

Studies on Impact Modification of Polystyrene (PS) by Ethylene–Propylene–Diene (EPDM) Rubber and Its Graft Copolymers.

II. PS/EPDM-*g*-(Styrene-co-Methylmethacrylate) Blends

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Synopsis

The toughness of a polymer blend is one of the major factors deciding its practical application. An impact modified polystyrene (PS) is usually a multiphase system consisting of the thermoplastics and an elastomeric component. The heterogeneous character of such a system and the interfacial adhesion between the components determine its impact strength. The graft copolymer of ethylene–propylene–diene (5-ethylidene-2-norbornene) rubber with styrene and methylmethacrylate is synthesized, characterized, and blended with polystyrene to improve its impact strength. It is observed that there is improvement in impact strength with the subsequent decrease of tensile strength. The improved impact strength has been discussed in terms of morphology, compatibility, and interfacial adhesion of graft copolymers with PS matrix.

INTRODUCTION

Impact modification of a glassy phase is possible if sufficient adhesion between the rubbery phase and glassy phase is present. But, generally, most of the polymers are incompatible with each other; hence grafting is necessary to bring about sufficient adhesion between the two phases. There is much in the literature available for the impact modifications of polystyrene [HIPS]^{1–3} where the grafted chain is compatible with the continuous matrix to impart adhesion between the rubbery phase and glassy polystyrene phase. Styrene and methyl methacrylate copolymer is grafted on polybutadiene to prepare high impact transparent or translucent material,⁴ transparent material with good brightness,⁵ and light-colored articles⁶ and to achieve impact modification of styrene–methyl methacrylate copolymer itself.⁷ The copolymer is grafted on EPDM rubber for coating purposes.⁸ Almost no research work is reported in the literature where the grafted chain of copolymer as a whole is used as an impact modifier of polystyrene. The adhesion between polystyrene matrix and styrene–methyl methacrylate grafted chain is possible as they make a semicompatible blend.^{9,10}

In the present investigation, styrene and methylmethacrylate copolymers are grafted on EPDM rubber. The graft polyblend is then melt-blended with polystyrene and their mechanical properties are studied.

TABLE I
Characteristics of Graft Copolymer

System	\bar{M}_w (copolymer)	η_c^a (dL/g)	η_g^b (dL/g)	% Grafting efficiency	Grafting percentage	Gel content (%)
EPDM- <i>g</i> -(styrene-co- methylmethacrylate) polyblend	2.29×10^4	0.135	1.21	20.2	60	16

^a η_c = intrinsic viscosity of styrene-methylmethacrylate copolymer.

^b η_g = intrinsic viscosity of graft copolymer.

EXPERIMENTAL

Materials

Methyl methacrylate (Laboratory Reagent supplied by Burgoyne Burbidges and Co., India) was made inhibitor-free by the usual procedure. The solvent *n*-heptane was distilled prior to its use. The other chemicals and solvents used here have already been specified in the first paper of this series.¹¹

Synthesis

The graft copolymer of EPDM was synthesized by solution precipitation technique. Typically, 10 g of EPDM was dissolved in *n*-heptane, then 45 mL of styrene and 45 mL of methyl methacrylate were added. The reaction mixture

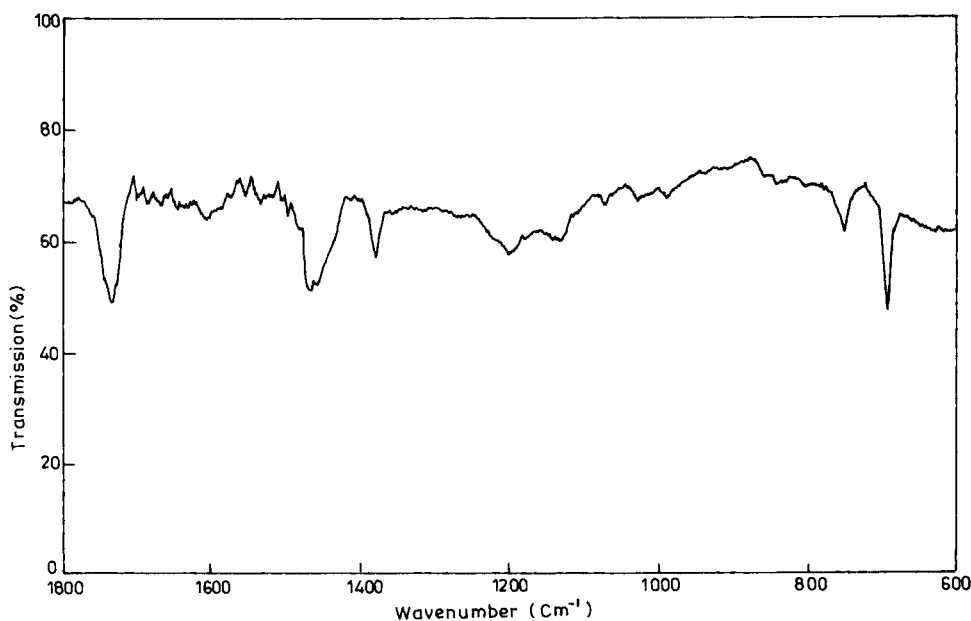


Fig. 1. IR analysis of graft copolymer.

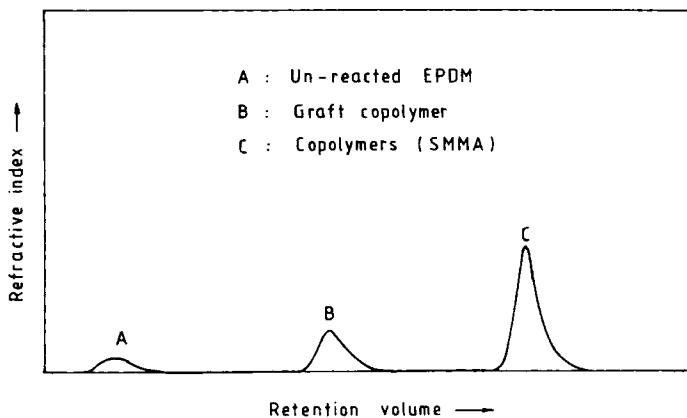


Fig. 2. GPC plot of graft copolymer.

was stirred for 0.5 h in nitrogen atmosphere to remove dissolved oxygen and insure complete mixing prior to reaction. Then 0.5 g of BPO was added and the reaction mixture was heated at 80°C for 10 h. A continuous stream of N₂ was flushed through the solution along with continuous stirring. The product was precipitated in excess of methanol and dried at 70°C in a vacuum oven overnight. The yield of product was about 77%.

Characterization

The Soxlet extraction procedure was followed for the separation of graft copolymer. The copolymer and homopolymer were extracted by using MEK

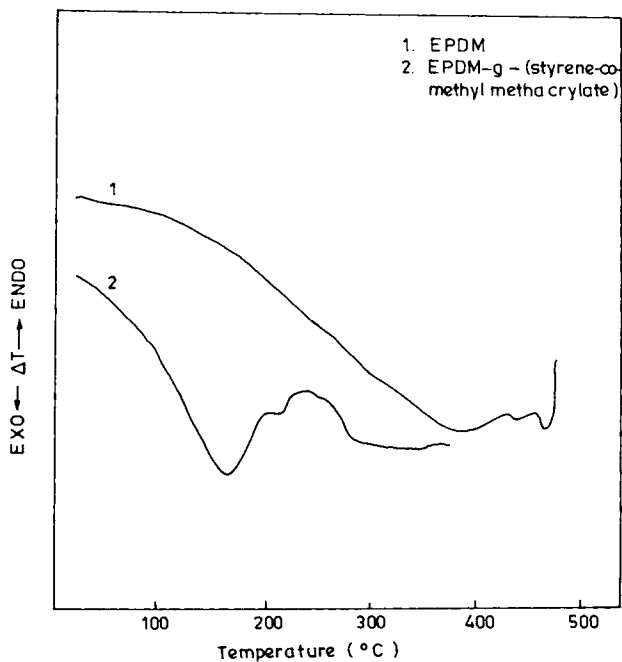


Fig. 3. DTA thermogram of graft copolymer.

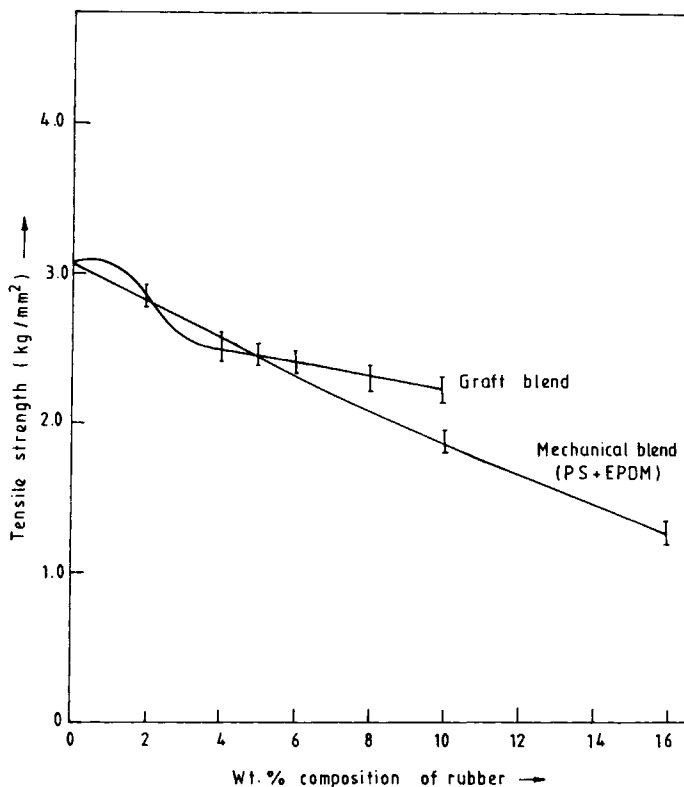


Fig. 4. Tensile strength of graft copolymer blends with PS as a function of rubber composition by weight.

solvent. Unreacted rubber was extracted by using petroleum ether. The remaining residue consists of the graft copolymer and gel. The graft copolymer was obtained by extracting it with benzene. The graft copolymer so obtained was repeatedly extracted with MEK and petroleum ether to remove homopolymer/copolymer and unreacted EPDM rubber to the maximum possible extent. The remnant graft copolymer was used for the characterization purpose. The intrinsic viscosity of graft was determined in solvent toluene at 30°C and the intrinsic viscosity of styrene-methyl methacrylate copolymer was determined in MEK solvent at 25°C. The following equation¹² was used for the determination of molecular weight of copolymer:

$$[\eta]_{\text{MEK}}^{25^\circ\text{C}} = 1.54 \times 10^{-4} (\bar{M}_w)^{0.675}$$

The characteristics of graft copolymer are given in Table I. The proton NMR spectra of styrene-methyl methacrylate copolymer was used to calculate the amount of constituents by standard integration method. The styrene and methyl methacrylate composition was found to be 49 : 51 by wt %, respectively.

The IR (Perkin-Elmer 577) analysis of graft copolymer shows (Fig. 1) the existence of methyl methacrylate ester peak at 1735 cm^{-1} and methyl peak at 1378 cm^{-1} . The characteristic MMA pattern is spread from 1280 to 1130 cm^{-1} .

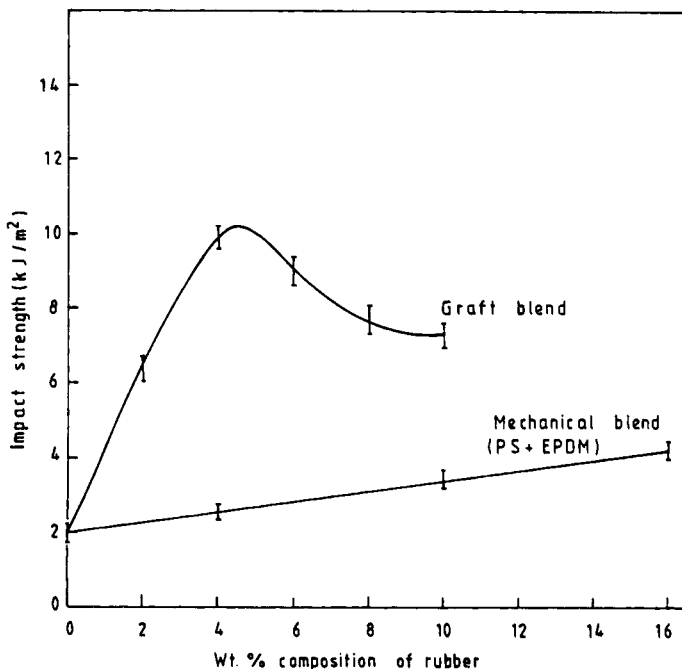


Fig. 5. Impact strength of graft copolymer blends with PS as a function of rubber composition by weight.

The characteristic ethylidene bands at 810 and 1680 cm^{-1} are very small. The 700 and 760 cm^{-1} bands are due to the out-of-plane deformation modes of the hydrogen atom attached to aromatic ring. The poorly resolved peaks of graft copolymer may be due to unclean fractions obtained from fractionation during Soxhlet extraction having spreading of molecular weight and composition of two copolymers plus gel and graft copolymer.

From the GPC chromatogram (Fig. 2), it can be seen that unreacted rubber was retained first, then graft copolymer, and lastly the copolymer of styrene and methyl methacrylate. DTA (Stanton Redcroft, U.K.) thermal analysis of graft copolymer (Fig. 3) from room temperature up to 350°C does not show second-order transition behavior (T_g) for the grafted chain. But the pattern of the curve for the graft copolymer is considerably different from the backbone EPDM rubber.

The processing, molding, and testing of blends were carried out according to the description given in the previous paper.¹¹

RESULTS AND DISCUSSION

Figure 4 represents the tensile strength vs. composition of EPDM. The tensile strength of the graft was measured up to 10 wt % of EPDM rubber content of graft copolymer. The tensile strength results for the graft copolymer blends show that, with the incorporation of rubber phase in the thermoplastics matrix, tensile strength decreases. The tensile strength decreases sharply between 2

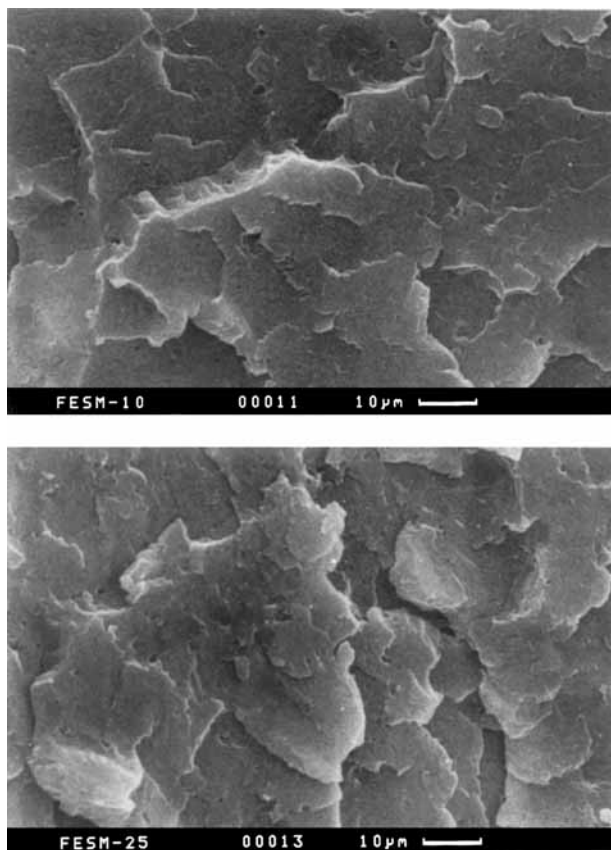


Fig. 6. Scanning electron micrographs, graft copolymer, and PS blends at (a) 2 wt % of rubber and (b) 4 wt % of rubber.

and 3 wt % of rubber in the case of graft blends and then there is a gradual decrease of tensile strength with respect to rubber composition. The higher decrease of tensile strength of graft copolymer blends than that of PS/EPDM blends between compositions of 2–4 wt % of rubber may be primarily due to the contribution of low molecular weight copolymers ($\bar{M}_w = 2.3 \times 10^4$) present in the graft polyblends. Secondly, in copolymers consisting of incompatible monomers units such as styrene and methyl methacrylate which increase the intermolecular spacing, producing poorer packing, lower density, and softer properties lesser than those in linearly additive values.¹³ The tensile strength of graft blends with PS at higher graft compositions then exceeds that of PS/EPDM blend system. Here, better adhesion than that of PS/EPDM blends due to the presence of higher grafts content at the interface of two phases is the contributing factor for the improvement of tensile strength.

The impact strength (Fig. 5) increases sharply and then decreases. The increase of impact strength up to 4.5 wt % of rubber is due to the increase of rubber composition. But the decrease of impact strength at higher composition may be due to increase in incompatibility of the blends because of increase of totally incompatible methacrylate component. This may lead to decrease in

adhesion of graftcopolymer and polystyrene and also to the agglomeration of graftcopolymers. These aspects have been discussed in details elsewhere.^{10,14}

The increase of impact strength can also be visualized by SEM microphotographs in Figure 6. The particle size of rubber as dispersed phase markedly influences the impact property of the blend.¹ The particle size is approximately in the range of 1–3 μm for the graft copolymer blends. The smaller particle sizes are more efficient to initiate craze formations to obtain the maximum impact strength. Another important reason for the improvement of impact strength may be due to the low copolymer occlusion within the rubber phase as indicated by lower graft efficiency and graft percentage. These would result in more flexible rubber particles of higher craze initiation and crack termination efficiency which enhance energy absorption during impact.¹⁵

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References

1. C. B. Bucknall, *Toughened Plastics*, Applied Science, London, 1977.
2. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York and London, 1976.
3. J. P. Kennedy and R. R. Smith, *Recent Advances in Polymer Blends, Grafts and Blocks*, L. H. Sperling Ed., Plenum, New York and London, 1974.
4. M. Starzak, B. Motysia, and M. Durak, *Polimery (Warsaw)*, **20**, 596 (1975).
5. T. V. Kudryavtseva, S. S. Ivanchev, E. I. Egorova, O. N. Romantsova, E. N. Ermina, V. P. Shamina, L. G. Mazora, M. A. Martynov, and K. A. Vylegzhanina, *Jpn. Pat.*, 78,117,093 (1978).
6. N. G. Gaylord and F. S. Ang, *Chemical Reactions of Polymers*, E. M. Fettes Ed., Wiley-Interscience, New York, London, Sydney, 1964.
7. L. A. Landers and W. C. Meisenheldev, *SPE J.* **20**, 621 (1964).
8. R. Muroi and K. Sato, *Jpn. Pat.*, 7,646,091 (1976).
9. R. J. Peterson, R. D. Corneliussen, and L. T. Rozelle, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **3**(10), 385 (1969).
10. S. Shaw and R. P. Singh, *Eur. Polym. J.*, **24**, 1163 (1988).
11. S. Shaw and R. P. Singh, *J. Appl. Polym. Sci.*, **40**, 685 (1990).
12. W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).
13. D. R. Deanin, *Polymer Structure, Properties and Applications*, Cahners Practical Plastics Series, 1972, Chap. 6.
14. S. Shaw and R. P. Singh, *Eur. Polym. J.*, **25**, 445 (1989).
15. E. P. Chang and A. Takahashi, *Polym. Eng. Sci.*, **18**, 350 (1978).

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