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Influence of untreated and novel electron beam modified surface coated silica filler on rheometric and mechanical properties of ethylene-octene copolymer

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Surface modified silica fillers have been developed by coating these with a silane coupling agent, triethoxyvinyl silane (TEVS) followed by electron beam irradiation at room temperature. These have been incorporated in an ethylene-octene copolymer rubber. Rheometric, mechanical, volume swelling and aging properties of the gum as well as the filled elastomers have been studied in details. A significant improvement in the above properties has been noticed for these vulcanizates, which clearly emphasizes that novel surface modified silica improves polymer-filler adhesion by the introduction of covalent bonds between the filler surface and the rubber chains. Filler-filler and polymer-filler interactions have been quantified with the help of a mathematical model correlating the modulus and the volume concentration of filler. The influence of electron beam treatment on silanized silica filler has also been demonstrated from the above model. © *2003 Kluwer Academic Publishers*

1. Introduction

Recent development of metallocene catalysts can produce homogeneous random polyolefin copolymers with both narrow molecular weight distribution and controlled branching [1]. The advent of Dow's INSITE$^{\text{TM}}$ constrained geometry catalyst technology leads to the production of a new class of elastomers based on homogeneous ethylene-α-olefin copolymers. In particular, copolymers with more than 8% octene possess low crystallinity and rubber-like behavior [2]. Commercially available ethylene copolymer with 25% octene content is elastomeric in nature and has a high filler loading capacity. Due to the saturated backbone of these polymers, they can be efficiently crosslinked by peroxide, irradiation or silane curing system.

Use of particulate fillers for improving the reinforcement properties of an elastomer has been studied extensively in numerous investigations. However, there is no such study in the case of this new elastomer. Among the nonblack fillers, the silicas provide the best reinforcing properties [3]. Wagner [4] has reviewed the use of reinforcing precipitated silica to improve rubber compound properties. It is well accepted that the surface characteristics of reinforcing fillers are the most important factors influencing their reinforcing effect in rubber [5].

Silicas are in general hydrophilic in nature. The presence of number of surface hydroxyl groups on the silica surface results in stronger filler-filler interaction which leads to poor filler dispersion of a silica filled rubber compound, which in turn adversely affects the reinforcing process due to lack of polymer-filler bonding [6]. A great deal of effort has been made in the past to treat the surface of reinforcing silica fillers with different organic compounds to make the surface of the silica hydrophobic [7, 8]. This chemically modified silica surface can enhance the filler dispersion in the rubber matrix and improve the polymer-filler interaction.

In our earlier work [9], a new method of silica surface modification by coating the silica fillers with an organosilane, TEVS (triethoxyvinyl silane) followed by electron beam irradiation of the coated filler has been reported. A significant improvement in hydrophobicity of the treated fillers has been observed from the characterization studies.

In this present study, both unmodified and modified silica fillers have been incorporated in an ethylene-octene copolymer. Although there is some work on these unfilled polymers [10–12], only a few studies have been carried out so far on the mechanical properties of the filled polymers [13–16] and there is virtually no literature reference on this topic where the above elastomer is reinforced with surface modified silica filler. Rheometric, mechanical, volume swelling and aging properties of the gum as well as the filled elastomers have been studied in details. Finally, a new parameter based on the mechanical properties has been proposed

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in order to explain the filler-filler and the polymer-filler interaction, which also demonstrates the influence of electron beam treatment on silanization process.

2. Experimental

2.1. Materials

The general purpose polyolefin elastomer, Engage 8150 was kindly provided by DuPont-Dow Elastomers, USA. The silica filler, VULKASIL S, specific surface area = 175 m^2/g, determined by nitrogen adsorption method according to ISO 5794/1, Annex-D; pH = 6.4 and volatile matter = 5.8% was provided by Bayer A.G., Germany. The silane coupling agent, triethoxyvinyl silane (TEVS, b.p. 160–161°C) was supplied by Aldrich Chemical Company Inc., Germany.

2.2. Filler modification

The surface modification of the silica fillers was done by coating with an organosilane, TEVS followed by irradiation of the coated filler via electron beam technique at room temperature. Dilute solution of TEVS was prepared at concentrations of 1%, 3% and 5% (by weight) in acetone. The solution (100 ml) was poured into the filler sample (100 g) till it completely wetted the surface of filler, under constant stirring for 20 min at room temperature. The samples were then dried in air for 30 min followed by grinding of dry fillers to obtain the surface coated fine powders. The treated fillers were then packed in polyethylene bags and irradiated by an electron beam accelerator (Model ILU-6) with different radiation doses ranging from 20 to 500 kGy (1 kGy = 0.1 Mrad) in air at 25 ± 2°C at Bhabha Atomic Research Center, Mumbai, India. The specifications of the electron beam accelerator were mentioned in details in our earlier communication [9]. Formulations of the various surface treated silica fillers are presented in Table I.

2.3. Preparation of the rubber-filler composite

In order to have a comparative study, both unmodified, and modified silica fillers were incorporated in the rubber. The formulations of the different mixes for peroxide curing as well as radiation curing are given in Tables II and III respectively. The mixing was carried out in two stages in a Brabender Plasticorder (PLE 330) at a rotor speed of 60 rpm. Firstly, the filler masterbatch (MB) was prepared at 100°C, while the final mixing (FM) was carried out at 80°C. The MB compounds were prepared as follows: (i) The rubber was loaded into the Brabender and allowed to soften for 1 min, (ii) the filler was incorporated into the rubber and was mixed for 3 min followed by a single pass through a two roll mill, and (iii) finally the compound was remixed in the Brabender for 2 min and passed through the two roll mill. In the second stage, in the case of peroxide curing, MB compounds so obtained were allowed to soften for 1 min in the Brabender and then DCP was added and mixed for 1min at 80°C and finally sheeted out through a two roll mill. On the other hand, in the case of radiation curing, instead of adding DCP the MB compounds were remixed for 2 min and then sheeted out through a two roll mill.

For peroxide curing, the sheeted out stocks were compression molded in an electrically heated hydraulic press at 150°C for 30 min at 5 MPa pressure and then cooled under pressure by water circulation through the hot mold. In the case of radiation curing, the sheeted out stocks without any curing agent were compression molded under the same condition for 3 min.

2.4. Rheometric properties

Rheometric properties of the uncured stocks were measured in a Monsanto Rheometer MDR 2000. All the results are found to be within ±3% experimental error.

TABLE I Formulations of the various surface treated silica fillers

Filler designation	VULKASIL S (g)	TEVS (g)	Radiation dose (kGy)
V	100	–	–
VV003	100	3	–
VV101	100	1	100
VV103	100	3	100
VV105	100	5	100
VV053	100	3	50
VV203	100	3	200
VV503	100	3	500

TABLE II Formulations of different mixes cured by dicumyl peroxide (DCP)

Mix designation	Ethylene-octene copolymer (phr)	Silica		DCP (phr)
		Type	Amount (phr)	
ED$_3$	100	–	–	3
EV00005	100	V	5	3
EV00015	100	V	15	3
EV00030	100	V	30	3
EV00050	100	V	50	3
EVV00305	100	VV003	5	3
EVV00315	100	VV003	15	3
EVV00330	100	VV003	30	3
EVV00350	100	VV003	50	3
EVV10305	100	VV103	5	3
EVV10315	100	VV103	15	3
EVV10330	100	VV103	30	3
EVV10350	100	VV103	50	3
EVV05315	100	VV053	15	3
EVV20315	100	VV203	15	3
EVV50315	100	VV503	15	3
EVV10115	100	VV101	15	3
EVV10515	100	VV105	15	3

TABLE III Formulations of different mixes cured by electron beam radiation technique

Mix designation	Ethylene-octene copolymer (phr)	Silica		Radiation dose (kGy) used for curing
		Type	Amount (phr)	
5E	100	–	–	50
5EV00015	100	V	15	50
5EVV10315	100	VV103	15	50

Cure behavior of the filled stocks was examined in terms of Westlinning and Wolf's 'α_F' values [17] defined by

$$\alpha_F = \left(\frac{\Delta L_f}{\Delta L_g} - 1\right) \Big/ W \tag{1}$$

where, ΔL_g, ΔL_f = maximum change in torque measured during vulcanization of the gum and the filled stocks respectively and W = weight fraction of filler to polymer.

2.5. Mechanical properties

Uniaxial stress-strain behavior of dumb-bell shaped specimens and tear strength of unnotched 90° angle specimens (die C) -all punched cut from the compression molded sheets were determined according to ASTM D412-98a and D624-98 test methods respectively, in a Zwick 1445 Universal Tensile Testing machine at a cross-head speed of 500 mm/min and temperature of 27 ± 2°C. Hysteresis loss at first cycle at 100% elongation was measured by subtracting the area under the force retraction curve from the area under force-deformation curve. All measurements were done in three replicates and the values were averaged. All the results are found to be within ±3% experimental error.

2.6. Atomic force microscopic studies

For AFM imaging, specimens were prepared by cryomicrotoming with the help of glass knives at −60°C using liquid nitrogen. The measurements were performed with a Dimension 3000 (Digital Instruments Inc., USA) atomic force microscope equipped with phase detection electronics and operating in the tapping mode under ambient conditions. The Tapping Mode Etched Silicon Probe (Model TESP), with a nominal tip radius of curvature of 5–10 nm, spring constant ranging from 20–100 N/m and resonance frequencies ranging from 200–400 kHz was used (information provided by the manufacturer). The setpoint ratio was adjusted between 0.7 and 0.8 at the resonance frequency of the cantilever with a scan rate of 1 Hz and a resolution of 256 samples per line for a 3×3 μm^2 scan size.

2.7. Equilibrium swelling studies

Previously weighed rubber samples were allowed to swell in toluene at ambient temperature (25°C) for 48 h, the equilibrium swelling time. The test pieces were taken out and the swollen weight was taken. Finally, they were allowed to dry in a vacuum oven to a constant weight. Volume fraction of the rubber in the swollen gel (v_r) was determined on the basis of simple additivity rule of volumes as follows:

$$v_r = \frac{(D - FA)\rho_r^{-1}}{(D - FA)\rho_r^{-1} + A_0\rho_s^{-1}} \tag{2}$$

where, v_r = volume fraction of rubber in the swollen gel, D = deswollen weight of the test specimen, F = weight fraction of the insoluble components, A = weight of the test specimen, A_0 = weight of the absorbed solvent, ρ_r = density of the rubber (0.868 g/cc), and ρ_s = density of the solvent (0.870 g/cc).

The values are found to be within ±1% experimental error. For cases where the crosslink density is not affected by the addition of filler, Kraus developed an equation to describe the relationship between equilibrium swell and filler loading [18]:

$$\frac{v_{r0}}{v_{rf}} = 1 - m\left(\frac{\phi}{1-\phi}\right) \tag{3}$$

where v_{r0} = volume fraction of rubber in the gum vulcanizate, v_{rf} = volume fraction of rubber in the filled vulcanizate, and ϕ = volume fraction of filler in the filled vulcanizate.

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

$$C = \frac{m - v_{r0} + 1}{3\left(1 - v_{r0}^{1/3}\right)} \tag{4}$$

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

2.8. Hardness

Hardness of the cured samples was measured using Durometer Type A hardness tester, (Shore Instrument & Mfg. Co., Inc., New York, U.S.A.) as per ASTM D2240 test method. The thickness of the samples used for measuring hardness was between 8–10 mm. The values are found to be within ±1% experimental error.

2.9. Aging studies

Tensile specimens punched cut from the molded sheets were kept in an air-aging oven for 36 h at 100°C. Modulus, tensile strength and elongation at break were determined in a Zwick 1445 Universal Tensile Testing machine at a cross-head speed of 500 mm/min and temperature of 27±2°C. The values of the above properties before and after aging indicated changes in properties during aging. All the values are found to be within ±3% experimental error.

3. Results and discussion

3.1. Influence of *untreated silica* filler on rheometric and mechanical properties of ethylene-octene copolymer

The rheometric properties of the unfilled and the untreated silica filled rubber cured by 3 phr of DCP are depicted in Fig. 1(i). Incorporation of silica filler results in an increase both in ML and MH values of the filled compound compared to those of the gum rubber. On gradual increase in the filler loading, there is a noticeable enhancement in the above two properties. Addition of 5 phr of silica filler causes slight increase in scorch time and optimum cure time by 23% and 8% respectively compared to the gum compound. However, with increasing the filler loading there is a significant drop in the above two properties. Combination of the above two properties reflects on the cure rate index where there is

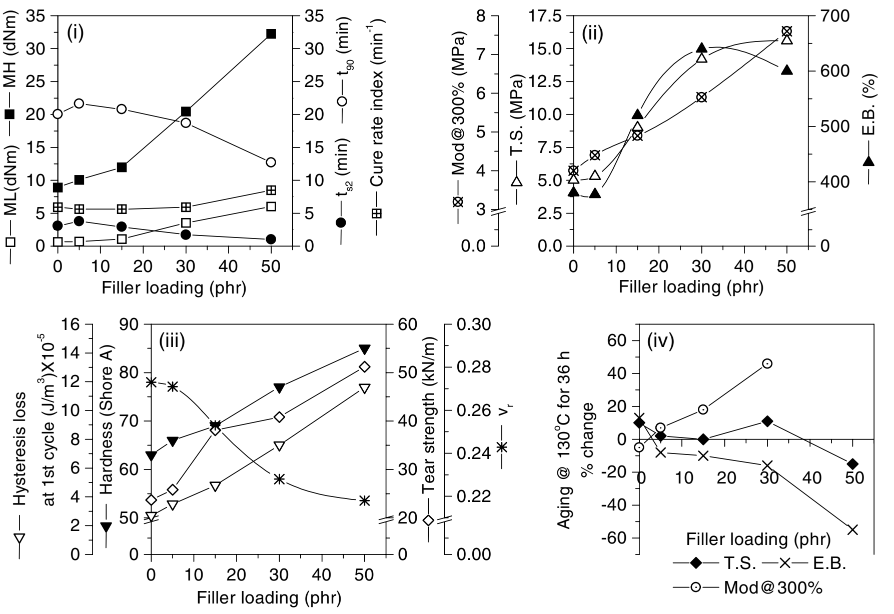

Figure 1 Influence of *untreated silica* filler on rheometric and mechanical properties of ethylene-octene copolymer.

no noticeable change upto 30 phr of filler loading; but at 50 phr of filler loading it is increased by 44%.

Tensile properties of the above compounds are presented in Fig. 1(ii). At 5 phr of silica filler loading, the TS and the modulus at 300% are increased by 6% and 10% respectively, whereas EB remains the same as that of the gum compound. Increasing filler loading to 15 phr, TS, EB and modulus values are increased by 80%, 37% and 23% respectively. Further increase in filler loading to 30 phr causes an enhancement in the above properties by 184%, 68% and 48% respectively. At a still higher dose of filler to 50 phr, TS and modulus values are increased by 212% and 90% respectively compared to the unfilled compound, whereas EB drops down by 58% compared to that of the 30 phr loaded compound.

From Fig. 1(iii) it is found that with respect to the filler loading of 5, 15, 30 and 50 phr, the tear strength increases by 9%, 61%, 72% and 116% respectively, hardness increases by 5%, 10%, 18% and 35% respectively and hysteresis loss at first cycle increases by 30%, 78%, 181% and 330% respectively. On the other hand, volume fraction of rubber in the swollen gel gradually drops by 1%, 7%, 16% and 20% respectively.

Aging properties of the above compounds are depicted in Fig. 1(iv). It is found that on increasing the filler loading, % change in the tensile properties also increases, which corroborates that the incorporation of unmodified silica fillers can not protect the base polymer.

Although there are some improvements in the mechanical properties by increasing the filler dose, the drop in properties like volume swelling and aging results suggests that the untreated silica fillers have poor interaction with the base polymer. Due to the hydrophilic nature of silica there is a poor adhesion between silica and this nonpolar matrix. This may lead to the formation of vacuole, which in turn reduces the volume fraction of rubber in the swollen gel. It also causes poor aging properties especially at the higher filler loading, suggesting a necessity of improving polymer-filler interaction in the silica filled ethylene-octene copolymer. So, an attempt has been made by incorporating the surface modified silanized silica in this copolymer.

3.2. Influence of electron beam *irradiated silanized silica* filler on rheometric and mechanical properties of ethylene-octene copolymer

Addition of 5 phr of electron beam irradiated silanized silica (VV103) in ethylene-octene copolymer does not cause much change in the ML value as compared to the gum compound [Fig. 2(i)]. Increasing the dose of the above filler by 15, 30 and 50 phr causes a significant increase in the ML value by 63%, 369% and 1906% respectively. However, the above increase in the ML value at 5, 15 and 30 phr levels are comparatively less than that of their unmodified counterpart. The lower ML value is indicative of lower compound viscosity, which may be due to less filler aggregation in the filled matrix with better filler dispersion. On the contrary, very high ML value is observed at a filler loading of 50 phr. A significant enhancement in the MH value by 17%, 53%, 169% and 517% is observed at these four different filler loadings, which are much higher than that of their unmodified counterpart. However, due to the silanization process a marginal drop in scorch time and optimum cure time is observed, which is more pronounced at the high filler loadings. On the other hand, combination of these two properties does not cause any noticeable change in cure rate index even at higher filler loadings.

The slope of the linear plot of the relative torque increase vs. filler loading defined as α_F is obtained from Equation 1. It can be used as a measure of cure behavior of the filled compounds. In Fig. 2(ii), α_F is plotted as a function of the volume fraction for the untreated (EV) and electron beam irradiated silanized (EVV103) silica fillers (ϕ). In both the cases, the changes in α_F upto a filler loading of 15 phr, are less. However at the higher

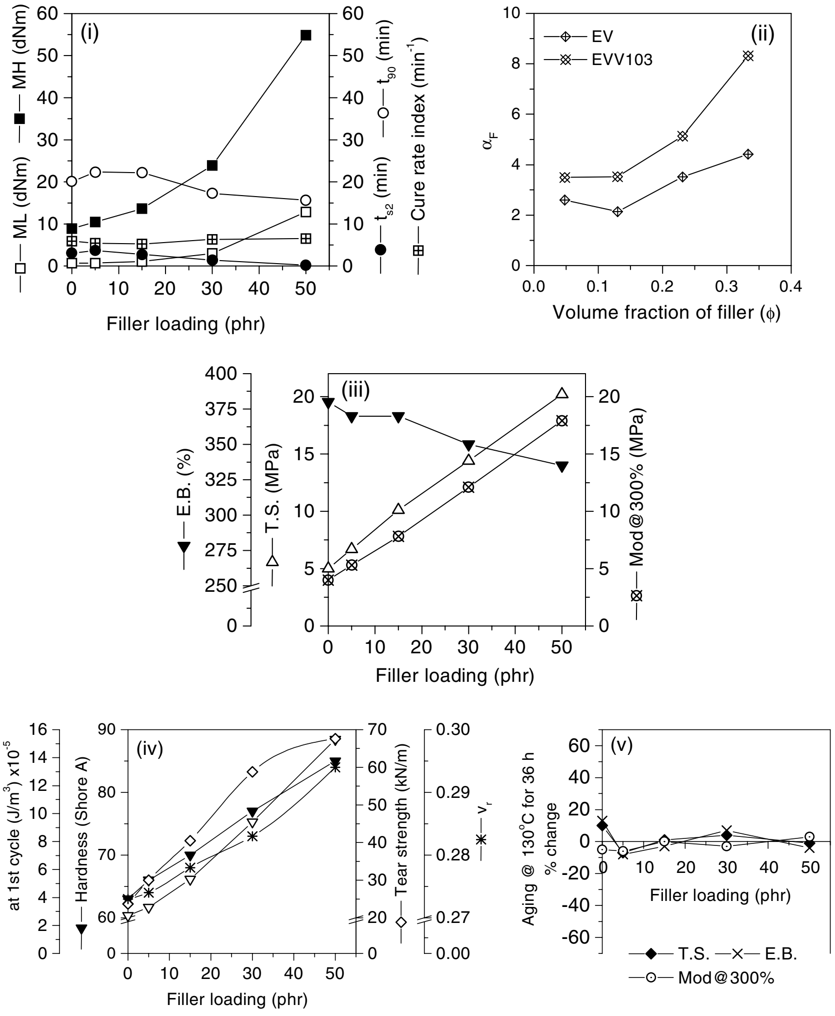

Figure 2 Influence of electron beam *irradiated silanized silica* filler on rheometric and mechanical properties of ethylene-octene copolymer.

filler loadings of 30 and 50 phr, a noticeable increase in α_F value is observed. It is interesting to note that the modified silica shows high α_F value at all the filler loadings compared to the unmodified filler. In the latter case, the change in maximum torque with the filler loading plays a dominant role over that of the minimum torque. Silanization process causes permanent bond formation between the polymer and the filler. This may lead to an apparent increase in volume fraction of rubber, which in turn provides the higher α_F values in the modified fillers.

Tensile properties of this irradiated and silanized silica filled ethylene-octene copolymer are presented in Fig. 2(iii). A steady increase in the TS value by 34%, 102%, 188% and 304% respectively and the modulus at 300% elongation by 33%, 95%, 203% and 348% is observed with the filler loading of 5, 15, 30 and 50 phr respectively. Compared to the unmodified filler, manifold improvement in the above two properties are observed in the case of the modified filler. But a slight drop in EB is observed in the case of modified filler as compared to the gum compound.

From Fig. 2(iv), it is found that the tear strength value is increased by 27%, 71%, 148% and 185% respectively; hysteresis loss at first cycle is increased by 22%, 96%, 248% and 467% with the filler loadings of 5, 15, 30 and 50 phr respectively and in both the cases, the above values are higher than those containing the untreated filler. However, an increase in hardness value with increasing the filler loading finds no change, when the results are compared with control samples. On the contrary in the case of the irradiated and silanized filler, a gradual increase in the volume fraction of rubber in the swollen material is observed with increasing the filler loading. The above phenomenon is explained in the light of polymer-filler interaction in the next section. Significant improvement is also observed in the case of aging properties [Fig. 2(v)], where the aged samples almost retain all the tensile properties of the unaged material even at a high filler dose of 50 phr.

Thus compared to the unmodified filler, the electron beam irradiated silanized filler shows better tensile properties, tear strength and a noticeable improvement in the cure properties, volume swelling and aging properties throughout the filler loading under consideration. All these observations clearly manifest the improvement in polymer-filler interaction after surface modification of the silica filler.

3.3. Effect of *radiation dose* on rheometric and mechanical properties of silanized silica filled ethylene-octene copolymer

In this present section, the silanized silica fillers have been treated with different radiation doses of 50, 100, 200 and 500 kGy, at a constant level of silane (3 phr)

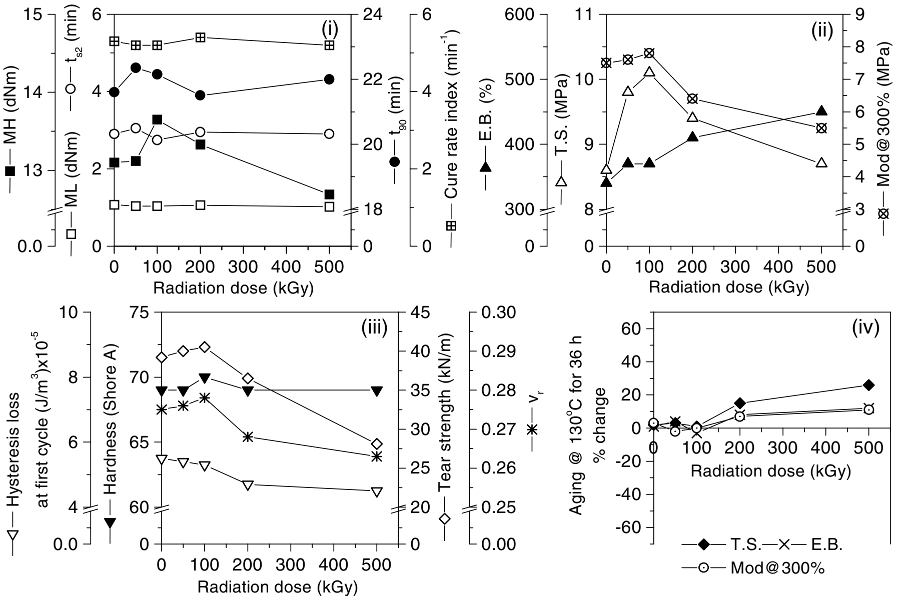

Figure 3 Effect of radiation dose on rheometric and mechanical properties of silanized silica filled ethylene-octene copolymer.

and the results are compared with the silane coated unirradiated sample in an ethylene-octene copolymer at 15 phr silica level.

Fig. 3(i) represents the rheometric properties of the above compounds. There is no significant change in ML values of the above mixes, whereas MH is found to be maximum in the case of 100 kGy irradiated silica. This is explained later. The radiation dose has not much influence on the scorch time and optimum cure time of these silanized silica filled rubber.

Tensile properties of the above mixes are presented in Fig. 3(ii). Compared to unirradiated silica, there is an increase in TS by 14% in the case of 50 kGy radiated silica, which is further increased by 17% in the case of 100 kGy radiated silica. However, at higher radiation dose of 200 kGy the above increment in TS is only by 9%. At a still higher radiation dose of 500 kGy, the TS becomes comparable to that of unirradiated one. There is an increase in EB by 9% in the case of 50 and 100 kGy irradiated silica, which further increases by 21% and 32% in the case of 200, and 500 kGy irradiated silica. A slight improvement in modulus at 300% elongation is noticed in the case of 50 and 100 kGy irradiated silica, but at further higher radiation dose a drop in modulus value is observed.

Fig. 3(iii) represents tear strength, hardness, volume fraction of rubber in the swollen gel and hysteresis loss at first cycle. There are marginal changes in tear strength and v_r at lower radiation dose (upto 100 kGy), whereas a noticeable drop in the above two properties is observed at higher radiation dose. With increasing radiation dose hysteresis loss gradually decreases. On the other hand, hardness of the electron beam modified silanized silica filled compound is comparable with that of the unirradiated one.

The aging properties of the above mixes are depicted in Fig. 3(iv). The change in tensile properties is more pronounced in the case of higher radiation dose. There is a definite improvement in the mechanical properties at lower radiation doses compared to the unirradiated filler. In earlier investigations it is observed that higher radiation dose facilitates degradation process [19]. In this case probably the surface activity of the filler gets destroyed at higher radiation doses which causes drop in physical properties. It is also found that the 100 kGy radiated filler shows optimum properties among all these irradiated fillers.

However, in this context it is necessary to examine the effect of electron beam irradiation on the silanization process. With respect to the control silica filler, even the low filler loading of 5 or 15 phr is found to be suitable for scrutinizing the effect of electron beam, although larger changes are observed at higher filler loadings. For example, at 50 phr of filler loading, the TS, the EB and the tear strength of unirradiated silanized silica filled compound (i.e., EVV00350) are 15.5 MPa, 285% and 62.6 kN/m respectively (Table IV). However, a noticeable enhancement in those properties by 30%, 18% and 8% respectively is observed in the case of 100 kGy irradiated silanized silica filled compound (EVV10350). Due to this low elongation at break property (285%), there is no value for the modulus at 300% elongation for the unirradiated silanized silica filled compound. Hence, the value at 200% elongation is compared. There is an improvement of 10% (from 11.1 MPa to 12.2 MPa) on irradiation after silanization. Similarly, as compared to the unirradiated counterpart, improvements in the aging properties are also noted in the case of irradiated silanized silica filled compound

TABLE IV Effect of electron beam irradiation on the silanization process

	EVV00350	EVV10350
Tensile strength (MPa)	15.5	20.2
Elongation at break (%)	285	335
Modulus @200% elongation (MPa)	11.1	12.2
Tear strength (kN/m)	62.6	67.6
Aging @ 130°C for 36 h		
(i) [a]Tensile strength (MPa)	13.2 (−15)	19.9 (−1)
(ii) [a]Elongation at break (%)	190 (−33)	320 (−4)

[a] Values in the parentheses indicate % changes after aging.

(EVV10350). For EVV00350, % changes in the TS and the EB properties after aging at 130°C for 36 h are 15% and 33% respectively, whereas practically no change in the above properties (1% and 4%, respectively) is noticed in the case of irradiated compound (EVV10350) even at this high filler loading.

The plausible reason for the improvements in the above properties may be as follows: due to the electron beam treatment of the silane coated silica filler, silane undergoes a chemical reaction with silica filler, which results in a permanent attachment of the coupling agent on the silica surface. However, it is evident that without any treatment (here, in the present study, electron beam treatment) no such interaction/reaction takes place between the filler and the silane at room temperature [20, 21]. Incorporation of electron beam treated silanized silica filler forms permanent covalent bonds/molecular linkages between silica filler and rubber matrix during the mixing and the molding stage. Although such coupling reaction takes place in the case of unirradiated compound but its extent suffers from the lack of pretreatment, which is clear especially from the aging properties at high filler loading.

3.4. Effect of *silane level* on rheometric and mechanical properties of silanized silica filled ethylene-octene copolymer

The rheological properties of the different mixes are presented in Fig. 4(i). There is no noticeable change in the ML values with different levels of silane loading. Compared to EV00015, an increase in the MH value by 6%, 15%, and 20% are observed in the case of the samples containing 1, 3 and 5 parts of silane modified silica irradiated at 100 kGy, designated as EVV10115, EVV10315 and EVV10515 respectively. However, variation of silane level does not have much effect on the scorch time, optimum cure time and cure rate index.

The tensile properties of the above compounds are presented in Fig. 4(ii). Compared to the control filler, an increase in the T.S. by 15% is observed in the case of 1 and 3 parts of silane treated filler and by 10% in the case of 5 parts silane treated filler. With increasing the silane level by 1, 3 and 5 parts a gradual increase in modulus at 300% by 25%, 59% and 71% respectively and a drop in E.B. by 8%, 26% and 32% respectively are observed.

Fig. 4(iii) depicts the tear strength, hardness, volume fraction of rubber in the swollen gel and hysteresis loss at first cycle. Addition of 1 part of silane does not cause much improvement in the above properties. However, with 3 and 5 parts of silane, an increase in tear strength by 7% and 12% respectively, an increase in hysteresis loss by 10% and 17% respectively and an increase in volume fraction of rubber in the swollen gel by 13% and 16% respectively are observed compared to that of the untreated filler. On the other hand, silane level has no significant effect on the hardness property.

From Fig. 4(iv) it is found that all the silane modified silica filled compound show excellent aging property as compared to the uncoated silica.

With increasing silane level from 1 part to 5 parts, increments in the properties like MH, modulus, tear strength and volume fraction of rubber in the swollen gel suggests that surface modification of silica fillers by triethoxyvinyl silane surely improves the polymer-filler interactions in the silica filled ethylene-octene copolymer.

3.5. Polymer-filler interaction

Two of the most characteristic phenomena in filler reinforcement are:

(i) a reduction in the capacity of the filled vulcanizates to swell in solvents and

(ii) a pronounced increase in the modulus of vulcanizates resulting from use of the filler.

These two phenomena are interrelated. The effects of filler loading, for both the cases of untreated and

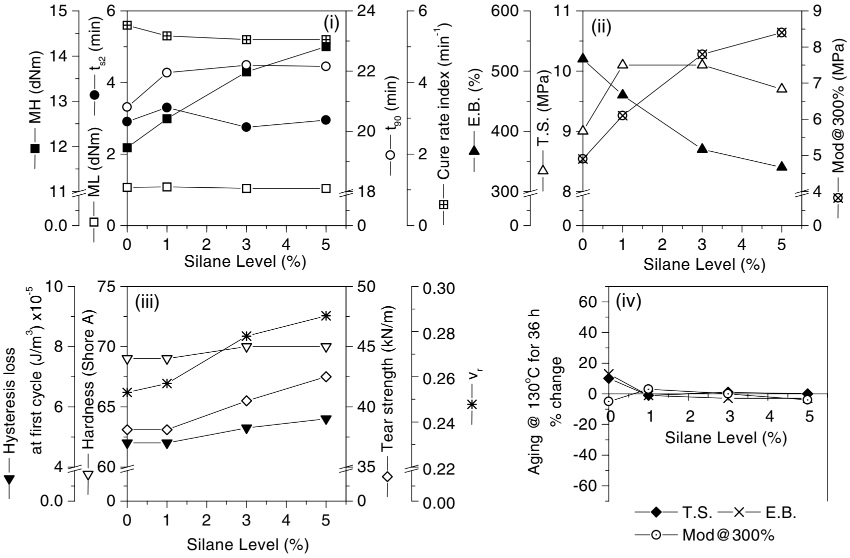

Figure 4 Effect of silane level on rheometric and mechanical properties of silanized silica filled ethylene-octene copolymer.

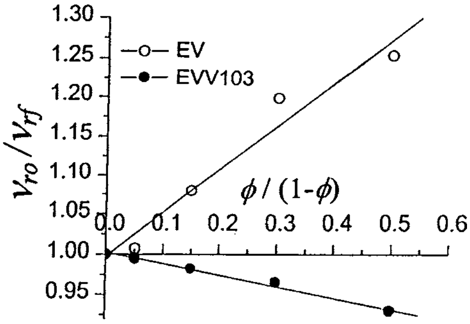

Figure 5 Kraus plots of swelling in toluene for untreated (EV) and electron beam irradiated silanized silica (EVV103) filled ethylene-octene copolymer.

electron beam irradiated silanized silica filled composites have been discussed in the previous sections. Here, in this section, an attempt has been made to quantify the polymer-filler interaction. Also, a new model for explaining the enhanced stress-strain properties of modified fillers has been proposed in the latter section.

3.5.1. Equilibrium swelling

As discussed earlier, the volume fraction of rubber in the swollen gel for the vulcanizates containing the electron beam irradiated silane modified fillers (EVV103) is much higher than that corresponding to the untreated compound (EV). The plots in Fig. 5 corroborate this fact quantitatively and show a trend of v_{ro}/v_{rf} against $\phi/(1-\phi)$ in both the cases, v_{rf} values being lower for unmodified filler loaded rubber, the ratio of v_{ro}/v_{rf} increases with $\phi/(1-\phi)$. From the slope of the plots, the '*m*' value obtained for the same is −0.55 and that of the modified filler loaded system is 0.135. Putting this value of '*m*' in the Kraus equation, the *C* value for the unmodified system is obtained as 0.168, which is increased to 0.818 in the case of modified system. Although the value of *C* is mainly dependent on filler-rubber interaction, it is found that both the primary and secondary structures of the filler have significant effect on *C* [22]. For reinforcing fillers such as carbon black and silica, the *C* values can directly be used to characterize the restriction of swelling caused by the filler. Here it is assumed that swelling is completely restricted at the particle surface and that the rubber matrix at some distance from the particle is swollen isotropically in a manner characteristic of the unfilled rubber. This suggests strongly that the restriction of swelling depends only on the fact that a firm bond between the rubber and the filler is established [23]. A negative value of '*m*' and a very low value of '*C*' in the case of untreated silica filled composites indicate that the solvent desorbs the rubber, opening up vacuoles and the restriction of swelling is less. The above process is rather enhanced with the addition of higher doses of filler. On the other hand, a five fold increase in the '*C*' value is observed after modifying the silica surface by the silanization process which manifests the higher swelling restriction in the silanized silica filled composites. This is also indicative of a coupling reaction which must have taken place between the filler surface and the polymer and which, indirectly would have led to an increase in the apparent crosslink density. In our earlier study we have observed that silanization of silica causes drastic improvement in hydrophobicity of the filler as obtained from dynamic wicking study [9]. Now from the present observations it can also be included that the surface modification of silica improves the adhesion between polymer and filler.

3.5.2. Mathematical model for filled elastomer

A mathematical model has been proposed in order to further envisage the effect of electron beam irradiation and the silanization process. Attempts have been made in the past by several workers to correlate the modulus with volume concentration of fillers [24–27]. In our present study it is observed that the ratio of the modulus of the filled to that of the gum vulcanizate basically follows an exponential nature with the volume concentration of filler. Hence, we have tried to explain the filler-filler and the polymer-filler interaction considering a generalized exponential equation correlating the modulus and the volume concentration of filler as follows:

$$E_f/E_g = ae^{b\phi} \tag{5}$$

where, E_g = modulus of the gum vulcanizate, E_f = modulus of the filled vulcanizate, ϕ = volume fraction of filler in the filled composite, and a, b = constants at a particular strain level.

Representative engineering stress-strain curves of untreated and 100 kGy irradiated silanized silica filled composites are shown in Fig. 6. The ratio of modulus of the filled to that of the gum compounds at different strain levels against the volume fraction of filler in the composites is curve fitted following Equation 5 (Fig. 7). It is observed that for all the cases of the filled vulcanizates, the experimental data nicely fit the above empirical equation. The '*a*' value remains constant and is equal to one. This is true for the entire strain level under consideration ($\lambda = 1.25$ to 4.00) and also independent of filler volume fraction and the filler system, i.e., both for untreated and silanized silica filled composites. But the value of '*b*' varies with strain levels and with the type of the filler.

By incorporating the value of '*a*', Equation 5 reduces to

$$E_f/E_g = e^{b\phi} \tag{6}$$

On expanding the above equation, one obtains,

$$E_f/E_g = (1 + b\phi + b^2\phi^2 + \cdots) \tag{7}$$

The above equation closely resembles that of the earlier models [24–26]. However, it is stated here that the factor '*b*' is responsible for the filler-filler and the polymer-filler interaction, although earlier workers have assumed a constant value of '*b*' for all the fillers.

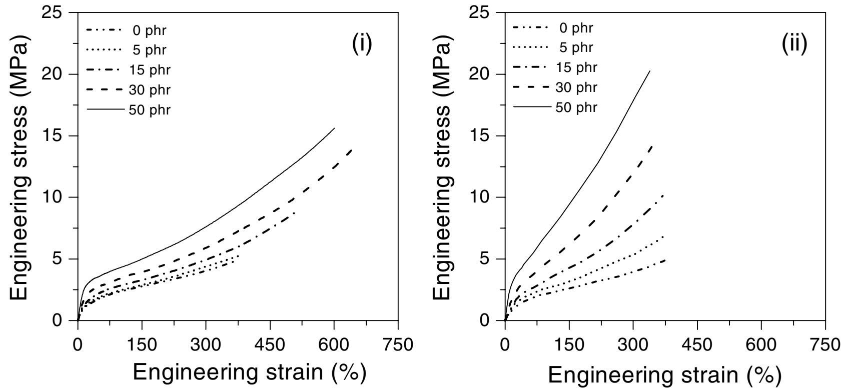

Figure 6 Representative stress-strain curves of (i) untreated (EV) and (ii) electron beam irradiated silanized silica (EVV103) filled ethylene-octene copolymer.

In Fig. 8 the 'b' values so obtained are plotted against the extension ratio. An entirely different nature of the curves for the unmodified and the modified silica filled composites is observed. The initial part of the curves (below $\lambda = 1.25$) is obtained by interpolation technique. In all the cases, a drop in the above curves is observed while increasing the extension ratio (upto $\lambda = 1.5$). This part of the curves resembles that of the Payne effect, which may be attributed to the breakdown of secondary structure of filler upon straining. The above effect is most significant in the case of untreated silica filled compounds (EV), which is noticeably reduced when the filler is replaced by the unirradiated silanized silica filler (EVV003). However, a further reduction is noted in the case of irradiated silanized silica filled compounds. The 'b' value obtained for untreated silica filled composites at $\lambda = 1.5$ is 3.35. Interestingly, at higher extension ratios (beyond $\lambda = 1.5$), there is no noticeable change in the 'b' values. On the other hand, in the case of irradiated silanized silica filled composites, the 'b' value at $\lambda = 1.5$ is 5.3. With $\lambda > 1.5$, there is a steady increase in the 'b' values and at $\lambda = 4$, $b = 8.6$, which is about 2.4 times higher than that of the untreated one. Although, the unirradiated silanized silica filled composite shows a similar trend, as that of its irradiated counterpart, but the values are noticeably lower (e.g., about 9.3% at $\lambda = 4$).

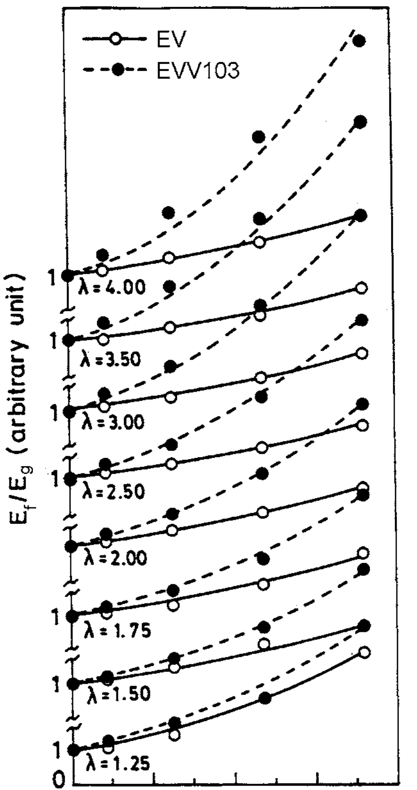

Figure 7 Representative plots of ratios of modulus of filled to that of the gum compound with respect to the volume fraction of filler for untreated (EV) and electron beam irradiated silanized silica (EVV103), in the composites at different strain levels.

As mentioned earlier, the initial high value of 'b' at a very low extension ratio followed by a faster decrease with increasing strain for the untreated silica filled compound may be attributed due to its strong filler-filler networking potential. Modification of the silica filler by silane coupling agent followed by electron beam treatment considerably reduces it. The atomic force microscopy studies further support the above findings. Fig. 9 depicts the Tapping mode AFM phase images (z-scale = 60 degree) showing the microdispersion of 15 phr loaded untreated (EV00015) and electron beam irradiated silanized silica filler in the ethylene-octene copolymer rubber (EVV10315). A noticeable reduction in the aggregates size and the occurrence in the primary silica filler particles are clearly visualized in the case

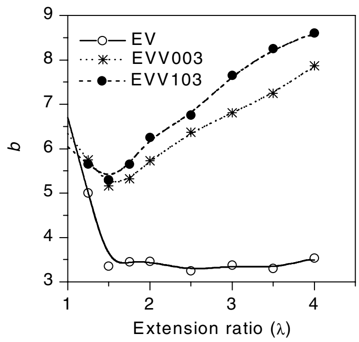

Figure 8 Plots of 'b' against extension ratio (λ) for untreated (EV), unirradiated (EVV003) and electron beam irradiated silanized silica (EVV103) filled composites.

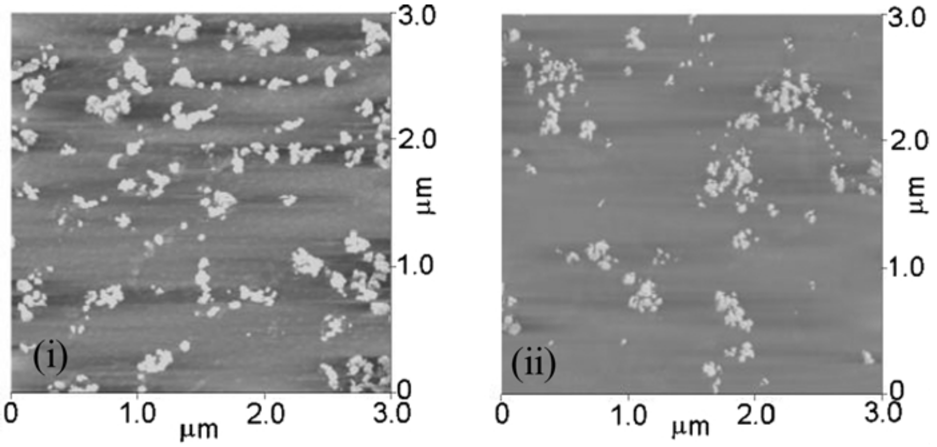

Figure 9 Tapping mode AFM phase images (z-scale = 60 degree) showing the microdispersion of 15 phr loaded silica filler in the ethylene-octene copolymer rubber (i) untreated silica filled rubber (EV00015) and (ii) electron beam irradiated silanized silica filled rubber (EVV10315).

of electron beam irradiated silanized silica filled compound. Due to the above modification, a significant drop in the parameter '*b*' at this low strain level is also noted in our earlier work, on the dynamic mechanical properties of silica filled ethylene-octene copolymer [28]. Thus in other words, the present investigations on mechanical properties are in good correspondence with that of the morphological studies and the dynamic mechanical properties.

At higher strain level (beyond $\lambda = 1.5$), after the destruction of filler-filler networking, polymer-filler interaction plays the dominant role. For untreated silica filled compounds, due to the lack of polymer-filler interaction, there is no change in the '*b*' values at higher extension ratios. On the other hand, the silanization of silica filler significantly increases the '*b*' values and the effect is more pronounced in the electron beam treated silanized silica filled composites. This clearly emphasizes that the pretreatment of silanized silica filler by electron beam irradiation successfully helps the silanization process by the introduction of covalent bonds between the filler surface and the rubber chains.

3.6. Mechanical properties of different surface modified silica filled ethylene-octene copolymer *cured by electron beam irradiation*

Owing to the saturated backbone of this ethylene-octene copolymer, radiation technique is also useful for curing this material in addition to peroxide curing. Moreover, peroxide may be adsorbed partially by silica, as a result of which the influence of the modified filler may be suppressed. Preliminary experiments indicate that ethylene-octene copolymer shows optimum properties when irradiated by electron beam technique at a dose of 50 kGy in air. Thus, in order to investigate the influence of surface treated silica fillers on this polymer, the filled systems were electron beam irradiated at the above radiation dose. The unfilled rubber, the unmodified silica filled rubber and the electron beam irradiated silanized silica filled rubber are designated as 5E, 5EV00015 and 5EVV10315 respectively [Table III]. The tensile properties of the unaged compounds are illustrated in Fig. 10(i). A distinct enhancement in the above properties is observed with this

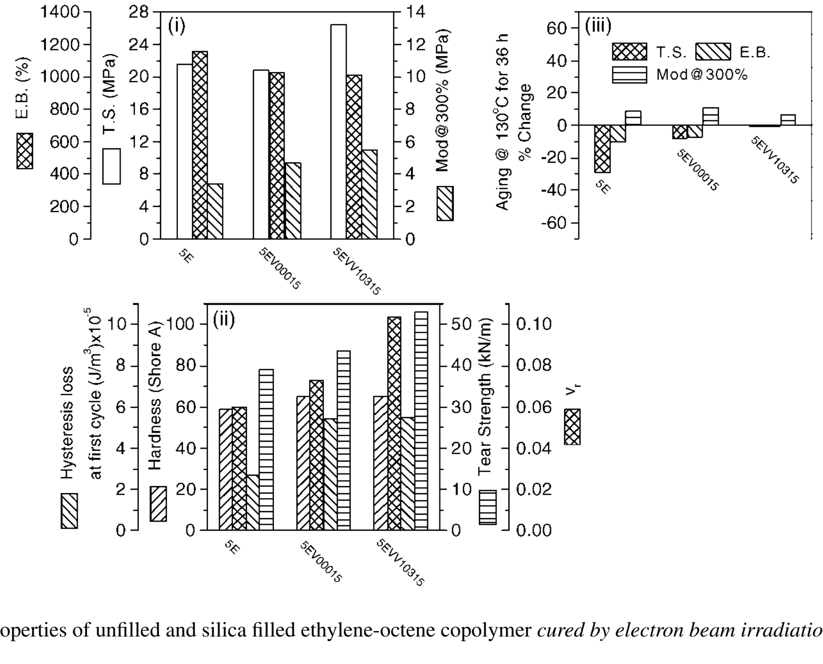

Figure 10 Mechanical properties of unfilled and silica filled ethylene-octene copolymer *cured by electron beam irradiation*.

modified filler. For example, the tensile strength, the elongation at break and the modulus at 300% elongation of unfilled rubber are 21.5 MPa, 1160% and 10.2 MPa respectively. Incorporation of untreated silica filler in the ethylene-octene copolymer results in a slight drop in tensile strength and elongation at break, however, the modulus at 300% elongation is increased by 38%. On the other hand, compared to this untreated silica filled compound, the tensile strength and the modulus values are increased by 27% and 17% respectively, in the case of silanized silica filled rubber, whereas, the latter does not show much change in the elongation at break.

The properties like, tear strength, hardness, volume fraction of rubber in the swollen gel and the hysteresis loss at first cycle of the above compounds are presented in Fig. 10(ii). With respect to gum compound, an enhancement in the tear strength by 12% and an increase in volume fraction of rubber in the swollen gel by 22% are observed in the case of untreated silica filled compound. The above increments are 35% and 73% respectively, in the case of silanized silica filled rubber, which elucidates a significant improvement in the polymer-filler interaction due to the silanization process. Although the incorporation of silica filler in the ethylene copolymer causes increase in hardness and hysteresis loss, the results are comparable both in unmodified and modified silica filled compounds. The silanization of the silica filler also shows noticeable improvements in the aging properties [Fig. 10(iii)] as compared to the gum and the untreated silica filled rubber, which suggest that the above enhancement in properties due to improvement in the polymer-filler interaction is also permanent, possibly by the introduction of covalent bonds between the filler surface and the rubber chains.

4. Conclusions

An extensive study is carried out to investigate the effect of filler-filler and polymer-filler interaction by the use of unmodified silica and silica modified with a silane coupling agent and electron beam. A new generation elastomer based on ethylene-octene copolymer was chosen as the candidate matrix material for the filled vulcanizates. The following observations have been made:

1. Although there are some improvements in the mechanical properties by increasing level of the control filler, but the drop in aging properties and volume swelling suggests that the untreated silica filler has poor interactions with the base polymer.
2. Treating the silica surface with a bifunctional silane followed by electron beam treatment causes a drastic improvement in the hydrophobicity of the filler. Incorporation of this modified filler into the nonpolar ethylene-octene matrix successfully overcomes the problems encountered with the control sample.
3. A definite improvement in the mechanical properties especially at the lower radiation doses is observed as compared to unirradiated silane coated silica. However, beyond 100 kGy, drop in the above properties is noticed which probably elucidates the decrease in surface activity at this high radiation doses.
4. In the case of peroxide curing system, while increasing the silane level from 1 to 5 parts, an improvement in the properties like MH, modulus, tear strength and volume fraction of rubber in the swollen gel suggests that surface modification of silica fillers by triethoxyvinyl silane surely improves the polymer-filler interactions in the silica filled ethylene-octene copolymer.
5. A five-fold increase in the 'C' value, as obtained from Kraus plot clearly manifests the extent of improvement in the polymer-filler interaction in the silanized silica filled composite.
6. A generalized mathematical model is also proposed in order to explain the filler-filler and polymer-filler interaction. This elucidates that after silanization of the silica surface with the bifunctional silane followed by electron beam treatment not only helps in reducing the filler networking potential but at the same time, the polymer-filler interaction is greatly strengthened by the introduction of covalent bonds between the filler surface and polymer chains. The influence of electron beam treatment on silanized silica filler can be easily demonstrated.
7. In contrast to untreated silica, silanized silica shows significant improvement in the whole property spectrum, achieved with ethylene-octene composites for both peroxide as well as electron beam radiation curing techniques.

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