

# **Studies on Impact Modification of Polystyrene (PS) by Ethylene–Propylene–Diene (EPDM) Rubber and Its Graft Copolymers. I. PS/EPDM and PS/EPDM-*g*-Styrene Blends**

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## **Synopsis**

Ethylene–propylene–diene (EPDM) rubber is an excellent rubber for outdoor use. High impact polystyrene (PS) containing EPDM rubber may show improved weathering resistance. PS is incompatible with EPDM; hence bulk polymerization technique is adopted for the synthesis of graft products which show limited compatibility with PS. Two initiators were chosen at two different working temperatures to produce high grafting efficiency and grafting percentage. In the present system, it is shown that the graft copolymer and polystyrene compositions show higher improved impact strength behavior than that of the products based upon simple dispersion of EPDM in polystyrene.

## **INTRODUCTION**

The poor weathering resistance of higher impact polystyrene and ABS blends, resulting from photooxidative attack on the unsaturated rubbers, greatly limits the outdoor use of these blends. Polystyrene blends containing saturated rubbers consisting of copolymers or terpolymers of ethylene and propylene have been reported in the literature.<sup>1–4</sup> EPDM rubber has excellent resistance to such factors as weather, ozone, and oxidation. It has good tensile strength and high resistance to heat.<sup>5</sup> EPDM is incompatible with PS.<sup>6</sup> The ability of rubber to improve the impact strength of brittle, glassy polymers depends on the rubber particle size, degree of crosslinking, and mechanical compatibility of the rubber phase with the matrix. This is usually achieved by grafting the matrix polymer onto the rubber backbone.<sup>7–10</sup> Styrene copolymerization with rubbers initiated by a mixture of initiators with different thermal stabilities is widely used for preparation of HIPS (high impact polystyrene) in industry. However, styrene copolymerizations with elastomers in the presence of initiator mixture are for all practical purposes not available in the literature.<sup>11</sup> The aim of this paper is to investigate the mechanical properties of blends of PS- and EPDM-grafted polyblend which was synthesized by using a combination of initiators which has not been reported earlier.

## **EXPERIMENTAL**

### **Materials**

Styrene was made free of inhibitor by usual procedure. Ethylene–propylene–diene monomer rubber [5-ethylidene-2-norbornene] was supplied by Exxon

(U.S.A.). Polystyrene (Polychem Industries, India) was used for blending purpose.

Benzoyl peroxide (AR grade, BDH, India) was recrystallized from chloroform prior to its use. Cumene hydroperoxide (70% in cumene) (Fluka, Switzerland) was used as received. Zinc stearate (commercial grade) was used as plasticizer. The thermal stabilizer (di-*tert*-butyl *para*-cresol) was supplied by Loba Chemie Australanal Co. (India). Benzoyl peroxide (BP) and cumene hydroperoxide (CHP) having different "working temperatures" were chosen as initiators.

### Synthesis

The styrene graft polyblend of EPDM was synthesized by bulk polymerization technique. Typically, 10 g of EPDM is dissolved in 75 mL of styrene and 0.1% benzoyl peroxide is added. The reaction mixture is heated at 80°C for 2 h under nitrogen atmosphere with continuous stirring. Then 0.3% cumene hydroperoxide is added with subsequent heating at 110°C for another 6 h. The sticky product is dissolved in benzene and precipitated in excess of methanol. The product was shredded into small pieces and dried in a vacuum oven at 70°C for 48 h. The yield of product was 75%.

### Characterization

The homopolymer polystyrene is extracted in Soxlet by using 50 : 50 MEK/acetone mixture. The unreacted rubber is extracted by using petroleum ether which dissolves only EPDM but not homopolystyrene. The remaining part consists of grafts and gel. The grafts are removed by using benzene. The graft copolymer is repeatedly extracted with MEK/acetone mixture and petroleum ether to remove homopolystyrene and unreacted EPDM rubber to the maximum possible extent. This graft copolymer was used for the characterization. The characteristics of graft copolymer are given in Table II. The intrinsic viscosities were measured in solvent toluene at 30°C. The molecular weight of EPDM was determined using the equation<sup>12</sup>

$$[\eta]_{\text{tol}}^{30^\circ\text{C}} = 3.1 \times 10^{-4} (\bar{M}_w)^{0.7}$$

The <sup>1</sup>H-NMR spectroscopy (Varian EM 360L, 90 MHz) study of graft copolymer (Fig. 1) shows the characteristic peak of methyl group of the propylene at about 1.1 ppm and the phenyl proton resonance at 6.2–7.2 ppm. The poly-

TABLE I  
Characteristics of the Materials Used

Name of material	% Composition by weight as determined by IR spectroscopy			Intrinsic viscosity (dL/g)	Mol wt	Density (g/mL)
	Ethylene	Propylene	Diene			
EPDM	42.7	47.9	9.4	1.585	1.4 × 10 <sup>5</sup>	0.86
PS	—	—	—	0.66	1.5 × 10 <sup>5</sup>	1.04

TABLE II  
 Characteristics of Graft Copolymer

System	$\eta_g^a$ (dL/g)	$\eta_h^b$ (dL/g)	$\bar{M}_v$ (homopolymer) PS	Graft efficiency (%)	Graft percentage	% Gel content	Wt percent of PS determined by $^1\text{H-NMR}$
EPDM- <i>g</i> -styrene polyblend	1.2	0.75	$2.7 \times 10^5$	39.57	338.4	13	83.2

<sup>a</sup> Intrinsic viscosity of graft.

<sup>b</sup> Intrinsic viscosity of homopolymer (PS).

styrene weight percent in the graft copolymer is calculated from the  $^1\text{H-NMR}$  spectra.<sup>4</sup>

Gel permeation chromatograms (Fig. 2) were obtained by the Waters Associates' instrument using dilute polymer solutions (0.125%) in toluene at room temperature and a flow rate of 1 mL/min. The chromatograph was equipped with five styragel columns ( $10^2$ – $10^5$  Å). The calibration of the GPC instrument was carried out using well-characterized polystyrene samples of known  $\bar{M}_n$  and  $\bar{M}_w$ . GPC curves show that, EPDM rubber having higher hydrodynamic volume than the EPDM–styrene-grafted species, the lower hydrodynamic volume of graft copolymer in comparison with EPDM rubber may be due to the influence of polymer–solvent interaction of the grafted chain.

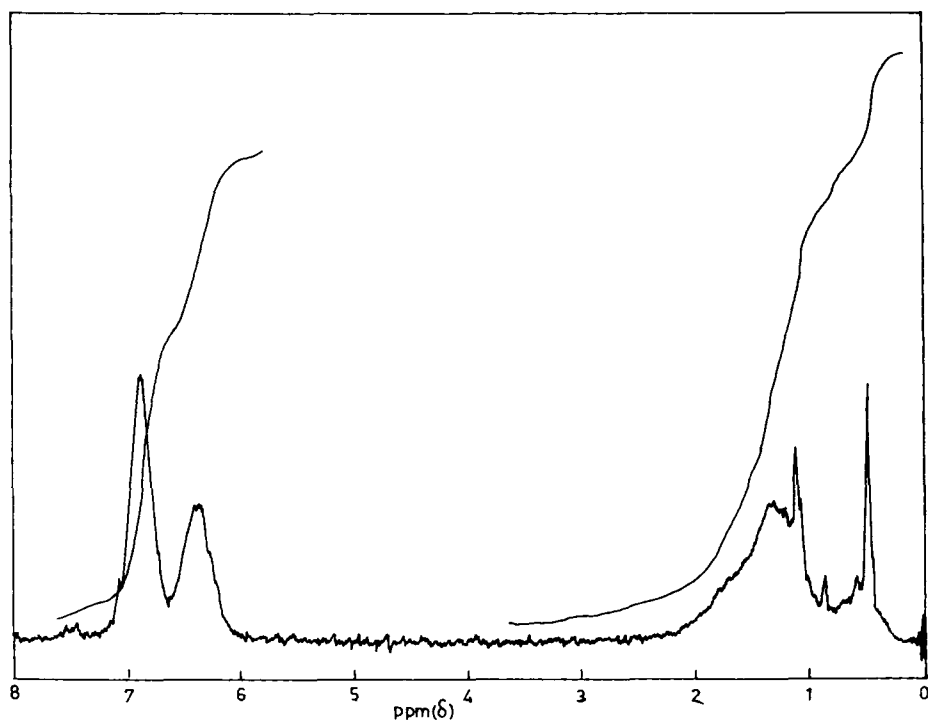


Fig. 1.  $^1\text{H-NMR}$  analysis of graft copolymer.

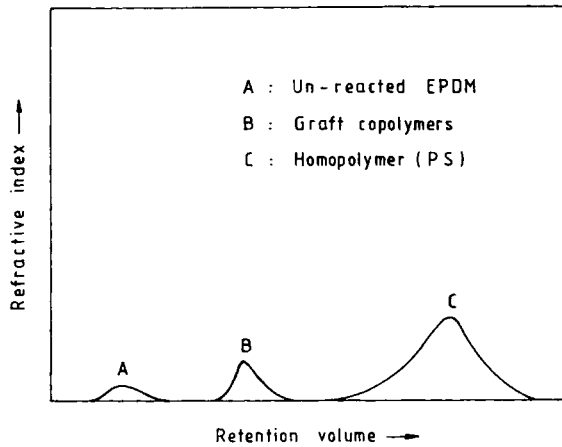


Fig. 2. GPC plot of graft copolymer.

DTA analysis (Fig. 3) has been performed by thermal analyser (Stanton Red Croft, U.K.) using dynamic nitrogen atmosphere up to 350°C. The samples were heated at the rate of 10°C/min. The shift of base line at 100°C is observed, indicating the glass transition temperature of the grafted polystyrene. The degradation temperature of EPDM is 458°C.

### Processing, Molding, and Testing

The graft polyblend and PS mixture is dry-blended with 0.3% di-*tert*-butyl *para*-cresol (Ionol) and 0.2% zinc stearate and then was extruded at 220°C by

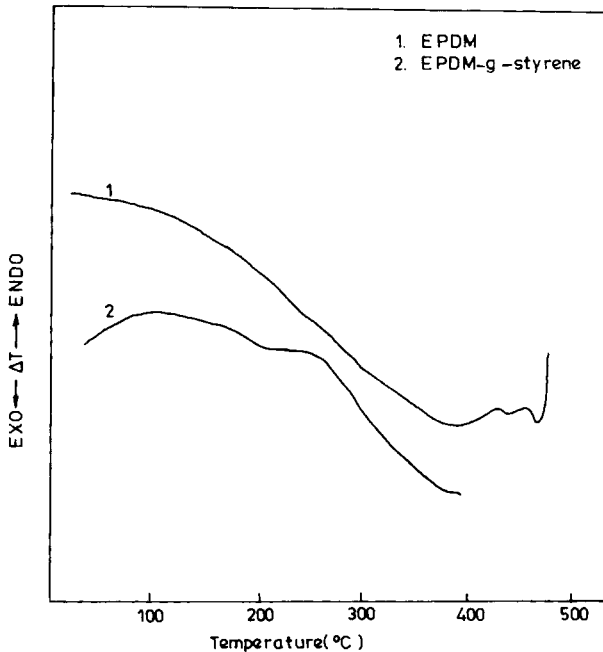


Fig. 3. DTA thermogram of graft copolymer.

Brabender Plasticorder and Extrusiograph. Finally the extrudate is compression molded into a flat sheet at 200°C. Tensile and impact specimens were prepared by cutting the sheet into strips and machining them according to ASTM standards. Tensile property measurements were done on an universal strength testing machine (Fu 10,000, GDR) at room temperature following the procedure described in ASTM D412. All the specimens for the Izod impact strength were prepared according to ASTM-256-256A. The notched Izod impact strength was measured, using an Avery Izod impact testing machine no. 6702 at room temperature. The Izod impact fractured surface of the test specimen was studied, using a scanning electron microscope (SEM) (Camscan, U.K.). The surfaces of the impact fractured specimens were coated with gold to avoid charging under an electron beam.

## RESULTS AND DISCUSSION

The grafting reaction takes place evidently by two ways, i.e., direct attack by hydrogen abstraction of initiator radical and chain transfer on the rubber. While the former is practically the sole one at low temperatures and at higher temperatures above (100°C), the chain transfer reaction also takes place.<sup>13</sup> The reason for high grafting efficiency and graft percentage which is also supported by NMR data is due to the higher resonance stabilization of allylic radicals on ENB (5-ethylidene-2 norbornene) portion of rubber with respect to styrene ones. Hence at higher temperatures with the introduction of second

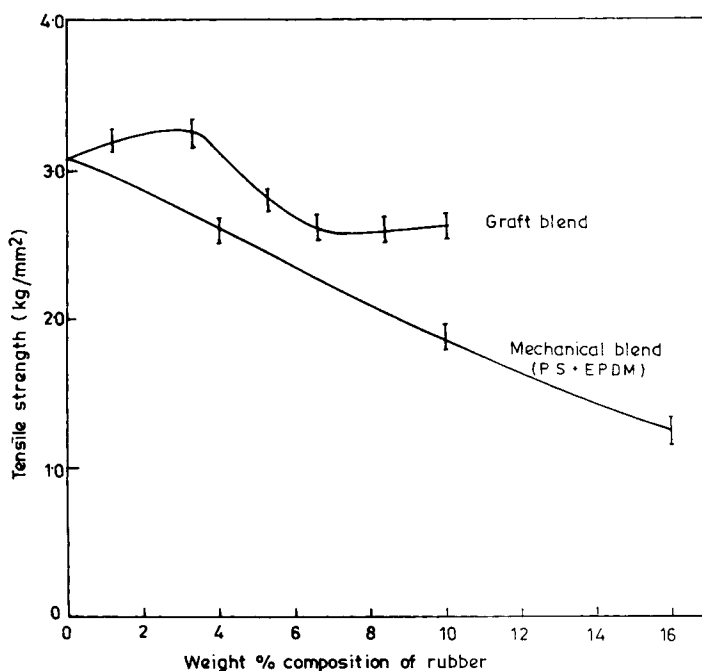


Fig. 4. Tensile strength of graft copolymer blends with PS as a function of rubber composition by weight.

initiator (Cumene hydroperoxide), the grafting reaction increases. Other reasons are higher rubber to monomer ratio and the addition of styrene to radicals formed on the secondary and tertiary carbon atoms.<sup>14</sup>

Figure 4 depicts the tensile strength vs. rubber concentration behavior of graft polyblend. The graft polyblend shows the initial increase of tensile strength then subsequent decrease. Figure 5 shows that the impact strength of graft polyblend increases sharply with respect to the PS/EPDM blend system. Here, the mechanical property study was made only up to 10% of rubber, which is sufficient for giving good impact strength.<sup>15</sup> The improved tensile strength and impact strength values for PS graft polyblend compared to those of the PS/EPDM blends are mainly due to (i) improved adhesion between the rubber and PS phase and (ii) increase of rubber phase volume due to very high grafting percentage and graft efficiency,<sup>16</sup> which reduces the inter particle distance (iii) and the gel content in the matrix. Suggestions made by several authors<sup>16-19</sup> on the mechanism of rubber toughening in polystyrene point out that rubber particles act as stress concentrators and catalyze the formation of fine craze structures (stress whitening) in the surrounding matrix which precedes crack propagation and prevents fracture. Moreover, the efficiency of craze formation decreases when the modulus of rubber phase volume increases.<sup>20</sup>

Electron micrographs (Fig. 6) illustrate irregular features on the fractured surface which account for greater energy absorption.

It is obvious that EPDM which is found as agglomerates in PS/EPDM blends is not there in PS/graft copolymer blends when it is present in form of graft copolymers. There is fine distribution of graft copolymers in the PS matrix. The decrease in the particle size increases the interfacial surface between rubber

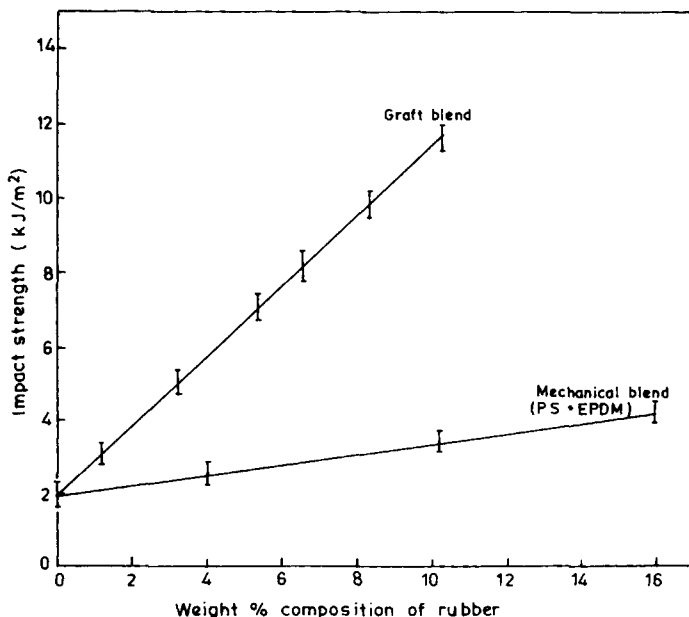


Fig. 5. Impact strength of graft copolymer blends with PS as a function of rubber composition by weight.

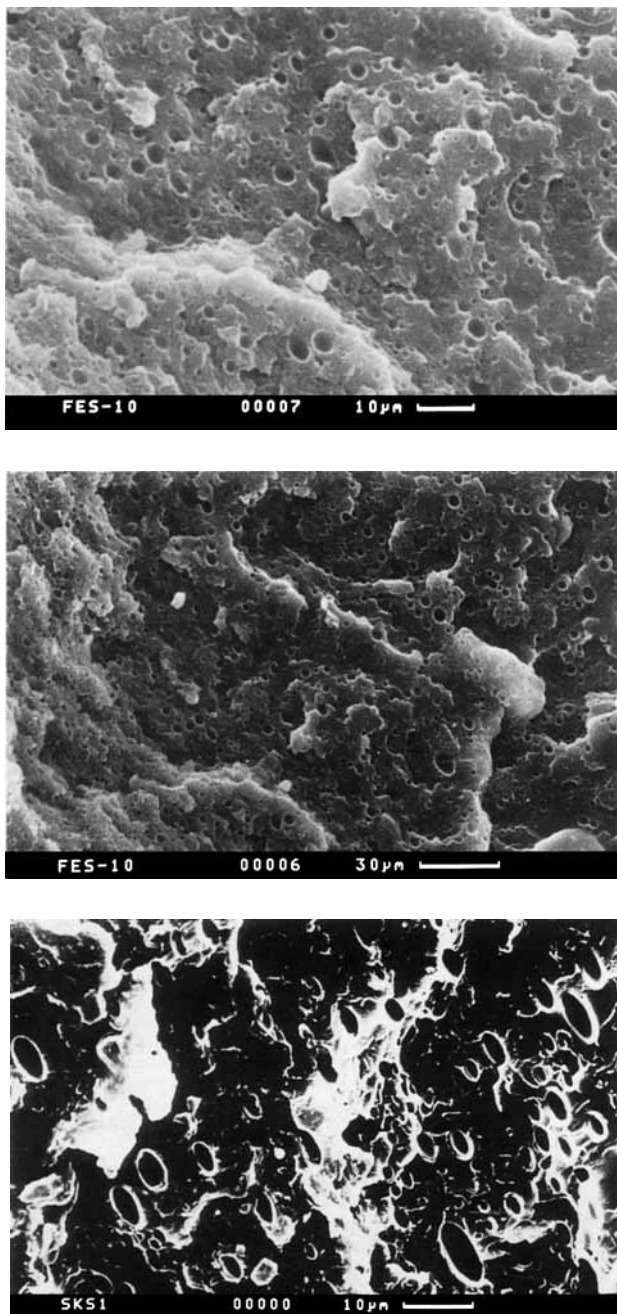


Fig. 6. Scanning electron micrographs: (a, b) graft copolymer and PS blend at 8.25 wt % of rubber; (c) EPDM/PS blend at 10 wt % of rubber.

particles and polystyrene matrix. This can favor the formation of more crazed matter during fracture with consequent increase of impact strength. In the present system, the gel content is increasing with the graft blend composition, contributing to the enhancement of impact strength. But the only amount of

gel content is not sufficient to account for major improvement of impact strength.<sup>21</sup> All the three factors as outlined above enhance the impact strength in PS-graft copolymer blends.

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