

# Influence of Untreated and Novel Electron-Beam-Modified Surface-Coated Silica Filler on the Thermorheological Properties of Ethylene–Octene Copolymer

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**ABSTRACT:** We developed surface-modified silica fillers by coating these with an acrylate monomer, trimethylolpropane triacrylate, or a silane coupling agent, triethoxyvinyl silane, followed by electron-beam irradiation at room temperature. These were incorporated in an ethylene–octene copolymer rubber. Thermorheological studies of the unvulcanized ethylene–octene copolymer and its untreated and modified silica-filled composites were done with a shear dynamic oscillating rheometer. Modification of the silica filler, especially via the silanization process followed by electron beam treatment, significantly reduced filler–filler networking as revealed from the log–log plots of storage

modulus and complex shear viscosity, and its real component. The rheological complexity of the compositions was analyzed from a double logarithmic plot of the storage modulus and loss modulus. The results obtained from the master curves constructed on the basis of the time–temperature superposition principle and the activation energy calculated from the Arrhenius equation for the flow of above these compounds further supported these findings. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2453–2459, 2003

**Key words:** surfaces; modification; silicas; electron beam irradiation; viscoelastic properties

## INTRODUCTION

The rheological characteristics of an unvulcanized rubber and its filled compounds are of considerable importance in both the processing and forming operations. All viscoelastic materials behave more or less like a solid (elastic) or liquid (viscous) depending on the rate at which they are deformed. This behavior is related to the fact that strained macromolecules tend to pull back to their original shape.<sup>1,2</sup> The various steps of rubber processing generally involve a flow state, and therefore, prediction of their performance and control require a knowledge of both the viscous and elastic properties of the rubber compound. Rheological measurements determine both the viscosity and elasticity of the fluid as a function of frequency.<sup>3</sup> The viscous behavior determines the throughput, and the elastic properties are important for the dimensional stability. The presence of a filler significantly influences the rheological properties of filled composites.<sup>4–10</sup> Recently, the processing behavior of finely divided silica in combination with a bifunctional silane was studied.<sup>11,12</sup>

In our previous article, we reported a new method of surface modification by the coating of the fillers with an acrylate monomer, trimethylolpropane triacrylate (TMPTA), or with an organosilane, triethoxyvinyl silane (TEVS), followed by the electron beam irradiation of the coated filler.<sup>13</sup> A considerable improvement in the hydrophobicity of the treated silica filler was observed from the characterization studies. The incorporation of these modified fillers in a new-generation elastomer based on a homogeneous ethylene–octene copolymer led to a significant improvement in its mechanical<sup>14</sup> and dynamic mechanical properties.<sup>15</sup> Also, the incorporation of these modified fillers in an ethylene–octene copolymer successfully reduced the filler–filler interaction, which in turn reduced the formation of big agglomerates and improved the filler dispersion in the rubber matrix.<sup>15</sup> Although, there has been some work on the rheological properties of the ethylene–octene copolymer, this has been done mostly on polyolefin blends where this copolymer was used as a second component in the blend.<sup>16–19</sup> There is virtually no literature on the reinforcement of this rubber with silica filler. This study dealt with the effect of the incorporation of untreated and novel electron-beam-modified surface-coated silica filler on the shear dynamic viscoelastic behavior of an unvulcanized ethylene–octene copolymer.

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**TABLE I**  
Formulations of the Various Surface-Treated Silica Fillers

Filler designation	VULKASIL S (g)	TMPTA (g)	TEVS (g)	Radiation dose (kGy)
V	100	—	—	—
VM103	100	3	—	100
VV003	100	—	3	—
VV103	100	—	3	100

## EXPERIMENTAL

### Materials

A general purpose polyolefin elastomer, Engage<sup>®</sup> 8150, was kindly provided by DuPont-Dow Elastomers (Freeport, TX). The silica filler, VULKASIL S (specific surface area = 175 m<sup>2</sup>/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. (Leverkusen, Germany). The acrylate monomer, TMPTA (flash point > 100°C, boiling point > 100°C, specific gravity = 1110 kg/m<sup>3</sup>), and the silane coupling agent, TEVS (boiling point = 160–161°C), were supplied by UCB Chemicals (Drogenbos, Belgium) and Aldrich Chemical Co., Inc. (Milwaukee, WI), respectively.

### Filler modification

We modified the surface of the silica fillers by coating them with an acrylate monomer, TMPTA, or with an organosilane, TEVS, followed by irradiation of the coated filler via the electron beam technique at room temperature. The specifications of the electron beam accelerator were mentioned in detail in our earlier article.<sup>13</sup> Formulations of the various surface-treated silica fillers are presented in Table I.

### Preparation of the rubber–filler composite

For a comparative study, both unmodified and modified silica fillers were incorporated into the rubber. The formulations of the different mixes are given in Table II. The mixing was carried out in a Brabender plasticorder (PLE 330) (Brabender OHG, Germany) at a rotor speed of 60 rpm at 100°C. First, the rubber was loaded into the Brabender and allowed to soften for 1 min. Then, the filler was incorporated into the rubber and was mixed for 3 min followed by a single pass through a two-roll mill. Finally, the compound was remixed in the Brabender for 2 min and passed through the two-roll mill.

The sheeted-out stocks were compression-molded in an electrically heated hydraulic press at 150°C for 3

min at 5 MPa of pressure and were then cooled under pressure by water circulation through the hot mold.

### Dynamic viscoelastic measurements

The rheological characterization of the molded compounds was carried out in oscillatory shear flow as a function of frequency ( $\omega$ ) and temperature using an ARES, 3A rheometer Rheometric Scientific, Inc. (Piscataway, NJ) with a 25-mm parallel plate geometry. Measurements were done at four different temperatures, 90, 110, 130, and 150°C, with a  $\omega$  ranging between 0.016 and 16.0 Hz under an imposed strain of 1%, which was selected from previously made strain sweeps to ensure a linear relation between the stress and deformation.

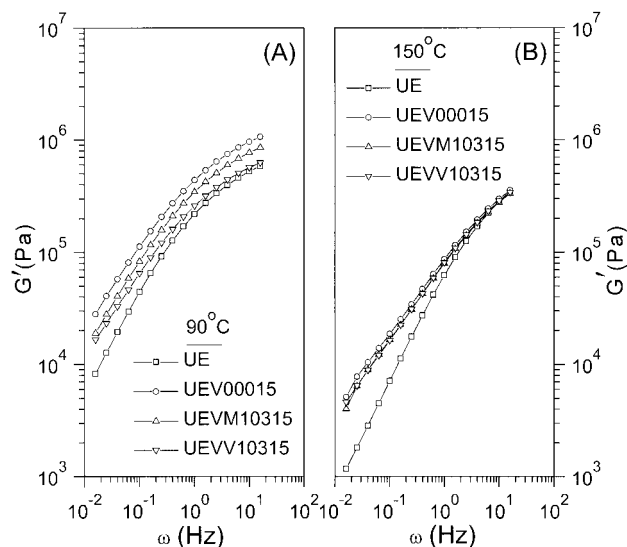
## RESULTS AND DISCUSSION

### Effect of the surface-modified silica filler on rheological properties: Dependence of dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) on ( $\omega$ )

The plots of  $G'$  versus  $\omega$  for the unfilled and uncured ethylene–octene copolymer and its 15-phr-loaded, untreated, and surface-modified silica-filled composites at 90 and 150°C are presented in Figure 1. With increasing  $\omega$ ,  $G'$  increased for all of the compounds, that is,  $G'$  was strongly  $\omega$ -dependent as the materials were stiffer at higher  $\omega$ 's. The unfilled ethylene–octene copolymer rubber (UE) showed lower  $G'$  values compared to its filled composites throughout the  $\omega$  range under consideration. Incorporation of the silica filler in the ethylene–octene copolymer rubber increased  $G'$  due to filler action, and the effect was more pronounced at lower temperatures and  $\omega$  lower  $\omega$ s. Interestingly,  $G'$  was also dependent on the filler type. For example, at 90°C, the  $G'$  of the untreated silica filled rubber (UEV00015) was  $2.8 \times 10^4$  and  $1.1 \times 10^6$  Pa at  $\omega = 0.016$  and 16.0 Hz, respectively. When this filler was replaced by acrylated and electron-beam-irradiated silica (UEVM10315),  $G'$  dropped to  $1.9 \times 10^4$  and  $0.9 \times 10^6$  Pa, respectively. A further reduction in these values to  $1.7 \times 10^4$  and  $0.6 \times 10^6$  Pa, respectively, was noted in the case of the silanized and elec-

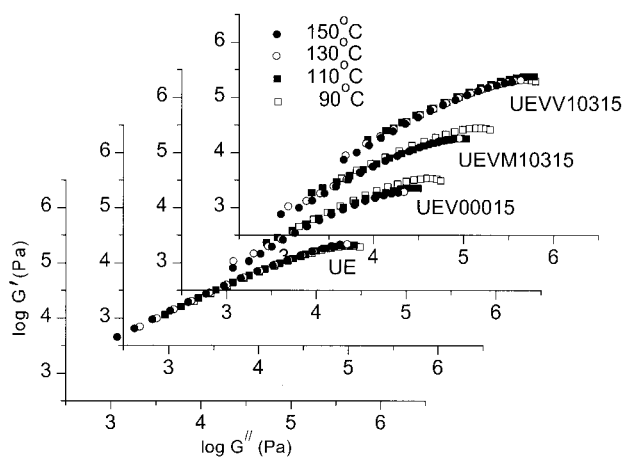
**TABLE II**  
Formulations of Different Mixes

Mix designation	Ethylene–octene copolymer (phr)	Silica	
		Type	Amount (phr)
UE	100	—	—
UEVM10315	100	VM103	15
UEV00015	100	V	15
UEVV00315	100	VV003	15
UEVV10315	100	VV103	15
UEVV10330	100	VV103	30
UEVV10350	100	VV103	50

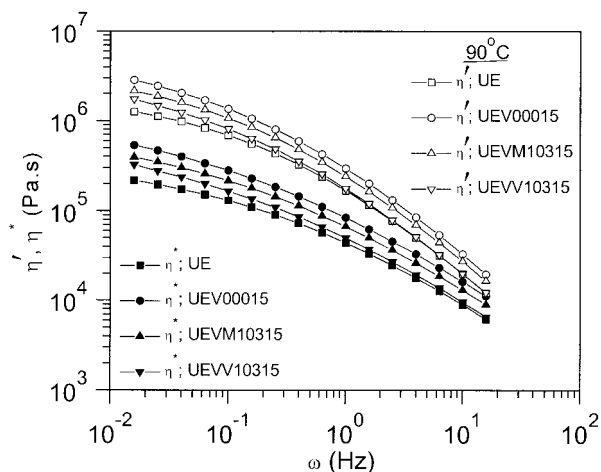


**Figure 1**  $G'$  versus  $\omega$  plots for unfilled and silica-filled ethylene-octene copolymer rubbers at (A) 90 and (B) 150°C.

tron-beam-irradiated silica-filled rubber (UEVV10315). This finding was presumably governed by the aggregate-aggregate interaction. Due to the presence of highly populated surface silanol groups, there was a tendency of silica filler aggregates to associate through strong hydrogen bonds to form agglomerates. This may have led to a chain-like filler structure, generally termed a secondary structure or filler network. In addition, rubber trapped within the filler agglomerates or secondary structure may have considerably increased the modulus value in the untreated silica filled compound. Also, as shown in Figure 1, at 150°C, the  $G'$  values of the filled polymers overlapped with the unfilled polymer at  $\omega$  ranges of 1–10 Hz, which implied the breaking of the filler-filler association from low shear to high shear. In our earlier study, the surface treatment of silica filler



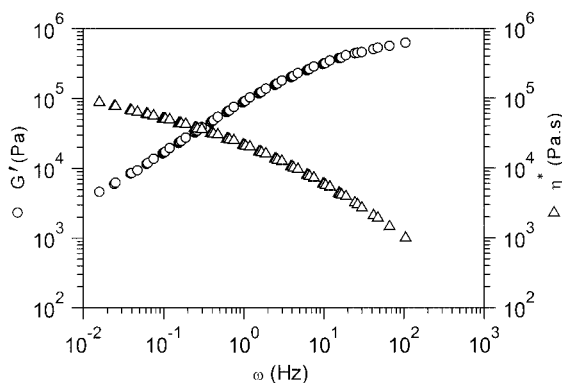
**Figure 2** Log-log plot of  $G'$  versus  $G''$  for unfilled and silica-filled ethylene-octene copolymer rubbers at different temperatures.



**Figure 3** Log-log plot of  $\eta^*$  and its real component  $\eta'$  against  $\omega$  for unfilled and silica-filled ethylene-octene copolymer rubbers at 90°C.

with acrylate and a silane coupling agent followed by electron beam treatment significantly improved the hydrophobicity of the filler,<sup>13</sup> and hence, it reduced the surface polarity of the silica filler, which in turn, helped to reduce the secondary structure formation and improved the filler dispersion. As a result, the acrylated and the silanized silica-filled compounds showed lower  $G'$  values compared to their untreated counterpart. Our earlier investigations based on the morphological studies of these silica-filled composites by atomic force microscopy clearly showed a reduction in filler aggregate size and improved filler dispersion in the rubber matrix due to this surface modification. A decrease in the minimum torque values observed in rheometric studies and reduction of structure breakdown due to these surface modifications were also noted in our earlier study,<sup>15</sup> which further supported these findings.

As mentioned earlier,  $G'$  is related to the elastic behavior of the material and may be considered the amount of stored energy, whereas  $G''$  represents the amount of dissipated energy. The dependence of  $G'$  and  $G''$  on the  $\omega$  measures the relative motion of the molecules in the bulk, which can provide important information about the flow behavior of melts. Figure 2 displays log-log plots of  $G'$  against  $G''$  (Han plot)<sup>20</sup> for the unfilled and uncured ethylene-octene copolymer and its untreated and surface-modified silica-filled composites at 15-phr loading at different temperatures. The unfilled rubber (UE) exhibited temperature independence in the Han plot, which could be ascribed to the thermorheological simplicity of the melt in the range of  $\omega$ s covered in this study. This implied that all of the relaxation processes that determined the observed rheological behavior of the polymer had the same dependency with temperature [the same flow activation energy ( $E_a$ )], that is, the melt was homogeneous at the four different tem-



**Figure 4** Representative master curves of  $G'$  and  $\eta^*$  of the silanized and electron-beam-irradiated silica-filled ethylene-octene copolymer rubber.

peratures (90, 110, 130, and 150°C) under consideration. For the melt containing untreated silica (UEV00015), the initial values were slightly scattered followed by a downward tailing, which may have been due to the formation of a heterogeneous melt structure. The acrylated and electron-beam-treated silica-filled compound (UEVM10315) behaved similarly to the untreated silica-filled compound, whereas the silanized and electron-beam-treated silica-filled compound (UEVV10315) showed a proximity toward the behavior of the unfilled rubber. Thus, the melt rheology of the untreated silica filled compound was highly influenced by the filler aggregation. Although the acrylate treatment somewhat reduced the filler-filler interaction, as noticed in the earlier cases, a considerable amount of this effect still persisted in this compound. However, the silane treatment successfully reduced the filler aggregation as a result of which the silanized and electron-beam-treated silica-filled compound behaved similarly to the unfilled rubber.

#### Effect of the surface-modified silica filler on rheological properties: Dependence of dynamic viscosity on frequency

In oscillatory dynamic mechanical analysis, two components of complex viscosity [ $\eta^*$ ; defined as  $\eta^* = \eta'$

–  $i\eta''$ , where  $\eta'$  is the real part of the viscosity and  $\eta''$  is the imaginary part of the viscosity) measure the dissipated and stored energy per cycle of oscillation, respectively. These are related with  $G''$  and  $G'$ , respectively, by the following equations:

$$\eta'(\omega) = G''(\omega)/\omega \quad (1)$$

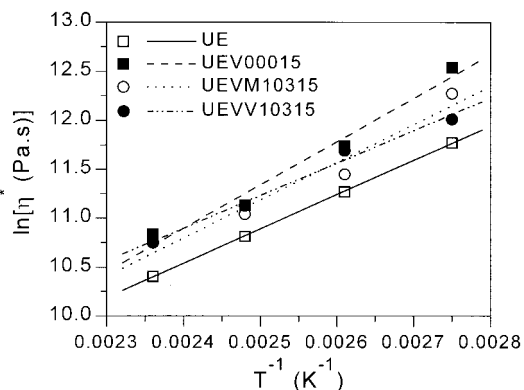
$$\eta''(\omega) = G'(\omega)/\omega \quad (2)$$

Figure 3 presents the dependence of the  $\eta^*$  and  $\eta'$  on the logarithm of the investigated frequencies for both the unfilled and the silica-filled compounds at 90°C. Both the unfilled and the silica-filled rubbers exhibited pseudoplastic behaviors; that is, with increasing frequency (which is a measure of shear rate), the viscosity decreased. The variation of  $\eta^*$  and  $\eta'$  with respect to frequency gave us an idea about the elastic and viscous components of the compound. Interestingly, in all of the cases,  $\eta^*$  was lower than  $\eta'$ . Like with  $G'$ , the unfilled ethylene-octene copolymer rubber showed lower viscosity values compared to its filled composites throughout the  $\omega$  range under consideration. The incorporation of the silica filler in the ethylene-octene copolymer rubber increased the viscosity, which may have due to the filler effect; for example,  $\eta^*$  values for UEV00015 were  $53.2 \times 10^4$  and  $1.1 \times 10^4$  Pa s at  $\omega = 0.016$  and 16.0 Hz, respectively. These were reduced to  $39.2 \times 10^4$  and  $0.9 \times 10^4$  Pa s, respectively, when this filler was replaced by acrylated and electron-beam-treated silica filler (UEVM10315). These values were further reduced to  $32.2 \times 10^4$  and  $0.6 \times 10^4$  Pa s, respectively, when the silanized and electron-beam-treated silica filler (UEVV10315) was incorporated.  $\eta'$  behaved similarly to  $\eta^*$ . As stated earlier, silanization followed by radiation treatment reduced the filler-filler interaction, and, consequently, the viscosity values decreased.

Due to the thermorheologically simple nature of these compounds, the time-temperature superposition principle was suitable for generating the master curves. The representative master curves of the  $G'$  and  $\eta^*$  viscosity of silanized and electron-beam-treated sil-

**TABLE III**  
Power Law Coefficients of Unfilled and Silica-Filled Composites at Different Temperatures

Composition	Temperature (°C)							
	90		110		130		150	
	$k$ (Pa s <sup><i>n</i></sup> )	$n$	$k$ (Pa s <sup><i>n</i></sup> )	$n$	$k$ (Pa s <sup><i>n</i></sup> )	$n$	$k$ (Pa s <sup><i>n</i></sup> )	$n$
UE	4.56	0.48	4.42	0.56	4.29	0.61	4.16	0.66
UEV00015	4.85	0.44	4.55	0.47	4.35	0.53	4.25	0.55
UEVM10315	4.75	0.45	4.44	0.48	4.31	0.54	4.22	0.56
UEVV10315	4.62	0.44	4.55	0.50	4.35	0.54	4.22	0.56



**Figure 5** Arrhenius plot for unfilled and silica-filled ethylene–octene copolymer rubbers at 0.1 Hz.

ica-filled (UEVV10315) ethylene–octene copolymer at the reference temperature of 150°C are presented in Figure 4. The shift factors obtained from these curves were used to derive the Williams-Landel-Ferry (WLF) coefficients  $C_1$  and  $C_2$  to quantify the temperature–frequency dependence of the dynamic properties of these compounds. The  $C_1$  and  $C_2$  values for the control silica-filled rubber (UEV00015) were 2.5 and 233.0, respectively. The values obtained for the acrylated and electron-beam-treated silica-filled compound (UEVM10315) were 2.3 and 241.6, respectively, comparable to that of the control compound, whereas a noticeable drop in those values (1.2 and 142.5, respectively) was observed for the silanized and electron-beam-treated silica-filled rubber (UEVV10315). Thus, the reduced effect of filler–filler interaction due to silanization was nicely reflected in these values.

All of these compounds showed pseudoplastic behavior with decreasing viscosity with increasing frequency.  $\eta^*$  was presumed to obey the power law against  $\omega$  by the equation

$$\eta^* = k(\omega)^{n-1} \quad (3)$$

The power law coefficients  $n$  and  $k$  for these compounds at different temperatures obtained from the log–log plot of  $\eta^*$  versus  $\omega$  are shown in Table III. The power law index,  $n$ , represents the pseudoplasticity of the compounds, which slightly increased with increasing temperature, suggesting less non-Newtonian behavior of the systems at higher temperatures. The  $n$  values did not alter when the filler was varied. However, the  $n$  values of the unfilled rubber were significantly higher than the filled systems except at 90°C, where the  $n$  values of the unfilled rubber were equal to those of the filled system. This behavior again indicated a change in the filler–filler association due to a change in shear rate. The power law coefficient,  $k$ , is a measure of viscosity at unit frequency. In all of the

cases, a slight decrease in  $k$  was observed with increasing temperature.

The  $E_a$  values for the flow of the blends were measured from the slope of the logarithmic plot of  $\eta^*$  at a fixed  $\omega$  against the reciprocal of the absolute temperature ( $T$ ), according to the Arrhenius equation

$$\eta^* = Ae^{E_a/RT} \quad (4)$$

where  $A$  is an arbitrary constant and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  is the universal gas constant. Figure 5 shows the Arrhenius plot for the untreated and the surface-modified silica-filled ethylene–octene copolymer rubber at a  $\omega$  of 0.1 Hz. The  $E_a$  values for these compounds at three different frequencies are shown in Table IV. In all cases,  $E_a$  decreased with increasing frequency. The untreated silica-filled compound (UEV00015) exhibited a higher  $E_a$  compared to the modified silica-filled compounds. A drop in  $E_a$  was noted when the control filler was substituted by the acrylated and electron-beam-treated silica filler. For example, at 0.1 Hz,  $E_a$  for the control and the previously mentioned modified filled rubber were 36.8 and 32.2 kJ/mol, respectively, which was further reduced to 27.6 kJ/mol in the case of the silanized and electron-beam-treated silica-filled compound. As mentioned previously, the surface modification of silica filler considerably reduced the filler–filler interaction, especially in the case of the silanized compound, and this was reflected in the  $E_a$  values.

#### Effect of filler loading and electron beam treatment on the surface modification of silanized silica filler and its influence on rheological properties

Figure 6 depicts the plots of  $G'$  with respect to  $\omega$  for the 15-, 30-, and 50-phr-loaded silanized and electron-beam-irradiated silica-filled ethylene–octene copolymer rubber at 90°C. With increasing frequency,  $G'$  increased for all of the compounds. However, the effect was more prominent at the lower filler loading. As usual,  $G'$  was higher at the higher filler loading. Figure 7 represents the plots of  $G'$  with respect to  $\omega$  for the 15-phr-loaded silica compounds (UEV00015, UEVV00315, and UEVV10315) at 90°C to show the effect of electron beam irradiation. The untreated sili-

**TABLE IV**  
Arrhenius Energy (in kJ/mol) for the flow of Unfilled and Silica-Filled Composites at Different  $\omega$ s

Composition	$\omega = 0.1 \text{ Hz}$	$\omega = 1.10 \text{ Hz}$	$\omega = 10.0 \text{ Hz}$
UE	29.1	19.8	10.2
UEV00015	36.8	30.7	23.0
UEVM10315	32.2	26.5	18.8
UEVV10315	27.6	21.2	13.2

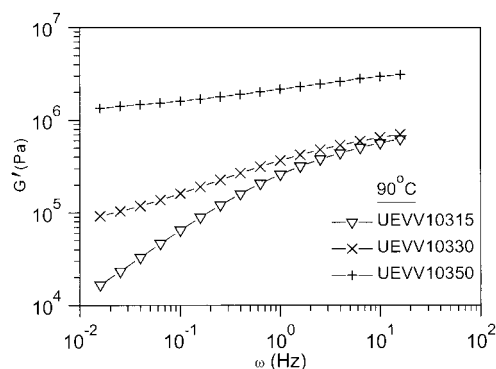
ca-filled rubber showed higher  $G'$  values compared to silanized silica-filled composites throughout the  $\omega$  range under consideration. For example, the  $G'$  values of the untreated silica-filled rubber (UEV00015) were  $2.8 \times 10^4$  and  $1.1 \times 10^6$  Pa at  $\omega = 0.016$  and 16.0 Hz, respectively. A slight drop in the  $G'$  values ( $2.4 \times 10^4$  and  $1.0 \times 10^6$  Pa, respectively) was noted when this filler was replaced by silanized filler without electron beam irradiation (UEVV00315). However, a noticeable drop in these values to  $1.7 \times 10^4$  and  $0.6 \times 10^6$  Pa, respectively, was encountered in the case of silanized and electron-beam-irradiated silica-filled rubber (UEVV10315). Similar trends were observed at higher filler loadings.

Like with  $G'$  UEVV00315 did not show any noticeable change in  $\eta^*$  as compared to the control compound (UEV00015). However, earlier, a considerable reduction in this property was observed in the case of silanized and electron-beam-treated silica-filled compound (UEVV10315). Thus, these findings imply that the silanization process became highly effective when these were pretreated with electron beam irradiation.

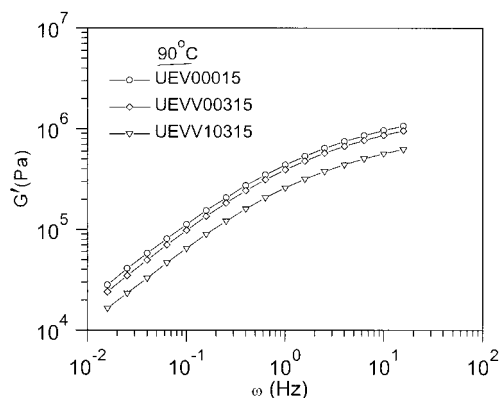
## CONCLUSIONS

Surface-modified silica fillers, developed by, coating with an acrylate monomer, TMPTA, or a silane coupling agent, TEVS, were incorporated in an ethylene-octene copolymer rubber. From the thermorheological studies of the unvulcanized rubber and its untreated and modified silica-filled composites, we concluded the following:

1. A considerable increment in  $G'$ , complex shear modulus, and its real component were noted when the control filler was incorporated in the unfilled rubber.
2. Compared to the control compound, a noticeable reduction in these properties were noted in the



**Figure 6** Plots of  $G'$  with respect to  $\omega$  for the 15-, 30-, and 50-phr-loaded silanized and electron-beam-irradiated silica-filled ethylene-octene copolymer rubber at 90°C.



**Figure 7** Plots of  $G'$  with respect to  $\omega$  for the 15-phr-loaded untreated silica, silanized and without electron-beam-irradiated silica and that of the silanized and electron-beam-irradiated silica-filled ethylene-octene copolymer rubber at 90°C.

case of modified fillers, which suggests a decrease in filler-filler interaction due to the surface treatment of the silica filler.

3. The double logarithmic plots of  $G'$  and  $G''$  showed more thermorheological simplicity of the melt of the silanized and electron-beam-treated silica-filled compound as compared to other filled composites. This may have been due to a significant reduction in the filler networking and a consequent improvement in the filler dispersion.
4. The results obtained from the master curves constructed on the basis of the time-temperature superposition principle and the  $E_a$  values calculated from the Arrhenius equation for the flow of these compounds further supported these findings.
5. Although the silica fillers modified by both of the surface coating agents showed property improvements, the silanized silica showed better improvement in the whole-property spectrum.
6. Also, the electron beam treatment of the coated filler had a significant role in this property improvement.

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## References

1. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; J Wiley: New York, 1980.

2. Lenk, R. S. *Polymer Rheology*; Applied Science: London, 1978.
3. Brydson, J. A. *Flow Properties of Rubber Melts*; Butterworth: London, 1970.
4. Leblanc, J. L. *Prog Polym Sci* 2002, 27, 627.
5. Kumar, N. R.; Bhowmick, A. K.; Gupta, B. R. *Kautsch Gummi Kunstst* 1992, 45, 531.
6. Osanaiya, G.; Leonov, A.; White, J. L. *Rubber Chem Technol* 1995, 68, 50.
7. Cotton, G. R. *Rubber Chem Technol* 1979; 52, 187.
8. Leblanc, J. L. *J Appl Polym Sci* 2000, 78, 1541.
9. Naskar, A. K.; Gala, D. P.; De, S. K.; Bhowmick, A. K. *Kautsch Gummi Kunstst* 2002, 4, 164.
10. Kader, M. A.; Bhattacharyya, A. K.; Bhowmick, A. K. *Polym Polym Compo* 2001, 9, 263.
11. Schaal, S.; Coran, A. Y. *Rubber Chem Technol* 2000, 73, 225.
12. Schaal, S.; Coran, A. Y.; Mowdood, S. K. *Rubber Chem Technol* 2000, 73, 240.
13. Ray, S.; Bhowmick, A. K. *J Appl Polym Sci* 2002, 83, 2255.
14. Ray, S.; Shanmugharaj, A. M.; Bhowmick, A. K. *J Mater Sci Lett* 2002, 21, 1097.
15. Ray, S.; Bhowmick, A. K. *Polym Eng & Sci* 2003.
16. Villar, M. A.; Faila, M. D.; Quijada, R.; Mauler, R. S.; Valles, E. M.; Galland, G. B.; Quinjani, L. M. *Polymer* 2001, 42, 9269.
17. Da Silva, A. L.; Rocha, M. C. G.; Coutinho, F. M. B.; Bretas, R.; Scuracchio, C. *Polym Test* 2000, 19, 363.
18. Rana, D.; Kim, H. L.; Kwag, H.; Choe, S. *Polymer* 2000, 41, 7067.
19. Rana, D.; Kim, H. L.; Kwag, H.; Rhee, J.; Cho, K.; Woo, T.; Lee, B. H.; Choe, S. *J Appl Polym Sci* 2000, 76, 1950.
20. Han, C. D.; Jhon, M. *J Appl Polym Sci* 1986, 32, 3809.