Compatibility and Viscoelastic Properties of Brominated Isobutylene-*co-p*-Methylstyrene Rubber/Tackifier Blends

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ABSTRACT: Brominated isobutylene-*co-p*-methylstyrene (BIMS) rubber has been blended with hydrocarbon resin tackifier and alkyl phenol formaldehyde resin tackifier, and the compatibility between the blend components has been systematically evaluated. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) studies show that BIMS rubber and hydrocarbon resin tackifier blends are compatible at all blend proportions studied. However, BIMS rubber and phenol formaldehyde resin blends exhibit very limited compatibility with each other and phase separation even at very low phenolic tackifier concentration. Morphological studies of the rubber–resin blends by scanning electron microscopy (SEM) corroborate well with the DMA and DSC results. From the DMA frequency sweep and temperature sweep studies, it is shown that the hydrocarbon resin tackifier acts as a diluent and causes a decrease in the storage modulus values (by reducing the entanglement and network density) in the rubbery plateau region. On the other hand, phenol formaldehyde resin behaves in the way similar to that of the reinforcing filler by increasing the storage modulus values (by increasing the entanglement and network density) in the rubbery plateau zone. The relaxation time estimated from the different zones of frequency sweep master curves provides information about the influence of the two tackifiers on the viscoelastic properties of the BIMS rubber in the respective zones. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1485–1497, 2008

Key words: BIMS; dynamic mechanical analysis; viscoelastic properties; compatibility; tackifier; rubber

INTRODUCTION

In the rubber industry, tackifiers are used to improve the tack and tack retention of compounded elastomers.[1–3] Tackifiers are generally added at lower concentration (between ∼ 1 and 15 phr) to improve the autohesive tack of the elastomers.[3] On the other hand, pressure sensitive adhesive blend compositions contain relatively very high amount of tackifier concentration (>30 phr) to achieve the required adhesive tack. Three major types of tackifiers are: hydrocarbon tackifiers, rosin and its derivatives, and phenol–formaldehyde resins.[1] Tackifying resins typically have a molecular weight of ca 2000 or less.

Brominated isobutylene-*co-p*-methylstyrene (BIMS) rubber is a new invention in butyl rubber series. BIMS rubbers are commercially known as Exxpro™ elastomers. Exxpro™ elastomers are highly evaluated in variety of tire compounds including inner liner,[4] side wall,[5] and treads.[6] Hubbard et al.[7] and Briddell and Hubbard[8] have shown that useful adhesives in either solvent or cured tape form can be formulated using BIMS in combinations with copolymers. Tse et al.[9] have studied the bonding and the debonding behavior of BIMS/tackifier pressure sensitive adhesive compositions through rheological and stress–strain characterization. Because BIMS elastomer is highly evaluated in the adhesive industry and in tire components (inner liner, side wall, and treads), the adhesive tack and the autohesive tack property of this elastomer is indispensable. Proper choice of tackifier is a prerequisite for achieving good adhesive and autohesive tack in any rubber–tackifier mixture. Bhowmick and coworkers[10] have investigated the autohesive tack and green strength of BIMS rubber and its blends with reference to level of bromination, fillers, nature of rubber, and blend ratio. Low molecular weight tackifiers are blended with this elastomer at lower concentration to enhance the autohesive tack and to prevent the tack degradation.[11,12] While dealing with rubber/tackifier mixtures, it is necessary to examine to what extent the components are compatible with each other because the compatibility has a greater influence on the phase

TABLE I
Composition of Mixes Prepared

Sr. no.	Designation	BIMS rubber	Hydrocarbon resin (phr)	Sr. no.	Designation	BIMS rubber	Phenolic resin (phr)
1	B	100	0	10	B	100	0
2	BE1	100	1	11	BSP1	100	1
3	BE3	100	3	12	BSP3	100	3
4	BE5	100	5	13	BSP5	100	5
5	BE7	100	7	14	BSP7	100	7
6	BE10	100	10	15	BSP10	100	10
7	BE15	100	15	16	BSP15	100	15
8	BE20	100	20	17	BSP20	100	20
9	BE30	100	30	18	BSP30	100	30

structure, physical properties, and practical performance (rheological properties) of the adhesive materials. In literature, there are several reports which explain the compatibility between various tackifiers and elastomers.[13–18] For example, Aubrey and Sherriff studied the viscoelastic and adhesion properties of the blends of natural rubber with pentaerythritol ester of hydrogenated rosin and poly(β-pinene) tackifiers.[16] Class and Chu investigated the effect of *tert*-butylstyrene and cycloaliphatic poly(vinyl cyclohexane) tackifiers on the viscoelastic properties of the natural rubber and styrene–butadiene rubber based adhesive compositions.[17] Hot melt pressure-sensitive adhesives or block copolymer/tackifier resin systems have also been studied.[19,20]

However, reports, which examine the compatibility between the BIMS rubber and the tackifiers are not available. Therefore, the compatibility of tackifiers with BIMS rubber is worth investigating. In this study, the compatibility of BIMS rubber with C_5-aliphatic unmodified hydrocarbon resin tackifier and Novolak-based alkyl phenol–formaldehyde tackifier has been systematically examined and the effect of compatibility on the viscoelastic behavior of the BIMS/tackifier blends has been reported. Ultraviolet–visible (UV–vis) spectroscopy, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) have been used to discern the tackifier compatibility with BIMS rubber.

EXPERIMENTAL

Materials

BIMS 3035 (grade: Exxpro™ 3035; benzylic bromine of 0.47 ± 0.05 mol % and 2.0 mol % of *p*-methylstyrene, Mooney viscosity of 45 ± 5 at ML_{1+8} 125°C and $M_w = 450,000$), Escorez™ hydrocarbon resin (grade: E1102; softening point, 96–104°C; Glass transition temperature, 50°C; $M_w = 2400$) were supplied by Exxon Mobil Chemical Company, Baytown, TX, and octylphenol–formaldehyde, thermoplastic phenolic resin tackifier (grade: SP1068; softening point, 85–

95°C; Glass transition temperature, 35°C) was supplied by Schenectady International, New York.

Preparation of rubber–resin blend

The mixes were prepared in a Brabender Plasticorder (model, PLE-330, capacity 65 mL) at 130°C and 110°C at 60 rpm for BIMS/hydrocarbon resin and BIMS/phenolic resin blends, respectively. BIMS was taken in the Brabender and sheared for 2 min and then the tackifier was added and mixing was continued for additional 3 min. The neat BIMS rubber was also mixed for 5 min under the same condition. The composition of the mixes prepared is reported in Table I.

UV–vis spectroscopy

The UV–vis spectra of the samples were recorded with a UV–vis spectrophotometer (Perkin–Elmer, Waltham, MA). UV–vis spectra (% transmittance) of the films of thickness 0.3 mm were recorded at room temperature (25°C). The samples were scanned in the wavelength region from 200 to 600 nm.

Measurement of glass transition temperature (T_g) by DSC

The T_g of neat BIMS rubber and rubber–resin blends was measured by DSC (DSC Q 100 from TA Instruments, New Castle, DE), in the temperature of −80 to 100°C at a heating rate of 10°C/min in nitrogen atmosphere. The T_g of the tackifiers was measured in the temperature range of 0–100°C at a heating rate of 10°C/min in nitrogen atmosphere. The samples of 5–10 mg were encapsulated in standard aluminum pans.

Dynamic mechanical analysis

Temperature ramp test

Temperature ramp test was carried out in a dynamic mechanical analyzer (DMAQ 800 from TA

Instruments, USA), in the temperature range of $-100°C$ to $100°C$ for pristine BIMS and BIMS/tackifier blends at a constant frequency of 1 Hz and at a constant strain of 0.1% in tension mode geometry. Because tackifiers are low molecular weight species, determination of T_g via tan δ peak requires special test geometry because tension mode geometry will not be able to resolve the tan δ peak of the tackifiers. Therefore, glass fiber cloth was impregnated with the tackifier powder at $110°C$ to a uniform thickness following a procedure given by Tobing and Klein.[21] Then the temperature sweep was carried in DMA, in the temperature range of $0–100°C$ for both the tackifiers at a constant frequency of 1 Hz and at a constant strain of 0.1%. Glass fiber cloth was chosen because it only exhibited glassy behavior throughout the test temperature $(0–100°C)$ range.

Frequency sweep test

The frequency sweep tests were carried out in a dynamic mechanical analyzer (DMAQ 800 from TA Instruments) in tension mode geometry. Measurements were made at 15 frequencies in the 0.01–25 Hz range at 0.1% strain and at different temperatures between -50 and $50°C$. All the results were reduced to $25°C$ and shifted to form master curves by applying time–temperature superposition principle and the results are presented as storage modulus E' against frequency.

Surface morphology study

Scanning electron microscope studies

The dispersion of tackifiers in the rubber matrix was examined by JEOL, JSM 5800 (Japan) scanning electron microscope (SEM) after sputter coating the samples with gold.

RESULTS AND DISCUSSION

Evaluation of compatibility between BIMS rubber and tackifiers

To examine the compatibility of BIMS/tackifier blends, the transparency of the films obtained by compression molding for 5 min at $110°C$ was checked by measuring the % transmittance of the UV–vis radiation through the films. Figure 1 shows the UV–vis spectroscopy of neat BIMS rubber and BIMS/tackifier blends. In both the visible (400–500 nm) and near ultraviolet (200–400 nm) regions, the % transmittance of UV–vis radiation is higher for the neat BIMS rubber. With the addition of the 10 phr of hydrocarbon resin tackifier, the % transmittance of UV–vis radiation decreases. This is perhaps due to the presence of the second component
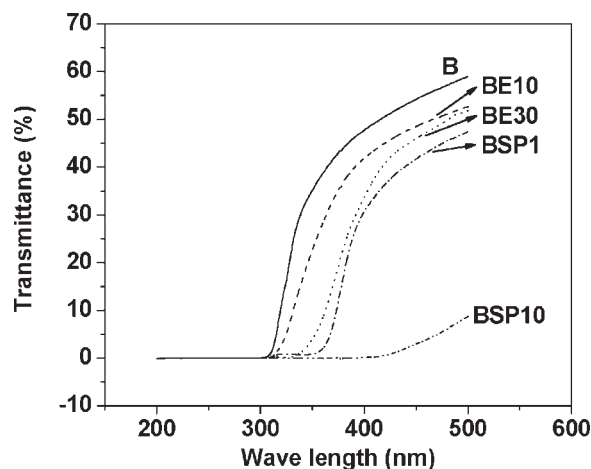

Figure 1 UV–vis spectra of B, BE10, BE30, BSP1, and BSP10.

in the BIMS rubber. However, even at 30 phr (BE30) of hydrocarbon resin concentration, there is only 13% reduction in the % transmittance of the UV–vis radiation from the total % transmittance of the neat BIMS rubber. This shows that BIMS/hydrocarbon resin mixtures are homogenous even at 30 phr resin concentration suggesting better compatibility between the blend components. On the other hand, the % transmittance of UV–vis radiation drastically decreases for the BIMS/phenolic resin blend. The sample containing 1 phr of phenolic resin tackifier (BSP1) shows 23% reduction in the % transmittance of UV–vis radiation from the total % transmittance of the neat BIMS rubber. This shows that BIMS/phenolic resin blends are not homogeneous even at lower resin concentration suggesting the limited compatibility between the blend components. However, the film transparency test alone does not provide unequivocal proof regarding the compatibility of a polymer pair, because an incompatible polymer pair may yield clear films when the refractive indices of the two polymers are equal. The final evidence in support of the compatibility is available from the glass transition temperature (T_g) studies. Therefore, the following paragraphs explain the results of the glass transition (T_g) studies of the BIMS/tackifier blends measured using DSC and DMA.

Evaluation of compatibility of BIMS rubber–hydrocarbon resin blends through DMA and DSC

The DMA of hydrocarbon resin tackifier impregnated in glass fiber cloth is shown in Figure 2. From the tan δ peak, the T_g is estimated as $77°C$ for the hydrocarbon resin tackifier. Dynamic storage modulus (E') and tan δ of neat BIMS rubber and rubber/resin blends (BE10 and BE30) are shown in Figure 3 (The results of other samples are omitted for clarity

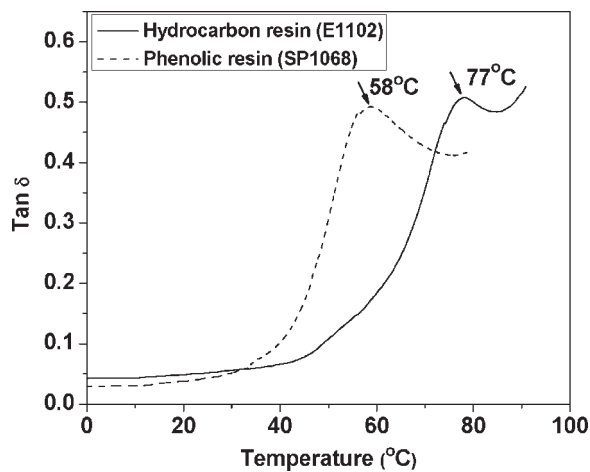**Figure 2** DMA tan δ peaks of hydrocarbon resin and phenolic resin tackifier impregnated in glass cloth.

in the figure). For BE10 and BE30, the tan δ peak temperature has shifted toward higher temperature and E' is depressed in the plateau region compared to the unmodified rubber (E' value of samples B, BE10 and BE30 at 25°C are 0.925, 0.476, and 0.347 MPa respectively) and there is no evidence of another peak in the tan δ curve, suggesting good compatibility between hydrocarbon resin and BIMS rubber. The dynamic mechanical properties of rubber–resin mixture suggest that BIMS/hydrocarbon resin mixtures are homogenous and compatible at all the proportions studied.

Previous investigators[22,23] have used Fox equation [eq. (1)] to analyze the glass transition of the homogeneous elastomer/tackifier blends and it has been suggested that Fox equation gives the most satisfactory agreement with observations of the tan δ peak temperature.[22]
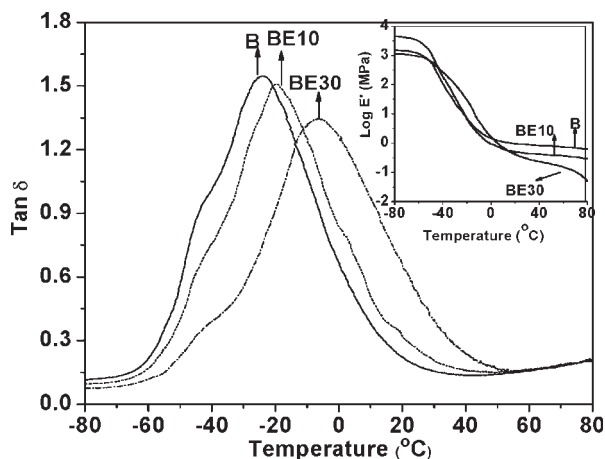
TABLE II
T_g Values of Neat BIMS and BIMS/Hydrocarbon Resin Blends from DMA

Sr. no.	Sample name	T_g (tan δ_{max}) (°C)
1	B	−24
2	BE1	−24
3	BE5	−21
4	BE10	−19
5	BE15	−13
6	BE30	−6

$$\frac{1}{T_{g,b}} = \frac{w_p}{T_{g,p}} + \frac{w_r}{T_{g,r}} \tag{1}$$

where $T_{g,b}$ = glass transition temperature of the blend; $T_{g,p}$ = glass transition temperature of the base polymer; $T_{g,r}$ = glass transition temperature of the resin; w_p = weight fraction of base polymer; w_r = weight fraction of resin.

Equation (1) can be rearranged to give

$$\frac{1}{T_{g,b}} = \frac{1}{T_{g,r}} + w_p \left(\frac{1}{T_{g,p}} - \frac{1}{T_{g,r}} \right) \tag{2}$$

Accordingly, a plot of $1/T_{g,b}$ versus W_p should be a straight line.[22,23] Here, while determining the glass transition temperature (T_g) of the polymer compositions through dynamic measurement techniques, the temperature at which tan δ is maximum is taken as the glass transition of the polymers. The T_g values of different BIMS/hydrocarbon resin blends are presented in Table II. The T_g values for BIMS/hydrocarbon resin blends have also been calculated from eq. (2), taking the experimental values of T_gs for neat rubber and the resin. The measured values of $1/T_{g,b}$ from the tan δ curves of Figure 3 and the theoretical values are plotted for the blends in Figure 4. For the hydrocarbon resin concentration up to 30 phr, the
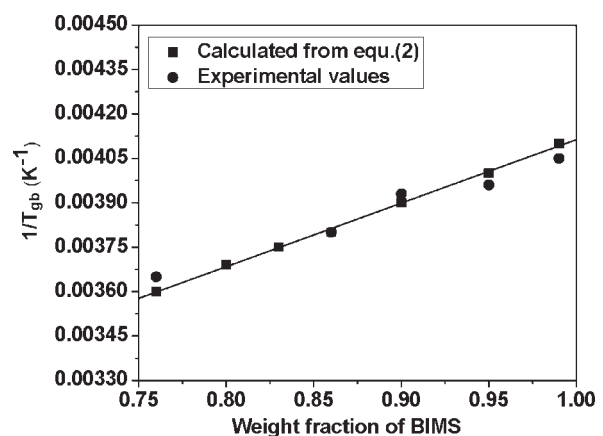

Figure 3 Tan δ versus temperature curves of B, BE10, and BE30. Inset: Log E' versus temperature curves of B, BE10, and BE30.

Figure 4 Comparison of experimental T_g values with the calculated T_g values for BIMS/hydrocarbon resin blends from eq. (2).

TABLE III
Effect of Hydrocarbon Resin Tackifier and Phenolic Resin Tackifier on the Viscoelastic Properties of the BIMS/Tackifier Blends

Sr. no.	Samples	Plateau modulus G_n^0 (MPa)	Entanglement spacing molecular weight (M_e) (g/mol)	Network density υ ($\times 10^{-4}$ mol/cm^3)	Monomer friction coefficient ζ_0 ($\times 10^{-5}$ Ns/m)
1	B	0.79	3345	2.9	4.07
2	BE1	0.72	3605	2.7	–
3	BE10	0.41	6398	1.5	7.41
4	BE30	0.23	11,017	0.9	44.66
5	BSP1	0.67	3569	2.7	–
6	BSP10	0.70	3400	3.0	10.71
7	BSP30	1.20	2219	4.5	45.70

plot is very linear suggesting the absence of the phase separation. Therefore, it can be hypothesized that up to 30 phr hydrocarbon resin concentration, the blends are homogeneous and compatible.

Commonly, tackifier, which has good compatibility with rubber will cause an increase in T_g, broadening of the transition region, and a decrease in the plateau modulus.[17] Here, the BIMS/hydrocarbon resin blends gave the similar behavior of tan δ and E'. Generally, the increase in T_g of the elastomer by the addition of tackifier indicates that addition of the tackifier results in a reduction in free volume available for local segmental motions. The evidence for this reduction is shown in the section "Time–temperature superposition from DMA." On the other side, in the rubbery plateau region, the storage modulus is determined primarily by the density of the entanglements. In this region the tackifier acts as a diluent and causes a decrease in the storage modulus values. The entanglement density in the plateau zone can be accurately estimated from the parameters like entanglement spacing molecular weight (M_e) and network density (υ) (moles of network strands per cubic centimeter). The aforementioned parameters have been calculated to understand the diluent effect of hydrocarbon resin tackifier in the plateau modulus.

The entanglement spacing molecular weight (M_e) can be estimated from the plateau modulus (G_n^0) as follows:[21,24,25]

$$M_e = \rho RT / G_n^0 \tag{3}$$

where ρ is the density of the polymer or blend, R is 8.31 $\times$ 10^7 dyne-cm/(mol K), T is the absolute temperature where G_n^0 is located, and G_n^0 is determined from the G' at the onset of the rubbery region (usually where tan δ reaches minimum following the prominent maximum). The G_n^0 and M_e values of the neat BIMS rubber and BIMS/hydrocarbon resin blends are reported in Table III.

It is seen that M_e value increases from 3345 to 11,017 for the compatible BIMS/hydrocarbon resin blends. This means that the hydrocarbon resin tackifier has significantly reduced the entanglement of the base polymer, and the hydrocarbon resin tackifier is essentially acting as a diluent in the plateau region. Furthermore, the plateau modulus could be related to the network density (υ) (the moles of network strands per cubic centimeter).[25,26] The relationship between the plateau modulus (G_n) and network density (υ) is given by the following equation:

$$G_n = g_n \upsilon RT \tag{4}$$

On rearranging the above equation, the network density can be calculated from the following equation:

$$\upsilon = G_n / g_n RT \tag{5}$$

In the above equation, (υ) is the moles of network strands per cubic centimeter, g_n is a numerical factor, and ρ is the density and R is the gas constant. g_n is generally taken as unity. The (υ) values of the compatible BIMS/hydrocarbon resin blends are reported in Table III. The network density (υ) value decreases with the increase in the concentration of the hydrocarbon resin tackifier. The effect of dilution on the plateau modulus (G_n) was given by Ferry[26] as

$$G_n \propto \phi_b^2 \tag{6}$$

where ϕ_b is the volume fraction of the base polymer. The plot of the plateau modulus as a function of volume fraction square of the base polymer for the compatible BIMS/hydrocarbon resin blends are shown in Figure 5. The plot is exactly linear, and it is consistent with Ferry's relationship. This further confirms diluent effect shown by the hydrocarbon resin tackifier in the plateau zone.
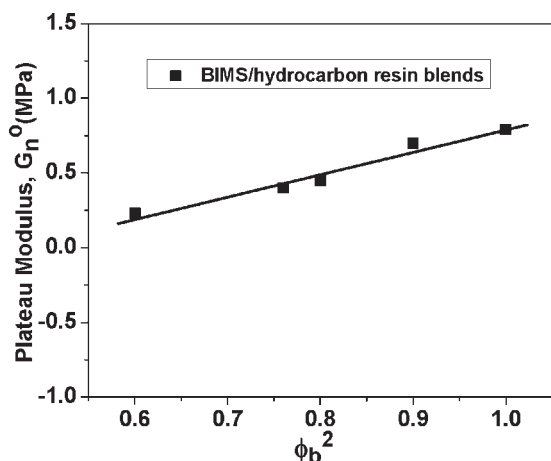
Figure 5 Dilution effect of hydrocarbon resin tackifier on the plateau modulus of the neat BIMS rubber.

It is also well known that the extent of phase separation is evaluated from the plateau modulus. According to Kraus and Rollmann,[20] quasi-equilibrium storage modulus of an entanglement network is given by the theory of rubber elasticity as

$$G_n^0 = (\rho/M_e)RT \qquad (7)$$

where ρ is the density, M_e is the entanglement spacing molecular weight, R is the gas constant, and T is the temperature. If immiscible filler is added to the elastomer (for example, polystyrene domains in styrene–isoprene–styrene block copolymer), the storage modulus of the mixture is expressed by Guth and Gold equation[24,27,28] as follows:

$$G_n^0 = (\rho/M_e)RT(1 + 2.5\,c + 14.1\,c^2) = G'_{(\tan\delta_{min})} \qquad (8)$$

where c is the filler volume fraction and T is the temperature at the minimum in tan δ. $G'_{(\tan\delta_{min})}$ is the storage modulus at the temperature of minimum in the tan δ, and this value is treated as plateau modulus by Kraus and Rollmann.[20,24] If a miscible diluent (tackifier) is further blended with the elastomer, its effect on the plateau modulus is described as[24]

$$G_n^0 = G'_{(\tan\delta_{min})} = \Phi_b^2(\rho/M_e)\,RT\,(1 + 2.5\,c + 14.1c^2)$$
$$(9)$$

where ϕ_b is the volume fraction of the rubber, whereas c is the volume fraction of the filler in the entire composition. Also ρ/M_e is the entanglement density of the unmixed (neat) elastomer. When this equation is applied to the miscible rubber–tackifier blends, $c = 0$ in eq. (9). Fujita et al.[24] have adopted the above practice for different miscible natural rubber–tackifier-based pressure-sensitive adhesive com-

positions. Here, we have followed the same practice for the compatible BIMS/hydrocarbon resin blends. Therefore, eq. (9) is rewritten as

$$G_n^0 = G'_{(\tan\delta_{min})} = \Phi_b^2(\rho/M_e)RT \qquad (10)$$

The plateau modulus values of compatible BIMS/hydrocarbon resin blends has been calculated from eq. (10) (as for the compatible BIMS rubber–hydrocarbon resin tackifier blends) and compared with the experimental values. Figure 6 compares the experimental plateau modulus values with the calculated plateau modulus values for the compatible BIMS/hydrocarbon resin blends. It is evident that the plateau modulus values calculated from eq. (10) show good agreement with the experimental plateau modulus values.

Estimation of the glass transition temperature (T_g) of the BIMS/hydrocarbon resin blends through DSC also corroborates the good compatibility between the BIMS rubber and the hydrocarbon resin tackifier. Figure 7 shows the DSC curves of neat BIMS rubber and BIMS/hydrocarbon resin blends. Only one well-defined glass transition is detected for each blend, which is quite close to the T_g of the neat BIMS rubber. This confirms the good compatibility between the BIMS rubber and the hydrocarbon resin. It may be noted that the T_g values measured by DSC are much lower than those by DMA because of the frequency effect in DMA.

The T_g value of the blend slightly increases with the increase in the resin concentration from 10 to 30 phr. This is due to the reduction in free volume of the blend with the increase in loading of the hydrocarbon resin.
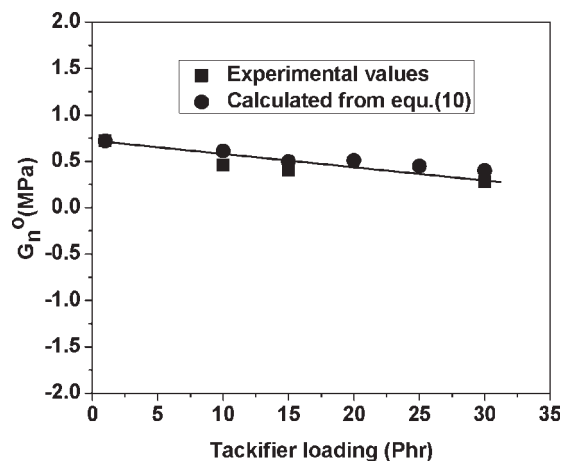

Figure 6 Comparison of the experimental plateau modulus values with the calculated plateau modulus values for the BIMS/hydrocarbon resin mixtures from eq. (10) as compatible blends.
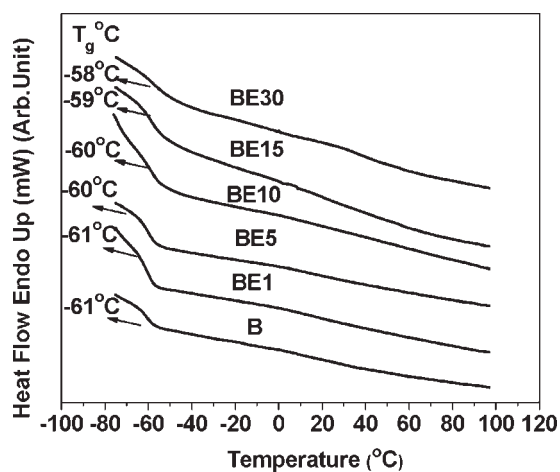
Figure 7 DSC thermograms for neat BIMS rubber and BIMS/hydrocarbon resin blends.

Evaluation of compatibility of BIMS rubber–phenolic resin blends through DMA and DSC

The DMA of phenol formaldehyde resin tackifier impregnated in glass fiber cloth is shown in Figure 2. From the tan δ peak, the T_g is estimated as 58°C for the phenol formaldehyde resin tackifier. Figure 8 shows the tan δ and log E' plots against temperature for neat BIMS rubber and BIMS/phenolic resin blends (BSP10 and BSP30). (The results of other samples are omitted for clarity in the figure.) For BSP10 and BSP30, there is no significant change in the tan δ peak temperature and a high temperature tan δ peak is apparent at ∼ 75°C on enlarging the scale. Also, at resin concentration of 30 phr, a second transition can be seen in the storage modulus curve at about 75°C, confirming the presence of second phase. Here, the rubber/tackifier mixture does not show the expected shift of the tan δ peak temperature and also there is only marginal depression of the storage modulus in the plateau zone up to 70°C (inset of Fig. 8). These suggest the limited compatibility between the phenolic resin and the BIMS rubber and also suggest the limited viscous flow behavior of the BIMS/phenolic resin mixtures (limited dilution effect of the phenolic resin tackifier). The entanglement spacing molecular weight (M_e) and network density (υ) (moles of network strands per cubic centimeter) values have been calculated to understand the effect of the phenolic resin tackifier.

In the case of BIMS/phenolic resin blends, it is interesting to note that the plateau modulus of neat BIMS rubber does not decrease with the increase in the loading of the phenol formaldehyde resin tackifier up to 70°C (Inset of Fig. 8). The plateau modulus (G_n^0) of neat BIMS rubber decreases marginally below 10 phr loading of the phenol formaldehyde resin tackifier. However, at higher loading of the phenolic resin tackifier (>10 phr), there is an abrupt

increase in the plateau modulus values, which results in the reduction of the entanglement spacing molecular weight (M_e) with the simultaneous increase in the network density (υ) values. The G_n^0, M_e, and υ values of the BIMS/phenolic resin blends are reported in Table III. This type of behavior of phenol formaldehyde resin tackifier can be rationalized by the limited compatibility between the BIMS rubber and the phenol formaldehyde resin tackifier.[17,29] At the temperature below the softening point of phenolic resin tackifier, the phenolic resin tackifier will phase separate in the BIMS rubber matrix due to its poor compatibility with the BIMS rubber. As long as the compound is below the softening point of the tackifier, the hard resin phase will act as additional filler in the uncured compound and will increase the stiffness of the stock. In line with this, here the addition of the incompatible phenolic resin tackifier (>10 phr) to BIMS rubber significantly increases the storage modulus (E') values of the BIMS rubber in the plateau zone of the DMA temperature sweep curves.

The experimental plateau modulus values and the calculated plateau modulus values for the incompatible BIMS/phenolic resin blends are shown in Figure 9. The calculated plateau modulus values from eq. (8) (as for the incompatible BIMS rubber–phenolic resin tackifier blends) show satisfactory agreement with the experimental plateau modulus values of the incompatible BIMS/phenol formaldehyde resin blend. This confirms the incompatibility nature of the phenol formaldehyde resin tackifier with the BIMS rubber.

Furthermore, the plot of the plateau modulus as a function of volume fraction square of the base polymer (Ferry's relationship for the effect of dilution on the plateau modulus) for the incompatible
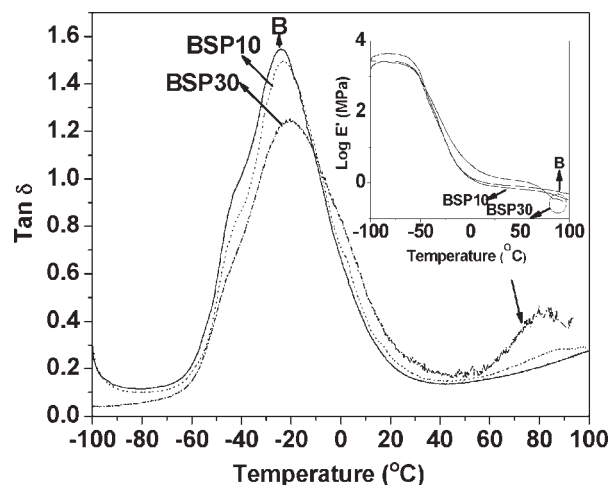

Figure 8 Tan δ versus temperature curves of B, BSP10, and BSP30. Inset: Log E' versus temperature curves of B, BSP10, and BSP30.
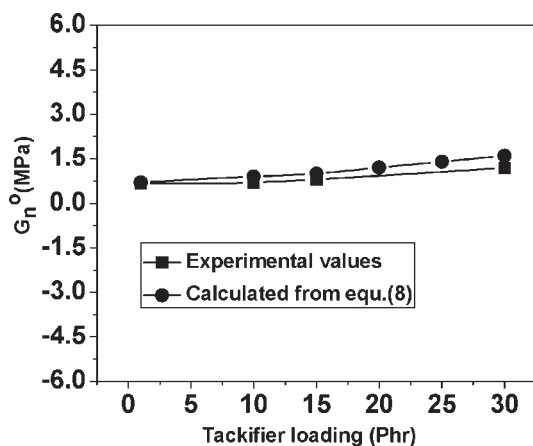
Figure 9 Comparison of the experimental plateau modulus values with the calculated plateau modulus values for the incompatible BIMS/phenolic resin mixtures from eq. (8) as incompatible blends.

Figure 10 Dilution effect of phenol formaldehyde resin tackifier on the plateau modulus of the neat BIMS rubber.

BIMS/phenol formaldehyde resin blend is shown in Figure 10. The plot is not linear and confirms the absence of the dilution effect in the plateau zone for the incompatible BIMS/phenol formaldehyde resin blends.

Hence, it is clear that phenol formaldehyde resin tackifier does not produce any significant diluent effect in the plateau zone. Therefore, it can be presumed that the phenol formaldehyde resin may show some mild reinforcing effect in the BIMS elastomer. The frequency sweep studies of the BIMS/phenol formaldehyde resin system discussed in the next section provide evidence for the mild reinforcement action of the phenol formaldehyde resin tackifier in the uncured BIMS rubber.

Estimation of the glass transition temperature (T_g) of the BIMS/phenolic resin blends through DSC also corroborates the limited compatibility between the BIMS rubber and the phenolic resin tackifier. Figure 11 shows the glass transition temperatures of neat BIMS rubber and BIMS/phenolic resin blends. Except for the samples BSP1 and BSP5, all other BIMS rubber–phenolic resin blends show two T_g values. This is a clear indication of phase separation of phenolic resin in the BIMS rubber matrix. The low temperature T_g values of the blends correspond well with T_g value of the neat BIMS elastomer and the high temperature T_g values of the blends correspond to the T_g value of the phenol formaldehyde resin tackifier.

Time–temperature superposition from DMA

Aubrey and Sherriff[15,16] state that the totally compatible or partially compatible tackifier causes a reduction in the modulus of an elastomer at low frequencies but an increase in modulus at high frequencies. It has been suggested that this favors high adhesive tack because bond formation is a low strain rate process, and bond separation is a high strain rate process.
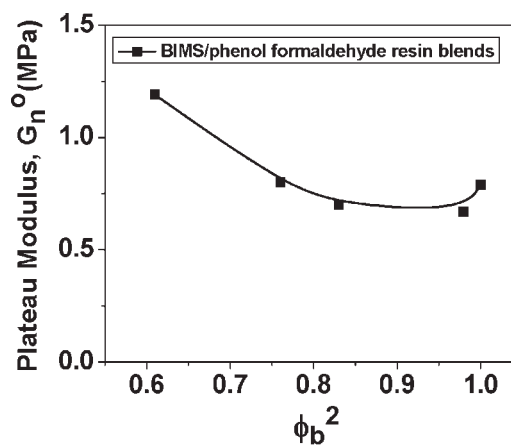
Since the behavior at high frequency is related to the behavior at very low temperature, and vice versa, the frequency sweep tests over a long range of temperature (-50 to $50°C$) can be used to understand the behavior at extreme temperatures outside the experimental range, using time temperature superposition method. Time–temperature superposition has long been used to obtain temperature-independent master curves for polymer systems by shifting values of storage modulus toward the frequency axis. One reference temperature should be chosen (here, it is $25°C$) and the viscoelastic variables of interest (e.g., storage modulus) at other temperatures are shifted to the corresponding values at that reference temperature. A horizontal shift factor, a_T, which is a function of temperature, enables to obtain the master curves. Using the Williams–Landel–Ferry (WLF) equation[30] given below
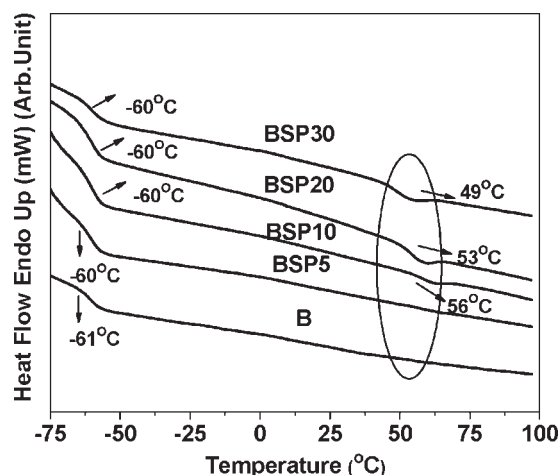

Figure 11 DSC thermograms for neat BIMS rubber and BIMS/phenolic resin blends.
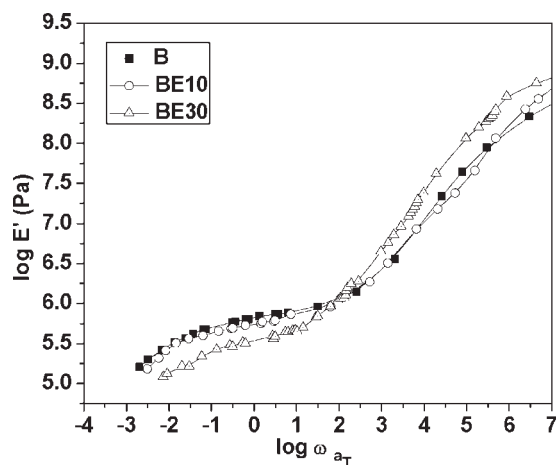
Figure 12 Master curves of log E' versus log frequency at 25°C of BIMS/hydrocarbon resin mixtures.

Figure 13 Master curves of log E' versus log frequency at 25°C of BIMS/phenolic resin mixtures.

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \qquad (11)$$

one can relate the shift factor, a_T, to the glass transition temperature, T_g ($T_g + 50°C$ is considered as the reference temperature) of a polymer and two constants, C1 and C2, which have been found to be characteristic of the polymer's molecular structure.

Figure 12 shows the log E' versus log frequency master curves of the compatible BIMS/hydrocarbon resin mixture measured using dynamic mechanical analyzer. At low frequency the addition of hydrocarbon resin results in a reduction of the storage modulus; simultaneously, the storage modulus increases at higher rates relative to that of the neat BIMS rubber. The magnitude of this reaction is small for the sample BE10 and rapidly increases as the resin concentration approaches 30 phr. Aubrey and Sheriff[15,16] have observed a similar trend for the blends of natural rubber with pentaerythritol ester of hydrogenated rosin tackifier and poly(β-pinene) tackifier. The decrease in storage modulus of the BIMS/hydrocarbon resin mixture at lower rates suggest the decrease in the resistance to flow at low rates (long times) due to the reduction of the viscosity (reduction of the entanglement density) and the increase in storage modulus at higher rates is due to the increased T_g accompanying the tackifier addition (decrease in free volume by the tackifier addition). The frequency sweep master curves of the compatible BIMS/hydrocarbon resin blends clearly elucidate the dilution effect of the hydrocarbon resin tackifier in the rubbery plateau zone.

Figure 13 shows the log E' versus log frequency master curves of incompatible BIMS/phenolic resin mixture measured using dynamic mechanical analyzer. The addition of the phenolic resin increases the storage modulus over the entire frequency scale
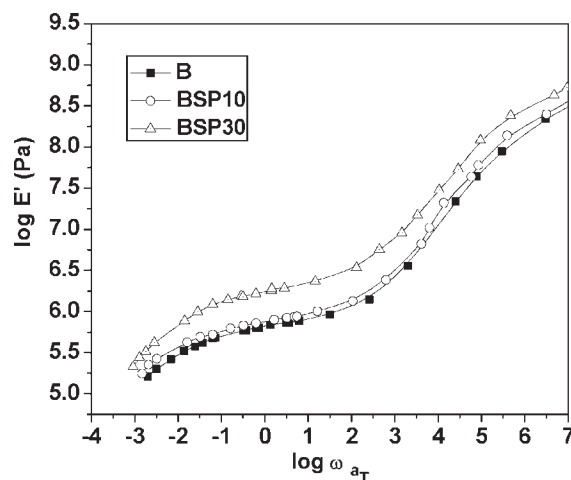
range similar to that of the reinforcing filler. The magnitude of this action is small at low resin concentrations (BSP10), but high at higher resin concentrations (BSP30). In general, in an uncured compound, the incompatible resin will exist in a phase-separated state and the hard resin will function as reinforcement up to the softening point of the resin.[29] The frequency sweep master curves of the incompatible BIMS/phenolic resin blends suggest the absence of the dilution effect of the phenol formaldehyde resin tackifier in the rubbery plateau zone.

C1 and C2 values of the neat BIMS rubber and BIMS/tackifier blends are reported in Table IV. C1 and C2 values of the neat BIMS rubber gradually increase with the addition of hydrocarbon resin tackifier. This increase can be attributed to the reduction of the free volume of the base polymer by the addition of the hydrocarbon resin tackifier. On the other hand, the C1 and C2 value of the base polymer abruptly increases with the addition of the phenolic resin tackifier. This can be attributed to the mild reinforcing effect of the phenolic resin tackifier in the BIMS rubber. Williams et al.[31] have shown that the constant C1 in the WLF equation [eq. (11)] may be identified as relating to fractional free volume:

TABLE IV
C1 and C2 Values of Neat BIMS Rubber and BIMS/Tackifier Blends

Sr. no.	Sample name	C1	C2
1	B	10.6	236.7
2	BE10	11.6	244.9
3	BE30	14.4	252.7
4	BSP10	18.6	346.8
5	BSP30	19.9	356.5

$$C1 = B/2.303 f_o \tag{12}$$

where B is the constant in the Doolittle equation,[32] generally assumed to be unity, and f_o is the fractional free volume as interpreted by Ferry.[26] The f_o/B values calculated based on the eq. (12) for the samples B, BE10, and BE30 are 0.040, 0.037, and 0.030 respectively. The f_o/B value of the neat BIMS rubber gradually decrease with the increase in the loading of hydrocarbon resin tackifier from 10 to 30 phr. Aubrey and Sherriff[16] have reported similar type of results for the blends of natural rubber with pentaerythritol ester of hydrogenated rosin and poly(β-pinene) tackifiers. The decrease in the fractional free volume of the neat BIMS rubber by the addition of the hydrocarbon resin tackifier clearly supports the increase in the glass transition temperature (T_g) value of the neat BIMS rubber with the increase in the loading of the hydrocarbon resin tackifier. On the other hand, the addition of 10 phr of phenol formaldehyde resin tackifier also decreases the fractional free volume of the neat BIMS rubber to 0.023. However, with the increase in the loading of the phenol formaldehyde resin tackifier from 10 to 30 phr, there is only meager reduction in the f_o/B value (0.023 and 0.022). Initial reduction of free volume is due to the mild reinforcement effect of the phenol formaldehyde resin.

Transition zone

Monomer friction coefficient (ζ_0). Another utility of DMA frequency sweep master curve data is to determine the monomer friction coefficient. Monomer friction coefficient is the average resistance force per monomer unit encountered when a polymer chain moves through its surroundings at a unit speed.[26] By assuming that Rouse model describes that high frequency response of the long chains in the transition zone, we have[26,33,34]

$$E'(\omega) = E''(\omega) = \rho \nu_0 N_a R_g \sqrt{\frac{\zeta_0 kT\omega}{8 m_0 M}} \tag{13}$$

where $E'(\omega)$ and $E''(\omega)$ are the storage and loss modulus, ω is the frequency, ρ is the density, N_a is the Avogadro's number, ν_0 is the volume fraction of the base polymer, R_g is the radius of gyration, k is the Boltzmann constant, T is the absolute temperature, m_0 is the monomer molecular weight, and M is the molecular weight of the base polymer. For BIMS rubber, the R_g value has been taken from the literature.[35] The monomer friction coefficient values of neat BIMS rubber and BIMS/tackifier blends have been calculated from the eq. (13) and the values are reported in Table III. The monomer friction

coefficient value increases with the addition of the hydrocarbon resin tackifier. The increase in the monomer friction coefficient value by the addition of compatible hydrocarbon resin tackifier can be rationalized by the increase in the glass transition temperature (reduction of the free volume) of the neat BIMS rubber by the addition of the hydrocarbon resin tackifier. In short, the segmental mobility is highly restricted due to the presence of the hydrocarbon resin tackifier in the BIMS rubber phase. This observation is very much consistent with the earlier findings of Aubrey and Sherriff[16] for the compatible natural rubber/terpene systems.

On the other hand, it is surprising to see the increase in the monomer friction coefficient values even with the addition of the incompatible phenolic resin tackifier to the BIMS rubber (Table III). Here, the increase in the monomer friction coefficient value by the addition of the incompatible phenolic resin tackifier can not be justified by the same explanation given for the compatible hydrocarbon resin tackifier, because there is no increase in the glass transition temperature of the neat BIMS rubber by the addition of the phenolic resin tackifier. Therefore, the possible reason for the increment of the monomer friction coefficient value by the addition of the phenolic resin tackifier can be due to the mild reinforcing action of the phenol formaldehyde resin tackifier in the BIMS rubber phase, which will restrict the segmental mobility. Also, any incompatible tackifier in uncured elastomer will remain in the highly phase separated stage at very low temperatures (well below the softening point of the tackifier).[29] Here, the phase separated phenolic resin tackifier will act as extra topological constraints for the free segmental mobility of the BIMS rubber molecules.

Onset of the transition zone. The onset of the transition zone with increasing frequency can be specified by the intersection of two tangents drawn to E' and E'' curves, as drawn in Figure 14.[36] The intersection frequency ω_{tr} is very close to the reciprocal of the relaxation time (τ_{tr}), which is the measure of the time required for complete configurational rearrangement of a piece of macromolecule caught between two crosslinks or two entanglement.[36–39] Here, the relaxation time (τ_{tr}) for the neat BIMS rubber and the BIMS/tackifier blends have been identified from the Figures 12 and 13 and the values are reported in Table V. It is seen that the relaxation time (τ_{tr}) of the neat BIMS rubber significantly increases with the increase in the loading of the compatible hydrocarbon resin tackifier from 10 to 30 phr. This suggests the existence of greater restrictions for a single BIMS rubber molecule to relax due to the constraints imposed by hydrocarbon resin tackifier. It is clear from the inset of Figure 3 that
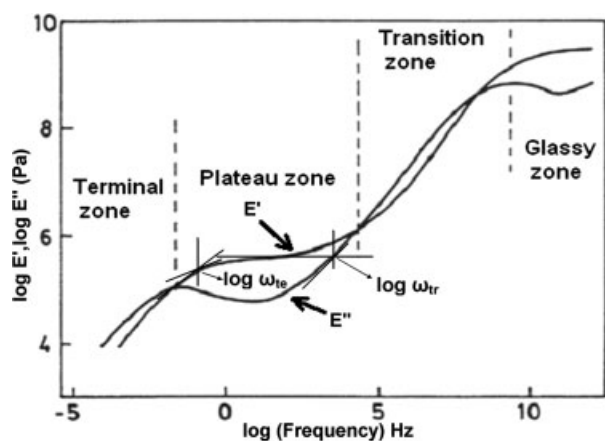
Figure 14 Typical E' and E'' master curve for a linear amorphous polymer.

addition of the hydrocarbon resin tackifier causes a change in the shape of the transition region in addition to the shift to the higher temperature. These suggest the presence of new relaxation processes associated with the constraints on the molecular motion by the hydrocarbon resin tackifier molecules. This phenomenon further explains the reason for the increase in the relaxation time (τ_{tr}) of the BIMS rubber by the addition of the hydrocarbon resin tackifier. On the other hand, there is only marginal increase in the relaxation time (τ_{tr}) of the neat BIMS rubber with the addition of the incompatible phenolic resin tackifier. This marginal increase in relaxation time (τ_{tr}) can be ascribed to the mild reinforcing action of the phenolic resin in the BIMS rubber matrix, which will also act as a constraint for the BIMS rubber molecule to relax faster. It is clear from the inset of Figure 8 that addition of the phenolic rein tackifier does not produce significant change in the transition region of the BIMS rubber.

Plateau and Terminal zone. The length of the plateau zone in the log ω axis is specified by log ω_{tr} − log ω_{te}, where ω_{tr} is the onset of the transition zone and ω_{te} is the left end of the plateau zone, defined by the intersection of two tangents drawn as shown in Figure 14.[36] The frequency ω_{te} is roughly the reciprocal of the relaxation time (τ_{te}) required for a molecule to completely rearrange its configuration by snaking itself through numerous entanglements.[36] Plasticization affects ω_{te} to a greater extent. As a result, the plateau length gener-

ally shrinks due to effect of the added diluent.[36] Generally, tackifiers act as a diluent in the plateau zone by reducing the modulus values of the base polymer to a greater extent. Here, the plateau modulus values of the neat BIMS rubber decreases with the increase in loading of the compatible hydrocarbon resin tackifier (Fig. 12). Furthermore, the lengths of the plateau zone (log ω_{tr} − log ω_{te}) of the BIMS/hydrocarbon resin blends are lower than that of the neat BIMS rubber (Fig. 12). This clearly confirms the dilution effect of the hydrocarbon resin tackifier in the plateau zone. The length of the plateau zone of the neat BIMS rubber and BIMS/hydrocarbon resin blends are reported in Table V. Moreover, the relaxation time (τ_{te}) of the neat BIMS rubber gradually decreases with the increase in loading of the hydrocarbon resin tackifier. This suggests that the hydrocarbon resin tackifier has significantly reduced the entanglement density of the BIMS rubber, which has actually resulted in a lower relaxation time (τ_{te}) of the BIMS/hydrocarbon resin blends. The relaxation time (τ_{te}) of the neat BIMS rubber and BIMS/hydrocarbon resin blends are reported in Table V.

On the other hand, the length of the plateau zone of the BIMS rubber increases by the addition of the incompatible phenolic resin tackifier (Fig. 13). Moreover, the addition of phenolic resin tackifier increases the plateau modulus values of the neat BIMS rubber (Fig. 13). Furthermore, the relaxation time (τ_{te}) of the neat BIMS rubber gradually increases by the addition of the phenolic resin tackifier (Table V). This behavior can be ascribed to the poor dilution effect and mild reinforcing action of the phenolic resin tackifier in the BIMS rubber matrix.

Morphological studies

The DMA studies (temperature sweep studies) of the BIMS/hydrocarbon resin blend prove the good compatibility between the blend components, whereas the SEM photomicrograph of sample BE10 shows some white resin particles on the rubber surface [Fig. 15(a)]. This observation is very similar to the results reported earlier for the compatible SBR/terpene tackifier blend.[23] It is well known that

TABLE V
Crossover Frequency and Relaxation Time Values of Neat BIMS Rubber and BIMS/Tackifier Blends

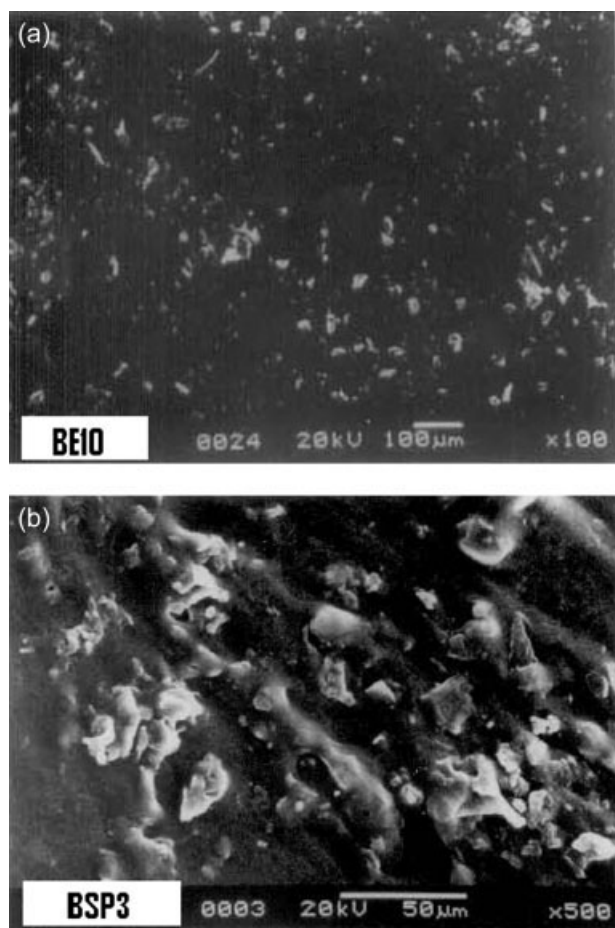| Sr. no.	Sample designation	log ω_{tr} (Hz)	log τ_{tr} (s)	log ω_{te} (Hz)	log τ_{te} (s)	log ω_{tr} − log ω_{te} (Hz)
1	B	2.03	0.49	−1.41	−0.71	3.43
2	BE10	1.18	0.85	−1.17	−0.85	2.34
3	BE30	0.71	1.41	−0.88	−1.14	1.58
4	BSP10	2.0	0.50	−1.46	−0.68	3.47
5	BSP30	1.90	0.51	−1.57	−0.63	3.47

Figure 15 (a) SEM photograph of sample BE10. (b) SEM photograph of sample BSP3.

tackifier/rubber blend, which is compatible in bulk undergo tackifier migration to surface region.[40,41] Despite the fact that the hydrocarbon resin particles are phase separated on the BIMS rubber surface, the dispersed hydrocarbon resin particles have not been identified as a distinct separate phase in the DMA studies of the BIMS/hydrocarbon resin blend (Fig. 3). On the other hand, SEM photomicrograph of the sample BSP3 shows bulk phase separation of the phenolic resin on the BIMS rubber surface [Fig. 15(b)]. This suggests the existence of the two distinct phases, which is also clearly recognized in the DMA studies of the BIMS/phenolic resin blend (Fig. 8).

CONCLUSIONS

BIMS rubber, which is highly evaluated in tire sector and pressure sensitive adhesive compositions, has been blended with hydrocarbon resin tackifier and phenol formaldehyde resin tackifier. The compatibility between various combinations of the blend components has been investigated by means of UV–vis spectroscopy, DMA, DSC, and SEM. The BIMS/hydrocarbon resin blends exhibit single T_g in the

DMA and DSC studies. However, BIMS/phenol formaldehyde resin blends exhibit two T_gs even at the tackifier concentration of less than 10 phr. In the DMA temperature sweep studies, the addition of hydrocarbon resin to BIMS rubber results in the reduction of the plateau modulus values with the concomitant increase in glass transition temperature (T_g). The reduction of the plateau modulus values is attributed to the reduction of the entanglement density and the network density of the base polymer by the addition of the hydrocarbon resin tackifier. On the other hand, the addition of phenol formaldehyde resin to BIMS rubber does not show any such type of behavior. Instead, phenol formaldehyde resin tackifier increases the plateau modulus values of the base polymer at a tackifier concentration greater than 10 phr. In the DMA frequency sweep studies, the addition of the hydrocarbon resin reduces the storage modulus of the BIMS rubber at lower frequencies (by reducing the entanglement and network density) and increases the storage modulus at higher frequencies. However, the addition of phenolic resin increases the storage modulus of the BIMS rubber throughout the entire frequency scale range similar to the action of the reinforcing filler. These observations are further substantiated from the decrease in the relaxation time (τ_{te}) values of the BIMS/hydrocarbon resin blends and from the increase in the relaxation time (τ_{te}) values of the BIMS/phenolic resin blends at the left end of the plateau zone in their respective frequency sweep master curves. The SEM photomicrograph of the compatible BIMS/hydrocarbon resin blend shows some controlled migration of the hydrocarbon resin tackifier to the rubber surface. On the other hand, the SEM photograph of the incompatible BIMS/phenolic resin blend shows excess phase separation of phenolic resin on the rubber surface.

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