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Synthesis and utilization of epoxidized polybutadiene rubber as an alternate compatibilizer in green-tire composites

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Abstract In the present study, epoxidized polybutadiene rubber (EBR) was synthesized from commercial-grade *cis*-polybutadiene rubber (BR) and was characterized by NMR, FTIR, differential scanning calorimetry, thermogravimetric analysis and surface energy by contact angle measurement. To circumvent the drawback of the existing compatibilizers, the EBR was successfully used as an alternate compatibilizer for a silica-based 'green-tire' composite. The significant rise of surface energy was observed after epoxidation of BR, which represents the enhancement of the polar character of the rubber chains and eventually leads to improved compatibility between silica fillers and rubber chains. Out of various epoxidation levels, EBR with 30 mol% epoxidation showed the best compatibilizing effect. The optimum loading of EBR was found to be 12% with respect to total silica content. Apart from using EBR alone as a compatibilizer, combination of EBR with commercial silane-coupling agents, namely, bis(triethoxy-silylpropyl) tetrasulphide (TESPT) and 3-aminopropyltrimethoxy silane, was also investigated. The physico-mechanical and dynamic properties of the compounds with a combination of TESPT:EBR (40:60–60:40) were comparable with those of the compound prepared using TESPT compatibilizer. The results observed with EBR-compatibilized samples revealed that EBR has a potential to be an effective compatibilizer which eventually could minimize the drawbacks associated while using commercial silane as a compatibilizer at the industrial scale.

Introduction

The development of 'green tires' with lower rolling resistance along with safety and fuel efficiency is the focus of the current tire research and developments. In fact, the 'green-tire' concept was introduced in early 90s and has emerged as a paradigm shift towards the improvements of tire's wet grip (safety) and rolling resistance (fuel efficiency) simultaneously [1–3]. Moreover, the impulsion and the advantages associated with 'green-tire' concept initiated the investigation and utilization of various types of novel fillers like nanosilica, nanoclay etc., to replace or to avoid the conventional carbon black [4, 5]. However, as compared to the carbon black, the use of other fillers such as nanosilica in the rubber composites encounters few major challenges such as [6–9];

- poor rubber–filler interaction due to difference of polar characteristics and
- filler agglomeration due to higher filler–filler interaction.

As a result of above-mentioned limitations, the rubber composites prepared using nanofillers lead to poor processability, inferior mechanical strength and unacceptable dynamic properties. However, such challenges can be resolved up to greater extent using compatibilizers or coupling agents which reduces the difference in polar characters of fillers and rubbers and leads to improved rubber–filler interactions [10, 11]. Typically, on industrial scale, the modification of silica surface is done by

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introduction of coupling agents or compatibilizers like silanes, which reduce the filler–filler interaction and also enhance the rubber–filler interaction through chemical linkages between the silica surface and rubber chains [12, 13]. However, from industrial production viewpoint, the use of silanes as compatibilizer has shown the following major disadvantages:

- the coupling reaction produces alcohols as by-products which may cause chronic defects in the final product [14];
- the higher material costs of the coupling agents; and
- the higher production costs due to the difficult processing behavior.

On the other hand, in the absence of silanes, the compatibility between fillers and rubbers can be enhanced by increasing the polar characteristics in the rubber chains which ultimately reduces the risks associated with their utilizations [15]. In the case of polyolefins, in general, functionalization such as epoxidation, carboxylation, oxidation, sulfonation, maleination etc., are known [16–18].

However, among the various functionalizations, the epoxidation of unsaturated –C=C– bond at mild reaction condition is a wonderful synthetic tool for introduction of versatile functionality to the rubber chain. The epoxidation of rubber chain is an excellent synthetic tool to increase the polar character by introduction of oxirane/epoxy ring to the rubber chain. The epoxidation of the rubber and polymer chains can be carried out by both methods: solution and melt-mixing [19, 20]. The epoxidation is carried out to serve dual purpose, to improve the functionality, and also to enhance the polar character of the non-polar rubber and polymer chains. Moreover, a controlled epoxidized rubber would possess both the polar group epoxy ring and non-polar hydrocarbon chain to interact with polar silica surface and a non-polar rubber chain, respectively. Advantageously, the epoxidized BR can also be co-cured with the main rubber matrix smoothly.

The silica and silane-based styrene–butadiene rubber/ polybutadiene rubber (SBR/BR) composites are currently being used in passenger car radial tire-tread [21]. In the present study, the commercial-grade high *cis*-polybutadiene rubber (BR) was epoxidized to synthesize epoxy-BR (EBR) at different epoxidation magnitude, and thus, prepared EBRs were used to replace and/or reduce the coupling agent from SBR/BR composites. Although the use of epoxidized polydienes has been reported as compatibilizer for silica filler in a few patents [22–25], however, a comprehensive study has not been reported on the effect of epoxidation levels on compatibilization in the open literature [26]. Therefore, the present study focuses on the following major aspects:

- epoxidation of tire-grade high *cis*-polybutadiene rubber (5, 10, 30, and 50 mol% epoxidation) to prepare the epoxidized polybutadiene rubber (EBR);
- evaluation of compatibilizing efficacy of thus synthesized EBR in silica-filled SBR/BR blend at various epoxidation levels and loadings;
- comparative study of EBR as a compatibilizer with commercially used silanes like bis(triethoxy-silylpropyl) tetrasulphide (TESPT) and 3-amino propyl trimethoxy silane (APS).

Experimental

Materials and methods

BR (Cisamer 01, ML_{1+4}@ 100 °C = 45; M_w = 3.5 × 10^5, *cis* content 96%) was obtained from Reliance Industries Ltd., India. SBR (1502, Mooney viscosity ML_{1+4}@ 100 °C = 48) was obtained from Japan Synthetic Rubber, Japan. Sulfur, stearic acid (98% purity), zinc oxide (ZnO), N-Cyclohexyl-2-benzothiazole sulphenamide (CBS) (98% purity), diphenyl guanidine (DPG), microcrystalline wax, precipitated silica, and bis(triethoxy-silylpropyl) tetrasulphide (TESPT) were purchased from Labort Fine Chem. Pvt. Ltd., India. N-(1, 3-dimethyl butyl)-N-phenyl-p-phenylenediamine (6PPD) was obtained from John Baker Inc., USA. 3-amino propyl trimethoxy silane (APS) was procured from Sigma-Aldrich Inc., USA. Naphthenic oil and di-tertiary-butyl-para cresol (DTBPC) were obtained from indigenous sources. *meta*-Chloroperbenzoic acid (MCPBA, 70%) was procured from Sigma-Aldrich, India.

Synthesis of epoxidized polybutadiene rubber (EBR)

A variety of different magnitude of epoxidation (5, 10, 30, and 50 mol%) of BR were conducted using modified protocol (Scheme 1) [27].

Typically for 10 mol% epoxidation, in a three-neck round-bottom flask equipped with magnetic stirrer, 16.2 g of BR (0.3 mol of C=C) was first dissolved in 1000 ml of toluene. A solution of 7.38 g of MCPBA (0.03 mol) in 300 ml of toluene was subsequently added drop-wise at room temperature into the rubber solution at such a rate that the MCPBA solution was added in 1 h. The reaction mixture was then further stirred for another 3 h. After 3 h, the stirring was stopped and epoxidized rubber was obtained by precipitation in methanol containing 0.5% DTBPC as an antioxidant. The rubber was decanted and then washed twice with methanol before subjecting to vacuum drying at room temperature for 5 h. The 10, 30,

Scheme 1 Epoxidation reaction of polybutadiene rubber
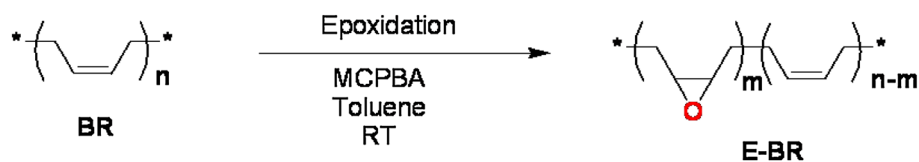
and 50 mol% epoxidized polybutadiene rubbers were designated as EBR10, EBR30 and EBR50 respectively.

Preparation of rubber composites

A variety of rubber composites were prepared by melt-mixing method. Mixing was carried out in a Brabender Plasticorder (PL2000, Germany), an internal mixer (volume 50 cm^3) adopting a three-stage mixing procedure at 60 rpm. Mixing temperature of first, second, and third stages was 120, 140 and 80 °C (unless otherwise mentioned). Different composites were prepared according to the formulations given in Table 1. The final curing of compound was done on compression molding at 145 °C and 10 MPa pressure at optimum cure time.

Testing methods of different composites

Dumbbell-shaped samples were cut from the molded sheets according to ASTM D412-96 for tensile strength and ASTM D624 for tear strength. The tensile strength, elongation at break, modulus and tear strength were determined on a Universal Testing Machine (Instron 3367, USA) with the crosshead speed of 500 mm/min. Hardness was measured using 6 mm-thick sample in Durometer (Wallace,

UK) according to ASTM D2240-97. For determining the abrasion resistance of the composites, cylindrical test pieces were molded. The tests were performed according to DIN 5316 in DIN Abrader (Zwick Roell, Germany). Cut and chip test was performed on Cut and Chip Tester (Alpha Technologies, USA). The conditions of testing were: sample speed 750 rpm, cut and chip cycle 60 rpm and cycle time 10 min. Circular sample of 50 mm diameter was used. Dynamic mechanical thermal analysis was done using DMA VA4000 (Metravib, France) in double sandwich shear mode. Strain sweep experiments were done in the range of 0.1–40% strain at 60 °C. Sample dimension was of 10 mm in diameter and 2.0 ± 0.2 mm of thickness.

The volume fraction of rubber in the swollen network, V_r, was calculated by equilibrium swelling method and crosslink density was subsequently calculated by the well-known Flory–Renner equation [28]. Rheology studies were carried out using Hybrid Rheometer from −120 to 100 °C at 10 Hz frequency and 0.1% strain [29]. The bound rubber content was determined as per method proposed by the reported literature [30]. The surface energy of the solid polymers was determined by contact angle measurement. Fowkes [31] proposed that the surface energy of a pure phase is a sum of the contribution from the dispersive γ_a^d and polar γ_a^p components, such that

Table 1 Formulation and designation of rubber composites

Ingredients	Formulation in phr[a]												
Sample name	A	B	C	D	E	F	G	H	I	J	K	L	M
SBR	70	70	70	70	70	70	70	70	70	70	70	70	70
BR	30	30	30	30	30	30	30	30	30	30	30	30	30
EBR (mol%)	–	–	–	8.4 (10)	8.4 (30)	8.4 (50)	5.6 (30)	17.5 (30)	35 (30)	4.2 (30)	3.4 (30)	5.0 (30)	5.0 (30)
Precipitated silica	70	70	70	70	70	70	70	70	70	70	70	70	70
TESPT	–	8.4	–	–	–	–	–	–	–	4.2	5.0	3.4	–
APS	–	–	8.4	–	–	–	–	–	–	–	–	–	3.4
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
6PPD	2	2	2	2	2	2	2	2	2	2	2	2	2
Wax	1	1	1	1	1	1	1	1	1	1	1	1	1
Naphthenic oil	8	8	8	8	8	8	8	8	8	8	8	8	8
Sulfur	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
CBS	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
DPG	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

[a] Parts per 100 parts of rubber

$$\gamma_a = \gamma_a^d + \gamma_a^p. \tag{1}$$

A contact angle meter, Kernco (Model G II) was adopted for contact angle measurement, using water and formamide as testing liquids. Contact angle of water and formamide on BR is 93.01° and 74.52°, respectively. Contact angle of water and formamide on EBR is 79.76° and 64.74°, respectively. Now

$$\cos\theta = -1 + \frac{2(\gamma_s^d \gamma_l^d)^{1/2}}{\gamma_l} + \frac{2(\gamma_s^p \gamma_l^p)^{1/2}}{\gamma_l}, \tag{2}$$

where γ_s^d and γ_s^p are the dispersive and polar components of solid's surface energy and γ_l^d, γ_l^p are the dispersive and polar components of liquid's surface energy. Using Eqs. 1 and 2, the surface energy of BR and EBR was calculated.

Results and discussion

Characterization of epoxidized polybutadiene rubber

As mentioned earlier, introduction of oxirane group into the rubber chain was aimed to increase the polar character of the polybutadiene rubber chain. The extent of epoxidation was calculated by a methods as described in the literature, e.g., ^{1}H-NMR (Bruker—400 MHz AVANCE-III, Germany) and FTIR (Nicolet 6700, USA) spectroscopy and addition of HCl in dioxane solution method [19, 20]. The extent of epoxidation was quantified by NMR spectroscopy. A new singlet at 2.9 ppm (–CH of epoxy) in EBR samples was observed in comparison to the NMR spectrum of BR (Fig. 1). The epoxidation of polybutadiene rubber was further confirmed by ATR–FTIR method. After epoxidation, in comparison to polybutadiene rubber, the appearance of new peaks at 809 and 1260 cm^{-1} (due to –C–O–C– stretching of epoxy group) was observed (Fig. 2). It was also noticed that the peak height increases with the extent of epoxidation. The typical ^{1}H-NMR resonance signals of BR and corresponding EBR30 samples are given below [19, 20, 27].

BR: ^{1}H NMR (400.13 MHz, CDCl$_3$): in ppm 0.911–1.444 (m, 0.12 H, –CH$_3$), 2.093 (s, 2.04 H, –CH$_2$), 5.026–5.395 (m, 1.02 H, =CH). **EBR**: ^{1}H NMR (400.13 MHz, CDCl$_3$): in ppm 1.251–1.500 (m, 0.71 H, –CH$_3$), 1.514–1.800 (m, 0.24 H, –CH$_3$), 1.951–2.291 (m, 2.71 H, –CH$_2$), 2.939–3.001 (m, 0.24 H, –C–O–C– Oxirane), 5.101–5.640 (m, 1.53 H, =CH).

The samples were also characterized and compared by thermal analysis such as DSC, TGA and DTG studies. The glass transition temperature (T_g) of a rubber changes expected to be increased on the introduction of oxirane ring. As shown in Fig. 3, similar kind of results was also observed in which the T_g was increased from −103 °C (BR) to −99 °C (EBR30). The change in T_g of the EBR is attributed to the fact that the presence of rigid polar bond in place of unsaturated group. Moreover, the single T_g value also implies the uniform distribution of epoxy group along with the BR main chain. The TGA and DTG studies have also been carried out to observe the effect of degradation pattern in the presence of oxirane ring into the BR chain (Fig. 4). A single pattern in the range of 300–480 °C in TGA curves and two distinct weight loss peaks in the DTG curves were observed. It is observed that the beginning of thermal degradation (T_{onset}) marginally delays on the introduction of oxirane ring in the BR chain. On the other hand, the maximum degradation temperature (T_{max}) increases by 2° from 448 to 450 °C.

A change in the surface energy of the rubber chains represents variance in the polar characters. To quantify the extent of variance of polar character, the surface energy of one of the synthesized epoxidized BR was compared with corresponding virgin BR. The surface energy of BR and EBR5 was calculated to be 24.72 and 29.79 mJ/m^2, respectively. Hence, it was observed that typically, 5% epoxidized BR has shown about 20% rise in the surface energy in comparison to the virgin BR. Such increment of surface energy clearly indicates that the polar character has been significantly increased after epoxidation of the BR. Finally, the ^{1}H-NMR, FTIR, DSC, TGA, and surface energy studies clearly signify that the presence of epoxy ring leads to increments of polar character in the BR chains.

Effect of different magnitude of epoxidation level of EBR as a coupling agent

The effect of different magnitude of epoxidation level of EBR on the mechanical properties of SBR/BR–silica composites is shown in Table 2. The lower mechanical properties were observed in the SBR/BR–silica composite without using compatibilizer (Sample A; Table 2) which may be due to higher filler–filler interaction and therefore, resulted poor dispersion of the silica filler in the rubber matrix. On the contrary, while using EBR10 and EBR30 as a compatibilizer, the tensile strength of the rubber composite was increased by 16 and 39%, respectively (Sample D and Sample E; Table 2) in comparison to the rubber composite without using compatibilizer (Sample A; Table 2). However, lower values of the physico-mechanical properties were observed while using higher magnitude of epoxidized, EBR50 (Sample F; Table 2). This could be due to higher polarity at 50% epoxidation level, which makes epoxidized rubber incompatible with non-polar SBR/BR blends. Although EBR50 with higher level of epoxidation may react better with silica but due to

Fig. 1 ^{1}H-NMR spectra of BR and EBR30 samples
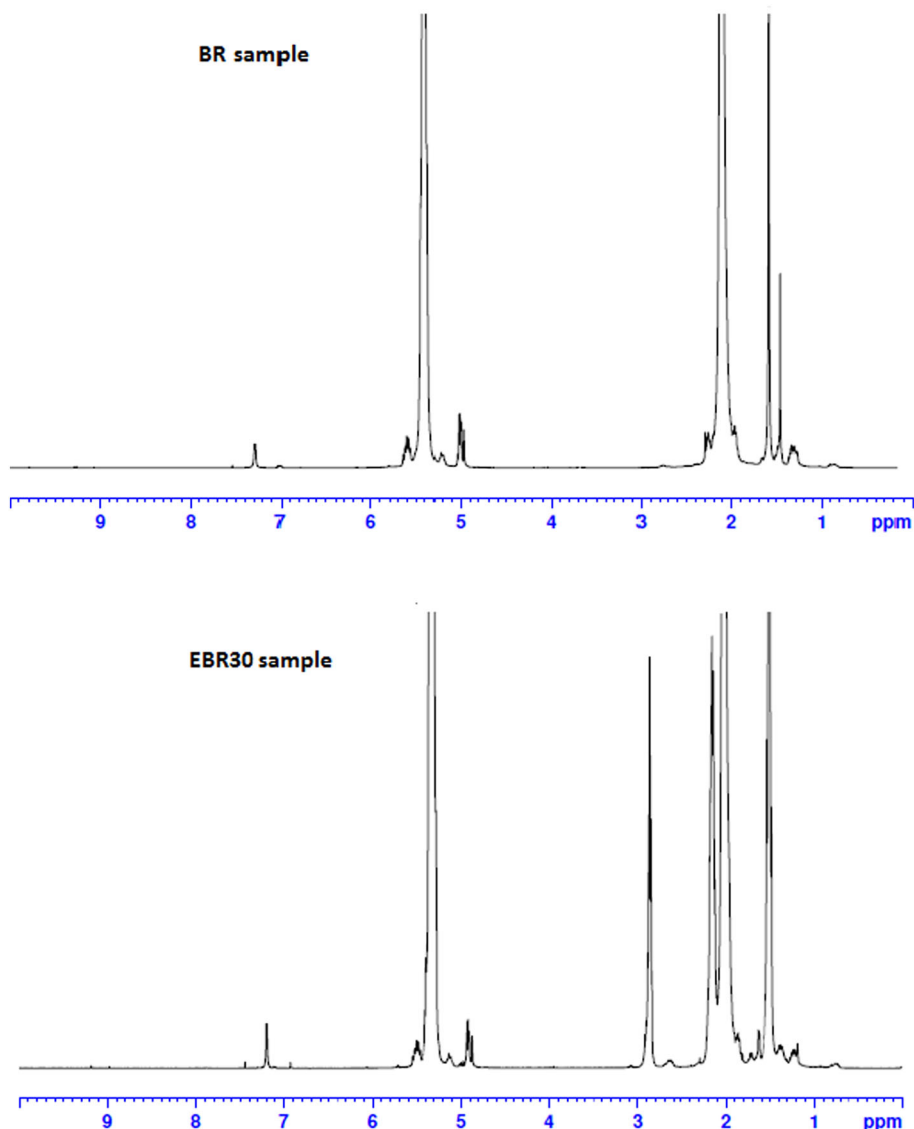
incompatibility with the SBR/BR blend matrix, the improved effect of compatibilization was not realized in the Sample F. Significantly higher improvement in the tensile strength was observed in the rubber composites sample containing the conventional silane-coupling agents, TESPT (95% increment, Sample B and Sample A; Table 2) and APS (51% increment, Sample C and Sample A; Table 2). Such improvements are due to better filler dispersion and filler–rubber interaction in the presence of conventional compatibilizers. The abrasion resistance and hardness values of the composites follow the trend: Sample B > Sample A > Sample E > Sample D = Sample F > Sample C (Table 2). The abrasion resistance and cut and chip are both closely related wear properties of the rubber composites.

The volume fraction of rubber in the swollen network (V_r) for the studied rubber composites follows the trend:

Sample B > Sample E > Sample C > Sample D > Sample A > Sample F (Table 2). The highest value of V_r was observed for the composite samples containing TESPT as a compatibilizer because of the presence of sulfur molecule in the TESPT (Scheme 2), which facilitated the crosslinking density of the silica–silane–rubber network. On the other hand, better V_r values were also observed while using EBR30 as a compatibilizer in the SBR/BR–silica composite (Sample E; Table 2) which further confirms that the presence of polar epoxidized BR improves the crosslink density in the composite sample in comparison to sample A.

In general, it has been observed that the acidic silica surface tries to make a strong hydrogen bond with basic cure activators and consequently the crosslink density reduces in the vulcanized rubber samples. To improve the crosslink density of silica-filled rubber, the silane-coupling
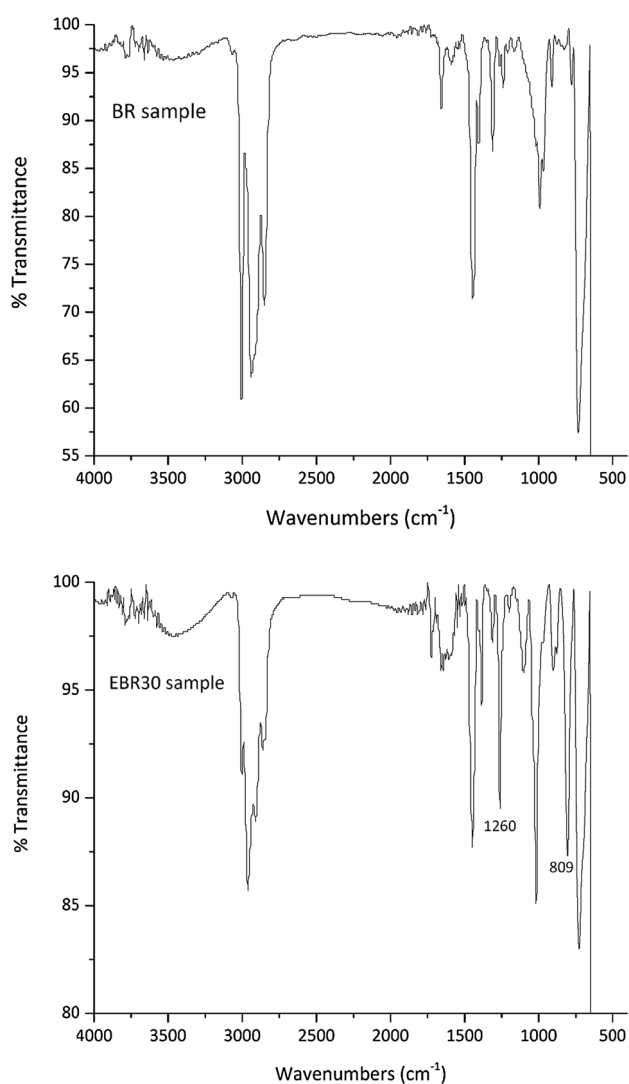
Fig. 2 FTIR spectra of BR and EBR30 samples

agents come into picture which basically prevents the adsorption of the curatives on the silica surfaces by modifying the silica surface and makes crosslinks between silica and rubber chain. The polarity of the polybutadiene rubber is increased in the presence of polar epoxy group. This enhances the strong interaction between rubber and silica in comparison to sample without silanes (Sample A). This might be the reason behind the improvement of crosslink density of Sample L in the presence of polar epoxidized BR.

Finally, it can be concluded that among the employed EBR samples, EBR30 showed a better improvement in the physico-mechanical properties while using as a compatibilizer in the SBR/BR–silica composites.

A proposed coupling reaction between silica surface and EBR is shown in Scheme 3. The surface silanol group of silica reacts with epoxy group of EBR, while the non-polar part of EBR is compatible with non-polar SBR/BR blend.

To support the proposed mechanism of Scheme 3, the FTIR spectra of EBR30 and the composites sample made from EBR30 and silica are compared (Fig. 5). It was observed that the peak at 810 cm^{-1} due to oxirane ring of EBR30 sample was disappeared in the composite sample of EBR30 and silica.

Effect of variation of EBR concentration on compatibilization

Out of the employed EBR samples, the EBR30 (30% epoxidized BR) showed encouraging compatibilizer properties. Therefore, to investigate the optimum loading level, further studies were carried out by variation of loading of EBR30 as 8, 12, 25 and 50 weight % of total silica content in the SBR/BR–silica composites. The highest tensile strength was observed at 12% loading (Fig. 6) as compared to higher (25 and 50%) as well as lower (8%) loading of EBR30. Other properties like modulus at 300% elongation, hardness, and tear strength also followed the similar trend (Figs. 6, 7). It may be presumed that at lower loading, the amount of epoxy groups may not be sufficient to interact with the polar silica filler. On the other hand, at higher EBR, loading increases the polarity difference between polar-EBR and non-polar SBR/BR created incompatibility and leads to inferior compatibilization effect.

Effect of EBR30 as partial substituent of silane

Though during our investigations, EBR samples showed encouraging results as a potential compatibilizer for SBR/BR–silica composites, however, the physico-mechanical properties were not observed better than the composites samples containing the conventional silanes, especially for TESPT. Similar observation was also reported earlier for other rubber composites samples [26]. Moreover, to observe the synergetic effects and also to minimize the disadvantages associated with the conventional silanes, another approach was undertaken by replacement of some part of conventional silanes by EBR samples SBR/BR–silica composites. A variety of SBR/BR–silica composites were prepared using different combination of TESPT and EBR30 samples. The ratio of TESPT:EBR30 was varied as 40:60 (Sample J), 50:50 (Sample K), and 60:40 (Sample L) and the results obtained are reported in Table 3.

As compared to the composite samples containing exclusively EBR as a compatibilizer (Sample E; Table 2), significant improvements (up to 31%) were observed for the tensile strength of composite samples containing the combination of EBR30:TESPT as compatibilizer (Sample L; Table 3). However, the expected synergy was not observed using a combination of TESPT and EBR in the composites as the mechanical and the wear properties were

Fig. 3 DSC curves of BR and EBR30 samples
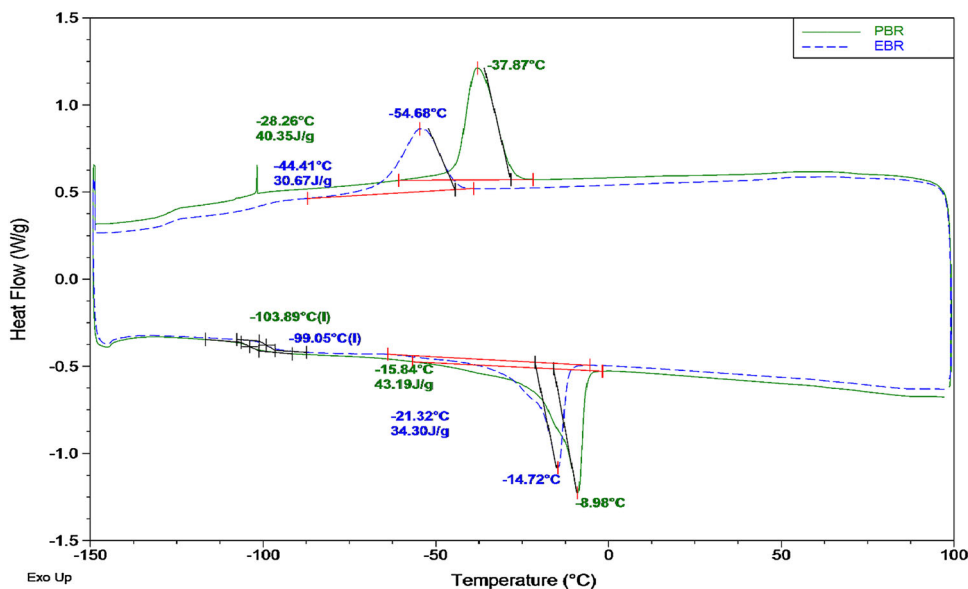
only comparable but not better than those of TESPT containing composite sample (Sample B; Tables 2, 3). Thus, it can be concluded that 40–60% of silanes can be substituted by EBR which can minimize the drawbacks associated while using only silane as a compatibilizer.

On the other hand, the Sample M (sample containing combination of EBR30:APS) showed mechanical properties inferior to both the composite sample containing alone APS (Sample C; Tables 2, 3) and EBR30 (Sample E; Table 2). The possible reason could be the non-availability of polar oxirane ring of EBR30 to function as compatibilizer because of the stoichiometric reaction between amino-group of APS and oxirane ring of EBR30 as represented in Scheme 4. Eventually, the remaining oxirane ring of EBR30 was not adequate to provide a better compatibilization effect into the SBR/BR–silica composite.

Rheology studies and bound rubber content

The cure characteristics such as scorch time (t_2), cure time (t_{90}), ML and delta torque of various important samples are given in Table 4. It was observed that except Sample M, all the samples have shown a significant decrease of ML value which indicates reduction of filler–filler interactions within the rubber matrix. Moreover, it was also observed that sample containing only TESPT compatibilizer (Sample B) has shown the highest extent of ML reduction followed by the Sample K and Sample L in comparison to the Sample A (without any compatibilizer). In addition, improved crosslinking efficiency, which is reflected by highest values for both M_H and delta torque for the sample containing only TESPT compatibilizer (Sample B) followed by Sample L and Sample K in comparison to Sample A (without any compatibilizer). Moreover, to

investigate the rubber–filler interaction, the bound rubber content values were also determined (Table 5). It was observed again that sample containing only TESPT compatibilizer (Sample B) has shown the highest percentage of bound rubber values followed by the Sample L, Sample K, and Sample M in comparison to the Sample A (without any compatibilizer).

Payne effect

To investigate further filler–filler interactions, the Payne effect studies were carried out. The Payne effect was calculated by the difference between the elastic modulus at 0.18 degree strain and at 2 degree strain $[\Delta G' = (G'@0.18 - G'@2.0)]$ in uncured and cured samples at 1 Hz and 100 °C (Figs. 8, 9). For the uncured samples, as expected, it was observed that there is a maximum reduction in $\Delta G'$ for Sample B due to the presence of TESPT coupling agent in the rubber matrix. Afterwards, the maximum reduction of $\Delta G'$ was occurred for Sample L (Fig. 8). This might be a favorable interaction between epoxy groups and the hydroxy (–OH) group onto the silica surface and, therefore, improve dispersion leading to reduction of Payne effect was observed. However, for the all cured samples, there is an increase in $\Delta G'$ magnitude was observed (Fig. 9) owing to the probable re-interaction of the filler particles by the low viscosity during crosslinking formation at higher temperature.

SEM microscopy studies

To investigate the dispersion of silica filler particles in the rubber matrix, the SEM microscopy studies of various samples were carried out. As shown in Fig. 10, the silica

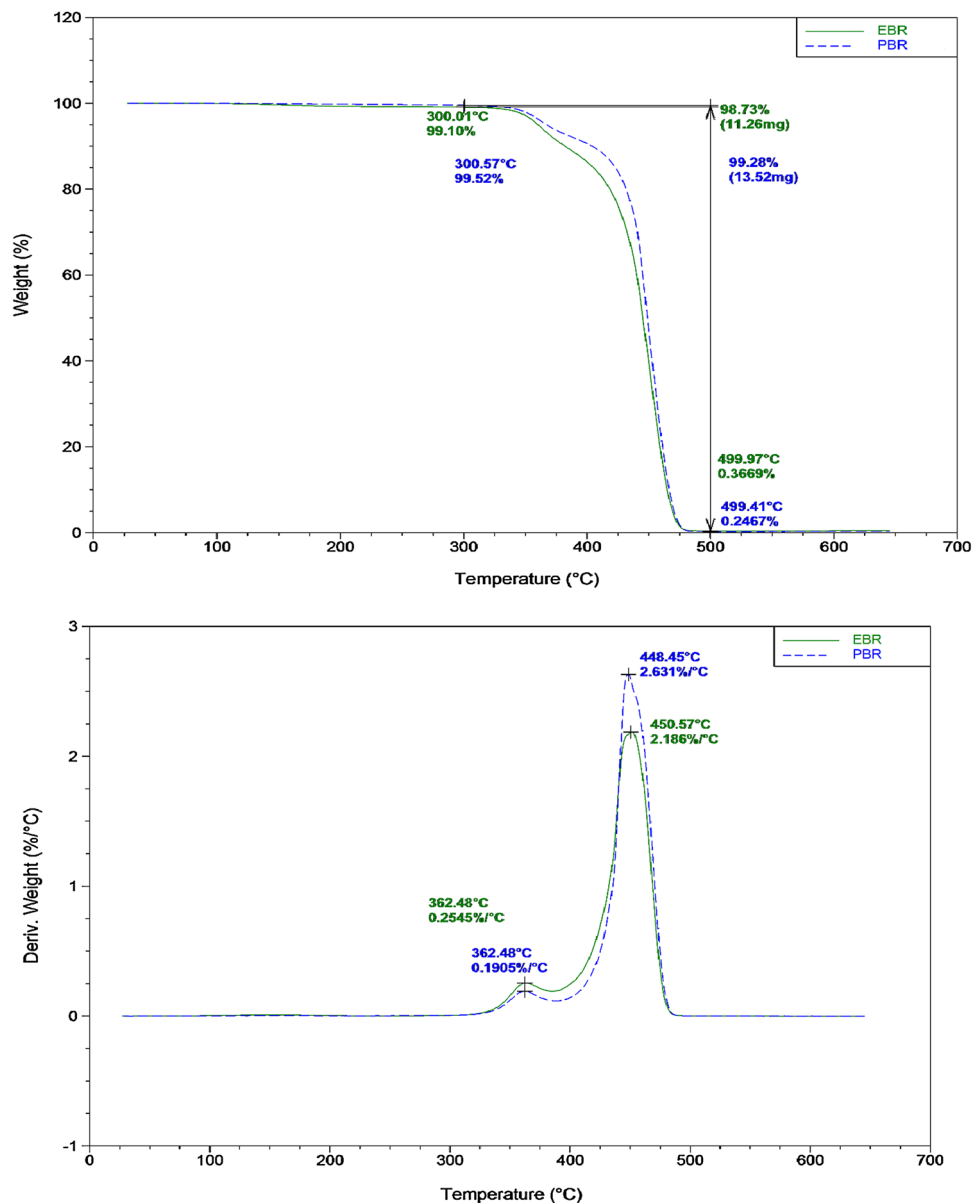**Fig. 4** TGA and DTG thermogram patterns of BR and EBR30 samples

Table 2 Mechanical properties of SBR/BR–silica composites containing various coupling agent

Properties	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
Tensile strength, MPa	5.40	10.55	8.13	6.29	7.51	4.75
Hardness, shore A	64	66	58	62	63	62
Elongation at break, %	555	377	460	303	560	595
100% modulus, MPa	1.60	3.92	2.80	2.71	2.45	1.52
300% modulus, MPa	3.28	6.09	5.90	3.17	4.31	3.04
V_r	0.182	0.281	0.186	0.185	0.221	0.156
Crosslink density $\times 10^{-4}$	0.80	2.55	0.85	0.83	1.32	0.54

Sample A composite sample without any compatibilizer, *Sample B* composite sample using TESPT as a coupling agent, *Sample C* composite sample using APS as a coupling agent, *Sample D* composite sample using EBR10 as a coupling agent, *Sample E* composite sample using EBR30 as a coupling agent, and *Sample F* composite sample using EBR50 as a coupling agent

Scheme 2 Proposed coupling reaction in the presence of TESPT
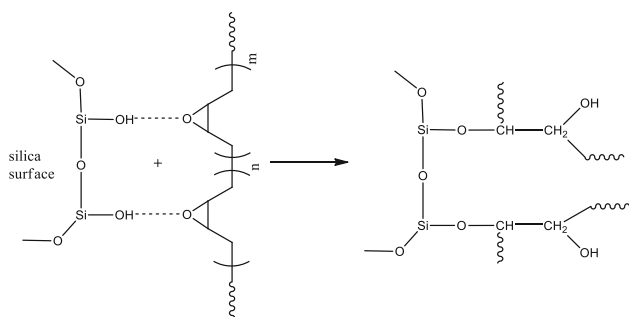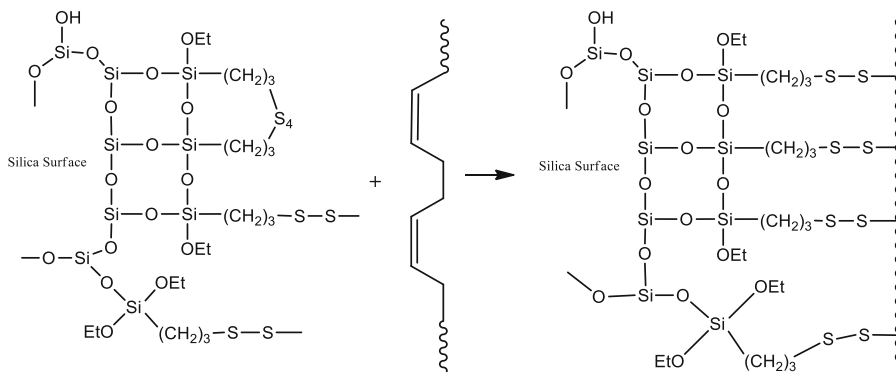
Scheme 3 Proposed coupling reaction in the presence of EBR

filler particles were uniformly dispersed in Sample B, Sample K, and Sample L, whereas an agglomeration of silica particles was observed in Sample A (without any compatibilizer). The observed SEM images clearly reflect that the utilization of EBR along with TESPT improved the silica filler dispersion by interaction between free –OH groups of silica surface with oxirane ring of EBR30 rubber chain to form strong interaction.

Dynamic mechanical properties

It has been reported that wet skidding resistance and rolling resistance of tires are generally determined by the tan δ value at temperatures of −20 to 0 and 50 to 70 °C, respectively [32]. Higher tan δ value at temperatures of −20 to 0 °C corresponds to improved wet skidding resistance, whereas lower tan δ value at temperatures of 50–70 °C relates to low rolling resistance. Therefore, to investigate the influence of employed compatibilizers EBR, TESPT, and APS in BR/SBR rubber matrix, the tan δ (loss factor) of various samples were compared (Fig. 11). It was observed that the tan δ at lower temperature (−20 to 0 °C) was higher for Sample B followed by Sample L as compared to those observed for the Sample A (without any compatibilizer). Therefore, both the Sample B and Sample L will show better wet skid resistance as compared to other Sample A, Sample K and Sample M. Moreover, the tan δ at
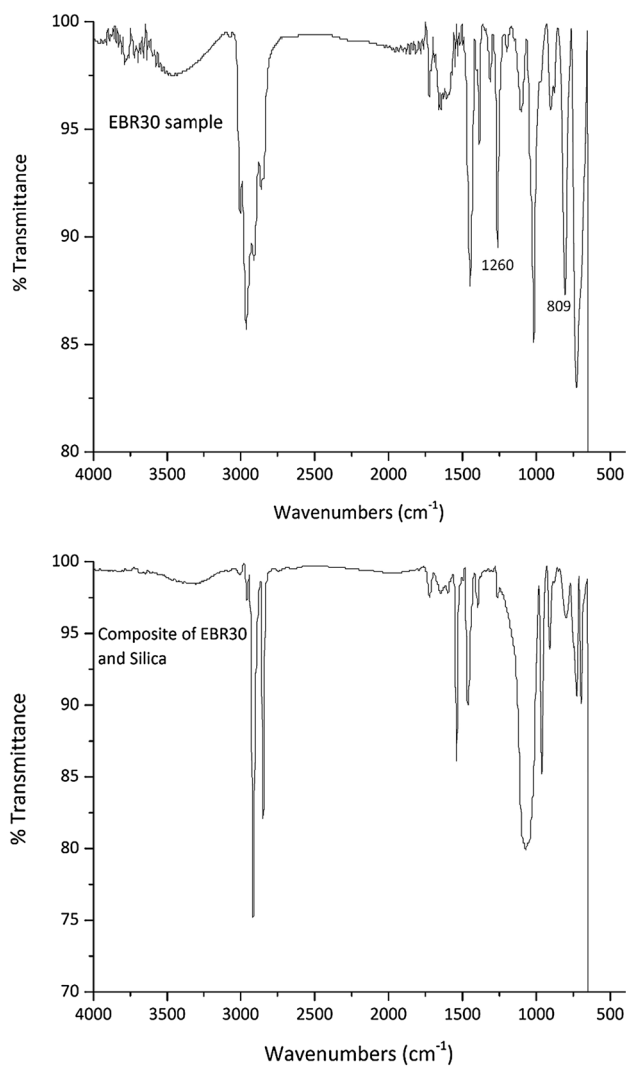

Fig. 5 FTIR spectra of EBR30 and composite of EBR30 and silica samples

higher temperatures (50–70 °C) was lower for the Sample B followed by Sample L as compared to those observed for Sample A (without any compatibilizer). Therefore, it can be concluded that the Sample B and Sample L would
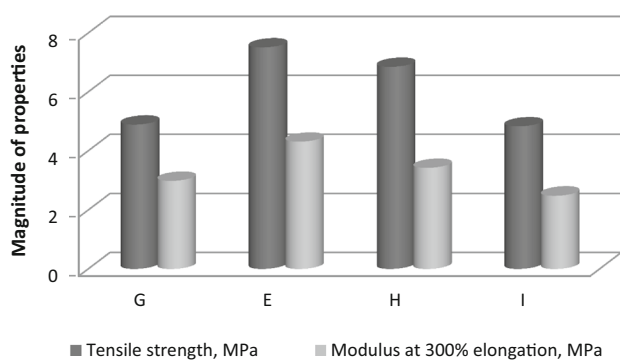
Fig. 6 Effect of variation of loading of EBR30 loading level on the tensile strength and modulus of the composite samples
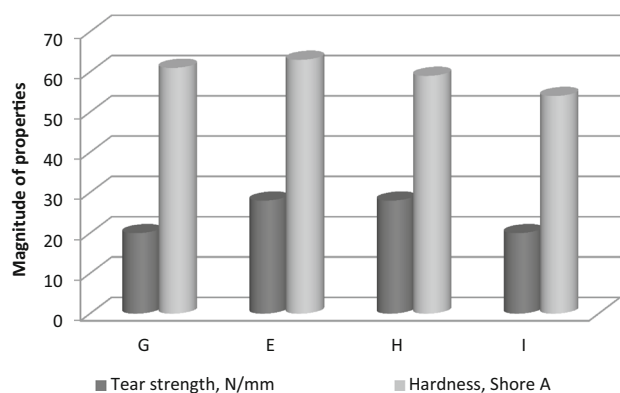

Fig. 7 Effect of variation of loading of EBR30 loading level on the tear strength and hardness of the composite samples. *Sample G* composite sample using EBR30 loading as 8% of silica content, *Sample E* composite sample using EBR30 loading as 12% of silica content, *Sample H* composite sample using EBR30 loading as 25% of silica content, and *Sample I* composite sample using EBR30 loading as 50% of silica content

show better rolling resistance and wet skid resistance than other Sample A, Sample K, and Sample M. Important to mention here that the Sample L (60 phr EBR30 and 40

phr TESPT silane as a compatibilizer) and Sample B (only TESPT silane as a compatibilizer) have shown comparable dynamic properties which further confirms potential effectiveness of EBR30 as a compatibilizer in green-tire composites.

Effect of EBR on viscoelastic properties of the composites

The viscoelastic behaviors of various composite samples as a function of strain percentage at 60 °C were also investigated for some of the samples (Fig. 12). The typical features of the Payne effect, i.e., a decrease in the storage modulus with increasing strain, can be seen for all the studied composite samples. The Payne effect amplitude, was calculated as a decrease in the magnitude of the non-linear effect was observed to follow the trend as Sample E < Sample L = Sample B < Sample C < Sample M. The efficient silanization of EBR30 sample can be seen from the observed lower values of the composite Sample E and Sample L, which reflects a better rubber–filler interaction in the composite samples.

Interestingly, unlike the physico-mechanical properties, the dynamic mechanical properties of EBR-containing composite samples were comparable with the corresponding composite sample containing the conventional silane like TESPT. Moreover, for the composite Sample M, ineffective silanization was observed which reduces rubber–filler interaction as explained in Scheme 4.

In addition, the Payne effect amplitude v/s V_r was also plotted (Fig. 13), where values followed a reverse trend in comparison to the trend observed for V_r. The higher V_r values can be observed in Sample B and Sample L due to additional crosslinking which caused by the presence of conventional silane TESPT in the composite sample.

Table 3 Physico-mechanical properties of different SBR/BR–silica composites sample containing combination various loading of TESPT and EBR30 compatibilizers

Properties	Sample B	Sample C	Sample J	Sample K	Sample L	Sample M
Hardness, shore A	66	58	64	66	74	61
Tensile strength, MPa	10.55	8.13	9.54	9.33	9.85	6.73
Elongation at break, %	277	460	340	309	386	425
100% modulus, MPa	3.92	2.80	2.81	3.24	2.94	2.38
300% modulus, MPa	6.09	5.90	8.56	8.95	7.73	4.95
Tear strength, N/mm	29	35	28	28	29	28
Abrasion loss, g/40 m	0.168	0.225	0.233	0.218	0.199	0.206
Cut and chip, g/10 min	2.83	3.28	2.46	2.82	2.83	3.21
V_r	0.311	0.209	0.231	0.265	0.243	0.183

Sample B composite sample using TESPT as a coupling agent, *Sample C* Composite sample using APS as a coupling agent, *Sample J* composite sample using combination of EBR30: TESPT (40:60 ratio), *Sample K* composite sample using combination of EBR30:TESPT (50:50 ratio), *Sample L* composite sample using combination of EBR30:TESPT (60:40 ratio), and *Sample M* composite sample using combination of EBR30:APS (60:40 ratio)

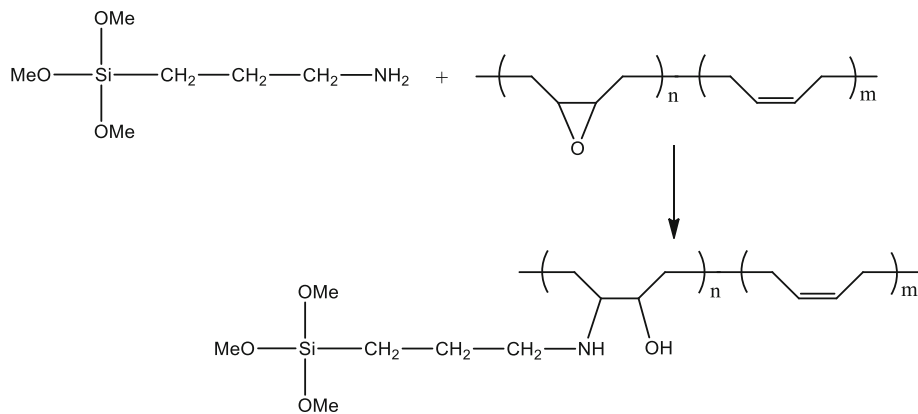**Scheme 4** Proposed reaction between the amino-group of APS and oxirane ring of EBR30

Table 4 Cure characteristics of various samples

	Sample A	Sample B	Sample K	Sample L	Sample M
M_L (d$N - M$)	4.9	3.3	4.2	4. 5	5.6
M_H (d$N - M$)	25.77	31.48	28.89	30.08	21.59
t_{s2} (min)	4.07	4.04	4.07	3.76	1.11
t_{90} (min)	10.01	17.39	15.33	14.34	5.74
ΔTorque ($M_H - M_L$) (d$N - M$)	20.87	28.15	24.65	25.43	15.98

Table 5 Bound rubber content

	Sample A	Sample B	Sample K	Sample L	Sample M
Bound rubber content (%)	46	79	69	74	51

Sample A composite sample without any compatibilizer, *Sample B* composite sample using TESPT as a coupling agent, *Sample K* composite sample using combination of EBR30:TESPT (50:50 ratio), *Sample L* composite sample using combination of EBR30:TESPT (60:40 ratio), and *Sample M* composite sample using combination of EBR30:APS (60:40 ratio)
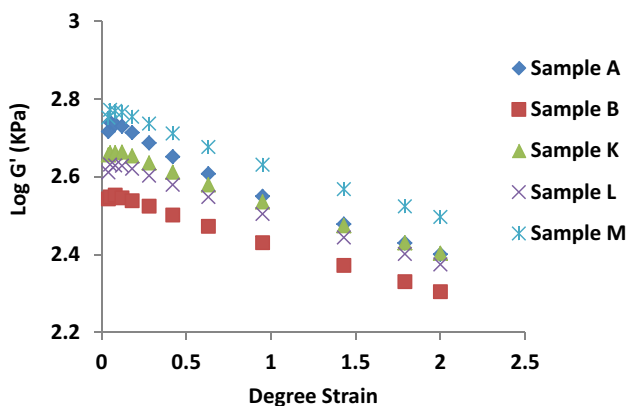
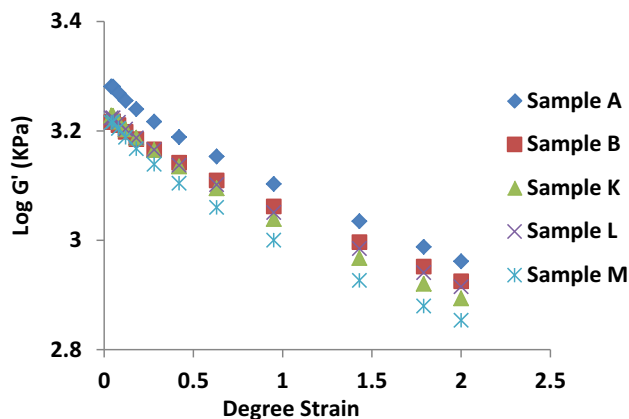**Fig. 8** Log storage modulus of uncured samples as a function of degree strain

Fig. 9 Log storage modulus of cured samples as a function of degree strain. *Sample A* composite sample without any compatibilizer; *Sample B* composite sample using TESPT as a coupling agent; *Sample K* composite sample using combination of EBR30:TESPT (50:50 ratio), *Sample L* com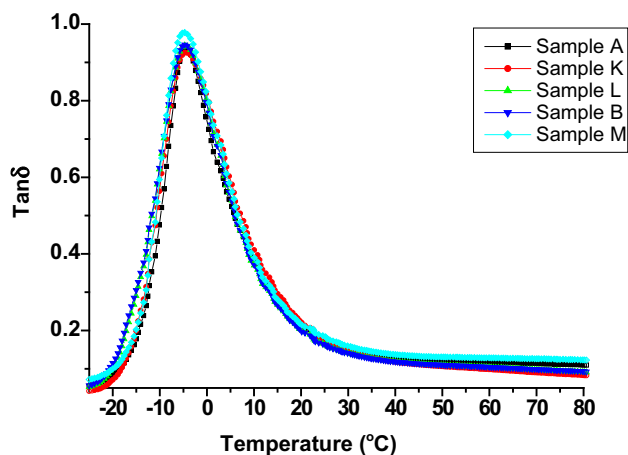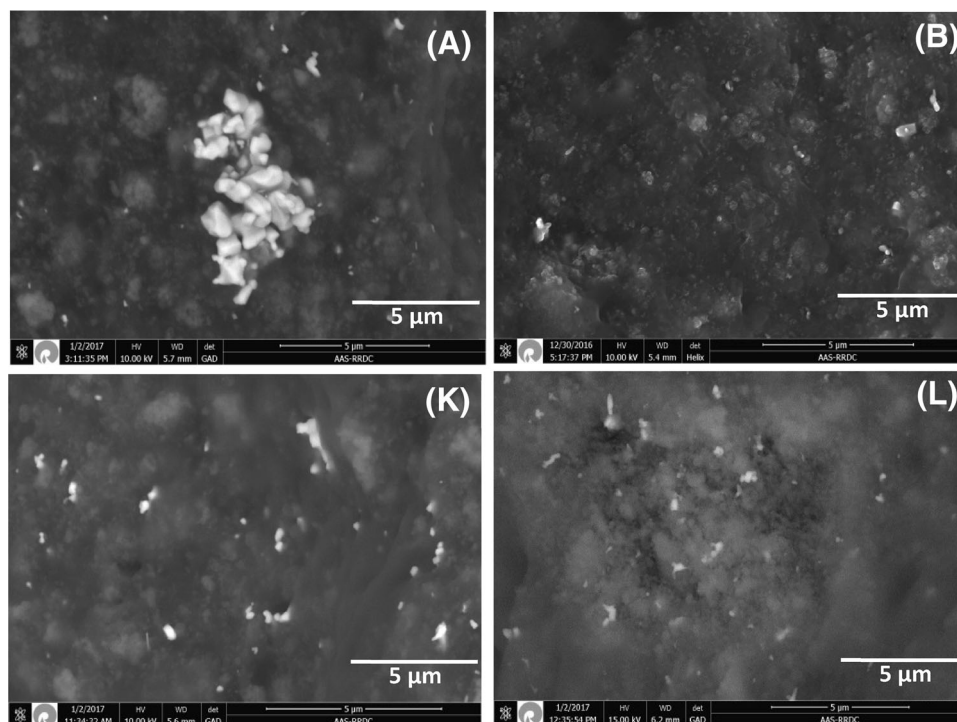posite sample using combination of EBR30:TESPT (60:40 ratio), and *Sample M* composite sample using combination of EBR30:APS (60:40 ratio)

Conclusions

In the present work, epoxidized polybutadiene rubber (EBR) was synthesized, characterized and used as a compatibilizer in SBR/BR–silica composite blend. With increasing epoxation level, the compatibilization effect increased till 30 mol% epoxation (EBR30) and then decreased at higher epoxation level (50 mol%). In addition, 12% loading was found as an optimum loading of

Fig. 10 SEM images of various samples. *Sample A* composite sample without any compatibilizer; *Sample B* composite sample using TESPT as a coupling agent; *Sample K* composite sample using combination of EBR30:TESPT (50:50 ratio), and *Sample L* composite sample using combination of EBR30:TESPT (60:40 ratio)

Fig. 11 Temperature dependence of tan δ values. *Sample A* composite sample without any compatibilizer; *Sample B* composite sample using TESPT as a coupling agent; *Sample K* composite sample using combination of EBR30:TESPT (50:50 ratio), *Sample L* composite sample using combination of EBR30:TESPT (60:40 ratio), and *Sample M* composite sample using combination of EBR30:APS (60:40 ratio)

Fig. 12 Plot of storage modulus versus percentage strain

EBR30 in composite sample. It was observed that although EBR can function as an effective compatibilizer, however, all the physico-mechanical properties obtained with commercial silane-coupling agent, TESPT was better than those of EBR-containing composite samples. The physico-mechanical properties of the composite sample containing combination of TESPT:EBR (40:60–60:40) were
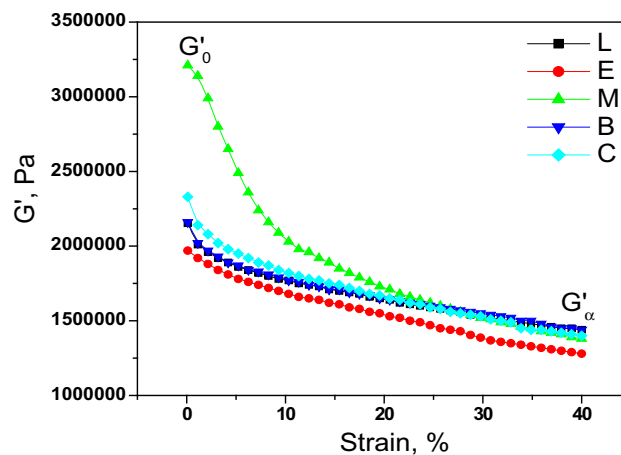
comparable with those of TESPT containing composite samples. On the other hand, the dynamic mechanical properties obtained while using the composite sample containing combination of TESPT:EBR (40:60) were comparable to the corresponding composite sample containing TESPT as a compatibilizer. The rheological, bound rubber content, Payne effect, and SEM results indicated the good compatibility between polar-EBR matrix and polar silica nanoparticles. The dynamic properties of the samples measured at low and high temperatures improved both good rolling as well as wet skid resistance. Finally, it can be concluded that in the Green-tire composite, 40–60% of the expensive conventional silanes can be replaced by
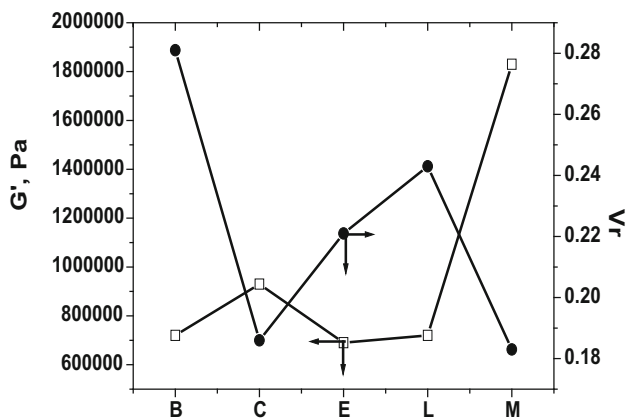
Fig. 13 Plot of Payne effect amplitude versus volume fraction of rubber. *Sample B* composite sample using TESPT as a coupling agent, *Sample C* composite sample using APS as a coupling agent, *Sample E* composite sample using EBR30 as a compatibilizer, *Sample L* composite sample using combination of EBR30:TESPT (60:40 ratio), and *Sample M* composite sample using EBR30:APS (60:40 ratio) as a compatibilizer

EBR30 sample without sacrificing the properties and reducing the advantages associated with silanes.

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