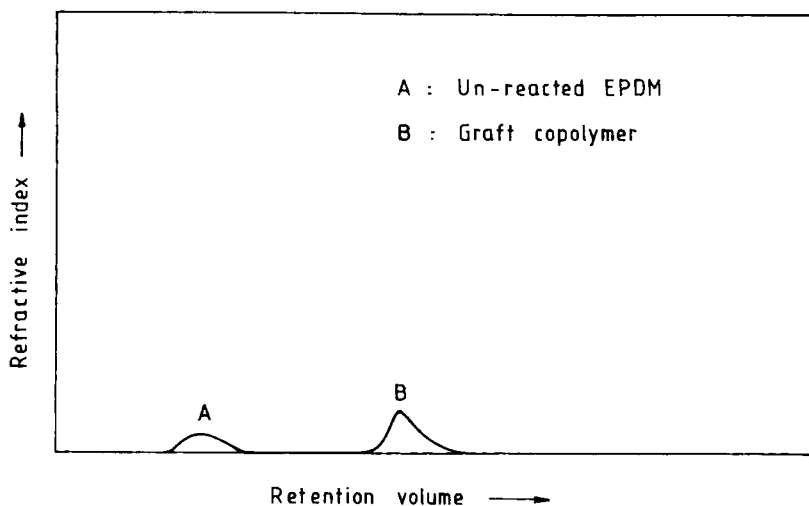


Fig. 1. GPC plot of graft copolymer.

transfer agent. The other chemicals and solvents used have already been specified in the first paper of this series.³

Synthesis

The graft copolymer of EPDM was synthesized by solution polymerization technique. Typically, 10 g of EPDM was dissolved in thiophene-free benzene. Then 95 mL of styrene and 2.5 g of maleic anhydride were added and stirred under nitrogen atmosphere for 0.5 h to remove dissolved oxygen and for thorough mixing of the reaction mixture. Subsequently, 0.71 g of benzoyl peroxide and 0.35 mL of *t*-dodecyl mercaptan were added with simultaneous stirring. The reaction mixture was kept at 85°C for 6 h with continuous stirring. The product is obtained after removing the solvent benzene by azeotropic distillation with distilled water. NaOH solution was added prior to distillation to neutralize the acid formed during the distillation process. The product was taken out from the reaction kettle, cut into small pieces, and vacuum dried at 70°C. The yield of product was about 61.3%.

To obtain the pure graft copolymer from the polyblend for the analysis purpose, a similar separation procedure as described in previous paper was followed.⁴

Characterization

The intrinsic viscosity of graft copolymer was determined in solvent toluene at 30°C and the intrinsic viscosity of styrene-maleic anhydride copolymer was determined in THF at 30°C. The characteristics of graft copolymers are given in Table I.

GPC chromatogram (Fig. 1) shows the unreacted EPDM and graft copolymer. The copolymer of styrene-maleic anhydride could not be detected as it could not be filtered before injecting the polymer solution into the GPC machine because of high viscosity. Hence the homopolymer free graft copolymer was used for the analysis.

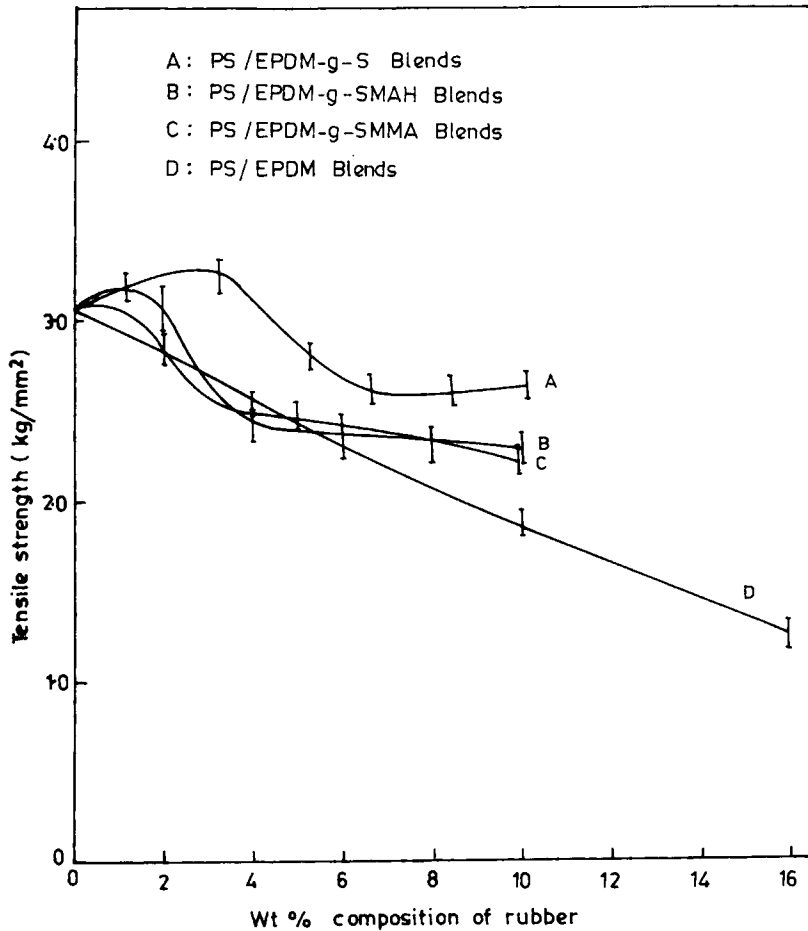


Fig. 2. Tensile strength of graft copolymer blends with PS as a function of rubber composition by weight.

RESULTS AND DISCUSSION

Tensile Strength

The tensile strength curves (Fig. 2) show that the incorporation of rubber results in the reduction of tensile strength of blends. However, the reduction occurs after a marginal initial increase in tensile strength at lower concentrations. Further among all PS blends, the performance of PS/EPDM-*g*-S blends has been the best. The following trend of tensile strength has been observed among all PS blends:

PS/EPDM-*g*-S > PS/EPDM-*g*-SMAH

> PS/EPDM-*g*-SMMA > PS/EPDM

Impact Strength

The impact strength plots (Fig. 3) show the impact strength goes on increasing with the increase of rubber concentration in the case of blends of PS/

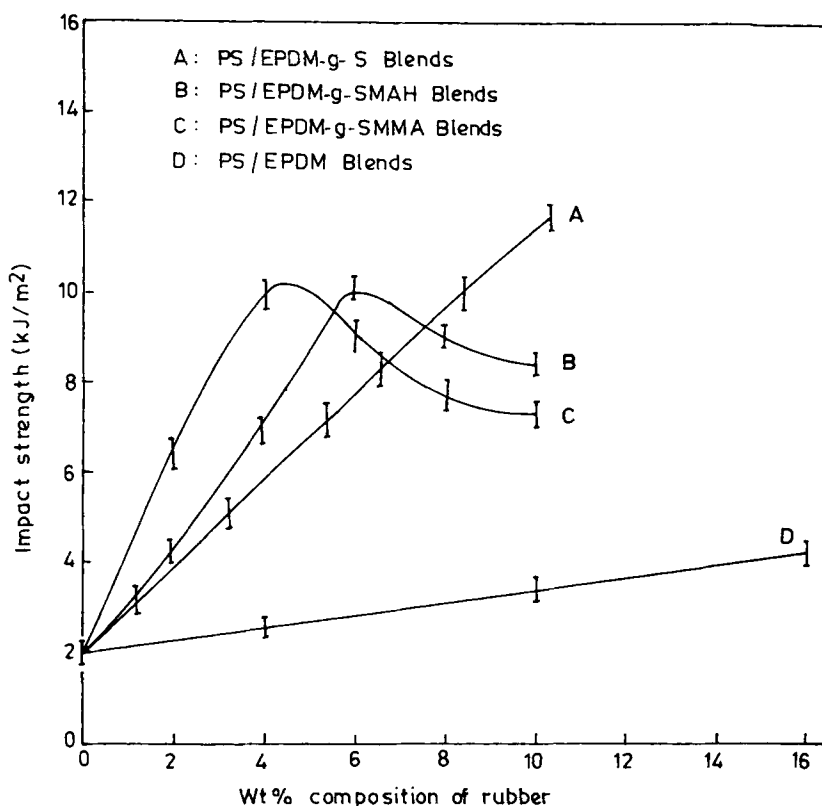


Fig. 3. Impact strength of graft copolymer blends with PS as a function of rubber composition by weight.

EPDM-*g*-S, whereas there is an optimum impact strength improvement in the case of other two modifiers. PS/EPDM-*g*-SMMA blends show maximum impact strength at lower concentrations of rubber in comparison with the PS/EPDM-*g*-SMAH blends. The following trend of impact strength has been observed:

PS/EPDM-*g*-S > PS/EPDM-*g*-SMAH

> PS/EPDM-*g*-SMMA > PS/EPDM

The results of the impact testing in Figure 3 show an increase in the impact strength of graft blends over the mechanical blends. It is clearly visible from these impact results that interfacial adhesion is an important factor in rubber toughening. However, the optimum values of impact strength for the other two grafted polyblends compared with the PS/EPDM-*g*-S blend may be due to the inclusion of incompatible methyl methacrylate and maleic anhydride comonomers into the matrix of the grafted species.⁵ It was also found that PS/EPDM-*g*-S blends are compatible for all compositions range whereas other two grafted blends are compatible at low concentration of grafted polyblends.⁶ Interfacial adhesion is also a factor that is important in rubber toughening; other factors

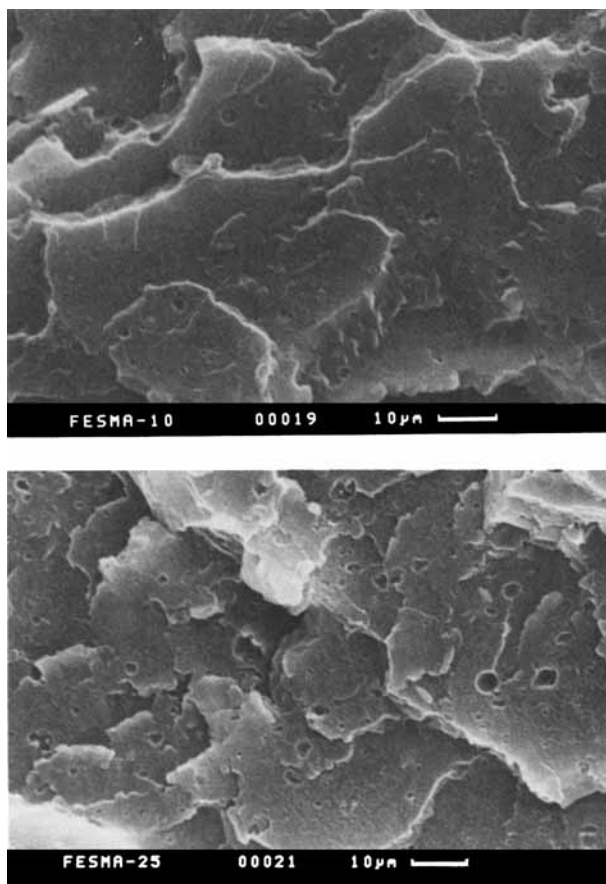


Fig. 4. Scanning electron micrographs of graft copolymer and PS blends at (a) 2 wt % rubber; (b) 6 wt % rubber.

are the nature of the matrix, the nature of the rubber, the concentration of the rubber phase, and the shape and size of the rubber particles. The dominant mechanism for deformation in polystyrene is craze formation and it is multiple craze formation that leads to toughness enhancement.⁷ Blends of polystyrene dissipate fracture energy mainly by matrix crazing and therefore the toughness is greatest at an optimum rubber particle size. Polystyrene requires an optimum rubber particle size of about $1.0 \mu\text{m}$ for best impact modification.⁷

Scanning electron microscopy was used to study the morphology of the blends and to correlate the structure with the impact properties. Figure 4 shows micrographs of some PS/EPDM-*g*-SMAH blends. Figures for other blends are shown in elsewhere.^{3,4} All the micrographs of the impact fractured surfaces show the rubber particle sizes of the graft blends are relatively smaller than those of mechanical blends. This is due to the increased interfacial interaction. As the compatibility of the blend increases, the minor rubber phase becomes more dispersed.

The semicompatible blends of PS/EPDM-*g*-SMAH and PS/EPDM-*g*-SMMA show a similar trend of mechanical properties. It can also be seen that

the small percentage of maleic anhydride as comonomer with styrene is more effective in reducing compatibility than a larger amount of methyl methacrylate, which is also reflected in having optimum impact strength at lower concentration of EPDM-*g*-SMAH.

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