Dynamic Mechanical Properties of Styrene-Butadiene Rubber Vulcanizate Filled with Electron Beam Modified Surface-Treated Dual-Phase Filler

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ABSTRACT: The influence of the electron beam modification of a dual-phase filler on the dynamic mechanical properties of styrene-butadiene rubber (SBR) is investigated in the presence and absence of trimethylol propane triacrylate or triethoxysilylpropyltetrasulfide. Electron beam modification of the filler results in reduction of the tan δ at 70°C, a parameter for rolling resistance, and an increase in the tan δ at 0°C, a parameter for wet skid resistance of SBR vulcanizates. These modified fillers give significantly better overall performance in comparison with the control dual-phase filler. This variation in properties is explained in terms of filler parameters such as the filler structure that leads to rubber occlusion and filler networking. These results are further corroborated using the master curves obtained by the time–temperature superposition principle. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2992–3004, 2003

Key words: fillers; reinforcement; rubber; radiation; viscoelastic properties; mechanical properties

INTRODUCTION

Fillers cause considerable changes in the dynamic properties of rubber, including the modulus and hysteresis. Some of the large volume uses of fillers are in applications such as tires, belting, and engine mountings, where the materials are subjected to rapid repeated deformations, although of relatively small magnitude, when compared with their ultimate breaking strength. The presence of a filler in rubber considerably modifies the low strain dynamic properties of a vulcanizate. It has been recognized that, for a given polymer and cure system, the surface area and structure of a filler, the hydrodynamic effect, and filler–filler and filler–polymer interactions influence the dynamic properties of rubber.[1] However, the dispersion state of these materials throughout the polymeric matrix is also important. To achieve good dispersion of filler by depressing the carbon black networking and increasing the filler–polymer interaction, surface modification is frequently used in the rubber industry.[2]

Recently, Cabot Corporation designed a new reinforcing filler (ECOBLACK) consisting of a silica phase distributed in a carbon phase. Its main feature in rubber compounding is its low filler–filler interaction, which reduces the carbon black networking in the vulcanizate, resulting in good dispersion of the fillers.[3] This filler provides improved dynamic properties, namely, high hysteresis at low temperature, which is necessary for the high wet grip resistance and low hysteresis at high temperature that imparts low rolling resistance relative to conventional carbon black.[4] The above properties are some requirements for developing a good tire tread composition.

However, filler–polymer interactions and the properties dependent on them need to be improved. In our earlier communication, we have demonstrated that electron beam modification of a dual-phase filler is a novel method to improve the mechanical properties of a filled styrene-butadiene rubber (SBR).[5] Like oxidation of carbon black, this surface treatment causes a considerable increase in the oxygen-containing functional groups on the surface. However, the extent of reactivity of the filler with the polymer is a function of the radiation dose and nature of the surface treatment. In this article we discuss the effect of electron beam treatment of the carbon black and the dual-phase fillers on the dynamic mechanical properties of SBR vulcanizates in the presence and absence of a radiation sensitizer like trimethylol propane triacrylate (TMPTA) and a coupling agent like triethoxysilylpropyltetrasulfide (Si-69).

EXPERIMENTAL

Materials

Fillers

The dual-phase filler and carbon black (N220) were supplied by Cabot Corporation (Billerica, MA) and

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TABLE I
Analytical Properties of Carbon Black and Dual Phase Fillers

Si No.	Fillers	Silica Content (%)	Nitrogen Surface Area (N_2 SA) (m^2/g)	External Surface Area (STSA) (m^2/g)	CDBP Adsorption (mL/100 g)
1	N220	—	122.0	120.0	101.0
2	CSDPF-A (CRX-2000)	4.8	154.3	121.4	101.0
3	CSDPF-E (CRX-2006)	5.7	210.8	136.7	104.0
4	CSDPF-F (CRX-2002)	2.6	102.6	87.1	103.0

Philips Carbon Black Company, respectively. The analytical properties are given in Table I.

Chemicals

TMPTA was supplied by UCB Chemicals and Si-69 was purchased from Degussa A.G.

Filler modification

The detailed procedures for modification of the fillers using an electron beam accelerator were discussed in our earlier communications.[6,7] The specifications of the electron beam accelerator and operating principles were reported elsewhere.[8,9]

Preparation of SBR vulcanizates

The compounds according to the formulation in Table II, except the sulfur and accelerator, were mixed in a Brabender plasticorder (PLE 330). In the final stage, the curatives were added in an open roll mill. The compounds were then cured to an optimum cure state according to optimum cure time (t_{90}) data obtained from a MDR-2000 instrument.

TABLE II
Compound Recipe

Si. No.	Ingredients	Loading (phr)
1	SBR-1502[a]	100.0
2	ZnO	5.0
3	Stearic acid	1.5
4	Antioxidant (TQ)[b]	1.0
5	Filler[c]	10-60
6	TBBS[d]	1.0
7	S	2.0

Zinc oxide (ZnO); sulfur (S) and stearic acid were procured from local suppliers.

[a] Styrene-butadiene rubber (SBR-1502) with 23.5% styrene content from Synthetic and Chemicals Ltd.

[b] Antioxidant trimethylol quinoline from R. T. Vanderbilt Co.

[c] Accelerator tertiary butyl benzthiazole sulfenamide from ICI chemicals (Rishra,India).

Designation of SBR vulcanizates

The SBR vulcanizates were designated as $SA_{x/y/z}$, $SB_{x/y/z}$, $SC_{x/y/z}$, and $SD_{x/y/z}$, where S and A represent SBR and N220, respectively; B, C, and D indicate dual-phase fillers; and x, y, and z represent the monomer or silane level, radiation dose (kGy), and filler loading (phr), respectively. These are given in Table III.

Dynamic mechanical properties

The dynamic properties of the filled vulcanizates were measured by means of a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific) using a rectangular specimen (30 × 10 × 1.5 mm) and operating in tensile mode. Data were acquired using RSI Orchestrator software on an Acer computer. Three types of tests were performed: temperature sweep (−80 to +80°C), strain sweep (0.001–10%), and frequency sweep (0.032–32 Hz).

Temperature sweep measurement

This measurement was carried out at temperatures ranging from −80 to 80°C at a heating rate of 2°C/min. The test frequency was fixed at 1 Hz, and the strain amplitude was set at 0.01% double strain amplitude (DSA).

Strain sweep measurement

In this case, DSAs ranging from 0.001 to 10% were applied with a frequency of 10 Hz at constant temperatures of 0 and 70°C. The data were taken at 5 points per decade and the full curves were recorded.

Frequency sweep measurement

A frequency sweep was carried out in the temperature range of −60 to 60°C and data were taken at every 5°C. A ramp and soak program was used to control the temperature profile. The specimen was soaked for 5 min at each temperature before testing. The storage modulus (E'), loss modulus (E''), and loss tangent (tan

TABLE III
Designation of Various Electron Beam Modified Dual-Phase Filler-Loaded SBR Vulcanizates

Si. No.	Sample Designation	Fillers	Type of Ingredients	Ingredients Level (%)	Radiation Dose (kGy)	Filler Loading
1	$SB_{0/0/20}$	CSDPF-A	—	—	—	20
2	$SB_{0/100/20}$	CSDPF-A	—	—	100	20
3	$SB_{3T/0/20}$	CSDPF-A	TMPTA	3	—	20
4	$SB_{3T/20/20}$	CSDPF-A	TMPTA	3	20	20
5	$SB_{3T/50/20}$	CSDPF-A	TMPTA	3	50	20
6	$SB_{3T/100/10}$	CSDPF-A	TMPTA	3	100	10
7	$SB_{3T/100/20}$	CSDPF-A	TMPTA	3	100	20
8	$SB_{3T/100/40}$	CSDPF-A	TMPTA	3	100	40
9	$SB_{3T/100/60}$	CSDPF-A	TMPTA	3	100	60
10	$SB_{3T/200/20}$	CSDPF-A	TMPTA	3	200	20
11	$SB_{1T/100/20}$	CSDPF-A	TMPTA	1	100	20
12	$SB_{5T/100/20}$	CSDPF-A	TMPTA	5	100	20
13	$SB_{3S/0/20}$	CSDPF-A	Si-69	3	—	20
14	$SB_{3S/100/20}$	CSDPF-A	Si-69	3	100	20
15	$SB_{1S/100/20}$	CSDPF-A	Si-69	1	100	20
16	$SB_{5S/100/20}$	CSDPF-A	Si-69	5	100	20
17	$SA_{3T/100/20}$	N220	TMPTA	3	100	20
18	$SD_{3T/100/20}$	CSDPF-F	TMPTA	3	100	20
19	$SC_{3T/100/20}$	CSDPF-E	TMPTA	3	100	20

TMPTA, Trimethylol propanetriacrylate; Si-69, triethoxysilylpropyltetrasulfide.

δ) were measured in the frequency range of 0.032–32 Hz. A 1% strain amplitude was used in all the measurements.

RESULTS AND DISCUSSION

Effect of irradiated, surface-treated dual-phase fillers on dynamic mechanical properties of SBR vulcanizates

Temperature dependence of storage modulus and tan δ

Figure 1(a) shows the temperature dependencies of E' for SBR vulcanizates loaded with 20 phr of unmodified and electron beam modified dual-phase fillers. The storage modulus of the electron beam modified filler loaded rubber ($SB_{0/100/20}$) is higher than that of the rubber containing the unmodified filler ($SB_{0/0/20}$) over the range of temperatures investigated (especially at lower temperature). Also, the addition of TMPTA or silane with or without a radiation dose increases the storage modulus in the glassy region when the samples are compared with $SB_{0/0/20}$. This can be understood from the values of the storage modulus at −70°C for these modified filler loaded SBR vulcanizates (Table IV). Figure 1(b) shows the temperature dependencies of the tan δ of those samples. The glass-transition temperature (T_g) of these modified filler loaded vulcanizates is also included in Table IV. Electron beam irradiation of the filler increases the T_g of the filled SBR by 3 units ($SB_{0/0/20}$ = −46°C, $SB_{0/100/20}$ = −43°C). This change in the T_g is mainly attributed to the increase in trapped rubber or occluded rubber, which loses its identity as a polymer and behaves like a filler. The presence of TMPTA and silane marginally affects the T_g of the polymer, although the values are

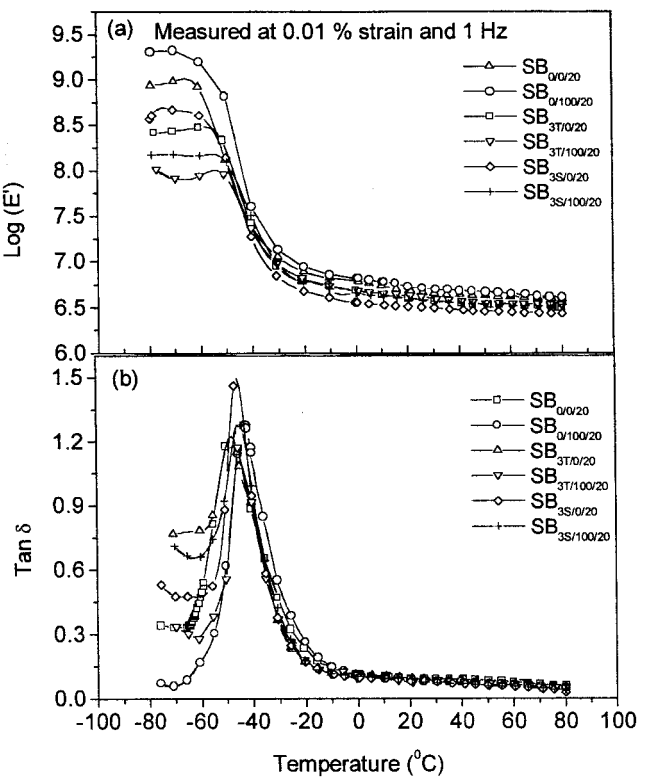


Figure 1 The variation of the (a) storage modulus (log E', Pa) and (b) tan δ with the temperature for electron beam modified filler loaded SBR vulcanizates.

TABLE IV
***E′* and Tan δ of Electron Beam Modified Dual-Phase Filler-Loaded SBR Vulcanizates**

			E′ ($\times 10^{-6}$ Pa)			Tan δ			
Si. No.	Samples	T_g (°C)	At −70°C	At 0°C	At 70°C	At −70°C	At T_g (°C)	At 0°C	At 70°C
1	$SB_{0/0/20}$	−46	56.5	5.17	3.24	0.332	1.092	0.116	0.073
2	$SB_{0/100/20}$	−43	2137.0	6.61	4.27	0.061	1.050	0.106	0.044
3	$SB_{3T/0/20}$	−45	275.0	4.93	3.31	0.758	1.200	0.093	0.052
4	$SB_{3T/100/20}$	−43	82.4	4.78	3.47	0.332	1.170	0.108	0.057
5	$SB_{3S/0/20}$	−45	466.0	3.66	2.76	0.480	1.460	0.096	0.040
6	$SB_{3S/100/20}$	−44	151.0	4.55	3.28	0.689	1.280	0.096	0.056

increased for the SBR vulcanizates containing electron beam modified surface-treated fillers because of the reason above. The tan δ values at the T_g is low for electron beam modified filler loaded vulcanizates ($SB_{0/100/20}$, $SB_{3T/100/20}$, $SB_{3S/100/20}$) compared to their respective unmodified counterparts ($SB_{0/0/20}$, $SB_{3T/0/20}$, $SB_{3S/0/20}$). The lower tan δ values at T_g, 0, and 70°C indicate better interaction of this modified filler with SBR vulcanizates because of physical and chemical adsorption.[10]

Strain amplitude dependence of storage modulus, loss modulus, and tan δ measured at 70°C

Strain sweep tests were performed in order to further investigate the effect of electron beam treatment of the filler on the polymer–filler and filler–filler interactions. Figure 2(a) shows the plot of the elastic modulus measured at 70°C and 10 Hz versus the DSA. The storage modulus of the irradiated filler loaded vulcanizate ($SB_{0/100/20}$) is higher than that of nonirradiated one ($SB_{0/0/20}$). The addition of TMPTA ($SB_{3T/0/20}$) and silane ($SB_{3S/0/20}$) reduces the storage modulus of the composites because of plasticizing effect. However, electron beam treatment of these fillers ($SB_{3T/100/20}$, $SB_{3S/100/20}$) significantly improves the storage modulus compared to its nonirradiated counterpart. This is probably due to the combined effect of surface oxidation of the dual-phase filler upon electron beam irradiation and the partial increase in primary and secondary structures.

From electron spectroscopy for chemical analysis studies[7] it was concluded that electron beam irradiation of the dual-phase filler increases the oxygen concentration (%) to 13.2 ($B_{0/100}$), 10.8 ($B_{3T/100}$), and 10 ($B_{3S/100}$) from 9.0 ($B_{0/0}$) on the surface when subjected to 100-kGy radiation doses in the presence and absence of TMPTA or silane. This introduction of oxygen-containing functional groups leads to the chemical reactivity between the filler and polymer matrix.[11,12] However, the chemical reactivity of the oxidized filler depends on the nature of the polymer that is used. Because SBR is nonpolar in nature, the chemical reactivity of the filler with the polymer is unexpected. However, previous reports suggest that introduction of oxygen atoms onto the surface produces free radicals during the high shear of mixing, which enhances the filler–polymer interaction.[12] Also,

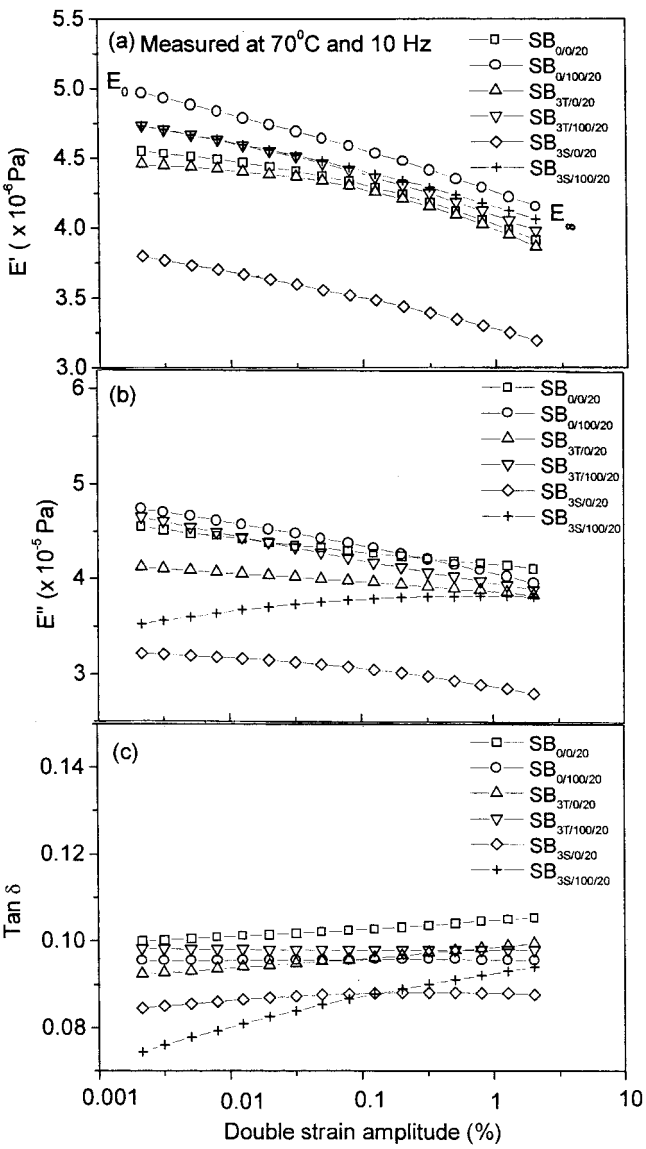


Figure 2 The variation of the (a) storage modulus (*E′*, Pa), (b) loss modulus (*E″*, Pa), and (c) tan δ with the double strain amplitude for electron beam modified dual-phase filler loaded SBR vulcanizates measured at 70°C.

TABLE V
E_0, E_∞, and ($E_0 - E_\infty$) Values of SBR Vulcanizates Loaded with Modified Fillers and Measured at 70°C

Si. No.	Samples	E_0 ($\times 10^{-6}$ Pa)	E_∞ ($\times 10^{-6}$ Pa)	$E_0 - E_\infty$ ($\times 10^{-6}$ Pa)
1	$SB_{0/0/20}$	4.55	3.91	0.64
2	$SB_{0/100/20}$	4.98	4.15	0.83
3	$SB_{3T/0/20}$	4.46	3.86	0.60
4	$SB_{3T/100/20}$	4.74	3.98	0.76
5	$SB_{3S/0/20}$	3.80	3.20	0.60
6	$SB_{3S/100/20}$	4.74	4.06	0.68

from transmission electron microscopy studies[6] it has been concluded that electron beam irradiation of the dual-phase filler in the presence and absence of TMPTA or silane causes an increase in primary and secondary structures. This is confirmed by the increase in the linear fractal dimension from $D = 1.26$ ($B_{0/0}$) to 1.36 ($B_{0/100}$), 1.41($B_{3T/100}$) and 1.39 ($B_{3S/100}$). This variation in structure significantly improves the rubber occlusion and rubber shell that enhances the storage modulus. Even though the primary structure is almost similar in $SB_{0/100/20}$ and $SB_{3T/100/20}$, the storage modulus is high for the former because of higher surface oxidation.

Generally, the storage modulus of a filled rubber decreases nonlinearly with the strain amplitude. This phenomenon was observed in 1950 by Warring[13] and later Payne and Whittaker,[14] who studied it extensively. Payne attributed the decrease in storage modulus when increasing the strain amplitude to the breakdown of the secondary structure of carbon black. The variation in the secondary structure with straining (i.e., the Payne effect) is generally expressed in terms of the difference ($E_0 - E_\infty$) in storage modulus at low (E_0) and high strains (E_∞). Due to the machine constraints, the E value at 5% strain has been taken as E_∞. Table V shows these results. Compared to that of the control ($SB_{0/0/20}$), the ($E_0 - E_\infty$) value is higher for the electron beam modified filler ($SB_{0/100/20}$) ($SB_{0/0/20} = 0.64 \times 10^6$ Pa, $SB_{0/100/20} = 0.83 \times 10^6$ Pa), indicating filler networking in the latter case. This is mainly attributed to the development of a polar microporous surface, resulting in the formation of more carbon black networking. The presence of TMPTA ($SB_{3T/0/20}$) or silane ($SB_{3S/0/20}$) lowers the Payne effect, which can be better understood from the ($E_0 - E_\infty$) values (Table V). The Payne effect is also influenced by the rubber trapped or caged in the filler network, which loses its identity as a polymer and behaves like a filler. TMPTA or silane occupies the pores and hence the rubber entrapment is less in these modified fillers, resulting in a lower Payne effect. However, electron beam irradiation of these modified fillers ($SB_{3T/100/20}$, $SB_{3S/100/20}$) increases the secondary structure that breaks down under high strain. This is responsible for the higher value of ($E_0 - E_\infty$) (Table V).

Shown in Figure 2(b) is the plot of E'' with the DSAs measured at 70°C and 10 Hz. The loss modulus, which is a measure of breakdown and reformation of secondary structures, decreases with strain, indicating that reformation of structures predominates in these SBR vulcanizates, except for the rubber loaded with electron beam modified silanized dual-phase fillers ($SB_{3S/100/20}$), in which the breakdown of the secondary structure takes place. The loss modulus at low strain is slightly high for the modified filler loaded SBR vulcanizates ($SB_{0/100/20}$), and it is almost constant at higher strain. This suggests that the breakdown of the secondary structures is more for $SB_{0/100/20}$ at low strain compared to the control filler loaded rubber ($SB_{0/0/20}$). The loss modulus of $SB_{3T/0/20}$ and $SB_{3S/0/20}$ is lower than that of the control. However, electron beam modified filler loaded SBR vulcanizates ($SB_{3T/100/20}$, $SB_{3S/100/20}$) display higher loss modulus than that of their counterparts ($SB_{3T/0/20}$, $SB_{3S/0/20}$) over the range of strains investigated. This result suggests that breakdown and reformation of structures is more pronounced in electron beam modified filler loaded SBR vulcanizates compared to their unmodified counterparts, possibly because of the higher secondary structure.

The tan δ, which is the ratio of the loss modulus to the storage modulus, is high for the unmodified filler loaded SBR vulcanizate [$SB_{0/0/20}$; Fig. 2(c)] compared to that of the modified filler loaded SBR vulcanizates. Even though the loss modulus is slightly high for $SB_{0/100/20}$ [Fig. 2(b)], the lower tan δ value may be attributable to a greater network portion that withstands dynamic deformation. This variation is ascribed to the chemical interaction between the filler and the polymer. The presence of TMPTA with or without a radiation dose lowers the tan δ value over the range of DSAs compared to that of $SB_{0/0/20}$. However, the electron beam irradiated silanized filler has a lower tan δ value at a lower DSA with a cross over at 0.1%. This indicates that at low strain the hysteresis loss is less pronounced in $SB_{3S/100/20}$ because of its stable secondary aggregates, whereas the reverse is true at high strain.

In order to understand the rolling resistance behavior of these modified filler loaded rubbers, the energy loss factor (E''/E'^2) has been calculated for these SBR vulcanizates and is plotted against the log(strain work) in Figure 3. The energy loss factor is low for modified filler loaded vulcanizates, indicating their lower hysteresis loss compared to the control filler loaded SBR vulcanizate ($SB_{0/0/20}$).

From the variation of the loss modulus and tan δ with the DSA, it is concluded that the breakdown of secondary structures is responsible for the variation of the hysteresis. This breakdown of the secondary structures, which are held together by weak van der Waal forces of attraction, leads to low strain hysteresis be-

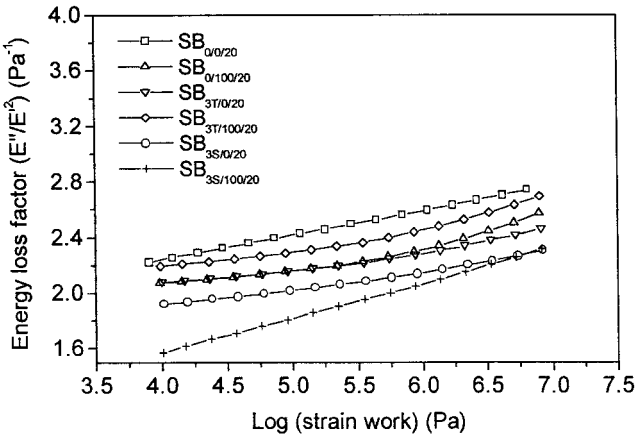


Figure 3 The variation of the energy loss factor (E''/E'^2, Pa^{-1}) with the log(strain work) (Pa).

havior. However, there is a significant amount of reformation of structures at high strain as evidenced from the decrease in the loss modulus with strain. Based on the assumption of the breakdown and reformation of structures, Kraus[15] theoretically derived the following equations for the storage modulus:

$$E = E'_\infty + \frac{(E'_0 - E'_\infty)}{1 + \left[\frac{\gamma}{\gamma_C}\right]^{2m}} \quad (1)$$

where E' is the storage modulus at different strain levels; E_∞' is the storage modulus after total destruction of the structures; γ is half the peak to peak test strain amplitude; and γ_c is the characteristic strain of the particular composite, which is generally expressed as follows:

$$\gamma_c = \left(\frac{k_m}{k_b}\right)^{0.5m} \quad (2)$$

where k_m is a rate constant for reformation of structures, k_b is a rate constant for breakdown of structures, and m is a constant.

On rearranging eq. (1) and by applying least squares fitting, the unknown parameters γ_c and m are calculated for these modified filler loaded SBR vulcanizates. The values of γ_c, which is a direct indication of the rate of breakdown and reformation of structures, decreases from 0.19 ($SB_{0/0/20}$) to 0.09 ($SB_{0/100/20}$) when the samples are subjected to a 100-kGy radiation dose. It further decreases to 0.058 ($SB_{3T/100/20}$) when modified with TMPTA, indicating that structure breakdown occurs at lower strain levels. This is further confirmed by the variation of another influencing parameter m, which is almost constant for $SB_{0/0/20}$ (0.33) and $SB_{0/100/20}$ (0.34) and increases for $SB_{3T/100/20}$ (0.38). However, it is found to be 0.64 ($SB_{3S/100/20}$) for the silane modified system. The lower value of γ_c and higher value of m indicates higher polymer–filler interaction in the silane modified system.

Strain amplitude dependence of storage modulus, loss modulus, and tan δ measured at 0°C

All the observations made from the results obtained at 70°C are also true when the values are compared at 0°C [Fig. 4(a)], but the difference between the low strain and high strain moduli is much greater because of the temperature dependence of filler–filler and filler–polymer interactions (Table VI). This can be well understood from the higher value of $(E_0 - E_\infty)$ for electron beam modified filler loaded rubber compared to the control ($SB_{0/0/20}$). These results are further re-

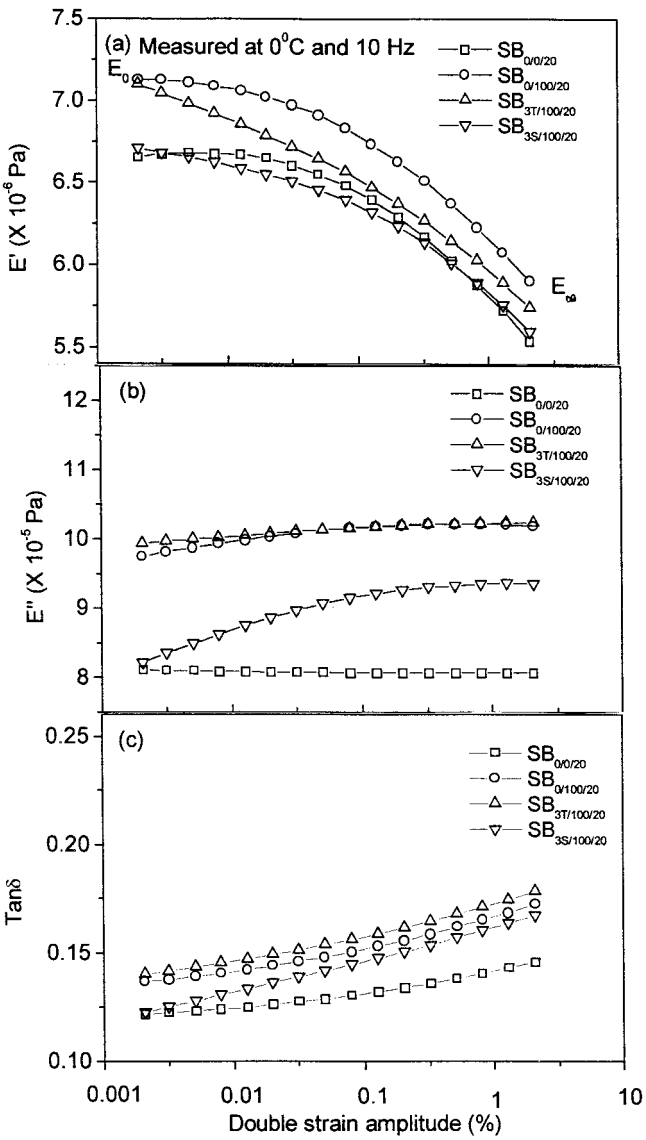


Figure 4 The variation of the (a) storage modulus (E', Pa), (b) loss modulus (E'', Pa) and (c) tan δ with the double strain amplitude for electron beam modified dual-phase filler loaded SBR vulcanizates measured at 0°C

TABLE VI
E_0, E_∞, and ($E_0 - E_\infty$) Values of SBR Vulcanizates Loaded with Modified Fillers as Measured at 0°C

Si. No.	Samples	E_0 ($\times 10^{-6}$ Pa)	E_∞ ($\times 10^{-6}$ Pa)	$E_0 - E_\infty$ ($\times 10^{-6}$ Pa)
1	$SB_{0/0/20}$	6.65	5.50	1.15
2	$SB_{0/100/20}$	7.13	5.90	1.23
3	$SB_{3T/100/20}$	7.10	5.70	1.40
4	$SB_{3S/100/20}$	6.71	5.50	1.21

flected in the tan δ values, which are high for the systems containing the modified fillers ($SB_{0/100/20}$, $SB_{3T/100/20}$, $SB_{3S/100/20}$) as compared to the control ($SB_{0/0/20}$). The value of E'', which is the measure of the hysteresis loss, is low for the control filler loaded system ($SB_{0/0/20}$) over the range of DSAs and the systems with the modified fillers ($SB_{0/100/20}$, $SB_{3T/100/20}$, $SB_{3S/100/20}$) display higher values [Fig. 4(b)]. The breakdown of the secondary structures over the range of strains is more pronounced in the modified filler loaded vulcanizates ($SB_{0/100/20}$, $SB_{3T/100/20}$, $SB_{3S/100/20}$) as evidenced from the higher values of ($E_0 - E_\infty$) compared to that of the control counterpart. The tan δ, which is the ratio of the loss modulus to the storage modulus, is also high for the modified filler loaded rubbers ($SB_{0/100/20}$, $SB_{3T/100/20}$, $SB_{3S/100/20}$) over the range of strains investigated [Fig. 4(c)]. This indicates the higher value of low strain hysteresis that can give higher wet grip resistance for these modified filler loaded vulcanizates.[16]

Frequency dependence of storage modulus, loss modulus, and tan δ for electron beam modified filler loaded SBR vulcanizates

Even though the above observations are useful to predict the behavior of these modified fillers in rolling and skid resistance, it is often necessary to understand the behavior of these systems at high frequencies ranging from 10 to 100 Hz because the rolling resistance is related to the movement of tires that corresponds to deformation at these frequencies. Also, in the case of skid or wet grip, the frequency of deformation is around 10^4–10^7 Hz at room temperature,[17] and it is thus necessary to know the dynamic properties at the appropriate high frequencies. Shown in Figure 5(a–c) are the master curves of the storage modulus, loss modulus, and tan δ for the unmodified ($SB_{0/0/20}$) and electron beam modified dual-phase filler loaded ($SB_{0/100/20}$) SBR vulcanizates. Following Wang et al.,[17] three temperature regions are identified from the master curves: high temperature (low frequency region), medium temperature (medium frequency region), and low temperature (high frequency region).

In the high temperature region (i.e., low frequency region) the E' is slightly higher for $SB_{0/100/20}$. At this zone, each filler aggregate consists of a thin rubber shell. The higher values of E' for $SB_{0/100/20}$ suggest higher filler–filler interaction in the filler aggregates. The E'' [Fig. 5(b)] is almost the same for the control and the modified filler, indicating that the hysteresis loss is almost the same at this imposed strain (1%) and there is no breakdown of filler aggregates. The tan δ, which is the ratio of E''/E', is low for $SB_{0/100/20}$ [Fig. 5(c)] because of higher filler–filler interaction without hysteresis loss in this temperature region.

As the frequency rises, the modulus of the modified filler loaded SBR vulcanizate ($SB_{0/100/20}$) is more than that of the control ($SB_{0/0/20}$), indicating higher polymer–filler interaction in this vulcanizate [Fig. 5(a)]. A

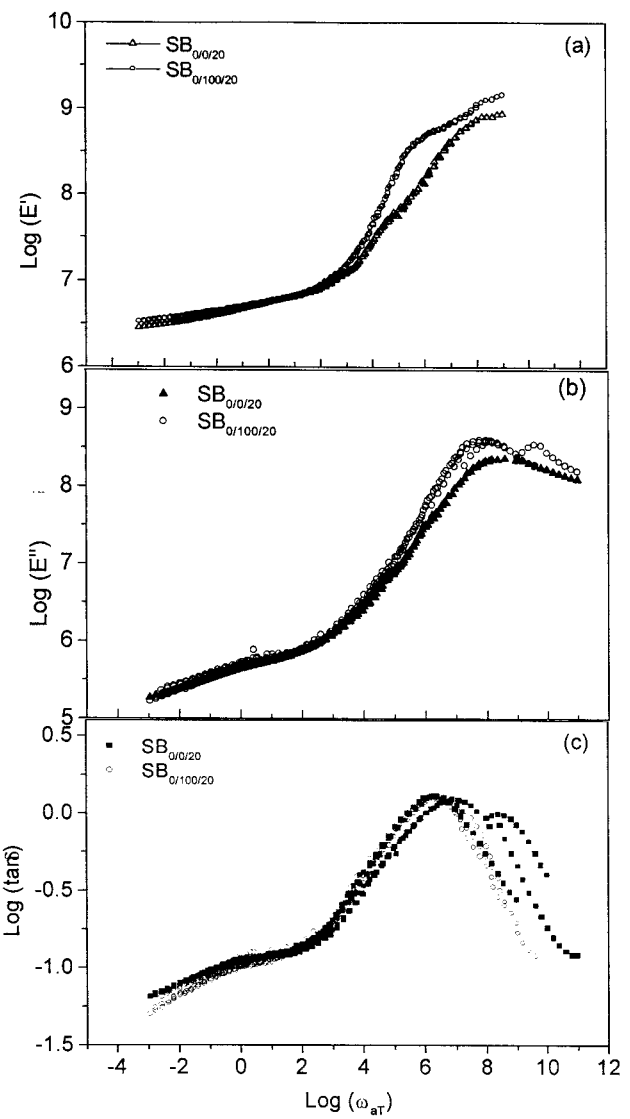


Figure 5 The master curves of SBR vulcanizates loaded with control ($SB_{0/0/20}$) and electron beam modified fillers ($SB_{0/100/20}$) for the (a) log(storage modulus) (Pa), (b) log(loss modulus) (Pa), and (c) log(tan δ).

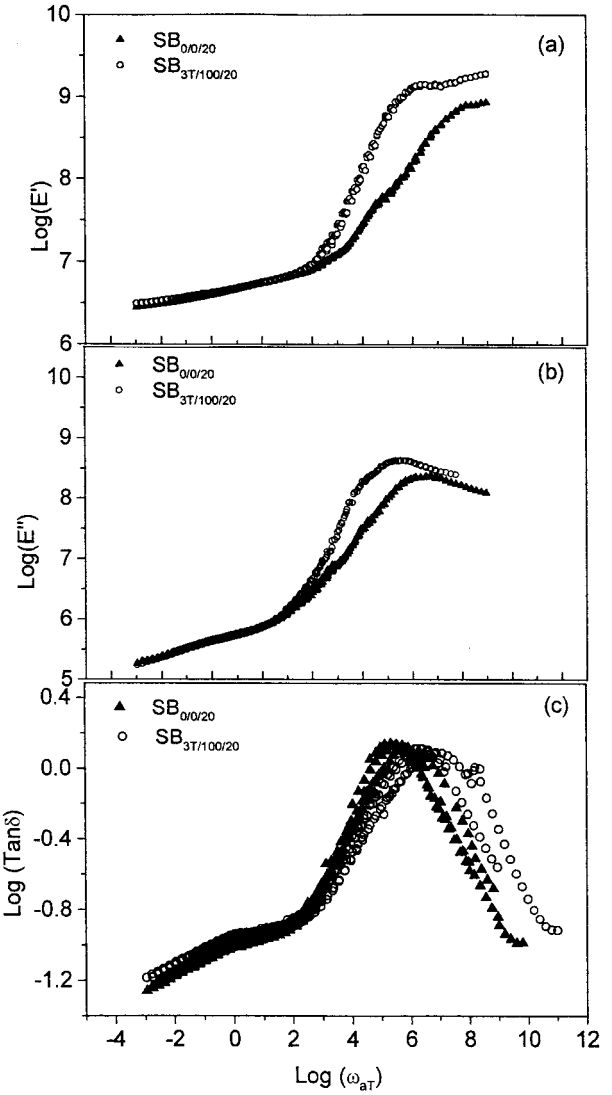


Figure 6 The master curves of SBR vulcanizates loaded with control ($SB_{0/0/20}$) and TMPTA modified fillers ($SB_{3T/100/20}$) for the (a) log(storage modulus) (Pa), (b) log(loss modulus) (Pa), and (c) log(tan δ).

layer of rubber shell develops around the filler aggregates because of the high polymer–filler interaction. Also, the rise in the hysteresis value is more for the modified system than its control counterpart [Fig. 5(b)]. The noncontinuous variation of the loss modulus and the storage modulus results in a featherlike feature in the tan δ [Fig. 5(c)] at this zone.

In the low temperature region, the storage and loss moduli of the modified system are higher than those of the control [$SB_{0/0/20}$; Fig. 5(a,b)]. This indicates that the amount of trapped rubber inside the filler network is very high in the modified primary and secondary structures that enhance the occluded rubber in the filler aggregates, resulting in the featherlike feature. This is because of the noncontinuous variation of the storage modulus and loss modulus [Fig. 5(c)].

Master curves of the E', E'', and tan δ for SBR vulcanizates loaded with unmodified ($SB_{0/0/20}$) and a representative TMPTA modified dual-phase filler ($SB_{3T/100/20}$) are shown in Figure 6(a–c). Compared to $SB_{0/0/20}$, E' and E'' are slightly higher for $SB_{3T/100/20}$ in the high temperature region (low frequency region). The higher modulus for $SB_{3T/100/20}$ compared to $SB_{0/0/20}$ is attributed to high filler–filler interaction [Fig. 6(a)]. The higher tan δ for $SB_{3T/100/20}$ compared to $SB_{0/0/20}$ in this zone indicates higher hysteresis loss [Fig. 6(c)].

In the medium temperature zone, the E' ad E'' are higher for $SB_{3T/100/20}$ compared to $SB_{0/0/20}$ [Fig. 6(a,b)]. In this zone the rubber shell, which forms around the filler aggregates, occurs more in $SB_{3T/100/20}$ because of higher polymer–filler interaction. Some aggregates may agglomerate together via a joint shell and some polymer trapped in this aggregate. As a result, the modulus of the rubber shell increases more rapidly than the modulus of the polymer matrix with a rise in the frequency, and this effect is more pronounced in $SB_{3T/100/20}$ compared to $SB_{0/0/20}$ because of its high structure. The same discussion would also be true for hysteresis because the rubber shell is close to or inside the transition zone. In the tan δ master curve, the rise in the peak transition occurs at higher frequency (lower temperature) compared to $SB_{0/0/20}$. This is attributed to the higher rubber shell thickness in $SB_{3T/100/20}$ compared to $SB_{0/0/20}$.

The dynamic properties of the polymer are governed by the Williams–Landel–Ferry (WLF) equation in the medium temperature zone and by Arrhenius equation at high temperature. Included in Table VII are the values of the WLF constants C_1 and C_2 and the Arrhenius factor for the control and electron beam modified filler loaded SBR vulcanizates. The Arrhenius factor, which is the measure of the activation energy, is about 108.0–127.8 kJ/mol.

Effect of TMPTA and silane level on dynamic mechanical properties of SBR vulcanizates

Figure 7(a) shows the variation of the storage modulus with the temperature for the modified dual-phase filler loaded SBR vulcanizates having different levels of TMPTA or silane. The storage modulus in the

TABLE VII
Fitting Parameters for SBR Vulcanizates Loaded with Modified Dual-Phase Fillers

Si. No.	Samples	WLF Factor C_1	WLF Factor C_2	Arrhenius Factor (kJ/mol)
1	$SB_{0/0/20}$	8.5	163.1	110.0
2	$SB_{0/100/20}$	5.7	131.0	108.0
3	$SB_{3T/100/20}$	8.8	159.0	127.8

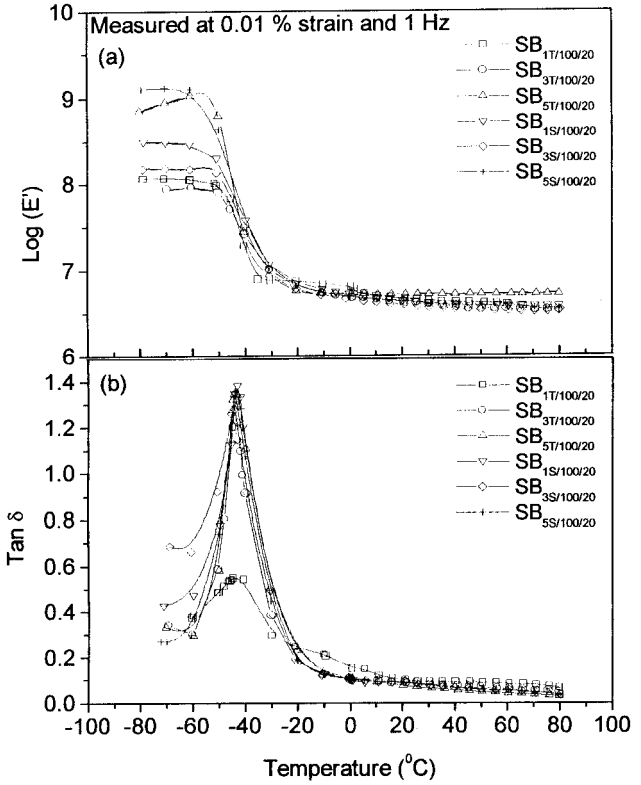


Figure 7 The variation of the (a) storage modulus (log E', Pa) and (b) tan δ with the temperature for SBR vulcanizates loaded with electron beam modified fillers with varying TMPTA or silane levels.

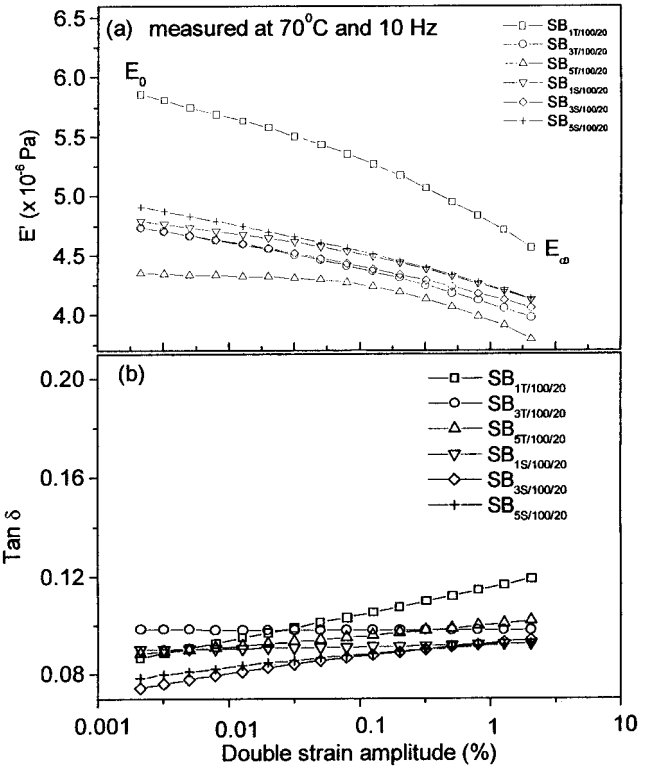


Figure 8 The variation of the (a) storage modulus (E', Pa) and (b) tan δ with the double strain amplitude for SBR vulcanizates loaded with electron beam modified fillers with varying TMPTA or silane levels measured at 70°C.

glassy region has a decreasing tendency with a lower level of TMPTA or silane, which increases significantly at a higher level of the monomer or silane coupling agent. Figure 7(b) shows the tan δ temperature curves for these systems. The rubber containing the filler modified with 1% TMPTA ($SB_{1T/100/20}$) shows a transition at −43°C, when loaded in SBR vulcanizates. At higher TMPTA levels and in the case of silanized dual-phase fillers, there is no significant variation in the T_g (Table VIII). The values of tan δ at −70°C, T_g, 0, and 70°C are included in Table VIII. The values of tan δ at 0 and 70°C are high for $SB_{1T/100/20}$ and decrease at higher TMPTA levels. However, in the case of the silane modified system, it is almost constant at 0°C and increases at 70°C with silane loading.

The above observation can be well explained by the variation of the storage modulus with the DSA [Fig. 8 (a)]. The storage modulus is high for $SB_{1T/100/20}$ over the entire range of DSAs and decreases with the TMPTA level. The $(E_0 - E_\infty)$ decreases from 1.26×10^6 ($SB_{1T/100/20}$) to 0.55×10^6 ($SB_{5T/100/20}$) with the increase in the TMPTA level (Table IX). This suggests that there is a significant variation in the secondary structure that forms the filler network in the SBR

TABLE VIII
E' and Tan δ of SBR Vulcanizates Loaded with Electron Beam Modified Dual-Phase Fillers Having Different TMPTA or Silane Levels

			E' ($\times 10^{-6}$ Pa)			Tan δ			
Si. No.	Samples	T_g (°C)	At −70°C	At 0°C	At 70°C	At −70°C	At T_g (°C)	At 0°C	At 70°C
1	$SB_{0/100/20}$	−43	2137.0	6.61	4.27	0.061	1.050	0.106	0.044
2	$SB_{1T/100/20}$	−43	88.4	6.52	3.98	0.381	0.580	0.211	0.086
3	$SB_{3T/100/20}$	−43	82.4	4.78	3.42	0.332	1.170	0.108	0.057
4	$SB_{5T/100/20}$	−44	888.0	5.23	5.14	0.331	1.340	0.109	0.058
5	$SB_{1S/100/20}$	−43	305.0	5.19	3.74	0.434	1.380	0.109	0.044
6	$SB_{3S/100/20}$	−44	151.0	4.55	3.28	0.689	1.280	0.096	0.056
7	$SB_{5S/100/20}$	−44	1310.0	4.91	3.60	0.266	1.290	0.103	0.058

TABLE IX
E_0, E_∞, and ($E_0 - E_\infty$) Values of SBR Vulcanizates Loaded with Modified Fillers Having Various TMPTA or Silane Levels

Si. No.	Samples	E_0 ($\times 10^{-6}$ Pa)	E_∞ ($\times 10^{-6}$ Pa)	$E_0 - E_\infty$ ($\times 10^{-6}$ Pa)
1	$SB_{1T/100/20}$	5.86	4.60	1.26
2	$SB_{3T/100/20}$	4.74	3.98	0.76
3	$SB_{5T/100/20}$	4.35	3.80	0.55
4	$SB_{1S/100/20}$	4.64	4.10	0.54
5	$SB_{3S/100/20}$	4.74	4.06	0.66
6	$SB_{5S/100/20}$	4.91	4.10	0.81

vulcanizates that decreases with the increase in the TMPTA level. Of course, in the case of silanized dual-phase filler loaded SBR vulcanizates, there is rise in the ($E_0 - E_\infty$) value from 0.54×10^6 to 0.81×10^6 when increasing the silane level from 1 to 5%, indicating a variation in the secondary structure at higher silane loading that is due to electron beam irradiation.

This is responsible for the high value of the low strain hysteresis loss at 70°C for $SB_{1T/100/20}$ as shown in Table VIII. Because the variation in the ($E_0 - E_\infty$) values for $SB_{3T/100/20}$ follows the same trend at both 0 and 70°C (Tables V, VI), the same behavior might also be expected for $SB_{1T/100/20}$ and $SB_{5T/100/20}$ at 0°C. Shown in Figure 8(b) is the plot of the variation in tan δ with the DSA for TMPTA and silane modified dual-phase filled SBR vulcanizates. The tan δ is low for $SB_{1T/100/20}$ at low strain and increases with the DSA. This is mainly attributable to the breakdown of secondary aggregates that enhance the hysteresis loss behavior. However, for $SB_{3T/100/20}$ and $SB_{5T/100/20}$, the breakdown and reformation of structures occur simultaneously, resulting in lower tan δ at higher strain values. The silanized dual-phase filler loaded vulcanizates follow the same trend. However, at higher silane loading ($SB_{3S/100/20}$, $SB_{5S/100/20}$), structure breakdown predominates over reformation.

Effect of radiation dose on dynamic mechanical properties of SBR vulcanizates loaded with acrylated dual-phase fillers

The variation of the storage modulus with temperature for the rubber loaded with acrylated filler irradiated at different radiation doses has been studied and the results are included in Figure 9(a). The storage modulus in the glassy region decreases with the radiation dose varying from 20 to 200 kGy. This is mainly attributed to a decrease in entrapped rubber that is due to crosslinked TMPTA, which occupies the pores of the carbon black surface. However, there is no significant variation in the storage modulus at the higher temperature at which the polymer is in rubbery state, except for $SB_{3T/20/20}$. Figure 9(b) is the plot of tan δ versus the temperature for the modified filler loaded vulcanizates. The glass-transition temperature of the SBR vulcanizates loaded with the modified fillers shows a negative shift in the tan δ peak when increasing the radiation dose from 20 to 200 kGy [Fig. 9(b)]. At lower radiation doses, surface oxidation predominates the crosslinking of the monomer; thereby increasing the storage modulus in the glassy region and shifting the tan δ peak to a higher temperature. However, filler subjected to higher radiation doses results in crosslinking of TMPTA, which reduces the trapped rubber in the filler aggregates and reduces the glass-transition temperature.

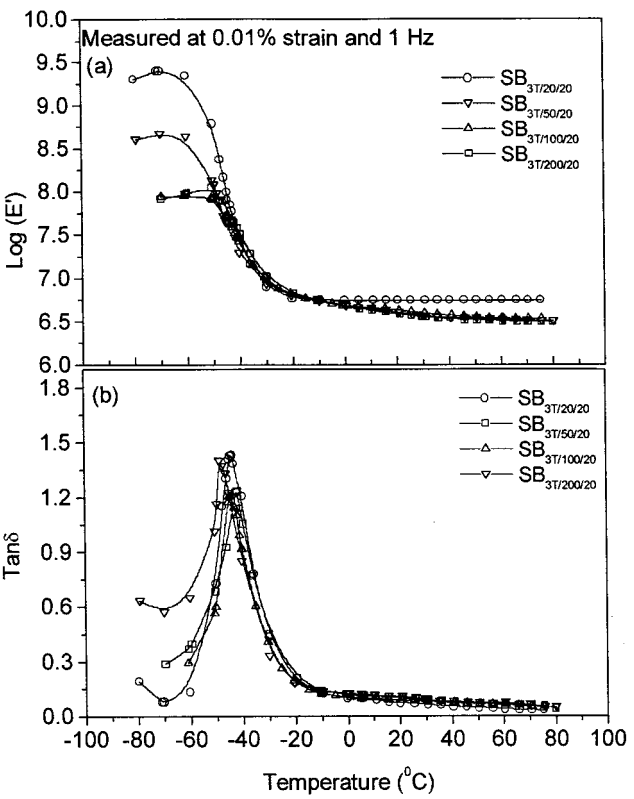
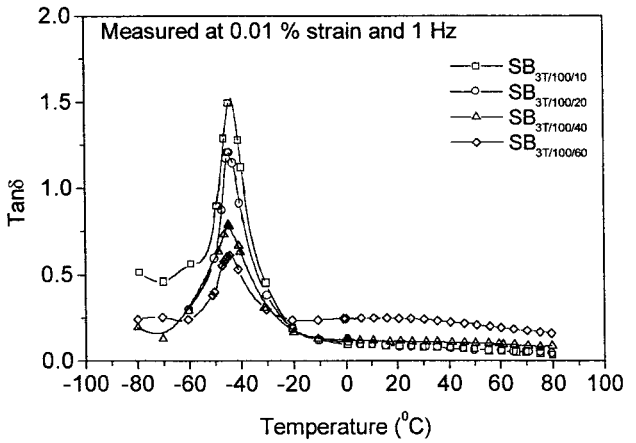
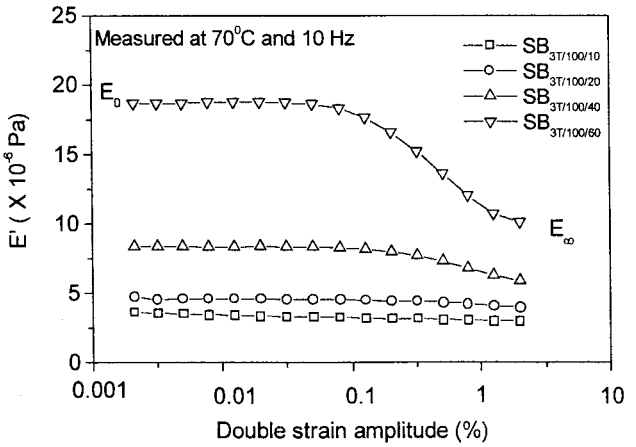


Figure 9 The variation of the (a) storage modulus (log E', Pa) and (b) tan δ with the temperature for SBR vulcanizates loaded with electron beam modified fillers subjected to varying radiation doses.



(a)



(b)

Figure 10 (a) The effect of filler loading on the tan δ versus temperature plot for electron beam modified filler loaded SBR vulcanizates. (b) The effect of the filler loading on the storage modulus (E', Pa) versus the double strain amplitude plot for electron beam modified filler loaded SBR vulcanizates measured at 70°C.

Effect of filler loading on dynamic mechanical properties of SBR vulcanizates

Figure 10(a) shows the tan δ–temperature curve of SBR vulcanizates filled with various filler loadings. The glass-transition temperature increases from −46 ($SB_{3T/100/10}$) to −43°C ($SB_{3T/100/20}$) and is almost constant at higher filler loadings. The tan δ peak height decreases with the loading of filler [Fig. 10(a)]. The decrease in tan δ with loading is attributed to the increase in occluded rubber in the filler aggregates. The tan δ is high for $SB_{3T/100/60}$ in the higher temperature region at which the matrix is in a rubbery state. This is mainly due to the breakdown of the filler network formed in the vulcanizates. This is further clarified from the plot of the storage modulus with the DSA [Fig. 10(b)]. The storage modulus increases with filler loading because of the increase in the effective volume fraction of filler. The decrease in the storage modulus with the strain amplitude increases with filler loading due to secondary structure breakdown, which is formed due to filler–filler networking at higher filler loading.

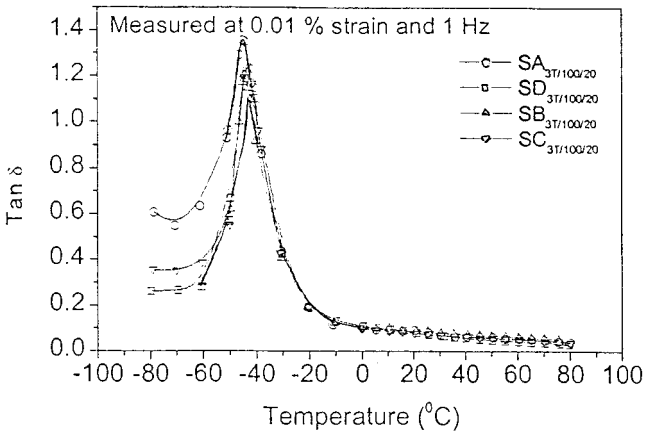


Figure 11 The variation of the tan δ with the temperature for SBR vulcanizates loaded with different modified fillers.

Effect of different modified fillers on dynamic mechanical properties of SBR vulcanizates

Figure 11 shows the tan δ–temperature curve of SBR vulcanizates loaded with different modified fillers having different silica content. The glass-transition temperature is almost constant for these modified fillers (Table X). With the increase in silica content, the filler–filler interaction increases, which results in the narrowing of the tan δ peak in the polymer transition zone. Figure 12(a) is the plot of the storage modulus with the DSA for modified fillers. The storage modu-

TABLE X
***E′* and Tan δ of SBR Vulcanizates Loaded with Different Electron Beam Modified Carbon Black and Dual Phase Fillers**

Si. No.	Samples	T_g (°C)	Tan δ			
			At −70°C	At T_g (°C)	At 0°C	At 70°C
1	$SA_{3T/100/20}$	−46	0.267	1.092	0.116	0.073
2	$SC_{3T/100/20}$	−42	0.344	1.050	0.106	0.044
3	$SB_{3T/100/20}$	−43	0.332	1.170	0.108	0.057
4	$SD_{3T/100/20}$	−43	0.554	1.200	0.093	0.052

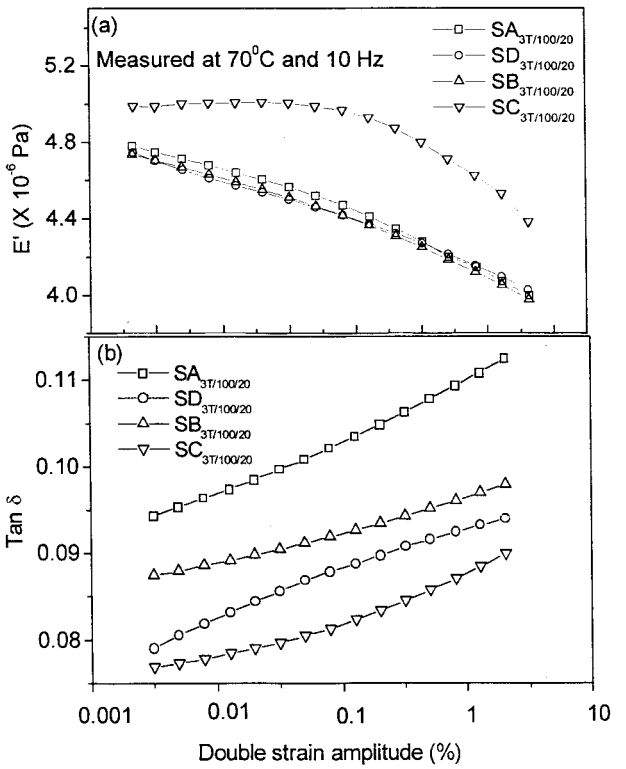


Figure 12 The variation of the (a) storage modulus (E', Pa) and (b) tan δ with the double strain amplitude for SBR vulcanizates loaded with different electron beam modified fillers measured at 70°C.

lus is high for $SA_{3T/100/20}$ over the range of strains investigated. However, it is almost constant for $SD_{3T/100/20}$, $SB_{3T/100/20}$, and $SC_{3T/100/20}$, which have increasing silica content. The value of $(E_0 - E_\infty)$, which is a measure of the Payne effect, is almost constant for $SA_{3T/100/20}$ (0.78×10^6) and dual-phase fillers such as $SD_{3T/100/20}$ (0.75×10^6) and $SB_{3T/100/20}$ (0.76×10^6). However, it is low for $SC_{3T/100/20}$ (0.56×10^6; Table XI). This indicates that the breakdown of secondary aggregates is less in $SC_{3T/100/20}$ at this imposed strain. Figure 12(b) shows the variation of the tan δ with the DSA for the modified fillers. The tan δ is high for carbon black over the range of strains, indicating that the breakdown and reformation of structure is more pronounced in the modified carbon black ($SA_{3T/100/20}$) in which weak van der Waal's forces hold filler aggregates together. However, it is low for modified dual-phase fillers, which is due to less developed filler agglomeration. This is responsible for the low value of hysteresis behavior measured at 70°C (Table X).

CONCLUSION

1. Electron beam modification of a dual-phase filler in the presence and absence of TMPTA or silane significantly improves the storage modulus of the modified filler loaded SBR composite. Also, from the strain sweep test, it is better understood that electron beam irradiation affects the primary and secondary structures of the filler that lead to higher rubber occlusion, resulting in a higher volume fraction of filler. This is responsible for the decrease of the tan δ value at 70°C and its increase at 0°C.
2. The higher storage modulus in the low temperature zone (high frequency region) in the master curve for the modified filler loaded SBR vulcanizate ($SB_{0/100/20}$) confirms higher rubber occlusion compared to the control counterpart ($SB_{0/0/20}$).
3. The lower tan δ in the high temperature region (low frequency region) in the master curve for $SB_{0/100/20}$ indicates that the hysteresis loss is less pronounced at this imposed strain level. This is in accord with the strain sweep test, which predicts that there is more reformation of the structure in $SB_{0/100/20}$ at higher strain level when compared to the control ($SB_{0/0/20}$).
4. The secondary structure that forms the filler network decreases with the TMPTA level and increases with the silane level when these modified fillers are subjected to a 100-kGy radiation dose.
5. The storage modulus in the glassy region decreases with the increase in the radiation dose from 20 to 200 kGy in the case of TMPTA modified dual-phase filler loaded SBR vulcanizates because of a decrease in rubber entrapment.
6. The tan δ peak decreases with the increase in filler loading, indicating that rubber occlusion and immobilization around the filler aggregates increases with loading.
7. With an increase in the silica content in the case of dual-phase fillers, the filler–filler interaction increases, which results in the narrowing of the tan δ peak in the polymer transition zone.

TABLE XI
E_0, E_∞, and $(E_0 - E_\infty)$ Values of SBR Vulcanizates Loaded with Different Modified Fillers

Si. No.	Samples	E_0 ($\times 10^{-6}$ Pa)	E_∞ ($\times 10^{-6}$ Pa)	$E_0 - E_\infty$ ($\times 10^{-6}$ Pa)
1	$SA_{3T/100/20}$	4.78	4.00	0.78
2	$SD_{3T/100/20}$	4.75	4.00	0.75
3	$SB_{3T/100/20}$	4.74	3.98	0.76
4	$SC_{3T/100/20}$	4.99	4.43	0.56

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