Electron Beam Modification of Dual Phase Filler: Surface Characteristics and its Influence on the Properties of Styrene-Butadiene Rubber Vulcanizates

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Abstract: The present work describes modification of dual phase filler by electron beam irradiation in presence of multifunctional acrylates like trimethylol propane triacrylate (TMPTA) or silane coupling agent like bis (3-triethoxysilylpropyltetrasulphide) and influence of the modified fillers on the physical properties of styrene-butadiene rubber (SBR) vulcanizates. Modulus at 300 % elongation increases whereas the tensile strength decreases with increase in radiation dose for the dual phase filler loaded styrene-butadiene rubber vulcanizates (SBR). However, modulus and tensile strength significantly increase, which is more, pronounced at higher filler loadings for TMPTA modified dual phase filler loaded SBR. These changes in properties are explained by the equilibrium swelling data and Kraus plot interpreting the polymer-filler interaction. Electron beam modification of the filler results in a reduction of tan δ at 70℃, a parameter for rolling resistance and increase in tan δ at 0℃, a parameter for wet skid resistance of the SBR vulcanizates. Finally, the influence of modified fillers on the properties like abrasion resistance, tear strength and fatigue failure and the improvement in the properties have been explained in terms of polymer-filler interaction.

1. Introduction

In last few years, in response to ever more demanding requirements from the tire industry, a great effort has been made by Cabot Corporation to develop functionalized carbon blacks to improve the tradeoff between wear resistance and rolling resistance. Carbon-silica dual phase filler commercialized as "ECOBLACK®" by Cabot Corporation, is a new generation reinforcing filler, which consists of two phases, a carbon phase with a finely divided silica phase (domains) dispersed therein. This unique filler can be produced by co-fuming process of carbon and silicon containing feed stocks in the carbon black reactor.[1] In more aspects, this carbon-silica dual phase filler (CSDPF) differs from the traditional fillers used as reinforcing agents in rubber industry. Depending upon the distribution of silica, surface coverage of silica and its content in carbon black, the dual phase fillers are classified into two series, namely

1. CSDPF 2000
2. CSDPF 4000 series

CSDPF 4000 series has much higher silica

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About 5 years research experience in the field of polymer technology, polymer composites and processing.
Able to work independently or in a team
Excellent problem solving, research analysis, decision-making and leadership skills.
Experienced in handling industrial research projects and different polymer testing equipment.
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coverage relative to CSDPF 2000, which is due to the silica domain distribution and high silicon content. Even within the CSDPF 2000 series, the dual phase fillers are classified as CSDPF-A, E and F depending upon the silicon content. This filler consists of a silica phase finely distributed in the carbon phase along with 90-99 % elemental carbon, oxygen and hydrogen as in traditional carbon black. Depending on the silicon content and surface area, dual phase fillers contain substantially more functional groups available to react with organosilane coupling agents than carbon black that can be understood by using trimethylchlorosilane (TMCS), as an analytical probe. ESCA and FT-IR experiments demonstrate that the carbon-silica dual-phase fillers are comprised of composite aggregates, each containing carbon and silica phases. In these dual-phase aggregates, the silica phase is intimately distributed with the carbon phase. The classification of dual phase fillers and their properties like surface area are included in Table 1

Although, carbon-silica dual phase fillers may find great commercial importance in the tire industries, especially in tire tread formulations, which lower rolling resistance and increase wet grip resistance compared to conventional carbon blacks or silica fillers, the ultimate properties like tensile strength, modulus, and hardness are lower compared to the conventional carbon black due to silicon doping.[2] Also, there is a drastic reduction in abrasion resistance of vulcanizates compared to those containing conventional carbon black of similar surface area due to doping of silica in carbon black surface.[2] This is due to the lower affinity of silica surface with elastomers.

Surface modification of fillers by surface oxidation or pretreatment with the surface modifiers significantly improves the property spectrum of the filler loaded vulcanizates.[3-5] In the present work, electron beam radiation has been used as tool to modify the surface of dual phase filler in the presence of multifunctional monomer, trimethylol propane triacrylate (TMPTA) or silane coupling agent, triethoxysilylpropyltetrasulphide (Si-69) and its influence on the properties of the styrene-butadiene rubber vulcanizates.

2. Experimental

2.1 Materials

Styrene-butadiene rubber (Synaprene-1502) was obtained from Synthetics and Chemicals Ltd., Bareilly, India. Carbon-silica dual phase filler, CSDPF-A with 4.7 % silica content was obtained

Table 1. Dual Phase Filler Classifications[1]

Sl. No	Filler samples	Trade mark of dual phase fillers	Silicon Content, %	BET Nitrogen Surface Area[a], m^2/g	TMCS[b] Uptake #/nm^2
1.	CSDPF-A[1]	CRX-2000	4.84	154.3	0.32
2.	CSDPF-E[1]	CRX-2006	5.73	210.8	0.31
3.	CSDPF-F[1]	CRX-2002	3.20	102.6	0.28
4.	CSDPF[1]	CRX-2124	4.1	171.0	0.32
5.	CSDPF[2]	CRX-4210	10.0	154.0	1.04

[1] represents the ECOBLACK CRX 2000 series
[2] represents the ECOBLACK CRX 4000 series
[a] BET is multipoint nitrogen surface area using the BET theory (ASTM D 4820)
[b] Number of trimethylchlorosilane (TMCS) uptake per nm^2 estimated using averaged surface areas from BET nitrogen surface area and statistical thickness surface area.

from Cabot Corporation, Boston, USA. Polyfunctional monomers, trimethylol propane triacrylate was obtained from UCB Chemicals, Belgium. Bis - (3 - triethoxysilylpropyl) tetrasulfide (Si-69) was obtained from Degussa A. G. Germany. Compounding ingredients like Zinc oxide (ZnO), stearic acid, Antioxidant (polymerized trimethyl quinoline), N-Tertiary Butyl-2-Benzothiazole-Sulphenamide (TBBS) and sulfur were obtained from local suppliers.

2.2 Filler modification

TMPTA solution was prepared at a concentration of 3% in acetone in a beaker. The solution (100 ml) was poured into the filler sample (100 g) till it completely wetted the surface of filler. The mixture was then stirred thoroughly for 20 min at room temperature. The sample was then dried in air for 30 min. All the samples (50g) were then packed in polyethylene bags of size 0.18 x 0.2 m^2. The same procedure was followed for modification of filler by triethoxysilylpropyltetrasulphide (Si-69). The packed samples were subjected to electron beam irradiation by using electron beam accelerator (Model ILU-6) at Bhabha Atomic Research Centre (BARC) Mumbai, India. Filler designation is included in Table 2.

2.3 Preparation of SBR vulcanizates

The compounds according to the formulation (Table 3) excepting sulfur and accelerator were mixed in a Brabender plasticorder (PLE 330) at a temperature of 80℃ and a rotor speed of 60 rpm using a two-stage mixing procedure. In the first stage of mixing, filler masterbatch was prepared by adding the ingredients as per the mixing specification shown in Table 3.

Table 3. Compounding Formulation for SBR Mixes

Sl. No	Styrene-butadiene rubber mixes	
	Ingredients	Loading (phr)
1	SBR-1502	100.0
2	ZnO	5.0
3	Stearic acid	1.5
4	Antioxidant (TQ)	1.0
5	Filler	10.0-60.0
6	TBBS	1.0
7	S	2.0

Final mixing with accelerator and sulfur was done in the same laboratory two roll Schwabenthon mill supplied by Baujahr, Germany at a temperature of 50℃ and a friction ratio of 1:1.1. The curing characteristics of the mixes were evaluated at a temperature of 160℃ with a moving die rheometer, MDR-2000 according to ASTM D 2084-98. Subsequent moldings were carried out in a Moore press (supplied by Castleton, Rocchdle, England) at a temperature of 160℃ pressure of 5 MPa, and optimum cure time (T_{90} in minutes) for tensile specimens, T_{90} + 5 minutes for abrasion resistance and compression set samples. Heat buildup specimens were cured for T_{90} + 10 minutes. Sample designation of the modified dual phase filler loaded SBR vulcanizates is included in Table 4.

Table 2. Designations of Electron Beam Modified Fillers

Sl. No	Filler designation	Type of filler	Type of ingredient	Concentration of ingredient (%)	Radiation dose (kGray)
1	$B_{0/0}$	CSDPF-A	-	-	-
2	$B_{0/100}$	CSDPF-A	-	-	100
3	$B_{3T/100}$	CSDPF-A	TMPTA	3	100
4	$B_{3S/100}$	CSDPF-A	Si-69	3	100

Table 4. Designation of Electron Beam Modified Filler Loaded SBR Vulcanizates

Sl. No	Sample designation	Type of filler	Filler loading (phr)
1	$SB_{0/0/10}$	$B_{0/0}$	10
2	$SB_{0/0/20}$	$B_{0/0}$	20
3	$SB_{0/0/60}$	$B_{0/0}$	60
4	$SB_{0/100/10}$	$B_{0/100}$	10
5	$SB_{0/100/20}$	$B_{0/100}$	20
6	$SB_{0/100/60}$	$B_{0/100}$	60
7	$SB_{0/200/20}$	$B_{0/200}$	20
8	$SB_{3T/0/20}$	$B_{3T/0}$	20
9	$SB_{3T/20/20}$	$B_{3T/20}$	20
10	$SB_{3T/50/20}$	$B_{3T/50}$	20
11	$SB_{3T/100/10}$	$B_{3T/100}$	10
12	$SB_{3T/100/20}$	$B_{3T/100}$	20
13	$SB_{3T/100/40}$	$B_{3T/100}$	40
14	$SB_{3T/100/60}$	$B_{3T/100}$	60
15	$SB_{3T/200/20}$	$B_{3T/200}$	20
16	$SB_{3S/0/20}$	$B_{3S/0}$	20
17	$SB_{3S/100/10}$	$B_{3S/100}$	10
18	$SB_{3S/100/20}$	$B_{3S/100}$	20
19	$SB_{3S/100/60}$	$B_{3S/100}$	60

2.4 Mechanical properties of the SBR vulcanizates

Tensile and tear specimens were punched out from the molded sheets using ASTM Die - C. The tests were carried out as per the ASTM D 412-98 method in a universal testing machine (Zwick 1445) at a crosshead speed of 500 mm/min at 25℃. The average of three tests was reported here.

2.5 Equilibrium swelling studies

The styrene - butadiene rubber (SBR) vulcanizates were swollen in toluene upto three days for equilibrium swelling at a temperature of 298 K. Experimental results were reproducible within ± 1%. The extent of swelling was measured by the volume fraction of rubber in the swollen gel and expressed by[6]

$$V_r = \frac{(D_s - F_f A_w)\rho_r^{-1}}{(D_s - F_f A_w)\rho_r^{-1} + A_s \rho_s^{-1}} \quad (1)$$

where V_r, D_s, F_f, A_w, A_s, ρ_r and ρ_s are volume fraction of rubber, deswollen weight of the sample, fraction insoluble, sample weight, weight of the absorbed solvent corrected for swelling increment, density of rubber and density of solvent respectively.

2.6 Kraus plot

Polymer-filler interaction in these SBR vulcanizates was examined using Kraus equation[7]:

$$\frac{V_{r0}}{V_{rf}} = 1 - m\left(\frac{\Phi}{1-\Phi}\right) \quad (2)$$

where V_{r0} = volume fraction of rubber in the gum vulcanizates.

V_{rf} = volume fraction of rubber in the filled vulcanizates

ϕ = volume fraction of filler in the filled vulcanizates

Polymer-filler interaction parameter "C" was calculated using the Kraus equation:

$$C = \frac{m - V_{r0} + 1}{\left(1 - V_{r0}^{\frac{1}{3}}\right)} \quad (3)$$

where m is the slope obtained from the linear plot of Equation (3).

2.7 Dynamic mechanical properties

The dynamic mechanical properties of the filled vulcanizates were measured by means of a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific Inc., NJ) using rectangular specimen of dimensions of 30 x 10 x 1.5 mm, in a tensile mode. Strain sweep test was carried out in the range 0.001 to 10 % at the constant frequency of 10 Hz measured at 0 and at 70℃. The data were taken 5 points per decade and the full curves were recorded.

3. Physical properties of filled vulcanizates

3.1 Abrasion resistance

The abrasion resistance of the samples was carried out according to ASTM designation D 394 method A against silicon carbide abrasive paper P 180 using DuPont abrader. The abrasion loss of the sample was calculated as volume loss in cc/hr

$$\text{Abrasion loss} = (\text{weight loss/specific gravity}) \times 6 \text{ cc/hr} \quad (4)$$

$$\text{Abrasion resistance} = 1/\text{Abrasion loss} \quad (5)$$

3.2 Fatigue to failure (FT-FT test)

Tensile fatigue to failure was carried out according to ASTM D 4482-94 with an extension ratio of 1.6 with tensile dumbbells molded with special inherent gripping facilities (to avoid slippage and damage of the grip due to the abrasion under the sinusoidally varying load) on a Monsanto Fatigue to failure tester, at 25℃ and at a frequency of 100 tension and relaxations cycles per minute.

4. Results and discussion

4.1 Effect of irradiation doses on the filler in the presence of TMPTA or silane

The tensile properties of the unmodified and the electron beam modified dual phase filler in the presence and in the absence of TMPTA or silane are included in Table 5. The values of modulus increases with radiation dose. On varying the radiation dose in the case of TMPTA modified filler, there is no change upto 50 kGy and the modulus increases slightly at higher radiation doses. However, silane coupling agent increases the modulus significantly.

This increase in modulus is governed by two factors.

1. Increase in surface fractal dimension due to filler aggregation compared to control sample ($SB_{0/0/20}$) resulting in entropy production in the fractal media under the exchange of mechanical momentum.

2. Increase in reactive functional groups on the surface that result in higher polymer-filler interaction.

From transmission electron microscopy (TEM) results, it has been concluded that electron beam irradiation in the presence and the absence of TMPTA or silane results in an increase of primary structure.[8] This variation in structure causes significant improvement in trapped rubber in filler aggregates that result in higher modulus. This is further confirmed from the increase in volume fraction of rubber in the swollen gel (V_r) as shown in Table 5. Tensile strength and elongation at break decrease for the electron beam modified fillers ($SB_{0/0/20}$ cf. $SB_{0/100/20}$ and $SB_{0/200/20}$) (Table 5). This may be due to the catroscopic tearing by growth of cracks initiated from accidental flaws, microvoids, dewetting on the surface and mainly attributed to higher aggregated structure. However, in the presence of TMPTA, there is no significant variation in tensile strength upto 50 kGy. The strength increases by about 16 % and 27 % at 100 kGy and 200 kGy radiation doses on the filler respectively. This is due to the increase in surface oxygen concentration and double bonds present in the basic structure of TMPTA. These TMPTA present on the surface may produce free radicals under high shear of mixing that enhances the polymer-filler interaction. There is also a possibility that residual double bond of TMPTA reacts with rubber in presence of vulcanizing agent. In the case of silane modified systems ($SB_{3S/0/20}$ and $SB_{3S/100/20}$), there is no significant variation in tensile strength compared to the control dual phase filler loaded system.

Table 5. Physical Properties of SBR Vulcanizates Filled with Electron Beam Modified Dual Phase Fillers

Sl. No	Samples	Modulus (MPa)			TS (MPa)	EB (%)	$(V_r)^b$
		100 %	200 %	300 %			
1	$SB_{0/0/20}$	1.09	1.93	3.09	12.40	700	0.172
2	$SB_{0/100/20}$	1.15	2.08	3.43	10.80	590	0.182
3	$SB_{0/200/20}$	1.34	2.54	4.22	9.40	484	0.181
4	$SB_{3T/0/20}$	1.09	1.88	3.02	12.80	710	0.171
5	$SB_{3T/20/20}$	1.09	1.87	3.02	12.50	684	0.176
6	$SB_{3T/50/20}$	1.07	1.87	3.01	13.20	715	0.177
7	$SB_{3T/100/20}$	1.10	1.93	3.14	14.80	741	0.187
8	$SB_{3T/200/20}$	1.10	1.70	3.30	15.20	725	0.188
9	$SB_{3S/0/20}$	1.20	2.32	3.42	12.00	620	0.183
10	$SB_{3S/100/20}$	1.24	2.37	3.88	12.30	596	0.186

Table 6. Effect of Filler Loading of Control and Modified Filler on the Physical Properties of SBR Vulcanizates

Sl. No	Samples	Modulus (MPa)			TS (MPa)	EB (%)	$(V_r)^a$
		100 %	200 %	300 %			
1	S_0	0.80	1.10	1.40	1.70	385	0.157
2	$SB_{0/0/10}$	0.98	1.43	2.15	7.60	710	0.168
3	$SB_{0/0/20}$	1.09	1.93	3.09	12.40	700	0.172
4	$SB_{0/0/60}$	3.09	6.89	12.34	20.90	417	0.222
5	$SB_{3T/100/10}$	0.93	1.42	2.12	7.00	607	0.168
6	$SB_{3T/100/20}$	1.10	1.93	3.14	14.80	741	0.187
7	$SB_{3T/100/40}$	1.70	3.38	5.65	26.80	751	0.192
8	$SB_{3T/100/60}$	3.16	6.85	12.30	27.70	529	0.211
9	$SB_{3S/100/10}$	0.93	1.43	2.13	7.50	715	0.171
10	$SB_{3S/100/20}$	1.24	2.37	3.88	12.30	599	0.186
11	$SB_{3S/100/60}$	3.32	10.63	14.20	25.50	445	0.260

[a] Calculated based on equilibrium swelling studies.

4.2 Effect of filler loading

Table 6. compares the effect of loading of control and modified fillers on the mechanical properties of SBR. 300 % modulus increases from 2.15 to 12.34 MPa in the case of control, 2.12 to 12.30 MPa in TMPTA and 2.13 to 14.20 MPa in silane modified systems. The increase in modulus is attributed to the increase in trapped rubber with loading and higher polymer-filler interaction. This is further confirmed from the increase in volume fraction of rubber in swollen gel with loading (Table 6). Tensile strength increases from 7.60 to 20.90 MPa in the case of control, 7.00 to 27.70 MPa in TMPTA and 7.50 to 25.50 MPa in silanized dual phase filler loaded system. Increase in oxygen content and higher polymer-filler interaction is responsible for the higher tensile strength in the case of modified systems. This is further evidenced from Vr results. It is worth mentioning that the electron beam modified surface treated fillers give superior tensile properties as compared to the one without treatment. However, it is more pronounced in TMPTA modified system, which may be due to trapped poly-TMPTA in filler aggregates

To examine the polymer-filler interaction of these modified fillers, we have plotted V_{ro} / V_{rf} vs. $\phi / (1-\phi)$ following Equation (2) (Figure 1). The values of the slope are tabulated in Table 6. The higher negative slope (-1.17) for silane modified fillers ($SB_{3S/100}$) shows the higher reinforcing ability compared to the control filler ($SB_{0/0}$) (slope value = -0.60). These results are consistent with 300 % modulus values as shown in Table 7. In the case of TMPTA modified fillers ($SB_{3T/100}$), the slope value (-0.69) is slightly more negative than the control filler (-0.60). This result reflects the lower modulus for TMPTA modified system as compared to the silane modified one. Polymer-filler interaction can also expressed in terms of interaction parameter 'C' calculated using Equation 3. These values are tabulated in Table 6. The 'C' value is higher for TMPTA modified and silane modified system than that of the control filler, indicating high reinforcing ability of the former.

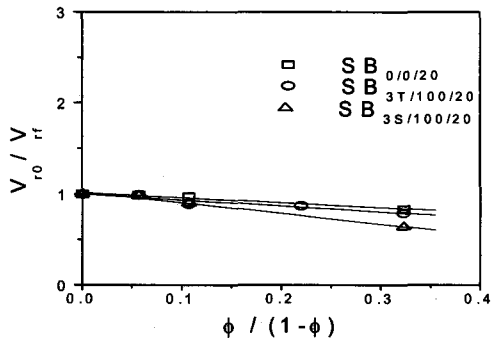

Figure 1. Kraus plot of SBR vulcanizates loaded with unmodified electron beam modified surface treated dual phase fillers.

Table 7. Results from Kraus Plot and Interaction Parameter for the Unmodified and Electron Beam Modified Surface Treated Dual Phase Filler Loaded SBR Vulcanizates

Sl. No	Samples	Slope (m)	C
1	$SB_{0/0/20}$	-0.60	1.06
2	$SB_{3T/100/20}$	-0.69	1.12
3	$SB_{3S/100/20}$	-1.17	1.36

4.3 Strain amplitude dependence of storage modulus, loss modulus and tanδ measured at 70℃ and at 0℃

Shown in Figure 2 (a) is the variation of storage modulus, loss modulus and tanδ for electron beam modified dual phase filler loaded SBR vulcanizates. The storage modulus of the irradiated filler loaded vulcanizates ($SB_{0/100/20}$) is higher than that of non-irradiated 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 ($SB_{3T/100/20}$ and $SB_{3S/100/20}$) significantly improves the storage modulus compared to its non-irradiated counterpart. This is probably due to the combined effect of

(i) Surface oxidation of the dual phase filler upon electron beam irradiation.

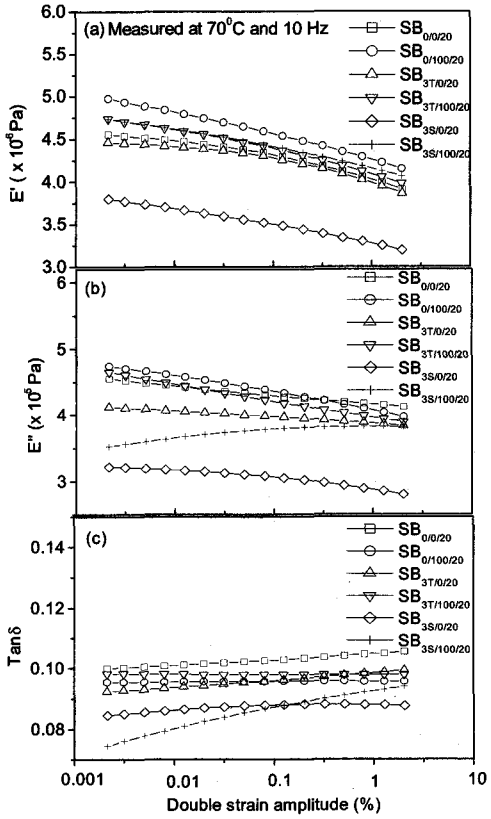

Figure 2. Variation of (a) storage modulus (E′) (in Pa), (b) loss modulus (E″) (in Pa) and (c) tan δ with double strain amplitude for electron beam modified dual phase filler loaded SBR vulcanizates measured at 70℃.

(ii) Partial increase in primary and secondary structures

Shown in Figure 2 (b) is the plot of loss modulus (E″) with the double strain amplitudes measured at 70℃ and 10 Hz. The loss modulus, which is a measure of breakdown and reformation of secondary structures, decreases with strain indicating that the reformation of structures predominates in the SBR vulcanizates except rubber loaded with electron beam modified silanized dual phase fillers ($SB_{3S/100/20}$), in which the break down of 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 is almost constant at higher strain. This suggests that the breakdown of secondary structures is more for $SB_{0/100/20}$ at low strain compared to 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 ($SB_{3T/100/20}$ and $SB_{3S/100/20}$) display higher loss modulus than that of their counterparts ($SB_{3T/0/20}$ and $SB_{3S/0/20}$) 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 loss modulus to the storage modulus, is high for the unmodified filler loaded SBR vulcanizates ($SB_{0/0/20}$) (Figure 2 (c)) compared to that of the modified filler loaded SBR vulcanizates. Even though the loss modulus is slightly high for ($SB_{0/100/20}$) (Figure 2 (b)), the lower value of tan δ 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 radiation dose lowers the tan δ value over the range of double strain amplitudes compared to that of $SB_{0/0/20}$. However, the electron beam irradiated silanized filler has a lower tan δ value at a lower double strain amplitude (DSA) with a cross over at 0.1%. This indicates that at low strain hysteresis loss is less pronounced in $SB_{3S/100/20}$ because of its stable secondary aggregates, whereas reverse is true at high strain. The lower tan δ for modified dual phase filler loaded system indicates lower rolling resistance compared to its control counterpart ($SB_{0/0/20}$).

All the observations made from the results obtained at 70℃ are also true when the values are compared at 0℃, 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. The higher tan δ values for the modified filler loaded SBR ($SB_{0/100/20}$, $SB_{3T/100/20}$ and $SB_{3S/100/20}$) as compared to the control system ($SB_{0/0/20}$) over the range of strain indicates higher wet grip resistance for the former.

4.4 Effect of irradiated dual phase fillers on the technical properties of styrene-butadiene rubber vulcanizates

Shown in Table 8 are the abrasion resistance values (hr/cc) of gum and irradiated filler loaded styrene-butadiene rubber (SBR) relative to the control system ($SB_{0/0/20}$). The abrasion resistance value is low for gum rubber compared to the filled systems. However, abrasion resistance values decreases by 2.5 % for irradiated filler loaded vulcanizates ($SB_{0/100/20}$) compared to the control system ($SB_{0/0/20}$). Since the unmodified ($SB_{0/0/20}$) and electron beam modified ($SB_{0/100/20}$) dual phase filler loaded rubber have same surface area, the main parameter, which is responsible for lower abrasion resistance for $SB_{0/100/20}$ is the aggregate size

Table 8. Abrasion Resistance, Tear Strength and Fatigue Failure Values of SBR Vulcanizates Filled with Unmodified/Electron Beam Modified Dual Phase Fillers

Sl. No	Samples	Abrasion resistance (hr/cc)	Tear strength (kN/m)	Fatigue failure (kcycles)
1	S_0	1.65 (80.5)*	34	10.80
2	$SB_{0/0/20}$	2.05 (100)	46	12.70
3	$SB_{0/100/20}$	1.99 (97.5)	44	13.60
4	$SB_{3T/0/20}$	2.06 (100.7)	46	12.60
5	$SB_{3T/100/20}$	2.22 (108.3)	42	20.20
6	$SB_{3S/0/20}$	2.38 (116.2)	43	22.80
7	$SB_{3S/100/20}$	2.44 (119.4)	42	24.20

distribution that exhibit higher abrasion rate at low severity.[9]

However, there is no significant improvement when the filler is treated with trimethylol propane triacrylate (TMPTA) ($SB_{3T/0/20}$), whereas it increases to 16.2 % by silane treatment (Si-69) ($SB_{3S/0/20}$). Electron beam modification of these surface treated dual phase filler loaded vulcanizates increases the abrasion resistance values by 8.3 % ($SB_{3T/100/20}$) and 19.4 % ($SB_{3S/100/20}$) compared to the control system ($SB_{0/0/20}$). At low severity, the contribution of structure in abrasion resistance is low and hence the improvement in abrasion resistance for $SB_{3T/100/20}$, $SB_{3S/0/20}$ and $SB_{3S/100/20}$ compared to $SB_{0/0/20}$ is due to higher surface activity of the filler[10] that enhances the polymer-filler interaction. From Table 8, it is inferred that mean fatigue life increases from 10.80 (S_0) to 12.70 kcycles ($SB_{0/0/20}$), on loading dual phase filler in SBR matrix. Several factors such as flaw size, impurities etc are responsible for the lower fatigue life of the SBR matrix (S_0). The mean fatigue life of SBR rubber filled with electron beam modified filler ($SB_{0/100/20}$) increases by 7.30 % compared to $SB_{0/0/20}$. This slight improvement in fatigue life is due to increase in energy dissipation that reduces the stress concentration near the tip of the crack growth, thereby reducing its rate. There is no improvement in fatigue life for $SB_{3T/0/20}$, whereas it increases to 22.80 kcycles (about 79.50 %) for $SB_{3S/0/20}$ compared to the control (12.70 kcycles). Electron beam modification of acrylated and silanized filler also improves the mean fatigue life of polymer significantly ($SB_{3T/100/20}$ = 20.20 kcycles (about 59.10 %); $SB_{3S/100/20}$ = 24.20 kcycles (about 90.60 %)). The higher reinforcing nature of these fillers reduces the strain energy during deformation, thereby increases the mean fatigue life of rubber. It has been well accepted that the cutting and chipping resistances of the tread compound are closely related to tearing energies. Presented in Table 8 are the tear strength of the gum, the unmodified and the modified dual phase filler loaded SBR systems. It is quite obvious that tear strength is low for gum SBR as it is non-crystallizable rubber. However, addition of the filler improves the molecular orientation that results in stick-slip tearing. The lower tear resistance for the control ($SB_{0/0/20}$) is mainly related to the lower polymer-filler interaction with which the slippage and detachment (dewetting) of polymer molecules on the filler surface occurs under stress. However, tear strength of electron beam modified filler loaded rubber ($SB_{0/100/20}$ = 44 kN/m) is marginally lower compared to unmodified filler loaded system ($SB_{0/0/20}$ = 46 kN/m). From TEM results, it has been confirmed that electron beam modification of dual phase filler results in the variation of primary and secondary structures,[8] which reduces the effective radius of the tear tip that results in lowering of tear resistance. There is no definite improvement in tear strength for acrylated filler loaded rubber ($SB_{3T/0/20}$ = 46 kN/m) whereas, it decreases for silanized filler loaded system ($SB_{3S/0/20}$ = 43 kN/m) (Table 7). Electron beam modification of acrylated ($SB_{3T/100/20}$ = 42 kN/m) or silanized filler ($SB_{3S/100/20}$ = 42 kN/m) also decreases the tear resistance of the rubber compared to the control ($SB_{0/0/20}$ = 46 kN/m). The lower tear resistance for $SB_{3T/100/20}$ is due to its high structure which is also responsible is responsible for lowering of tear resistance for $SB_{3S/100/20}$

5. Conclusions

Styrene-butadiene rubber vulcanizates filled with electron beam modified dual phase filler in the presence of multifunctional monomer, TMPTA or silane coupling agent, triethoxysilylpropyltetrasulphide (Si-69) significantly improves the tensile strength

significantly, especially at higher loading of modified filler. Electron beam modification of dual phase filler lowers the tan δ at 70℃ and increases the tan δ at 0℃ over the range of strain indicating lower rolling resistance and higher wet grip resistance for the SBR vulcanizates. Higher abrasion resistance for the modified filler loaded vulcanizates indicates the higher polymer-filler interaction.

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