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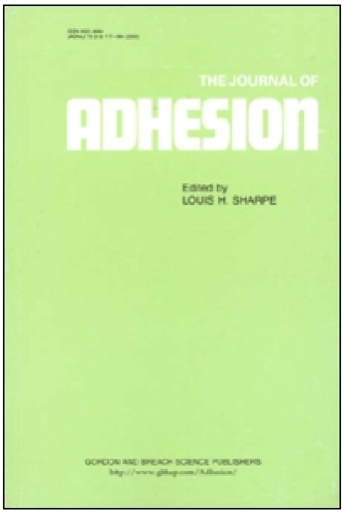

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Tack and Green Strength of Blends of Bromobutyl and EPDM Rubbers. I. Unfilled Gum Blends

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Tack and Green Strength of Blends of Bromobutyl and EPDM Rubbers.
I. Unfilled Gum Blends

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Polymer blends are gaining importance in recent years because they provide a compromise of properties. In this paper, tack and green strength of several blends of EPDM and bromobutyl rubbers (BIIR) have been studied over a wide range of temperaures, contact times and rates.

Tack increases with increase in contact time and with increase in contact temperature up to 47°C for a particular blend. At a much higher temperature the tack strength falls gradually. Green strength increases with increase in bromobutyl content and decreases with temperature. Tack index, a ratio of tack strength divided by the cohesive strength under the same geometry, decreases slowly with the test temperature. At a 50:50 ratio of BIIR:EPDM, the two rubbers form an interpenetrating network as observed under the phase contrast microscope.

KEY WORDS Tack strength; Green strength; Contact time; Bromobutyl rubber; EPDM rubber; Tack index.

INTRODUCTION

Polymer blends have been gaining technological importance because they provide a compromise in properties over the single polymers. In many critical applications such as tyres, belting, etc., blends are useful. Properties of many of these blends are not fully understood. One such blend consists of bromobutyl rubber (BIIR) and ethylene propylene diene (EPDM) rubber used in making conveyor belting.

Few studies have been done on tack and green strength of these two elastomers. Hamed[1–3] has reported tack and green strength of filled and unfilled Natural Rubber (NR), Styrene Butadiene Rubber (SBR) and their blends. Molecular contact,[4,5,6] interdiffusion[7–11] and high cohesive strength are responsible for tack development. Adhesive tack of EPDM rubber has been discussed recently by Bhowmick, *et al.*[12] At a high test rate, tack increases. For unvulcanized soft elastomers the scale of the contact zone has also an effect.[13,14] Some authors[15,16] believe that chain cavities in a polymer chain, consisting of intra-chain free space and inter-chain free space play an important role. Intra-chain free space is a collation of free volume regions contained in cavities, associated with structural features of the rubber chain. NR, having larger size cavities than SBR, shows higher tack than SBR. EPDM has only very few cavities in its propylene segments and shows very poor tack. The existence of strain-induced crystallization in NR, in addition to its high raw tensile strength, enhances its tack strength to a great extent.[17–19] Hamed[20] has also made a similar observation but pointed out that crystallinity or semicrystallinity in materials severely limits chain mobility for tack bond formation. For this reason EPDM and EPM rubbers exhibit poor tack. Bister *et al.*[6] and Wool[21] have derived a relation for the dependence of tack strength on contact time.

This paper presents the results of the tack and green strength of EPDM and BIIR elastomers and their blends over a wide range of compositions, temperatures (both testing and contact) and rates. Morphology and rheological behaviour of blends are also reported.

EXPERIMENTAL

Raw materials

EPDM rubber (Royalene 521, viscosity ML4 @ 100°C, 45, $\bar{M}_v = 8.9 \times 10^4$ g/g·mole, supplied by UniRoyal Chemical, Naugatuck, USA) and Bromobutyl rubber (BIIR) (Polysar Bromobutyl ×2, viscosity ML4 @ 100°C, 37.5, $\bar{M}_v = 7.91 \times 10^5$ g/g·mole, supplied by Andrew Yule and Co. (P) Ltd., Kalyani, Nadia) were used. Seven different blend compositions were chosen. Ratios of EPDM to BIIR in these blends were 100:0 (M1), 80:20 (M2), 70:30 (M3), 50:50 (M4), 30:70 (M5), 20:80 (M6) and 0:100 (M7).

Mixing procedure

The mixes were prepared in a laboratory-size Brabender plasticorder (PLE 330). The sheets of the elastomers made by passing the elastomers through two-roll mill were cut into narrow ribbons and fed in the Brabender. The torque of the EPDM was lowered in the Brabender from an initial value of 56 Nm to a value of 33 Nm at 64°C and 25 rpm rotor speed. The initial torque of BIIR was 25 Nm and was used as such. For preparing blends elastomer ribbons were fed alternatively at a head temperature of 62 ± 2°C. A mixing time of five minutes was allowed in each case for final blending.

Sample preparation and determination of tack strength and tack index

For determination of tack strength, sheets of 2.5 ± 0.05 mm thickness were prepared in an electrically-heated hydraulic press. One side of the sheet was backed by cloth. Sheeting was done at 100°C for 5 minutes between smooth aluminium foils. From these sheets narrow strips (1 cm × 6 cm) were cut. The aluminium foils were removed and the strips were allowed to come in contact quickly over a length of 4 cm. A dead load of 700 gms was applied. The time and temperature of contact were varied. The force of separation of the two strips was measured in an Instron machine (1195 model) using a T-peel geometry as shown in Figure 1. A separation rate of 500 mm/min was used. The tack strength was calculated by using the relation,

$$G_a = \frac{2F}{w} \tag{1}$$

where,

G_a = fracture energy per unit area

F = average force required for peeling

w = width of the strip.

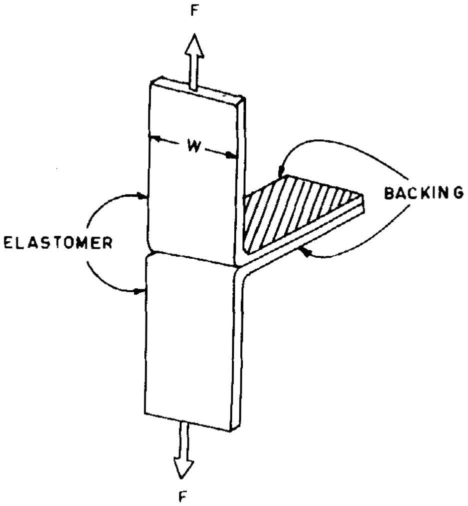

FIGURE 1 T-peel test geometry.

Using the same sample pieces, cohesive strength of the samples was measured for different blends. Two strips (1 cm × 6 cm) were pressed together and the force of separation was measured. Tack index was obtained by taking the ratio of tack strength to cohesive strength.

Determination of gum strength

The tensile strength of the various blends was measured according to ASTM D412-51T, using dumbell-shaped specimens in the Instron machine (1195 model) at different rates and temperatures. Sheets of about 2.5 mm thickness were prepared in the press at a temperature of 100°C for 5 mins.

Rheological measurements

Rheological measurements were carried out by using a capillary rheometer MCR 3210 attached to an Instron Universal Testing Machine, model 1195. The capillary length to diameter ratio (lc/dc) was 40 with an angle of entry of 90°. The sample was preheated inside the barrel for 5 minutes and then extruded through the capillary at pre-selected speeds ranging from 0.5 to 200 mm/min of the cross-head. Forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and the cross-head speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations, involving the geometry of the capillary and the plunger:[22]

$$\tau_w = \frac{F}{4A_p(\mathrm{lc}/\mathrm{dc})} \tag{2}$$

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'}\right) \cdot \frac{32\theta}{\pi dc^3} \tag{3}$$

where F is the force applied at a particular shear rate, A_p is the cross-sectional area of the plunger, lc the length of the capillary and dc the diameter of the capillary. 'θ', the volumetric flow rate, was calculated from the velocity of the cross-head and diameter of the plunger. 'n'', the flow behaviour index defined by $d(\log \tau_w)/d(\log \dot{\gamma}_a)$, was determined by regression analysis of the values of τ_w and $\dot{\gamma}_a$, obtained from the experimental data. $\dot{\gamma}_a$ is the apparent wall shear rate calculated as $32\theta/\pi dc^3$. The shear viscosity η was calculated from τ_w and $\dot{\gamma}_w$.

Study of morphology

Morphology of the unfilled gum blends was studied in a Karl–Zeiss phase contrast microscope. Very thin films (thickness of about 0.1 mm) were prepared by pressing a very small quantity of sample between two aluminium foils at a temperature of 100°C for 5 mins. A portion of the thin film was cut and mounted on a slide by using glycerine and tested under the microscope. Photographs were made with a slow-speed camera.

RESULTS AND DISCUSSION

Tack strength and tack index

Tack strength of gum blends at different contact times at room temperature is shown in Figure 2. In all the cases, tack increases

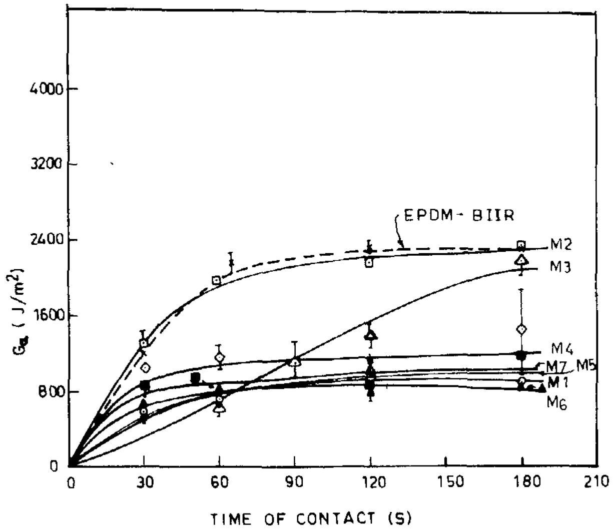

FIGURE 2 Tack strength of gum blends and EPDM to BIIR at different contact times at 24°C.

initially with contact time and ultimately reaches a plateau. The initial increase of tack is due to gradual interdiffusion of rubber molecules and to increasing surface contact during the bonding step caused by flow under stress. At about 180 seconds, interdiffusion is almost complete and the equilibrium is reached. Figure 2 shows also the tack strength of the EPDM/BIIR joint. The result for this case is almost identical, *i.e.*, adhesion increases with time of contact and reaches a plateau. The blend containing 80% EPDM and 20% BIIR gives the highest value of tack strength at room temperature. The value is similar to the tack strength of the EPDM/BIIR joint. The high tack strength between EPDM and BIIR may be attributed to their similar solubility parameters ($\delta_{\mathrm{EPDM}} = 7.95$; $\delta_{\mathrm{BIIR}} = 7.84$).

Figure 3, a plot of logarithm tack strength *versus* the logarithm contact time for $t < t_{\mathrm{plateau}}$ shows that the tack strength is proportional to (contact time).$^{1/2}$ It has previously been reported[21] that tack strength G_a is given by

$$G_a \sim t^{1/2} M^{-1/2} R^{1/2} \tag{4}$$

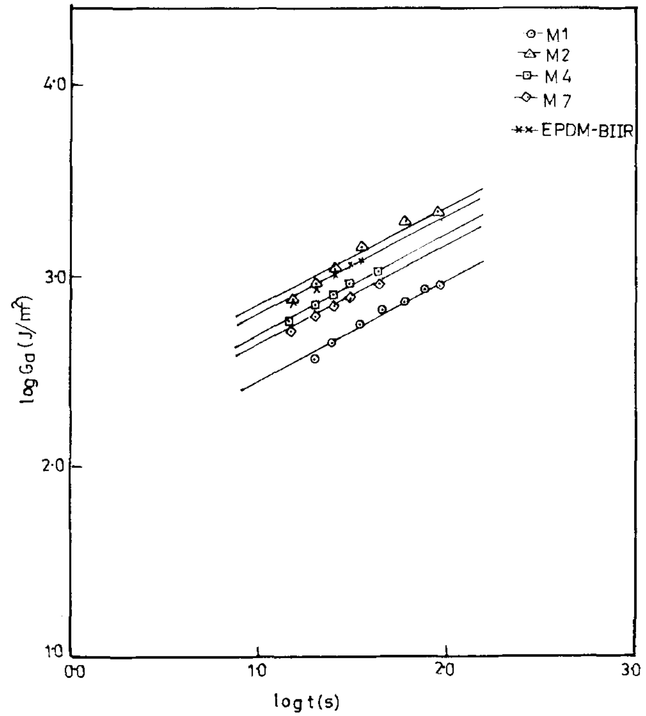

FIGURE 3 Plot of logarithm tack strength *versus* logarithm contact time of several gum blends and EPDM-BIIR at 24°C.

where,

R = rate of testing

M = molecular weight

t = time of contact

For the same set of samples when R and M are the same,

$$G_a \sim t^{1/2} \tag{5}$$

Hence our experimental values are in accord with the theory. For all the BIIR-EPDM blends, this relationship has been found to be true. Skewis[18] also found similar results for SBR and butyl rubber.

Bhowmick *et al.* reported similar dependence for EPDM/NR and EPDM/CR joints.[12]

The initial increase in tack strength resulting from incorporation of BIIR may be due to the presence of polar groups in the matrix. The highest value in the case of 80:20, EPDM:BIIR, at 24°C may, however, be due to a combinatorial effect of polarity and molecular weight. The same blend has the highest value of shear viscosity at shear rates of $20\,s^{-1}$ to $2500\,s^{-1}$, indicating the fact that the resistance to deformation is greater (Figure 4).

The approximate diffusion coefficient, D, of an elastomer may be estimated[21] from,

$$D \sim M^{-2} \tag{6}$$

where M is the molecular weight. The viscosity average molecular weight for BIIR and for EPDM are 7.91×10^5 and 8.9×10^4 respectively. The ratio of the diffusion coefficients of BIIR and EPDM calculated from relation (6) is 0.0125. It must be noted here that BIIR, having a lower diffusion coefficient, will diffuse less rapidly than EPDM in the blends. The maximum in the plot of tack

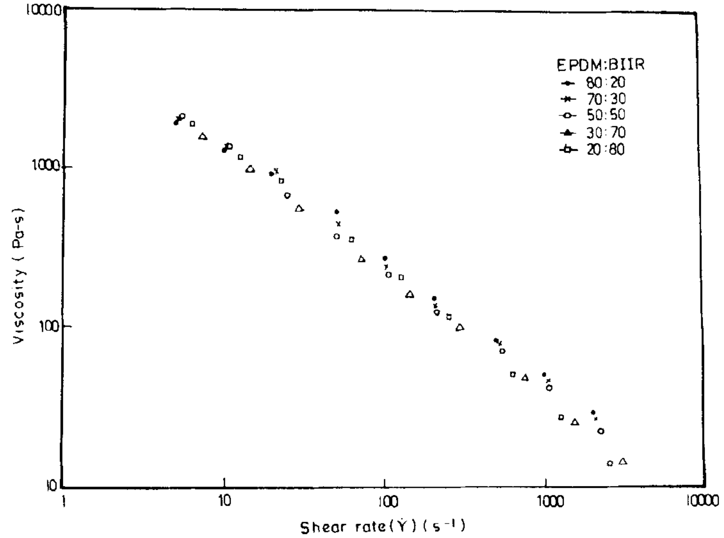

FIGURE 4 Logarithmic plot of shear rate *versus* viscosity of different blends at 100°C.

strength *versus* blend composition probably arises from the combined effects of diffusion and polarity.

A plot of tack strength *versus* blend ratio (Figure 5) shows that the blend of EPDM:BIIR, 80:20, gives the maximum tack strength at room temperature. It decreases slowly with increase of BIIR content after the maxima. The decrease of tack strength with incorporation of BIIR after the maxima is due to lesser diffusion of high molecular weight BIIR. The tack of pure EPDM, however, is improved by the addition of BIIR. Tack strength at different temperatures has also been plotted in Figure 5 for various blends. It shows an optimum at 47°C and then gradually decreases. The increase of tack strength with increase in temperature is due to higher rate of interdiffusion of macromolecules. However, at very high temperature, the green strength of BIIR falls rapidly (shown later); hence the tack strength decreases. The polar nature of BIIR and its matching solubility parameter are probably responsible for the increase of tack of EPDM with incorporation of BIIR.

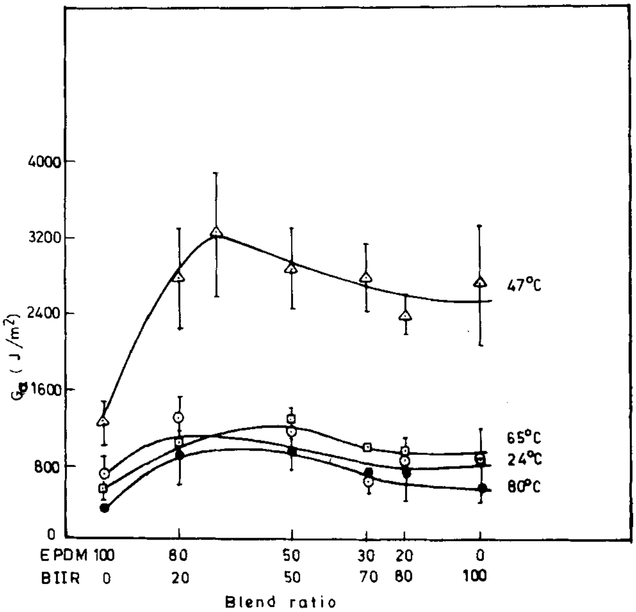

FIGURE 5 Relationship between tack strength and blend compositions at different temperatures.

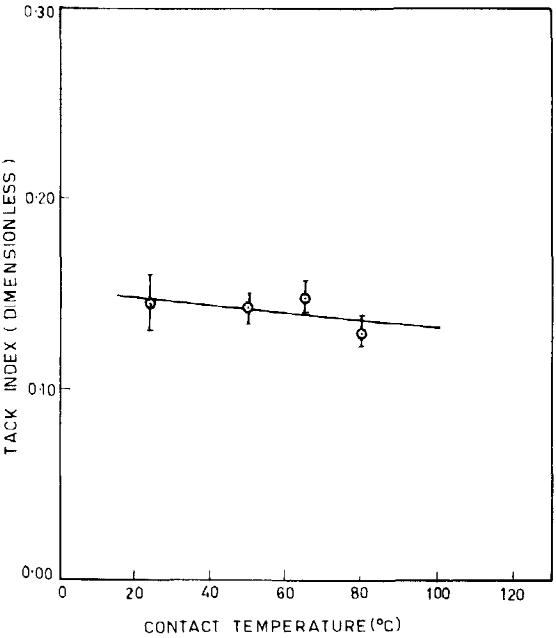

FIGURE 6 Tack index of a 50/50 EPDM/BIIR blend at different temperatures.

Figure 6 is a plot of tack index (ratio of tack strength and cohesive strength under the same geometry) of a 50:50 blend of EPDM and BIIR against contact temperature. With the increase of temperature the tack index goes down slowly. Similar behaviour has been observed by Skewis[17] for natural rubber. This can be explained by the fall in cohesive strength with temperature.

Green strength

The maximum strength that an adhesive joint can achieve is the cohesive strength of the weaker substrate. In order to understand the cohesive fracture, the green strength of all the blends was studied.

Measurement of green strength of different gum blends at different rates of test shows that the green strength of a particular blend increases rapidly with increase in test rate (Figure 7). This property also increases in value with increase in BIIR content in the

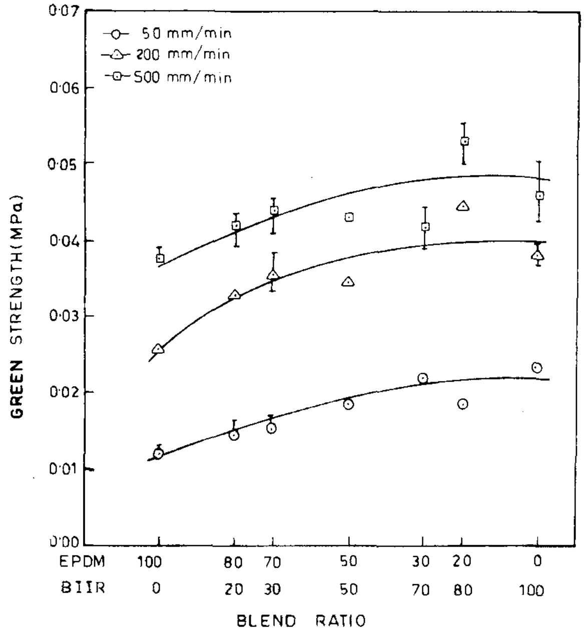

FIGURE 7 Green strength of gum blends at different test rates at 24°C.

blend at a particular test rate. At higher test rates, the coiled elastomer molecules do not have sufficient time to relax. Breakage of these coiled molecules requires a large amount of energy; hence the green strength is high. During testing at low rate the coiled elastomer molecules have sufficient time to relax and uncoil. Flow and rupture of the uncoiled chains require less energy; hence the green strength is low.

The green strength decreases with increase in test temperature (Figure 8). The blend containing higher amount of BIIR has higher tensile strength at a particular temperature. The decrease in strength is due to reduction of viscosity of the elastomers at higher temperature. This is evident from the decrease of the Brabender torque value [$\text{Torque}_{\text{EPDM}}$ (at 30°C) = 43 Nm, $\text{Torque}_{\text{BIIR}}$ (at 30°C) = 29 Nm, $\text{Torque}_{\text{EPDM}}$ (at 80°C) = 30 Nm, $\text{Torque}_{\text{BIIR}}$ (at 80°C) = 20 Nm, at a rotor speed of 25 rpm].

The green strength (σ_b) has been plotted against viscosity average

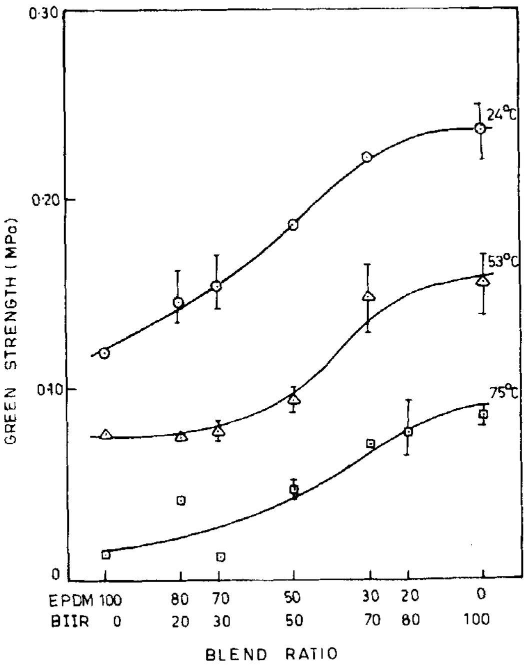

FIGURE 8 Green strength of gum blends at different temperatures and at 50 mm/min test rate.

molecular weight $\bar{M}$ in Figure 9. The relation between green strength and test rate (ε) is shown on the same plot. It must be mentioned here that the molecular weight was calculated theoretically by taking the weight fraction of each component (ϕ_1 and ϕ_2) as follows:

$$\bar{M} = \phi_1 M_1 + \phi_2 M_2 \tag{7}$$

where M_1 and M_2, the molecular weights of individual components, have been determined from viscometric measurement. From Figure 9 it is evident that the slope of the plot of σ_b *versus* $\bar{M}$ is approximately one-fourth. Straight lines with a slope of one-half are drawn through the points for the plot of σ_b against test rate (ε). It has been observed that most of the points fall on the lines. Hence,

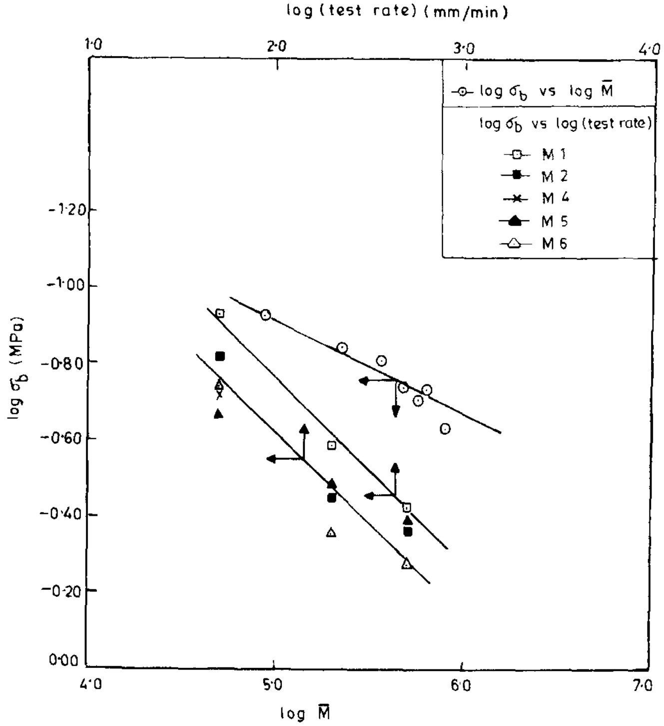

FIGURE 9 Logarithmic plot of green strength of different blends against molecular weights of the blends and test rates.

we could write the following relations,

$$\sigma_b \sim \bar{M}^{1/4} \tag{8}$$

$$\sigma_b \sim \varepsilon^{1/2} \tag{9}$$

MORPHOLOGY

It is well known that the morphology of rubber blends determines the physical properties of many blend systems.[23] Hence a study of morphology was undertaken. The EPDM phase appears white and the BIIR phase appears dark under the phase contrast microscope.

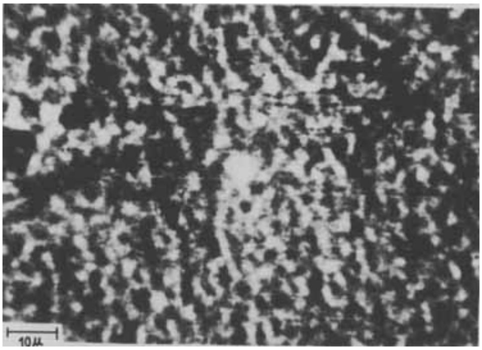

FIGURE 10 Morphology of 50/50 EPDM/BIIR blend.

A 50:50 blend of both the elastomers reveals that the elastomers form a homogeneous interpenetrating network. Gardiner[24] found similar results for an EPDM and butyl rubber blend. With the increase in one of the components in the blend the morphological structure changes marginally (shown in Figures 10 and 11). The elongated particles become smaller in size and spherical in shape as shown for a 20:80 blend of EPDM:BIIR. We do not see, however, any discrete particles of the small component distributed in the matrix of the large component as observed by Gardiner[24] for chlorobutyl/SBR and NR/SBR blends. The similarity in morphological structure may be due to the similar values of solubility parameter ($\delta_{S\,\mathrm{EPDM}} = 7.95$ and $\delta_{S\,\mathrm{BIIR}} = 7.84$). From this morphological study of the blends the difference in the tack strength

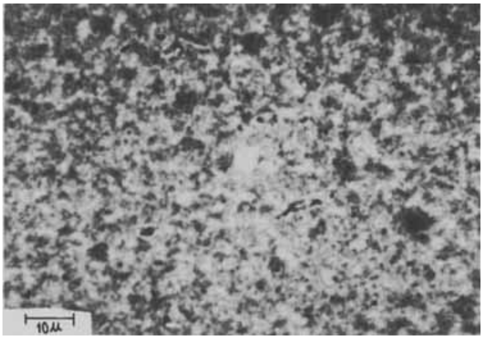

FIGURE 11 Morphology of 20/80 EPDM/BIIR blend.

could not, however, be explained. Hence, we would propose that the reasons for the differences in tack strength and green strength of the various blends lie with the polarity of the BIIR phase and the rheological behaviour of the blends.

SUMMARY

Tack and green strength of EPDM, BIIR and their blends (unfilled) have been reported at different temperatures, contact times and test rates. Poor tack of EPDM was improved by the incorporation of BIIR. At room temperature, the blend containing 80% EPDM and 20% BIIR gave the highest value of tack strength probably due to changes in the rheological behaviour and polarity of the system. Tack strength of the pure elastomers and their blends varied as the square root of the contact time (t) at $t < t_{\text{plateau}}$, where t_{plateau} is the time of contact for attaining an almost constant tack strength. Interdiffusion, increase in surface contact during the bonding step and gum strength of the blends are the main factors affecting tack in elastomers. With the rise of temperature, the tack of the blends increases up to a maximum and then falls. Green strength increases with the rate of test and BIIR content in the blend. With rise of temperature the gum strength falls. This is due to decrease in viscosity of the blends at higher temperature. The green strength varies as the one-fourth power of the molecular weight and as the square root of the test rate.

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