

Effect of Controlled Electron Beam Irradiation on the Rheological Properties of Nanosilica-Filled LDPE-EVA Based Thermoplastic Elastomer

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ABSTRACT: The effect of controlled electron beam irradiation on the rheological properties of a model LDPE-EVA thermoplastic elastomer (TPE) system filled with silica nanoparticles is explored in this article. The pristine silica particles were mixed with LDPE-EVA system in molten condition by varying the sequence of addition and amount of nanosilica. In one composition, Si69 was used to improve the state of dispersion of nanosilica. The rheological behavior of irradiated TPE systems is influenced remarkably by irradiation dose, loadings of silica, variation of sequence, and addition of Si69. All filled TPE systems register an increase in elastic response with increasing frequency and with increase in irradiation dose. Upon irradi-

ation, melt viscosity increases when compared with the unirradiated samples because of the crosslinking effect and improvements in interfacial bonding. The viscoelastic response varies markedly with the temperature. The radiation sensitizing effect of silica is reflected from the rheological data. The dynamic and steady shear rheological properties do not follow a simple correlation. Finally, the rheological behavior is correlated with the morphology of the irradiated systems processed at various shear rates. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2153–2166, 2011

Key words: thermoplastic elastomer; nanocomposite; silica; electron beam irradiation; rheology

INTRODUCTION

The field of processing of polymers by using high-energy irradiation is being continuously broadened over the past decades.¹ Controlled radiation crosslinking, in particular, offers an opportunity to considerably improve the range of properties of TPE systems as an alternative to dynamic vulcanization. This technique aids in inter-crosslinking the dispersed and continuous phases. Chattopadhyay et al.^{2,3} showed that the electron beam processing of polyolefin-based TPE blends at low radiation dose to be a potential alternative to dynamic vulcanization. The stress-strain behavior as well as morphological and rheological characteristics of radiation-crosslinked PVC/ENR blend were examined by Ratnam and Ahmad.⁴ It was mentioned there that the radiation-induced crosslinking increased the apparent shear stress and viscosity with increase in the irradiation dose. Ellul et al.⁵ evaluated crosslink densities

and phase morphologies in the thermoplastic vulcanizates (TPVs) based on PP-EPDM blends. The effects of dynamic crosslinking on rheological, mechanical, dynamic mechanical properties, and morphology of different blends were evaluated by different researchers.^{6–8} It was reported there that the dynamically vulcanized samples registered an increase in the viscosity with the extent of crosslinking. Characterization and properties of nanosilica-filled thermoplastic vulcanizates were studied by Chatterjee and Naskar.⁹ It was reported there that at low strain amplitude, the G' and G'' of nanosilica-filled TPVs were higher than those of virgin TPVs. Both the storage and complex modulus increased further with increasing nanosilica concentrations. Rheological behavior of different filled polymer systems with carbon black and nanofillers was investigated by different researchers.^{10,11}

In one of our recent publications, we have reported a comparative study of dynamic and capillary rheology of pristine nanosilica-filled LDPE-EVA-based TPE system with variations in sequence of silica addition, their loading, and with the use of coupling agent.¹² We have also demonstrated the details of the dynamic rheological properties and capillary rheology of such system and have derived the correlation between them. The rheological behaviors have also been correlated with the resultant morphology of such system at various shear rates.

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However, no investigation has been found in the literature that deals with the studies of rheological properties of radiation crosslinked nanosilica-filled TPE systems including LDPE-EVA. Dynamic vulcanization imparts compounding complexity, trims down the purity of the TPE systems, and affects the reprocessibility of the TPE systems. Chattopadhyay et al. established that in EVA (45% VA)-LDPE blend, the irradiation effect at low irradiation dose (20 kGy) was limited to the amorphous portion of the concerned blends. This particular dose gave the best compromise between the permanent set and reprocessibility. Above 50 kGy dose, the gel fraction increased, processibility decreased, and EVA-LDPE TPE system progressively became a thermoset.^{2,3,13,14} On the basis of these literature survey, we have chosen electron beam irradiation technique at lower dose levels (20 kGy and 40 kGy dose) to modify the properties of the silica-filled LDPE-EVA TPE system by selectively strengthening the weaker EVA phase and interface without affecting the thermoplastic phase to a great extent. This may finally freeze the morphology with improved interfacial bonding. Thus, the reprocessing characteristics and thermo-plasticity of the TPE can also be retained considerably. Thus, we shall mention these dose levels as the "controlled dose" in this work. In one of our earlier publications, we have reported the simultaneous effect of nanosilica reinforcement and electron beam irradiation on this system highlighting the structure-property correlation of such TPE systems.¹⁵

In this work, our aim is to explore the effect of controlled dose of electron beam irradiation on the rheological (oscillatory and steady state) characteristics of this particular filled TPE system and to correlate this property with the resultant morphology at different shear rates.

EXPERIMENTAL

Materials

The plastic used for this work was low density polyethylene (LDPE)-Indothene MA 400 supplied by IPCL, Vadodera, India (0.918 g/cm³ density as per ASTM D-1505, MFI as per ASTM D-1238 at 190°C using 2.16 kg load 30 g/10 min melt index). The elastomer used was ethylene vinyl acetate copolymer (EVA) containing 40% vinyl acetate (EVA-40) (0.967 g/cm³ density as per ASTM D-792, MFI as per ASTM D-1238 at 190°C using 2.16 kg load: 3 g/10 min) purchased from Bayer Co., Ltd. (Leverkusen, Germany). The silicon dioxide nanoparticles (size \sim 10–15 nm) were procured from Aldrich Chemical Co. Ltd., USA. Bis-[3-(triethoxysilyl) propyl] tetrasulphide (Si69) was purchased from Degussa, Germany. Methyl ethyl ketone (MEK) (density

\sim 0.804–0.805 cm³) used for evaluation of swelling index of selected nanocomposites was purchased from Merck Specialities Private Ltd., Worli, Mumbai.

Sample preparation

Mixing in molten condition was carried out with EVA (60 wt %) and LDPE (40 wt %) with various loading of silicon dioxide nanopowder (1.5, 3, and 5 wt %, respectively) in a Brabender Plasticorder (PLE-330) (Duisburg, Germany) at 130°C and 80 rpm rotor speed by varying two different sequences of addition of ingredients. In sequence 1, LDPE was initially allowed to melt for 4 min at 130°C, followed by EVA addition at the same temperature. Thereafter, at the same temperature, the silica particles were added to the mixture in molten condition. The total mixing time was 10 min. The mixes so obtained were sheeted out through an open mill set at a 2-mm nip gap.

In sequence 2, initially EVA was made soften for 4 min at 110°C, which was followed by addition of silica particles for another 4 min at the same temperature to prepare the masterbatch comprising EVA and silica. Thereafter, LDPE was allowed to melt for 4 min at 130°C, followed by addition of EVA-silica particle mixture (that was previously made at 110°C). Mixing was carried out for 2 min at 130°C. The mixes so obtained were also sheeted out using an open mill set at a 2-mm nip gap. In one composition prepared by the sequence 2, Si69 was used as a coupling agent along with 3 wt % nanosilica to chemically modify pristine nanosilica and to improve its dispersion in the polymeric matrix.

For both the sequences, after the initial mixing (as depicted earlier), the mixtures were remixed again in the Brabender Plasticorder for another 2 min at 130°C to achieve more homogeneity.

The control (unfilled) blend was prepared by first allowing the LDPE to melt for 4 min at 130°C, followed by EVA for 6 min. The mixes were also sheeted out using a two roll mill set at a 2 mm nip gap. This was then remixed for another 2 min.

All the nanocomposites so prepared were compression molded between two Teflon sheets for 3 min at 150°C with a preheat time of 1 min and with a load of 5 Tonnes on platens (18 \times 15 cm²), in an electrically heated hydraulic press to obtain films of 0.03–0.04 cm thickness. The moldings were cooled under compression to maintain the overall dimensional stability.

Conditions for electron beam irradiation

The molded samples were irradiated in air at room temperature of 25°C \pm 2°C by using an electron beam accelerator (model RDI-Dynamitron; DPC-2000

TABLE I
Sample Designation^a

Composition	LDPE (wt %)	EVA (wt %)	SiO ₂ (wt %)	Sequence of addition	Radiated sample designation (ID)		
					0 kGy	20 kGy	40 kGy
C	40	60	0	–	C	C/2R	C/4R
CS/1.5-2	40	60	1.5	2	CS/1.5-2	CS/1.5-2/2R	CS/1.5-2/4R
CS/3-1	40	60	3	1	CS/3-1	CS/3-1/2R	CS/3-1/4R
CS/3-2	40	60	3	2	CS/3-2	CS/3-2/2R	CS/3-2/4R
CS/3-Si69-2	40	60	3+10% Si69 w.r.t silica	2	CS/3-Si69-2	CS/3-Si69-2/2R	CS/3-Si69-2/4R
CS/5-2	40	60	5	2	CS/5-2	CS/5-2/2R	CS/5-2/4R

^a C, Control EVA (60 wt %)/LDPE (40 wt %) blend; S, silica; R, irradiation.

Control System, USA) under forced air cooling at the NICCO Corporation Limited, Kolkata. The radiation dose of 20 kGy and 40 kGy, respectively, were used. The energy of the electron beam accelerator was 2 MeV. The average beam current was 0.5–50 mA. The accelerating voltage frequency was 100 KHz. The dose rate was ~ 6.6 kGy/s for 20 kGy. The details of the samples and their appropriate designations are given in Table I.

Measurement of rheological properties

Monsanto processibility tester (MPT)

The melt flow characteristics of the nanosilica-filled LDPE-EVA blends were evaluated by using a Monsanto Processability Tester (Capillary rheometer; model number: 83077; Monsanto Company, Akron, USA), which is a computer-controlled, high-pressure capillary rheometer with a barrel radius of 9.53 mm. The details of the instrument were discussed in our recent publication.¹² The TPE films were cut into small pieces and fed into the hot barrel after compaction. The capillary die used was 30-mm long, 1-mm in diameter, having L/D ratio of 30 : 1, with a conical entry having multiple cones of 45° and 60°, which are known to minimize the pressure drop at the entrance. The extrusions were performed at three different temperatures (110°C, 120°C, and 130°C, respectively) and at six different shear rates in the range of 12.25 s⁻¹–1225 s⁻¹. The apparent shear stress (τ_{app}), apparent shear rate ($\dot{\gamma}_{app}$), and apparent shear viscosities (η_{app}) were calculated by using the standard equations.¹⁶

The error in measurement in viscosity was limited to ±1%. The flow behavior index (n) and consistency index (k) were calculated by using the Power Law model.¹⁶ The extrudate swell measurements were directly obtained from the MPT at different shear rates through a microprocessor-controlled laser beam assembly according to the following equation:

$$\text{Extrudate swell} = [(de - dc)/dc] \times 100 \quad (1)$$

where de and dc are the extrudate diameter and the capillary diameter, respectively. The diameters of the extrudates were measured at several points with a traveling microscope fitted with a micrometer. The error in measurement in extrudate swell was limited to ±2%.

Rubber process analyzer (RPA)

Dynamic rheological (linear and nonlinear) viscoelastic properties of blends were measured by using the Rubber Process Analyzer (RPA2000; Alpha Technologies, Akron, USA). The details of the instrument were given in our earlier publication.¹² The linear viscoelastic (LVE) region of the blends was initially determined by strain sweep at a test frequency of 0.5 Hz. In the strain sweep test, the strain amplitude was programmed to change in steps from 1.40% to 697.50% at a constant temperature (50°C) and at a constant frequency of 0.5 Hz, respectively. Thereafter, the frequency sweep test was performed where the oscillating frequency was programmed to change in steps from 0.033 Hz to 33.333 Hz within the LVE, at constant strain amplitude of 2.79% and constant temperature conditions (130°C). The stress relaxation was also carried out by using RPA at 120°C, with constant strain amplitude of 69.75%. The samples were allowed to relax at constant deformation and the resultant decay of dynamic stress was followed for 120 s. Percentage error in the dynamic rheological measurements was found to be ±1.5%.

Swelling studies

Swelling tests were performed according to ASTM D-3616. Weighed samples were immersed in methyl ethyl ketone (MEK) at room temperature for 24 h (equilibrium swelling time, determined by experiment). The surface of the swelled samples was then immediately blotted with tissue paper and the samples weighed. The swelling index is defined as:

$$\text{Swelling index} = W_s/W_1 \quad (2)$$

where W_s and W_1 are the weights of the swelled (upto equilibrium swelling) and the dried samples, respectively. The percentage errors in the measurements of swelling index were limited within $\pm 1.5\%$.

Microscopy studies

Transmission electron microscopy (TEM)

For the transmission electron microscopic (TEM) observations, the compression molded specimens (extruded at 612.5 s^{-1} shear rate) were dried in vacuum oven overnight at ambient temperature. Then the specimens were cut into ~ 50 -nm-thick sections on a LEICA ULTRACUT UCT (Austria) microtoming apparatus equipped with a diamond knife. The section was cut at 1.0 mm/s at $\sim -50^\circ\text{C}$ in liquid N_2 atmosphere. The ultra thin sections were mounted on 300-mesh copper grids and were dried in desiccators. The sections were then examined on a high-resolution transmission electron microscope (HRTEM) (JEOL JEM 2100, Japan) operated at an accelerating voltage of 200 kV with a resolution of 1.9 Å. Similar experiment was also carried out for some selected and irradiated samples (before extrusion).

Field Emission scanning electron microscopy (FESEM)

The nanoscale bulk morphology of the composite was observed with FESEM. The samples (extruded at 1225.0 s^{-1} shear rate) were vacuum-dried and then ~ 20 micrometer scales from the surface of 1mm thick film was removed at -50°C using the diamond knife of a LEICA ULTRACUT UCT (Austria) microtoming device. The samples were then coated with a thin layer of gold with a sputter coater equipped with a quartz crystal microbalance thickness controller. They were then imaged at high magnifications (e.g., $100,000\times$) with a Leo 1530 field emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany).

RESULTS AND DISCUSSION

MPT studies (melt viscosity by capillary flow)

Figure 1(a) shows the variation of the melt viscosity with the shear rate (at 120°C) for silica-filled LDPE-EVA systems at 20 kGy radiation dose. Similar experiments were also performed at 110°C and 130°C for C/2R, CS/3-1/2R, and CS/3-2/2R, respectively, and are represented in Figure 1(b,c). Figure 1(d) shows the effect of radiation dose on the melt viscosity over a range of shear rate at 120°C . All the radiation-induced crosslinked samples register higher viscosity when compared with the unirradiated samples (e.g., in comparison with the

unirradiated samples, the percentage of improvement in the melt viscosity at 12.25 s^{-1} shear rate are $\sim 64\%$, $\sim 88\%$ and $\sim 93\%$ for C/2R, CS/3-1/2R, and CS/3-2/2R, respectively). The detailed rheological behavior of filled unirradiated samples has been presented in one of our earlier publications.¹² In addition, the melt viscosity increases with increase in the radiation dose [Fig. 1(d)] because of the radiation-induced crosslinking effect.⁴ Increase in the viscosity with the radiation dose is more pronounced in the low shear region than that in the high shear region where flow curves converge, indicating increased crosslinking at higher dose (e.g., in comparison with 20 kGy radiation dose, the percentage of improvement of the melt viscosity at 40 kGy dose and at 12.25 s^{-1} shear rate are $\sim 104\%$, $\sim 66\%$, and $\sim 81\%$ for C/4R, CS/3-1/4R, and CS/3-2/4R, respectively). In literature, it was also reported that the dynamically vulcanized PP/EPDM blends showed higher melt viscosity due to the reduced free volume and the restricted intermolecular slippage when compared with the uncrosslinked one.⁸ The melt viscosity decreases with the increase in the rate of shear, showing the pseudoplastic or shear thinning nature of the samples.^{4,7}

In our system, silica particles play dual functions, namely, as reinforcing filler¹² and as radiation sensitizer.¹⁵ In all the compositions, EVA domains have been found to exist as dispersed phase in the continuous matrix.¹⁷ However, it has been found that in CS/3-1, in the continuous phase, due to intermixing of EVA and LDPE silica particles remained associated in both phases as well as in the interface. This intermixing phenomenon has been proven by extensive FTIR and TEM analysis in one of our recent publications.¹⁵ Because of intermixing, crystallinity of LDPE matrix was reduced.¹⁷ On the contrary, for CS/3-2 no such intermixing was found as the silica-EVA masterbatch was prepared previously before mixing them with LDPE. Here, silica particles were mostly found to be associated with the EVA domains. Also, in C, EVA portion was not found to be intermixed with the continuous LDPE phase. Thus, both at 110°C and 120°C , residual crystallinity (unmolten) of C and CS/3-2 are more than that of CS/3-1. Upon addition of coupling agent, a finer scale of nanosilica dispersion took place. Silica was also found to be well diffused in the continuous matrix and in the interface because of the significant reduction of filler-filler interaction.^{15,18}

Upon irradiation (at 20 kGy dose), crosslinking occurs, leading to improved interfacial bonding. The improvement in interfacial bonding upon irradiation has been evident by swelling-deswelling kinetic analysis of such system in one of our recent publications.¹⁹ The effect due to crosslinking prevails over the reduction in crystallinity in case of CS/3-1/2R.

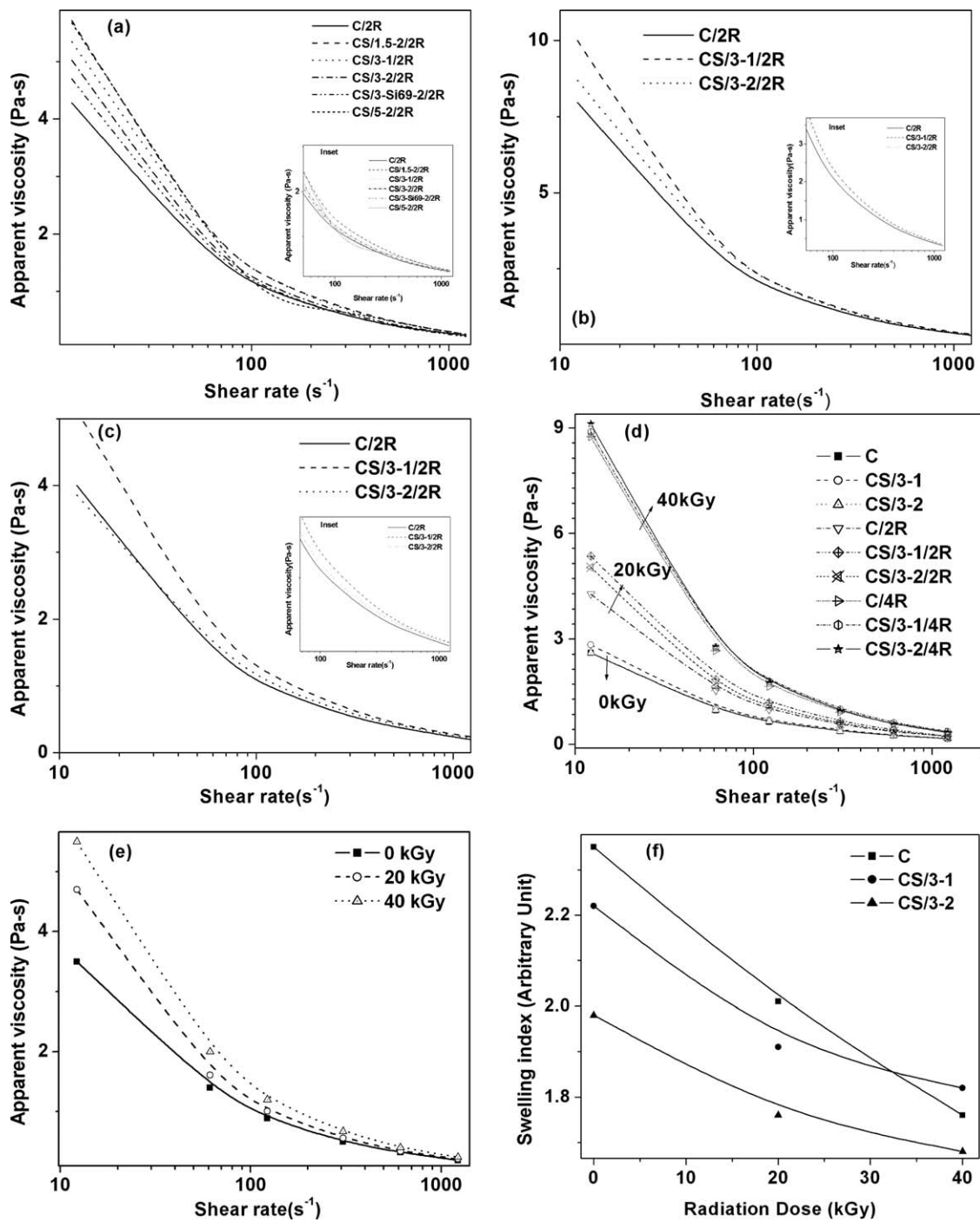


Figure 1 Apparent shear viscosity versus apparent shear rate. (a) Silica-filled 60 : 40 EVA-LDPE TPE systems irradiated at 20 kGy at 120°C. (b) C/2R, CS/3-1/2R, and CS/3-2/2R at 110°C. (c) C/2R, CS/3-1/2R, and CS/3-2/2R at 130°C. (d) Effect of radiation dose on silica-filled 60 : 40 EVA-LDPE TPE systems at 120°C. (e) Effect of radiation dose on CS/3-Si69-2 at 120°C. (f) Variation of swelling index with radiation dose for C, CS/3-1 and CS/3-2.

Thus, viscosity of CS/3-1/2R is higher than that of C/2R and CS/3-2/2R [Fig. 1(a)]. It has also been pointed out that in case of samples prepared by sequence 2, more crosslinking occurs in dispersed EVA domains (silica filled) than that in the continuous matrix. Thus, in case of CS/3-2/2R, because the crosslinking mostly takes place in silica-filled EVA domains (EVA is more susceptible for radiation

crosslinking and silica acts as radiation sensitizer), a negligible amount of crosslinking takes place in LDPE phase. As a result, chance of rolling effect of polymer molecules over the silica filled rigid EVA domains or ball bearing effect (under melt flow condition) becomes more than that is present in CS/3-1/2R. Normally, the presence of a rigid particulate filler leads to an increase in melt viscosity due to the

TABLE II
Flow Behavior Index (n) and Consistency Index (k) at 110°C, 120°C, and 130°C
of LDPE-EVA Nanocomposites

Sample ID	110°C		120°C		130°C	
	k (kPa s ^{n})	n	k (kPa s ^{n})	n	k (kPa s ^{n})	n
C/2R	42.67	0.34	20.78	0.37	19.23	0.37
CS/3-1/2R	58.63	0.29	28.03	0.34	26.16	0.34
CS/3-2/2R	49.11	0.32	26.17	0.33	17.59	0.40

greater resistance they offer to flow.²⁰ However, in some cases, the reverse trend is also observed.²¹ As the viscosity of polymer melts depends on the inter-layer interaction, interlayer slip or inhomogeneous flow may account for the decrease in viscosity. Kumar et al.²² reported a decrease in the shear viscosity of silica and carbon black-filled compounds up to 10 phr of filler loading in NR. The addition of both unmodified and modified nanoclays to styrene butadiene, polybutadiene, and acrylonitrile butadiene rubber was found to decrease the shear viscosity of the nanocomposites compared to the gum rubber.²³ Xie et al.²⁴ reported that the “ball bearing” effect of the spherical nanoparticles decreased the apparent viscosity of the PVC/CaCO₃ nanocomposite melts, and the viscosity sensitivity on shear rate of the PVC/CaCO₃ nanocomposite was higher than that of pristine PVC. In case of CS/3-2/2R, similar observation is found. Hence, it has been presumed that the polymer chains slip past or roll over the nanosilica-filled and crosslinked rigid EVA domains. In case of CS/1.5-2/2R, because of low loading, silica particles are finely dispersed, which enhance the radiation sensitizing effect of silica particles. Finer dispersion of nanosilica at 1.5 wt % loading has also been evident from TEM analysis as depicted in the next section. The radiation sensitizing effect becomes prominent when the silica particles are finely dispersed and exist as isolated particles. Thus, the surface area of the polymers in contact with the fillers increases effectively. This ultimately leads to the improvement in the sensitizing effect of silica. Thus, viscosity of CS/1.5-2/2R is very high because of the crosslinking and the silica reinforcement effect (involving EVA domain and interface). In CS/5-2/2R, aggregation tendency of silica particle is more (evident from TEM analysis depicted in the next section); still diffusion tendency of silica particles to the interface is high. Because of the higher atomic number of silica particles, radiation crosslinked interfacial area (also to some extent to the continuous matrix) is accordingly more.¹⁵ Thus, initially viscosity is high. But after a certain shear rate, structural breakdown of EVA domains with aggregated silica particles occurs. Thus, viscosity falls. It has also been evident from TEM analysis as described in the next section. Interestingly, CS/3-

Si69-2/2R shows lower viscosity than that of the other filled samples. The role of Si69 to act as a radiation scavenger¹⁵ is evident from here. For better understanding this scavenging effect, a comparative plot of unirradiated and irradiated silane loaded sample at 120°C is shown in Figure 1(e). Here, the percentage enhancement of viscosity with irradiation dose is insignificant when compared with other silica-filled samples [Fig. 1(d)]. At 110°C, the viscosity follows the order CS/3-1/2R > CS/3-2/2R > C/2R [Fig. 1(b)]. The explanation is same as mentioned earlier. At 130°C, both EVA and LDPE are in the molten state. Thus, the effects of crosslinking can be better realized at this temperature. Thus, in comparison with C/2R and CS/3-2/2R, viscosity of CS/3-1/2R is distinctly higher [Fig. 1(c)]. The viscosities of filled samples irradiated at 40 kGy are marginally higher than those of irradiated at 20 kGy [Fig. 1(d)]. The extent of crosslinking in a polymeric matrix can be qualitatively evaluated by computing the equilibrium swelling index. Thus, to further establish the marginal change at 40 kGy, a comparative plot of swelling index as a function of radiation dose for filled and unfilled samples is shown in Figure 1(f). From this figure, it is clear that for filled samples, the swelling indices at 20 kGy and 40 kGy dose are very close to each other, whereas for the unfilled control blend, the swelling index decreases steadily with increase in irradiation dose. The detailed swelling analysis has been depicted in one of our recent publications.¹⁵

Using power-law equation, the flow behavior index (n) and the consistency index (k) are calculated and are presented in Table II. The composite systems show a pseudoplastic behavior (since $n < 1$). The variation of “ n ” can be explained on the basis of residual crystallinity, radiation-induced crosslinking, and ball bearing/rolling effect (at 110°C and at 120°C). However, at 130°C, the contribution due to the ball bearing mechanism and due to the residual crystallinity would be negligible. The increase in temperature tends to increase the free volume of the system and thus the k -value (approximately equal to zero shear viscosity) decreases. Also, upon filler loading, the free volume of the system decreases, so the k -value increases. Interestingly, at 110°C, 120°C, and 130°C, k is lower in CS/3-2/2R than that of CS/

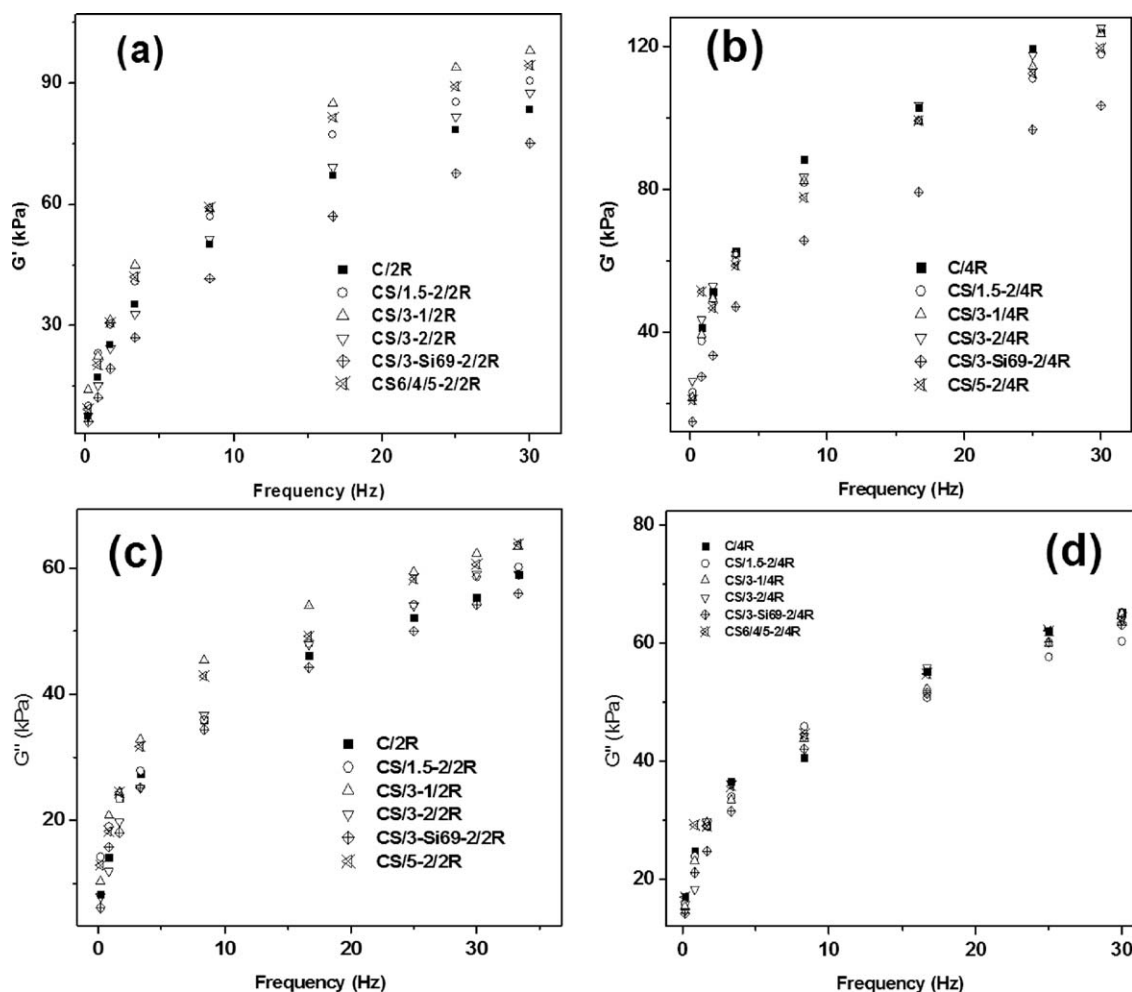


Figure 2 Frequency sweep test at 130°C and 2.79% strain. (a) Elastic modulus (G') as a function of frequency in EVA-LDPE systems filled with various silica loadings at 20 kGy. (b) Elastic modulus (G') as a function of frequency in EVA-LDPE systems filled with various silica loadings at 40 kGy. (c) Loss modulus (G'') as a function of frequency in EVA-LDPE systems filled with various silica loadings at 20 kGy. (d) Loss modulus (G'') as a function of frequency in EVA-LDPE systems filled with various silica loadings at 40 kGy.

3-1/2R. It further proves that in this particular sample (prepared by sequence 2), ball bearing effect takes place that becomes more prominent upon irradiation.

Oscillatory shear flow–RPA studies

Frequency sweep

Figure 2(a,b) exhibit the elastic modulus (G') as a function of test frequency, at 20 kGy and 40 kGy radiation dose, respectively. It is clearly seen that all blends (filled and unfilled) at both dose display an increase in elastic response with increasing frequency due to increasingly imposed restriction on polymer.¹¹ Accordingly, the elastic modulus is higher in the irradiated samples than that of the unirradiated ones. CS/3-1/2R shows highest extent of elastic response as reflected from its higher G' value combining with comparable G'' over the range

of frequency studied here. But at 40 kGy dose, a similar G' and G'' values are obtained for almost all compositions. Interestingly, at both dose, CS/3-Si69-2 registers lower elastic modulus. This is possible because Si69 acts as a radiation scavenger as mentioned in our earlier publication.¹⁵ Overall, the increase in the elastic modulus (G') with increase in the irradiation dose is attributed to the radiation-induced crosslinking of the silica-filled TPE systems.

Figure 2(c,d) represents loss modulus (G'') of silica-filled blends as a function of frequency, at 20 kGy and 40 kGy dose. G'' increases with test frequency. This is due to the higher energy required for molecular viscous response. The value of G'' is obviously lower than that of G' in the range of mid to higher frequencies at both irradiation dose, implying the elastic-dominant response in all the blends.

In the terminal region, the characteristics of homopolymer, i.e., $G' \sim \omega^{n_1}$ ($n_1 = 2$) and $G'' \sim \omega^{n_2}$ ($n_2 = 1$)

TABLE III
Slopes of $\log G'$ and $\log G''$ Versus $\log \omega$ (ω = Angular Frequency) at 130°C, Respectively (n_1 and n_2), for Various Samples as Measured by RPA

Sample ID	n_1	n_2
C/2R	0.45	0.36
CS/1.5-2/2R	0.41	0.28
CS/3-1/2R	0.39	0.34
CS/3-2/2R	0.48	0.40
CS/3-Si69-2/2R	0.48	0.40
CS/5-2/2R	0.44	0.31
C/4R	0.32	0.26
CS/1.5-2/4R	0.31	0.26
CS/3-1/4R	0.33	0.27
CS/3-2/4R	0.30	0.30
CS/3-Si69-2/4R	0.37	0.29
CS/5-2/4R	0.31	0.25

can be observed, where ω is the angular frequency in rad/s.²⁵ From the plot of $\log G'$ and $\log G''$ versus $\log \omega$ (not shown here), slopes are calculated (n_1 and n_2 , respectively, all the fittings are obtained with 99% confidence) and are represented in Table III. From the values of " n_1 " and " n_2 ," respectively, it is clear that at 130°C, flow is restricted more in irradiated samples when compared with that of unirradiated samples.¹² This effect becomes predominant with increase in the radiation dose. This again reflects the radiation-induced crosslinking effect. The " n_2 " values reflect that the loss modulus becomes stronger function of angular frequency upon increase in silica loading within sequence 2. However, both " n_1 " and " n_2 " values do not follow definite trend within the same irradiation dose level.

Figure 3(a,b) shows a modified Cole-Cole plot of silica particle-filled LDPE-EVA systems irradiated at 20 kGy and 40 kGy dose. In the low frequency

region, there are some scattered data for the filled samples. But in the higher frequency region, all the curves are super imposed on a single master curve. This is an indication that at low frequency (near terminal region) the relaxation mechanisms for filled systems are different than that of the control one, whereas at higher frequencies (near rubbery plateau), the gross relaxation mechanisms are similar for all systems.

Figure 4 exhibits the complex viscosity (η^*) as a function of frequency at 130°C, at 20 kGy dose. Clearly, both unfilled and filled blends at both dose exhibit rheological behavior of the pseudo-plastic fluids.⁹ Overall, upon irradiation, viscosity increases when compared with the unirradiated samples. The viscosity increases with the increase in the radiation dose. The observations are in line with the results obtained from the capillary rheometer. At 40 kGy dose, the viscosity of all the samples merges over the range of frequency studied here (not shown).

Strain sweep

To precisely understand the behavior of change in modulus over the % strain, strain sweep was performed. The ratio of stress at various strain percent with respect to initial stress for the samples irradiated at 20 kGy (at constant and low strain %) at 50°C are calculated and tabulated in Table IV. Results of variation of dynamic storage modulus versus percent strain at 20 kGy are illustrated in Figure 5. The contribution of each phase and the interface on stress ratio for unirradiated samples has been explained in our earlier publication.¹² Interestingly, CS/3-1/2R shows higher stress ratio both at low and high strain region than that of all samples

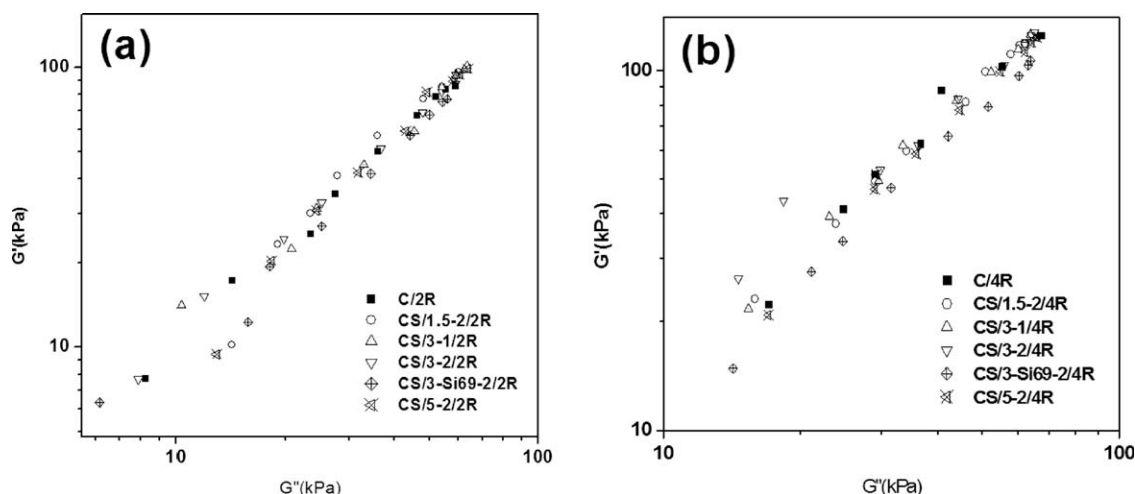


Figure 3 (a) Elastic modulus (G') as a function of Loss modulus (G'') in EVA-LDPE systems filled with various silica loadings at 20 kGy. (b) Elastic modulus (G') as a function of Loss modulus (G'') in EVA-LDPE systems filled with various silica loadings at 40 kGy.

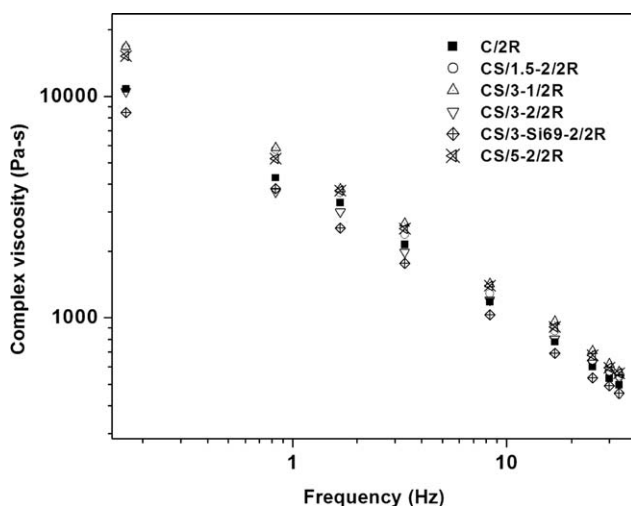


Figure 4 Complex viscosity (η^*) as a function of frequency in EVA-LDPE systems filled with various silica loadings at 130°C at 20 kGy.

excepting CS/3-Si69-2/2R. It again invokes the possibility of better interfacial bonding which outweigh the effect of changes in crystallinity in this case than that of other samples.¹⁷ In CS/3-2/2R, interfacial bonding is inferior such that strain retention capacity at moderate range of elongation is less. The stress ratio for all samples begins to fall at higher strains when compared with that of unirradiated samples.¹² At such high strains, possibly only EVA domain contributes to the dynamic modulus. Within sequence 2, the stress ratio increases with the nanosilica loadings. However, CS/3-Si69-2/2R gives interesting contrast. Although because of the radiation scavenging activity of Si69, interfacial bonding gets restricted, but the effect owing to compatibility prevails over the former. However, in this case, the absolute modulus values are far less over the %

strain (Fig. 5). It reflects limited crosslinking and thereby scavenging effect of Si69.¹⁵ At 40 kGy, all samples register similar trend but with less contrast because at this dose level selectivity of crosslinking diminishes (not shown here). At very high strain, Payne effect is observed in all the irradiated samples. Overall, the stress ratio is more for all irradiated samples when compared with that of unirradiated ones.¹²

Comparison between the capillary and dynamic rheology

Effect of frequency or shear rate

Generally, by using Cox-Merz concept²⁶ shown in eq. (3), it is possible to compare the oscillatory shear viscosity as a function of test frequency to the steady shear viscosity as a function of shear rate at 130°C.

$$\eta^*(\omega) = \eta(\dot{\gamma}) \tag{3}$$

In our earlier publication,¹² we have derived a good correlation between dynamic and capillary rheological results for the unirradiated samples following Cox-Merz concepts. Interestingly, in the irradiated systems, from Figure 6, it is observed that there is a significant difference between dynamic and capillary rheological data. In all cases, the apparent viscosity (η_{app}) is higher than the complex viscosity (η^*).

The deviation mainly originates from the cross-linking effect. In RPA, the flow is localized and restricted. But on contrary, the capillary flow is not localized (longer range). It is rather translational involving Brownian motion of molecules as a whole. Hence, the effects of crosslinking are more pronounced in capillary flow.

TABLE IV
Stress Ratio at Different Percent of Strain at 50°C and at 0.5 Hz Frequency

Strain (%)	Stress ratio at different percent of strain					
	C/2R	CS/1.5-2/2R	CS/3-1/2R	CS/3-2/2R	CS/3-Si69-2/2R	CS/5-2/2R
4.19	1.43	1.43	1.43	1.43	1.45	1.43
5.58	1.82	1.82	1.83	1.83	1.87	1.82
6.98	2.18	2.19	2.20	2.19	2.26	2.19
13.95	3.55	3.60	3.63	3.59	3.83	3.60
20.93	4.46	4.54	4.62	4.53	4.92	4.55
34.88	5.54	5.70	5.83	5.67	6.29	5.72
69.05	6.64	6.91	7.18	6.92	7.78	6.99
105.04	6.86	7.29	7.70	7.35	8.35	7.45
139.50	6.78	7.25	7.83	7.40	8.51	7.50
279.00	6.00	6.45	7.40	6.68	8.16	6.89
418.50	4.98	5.03	6.18	5.33	6.84	5.56
558.00	4.23	4.11	5.08	4.32	5.71	4.53
697.50	3.63	3.44	4.32	3.54	4.85	3.76

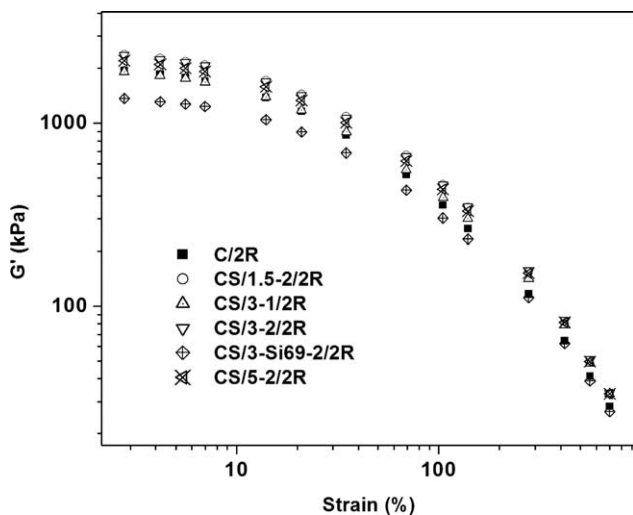


Figure 5 Dynamic strain sweep test of EVA-LDPE TPE systems filled with various silica loadings at a test frequency of 0.500 Hz and at 50°C, irradiated at 20 kGy dose.

Comparison of extrudate swell value (MPT) with stress relaxation (RPA)

The extrudate swell values at various shear rates for C/2R, CS/3-1/2R, and CS/3-2/2R are represented in Table V. The extrudate swell value is observed to increase upto certain shear rates following a decrease.⁶ But the value of shear rate (from where decrease starts -critical shear rate) is found to be highest in C/2R followed by CS/3-1/2R. The critical shear rate for CS/3-2/2R is lowest amongst all. In CS/3-2/2R, due to the ball bearing mechanism, the stored energy release and elastic recovery of deformation of the melt are relatively less when it leaves the channel. In case of CS/3-1/2R, at 12.25 s⁻¹ and 61.25 s⁻¹ shear rate, i.e., initially both crosslinked continuous matrix and the interface are contributing. Thus, the extrudate swell value is less when compared with that of the CS/3-2/2R. This again indirectly proves improved interfacial bonding in

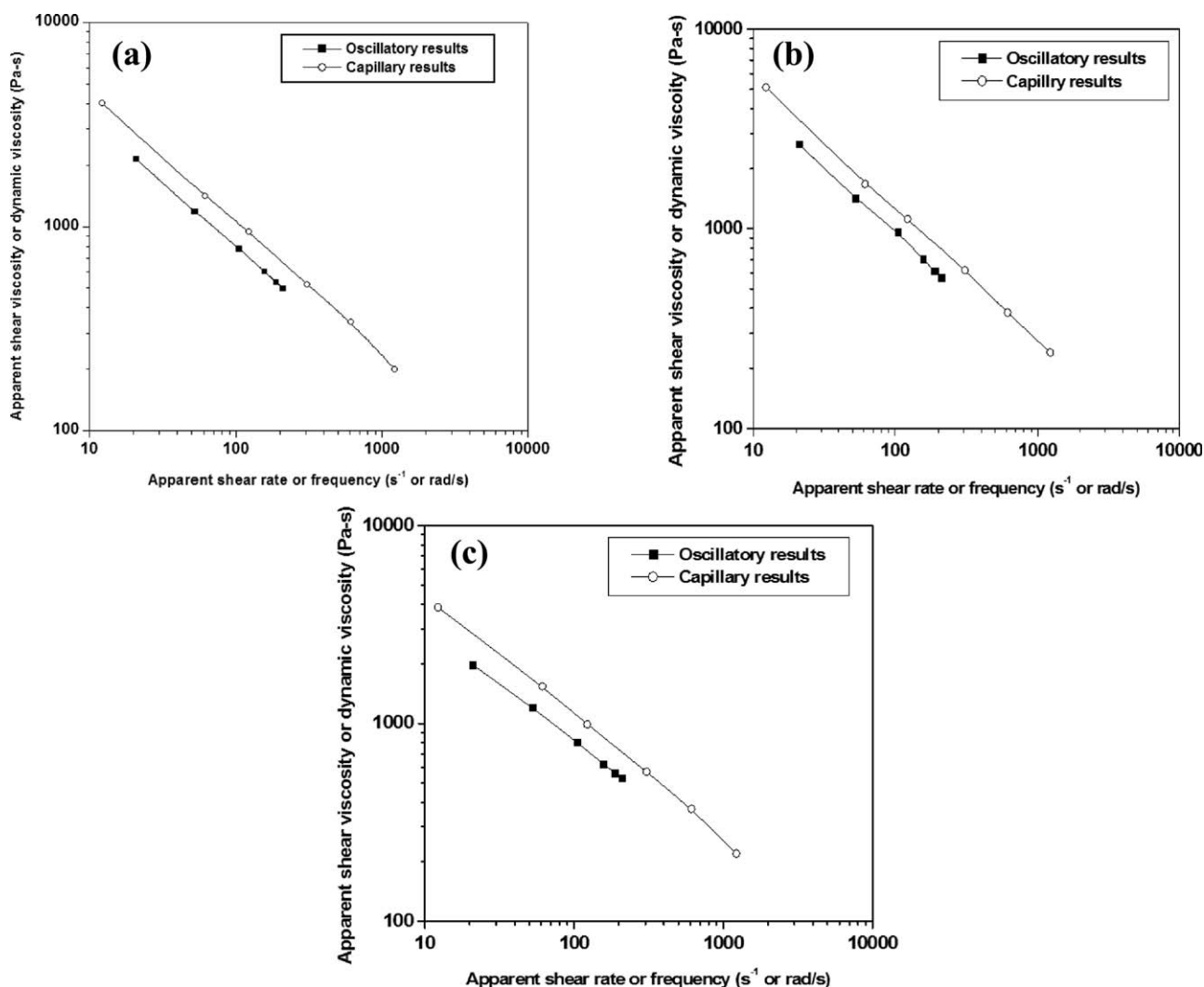


Figure 6 Superimposed plots of oscillatory viscosity determined from RPA2000 and steady shear viscosity determined from capillary rheometer as a function of frequency or shear rate in EVA-LDPE systems filled with various silica loadings on varying sequences, (a) C/2R, (b) CS/3-1/2R, (c) CS/3-2/2R.

TABLE V
Extrudate Swell Value of C/2R, CS/3-1/2R,
and CS/3-2/2R at 120°C

Shear rate (s ⁻¹)	Extrudate swell (%)		
	C/2R	CS/3-1/2R	CS/3-2/2R
12.25	106	99	116
61.25	118	115	122
122.50	128	118	115
306.25	131	110	109
612.50	103	110	104
1225.00	112	99	98

case of CS/3-1/2R. Finally, at very high shear rate, the extrudate swell value decreases in both sequences, where the crosslinked EVA domain is mainly contributing.

From the stress relaxation experiment (dynamic, encompassing nonlinear region), we have calculated relaxation frequency at 120°C, for C/2R, CS/3-1/2R, and CS/3-2/2R, respectively. The values are 26.426 s⁻¹, 23.056 s⁻¹, and 19.653 s⁻¹ respectively. Accordingly, the relaxation time is less for CS/3-1/2R (more elastic) than that of the CS/3-2/2R. This is well correlated with the extrudate swell value (within

12.25 s⁻¹–61.25 s⁻¹ shear rate regions). But at very high shear rates, both extrudate swell and stress relaxation cannot be correlated. Similar observations are noted for samples irradiated at 40 kGy dose (not reported here).

Morphology of extrudates

Transmission electron microscopy (TEM)

To observe the state of dispersion of silica particles in the bicomponent polymeric matrix, TEM analysis was performed for some selected irradiated samples (before extrusion) prepared by sequence 2. The comparative TEM photomicrographs are shown in Figure 7. The gray and the white regions correspond to LDPE matrix and intermixed (LDPE-EVA) portion, respectively. Besides these, a dark phase also appeared which represents the inter-mixed portion of silica-filled EVA domains. In all cases, the intensity of the black color varies amongst the dispersed particles.

From Figure 7, it is evident that with 1.5 wt % loading silica particles are more finely dispersed [Fig. 7(a)] in comparison with the samples having 3

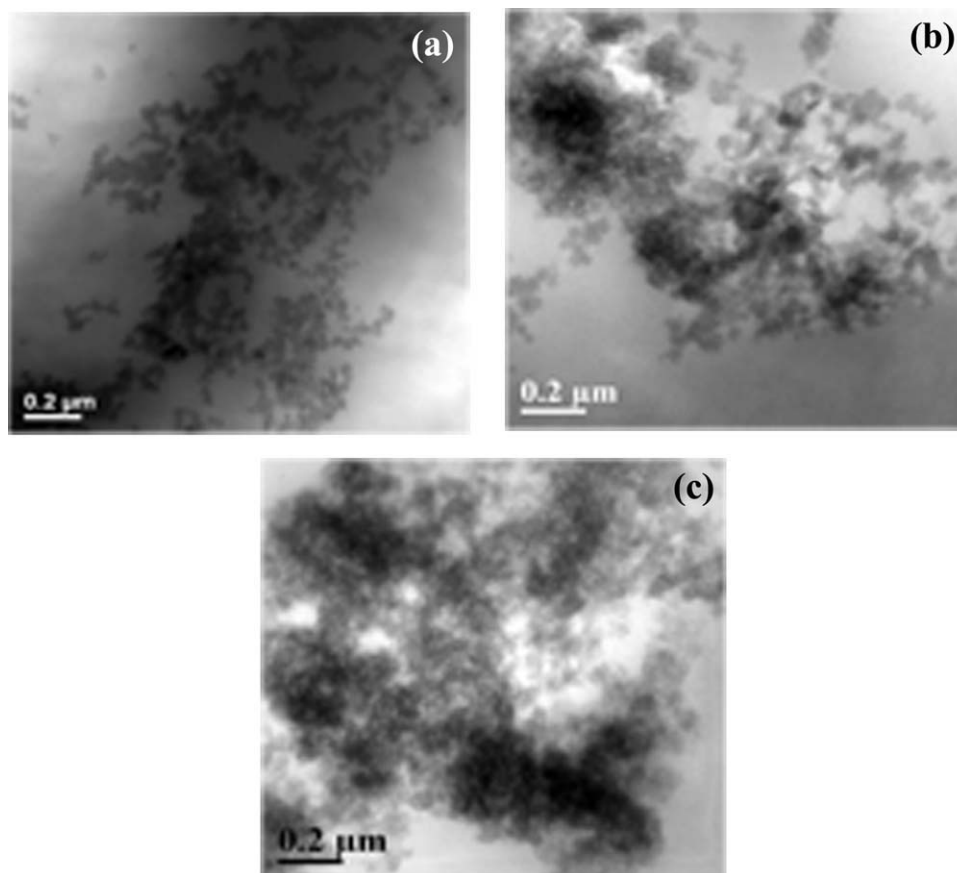


Figure 7 Transmission electron photomicrographs of irradiated samples (before extrusion) of 60 : 40 EVA-LDPE TPE systems with various loadings of nanosilica particles: (a) CS/1.5-2/2R, (b) CS/3-2/2R, and (c) CS/5-2/2R.

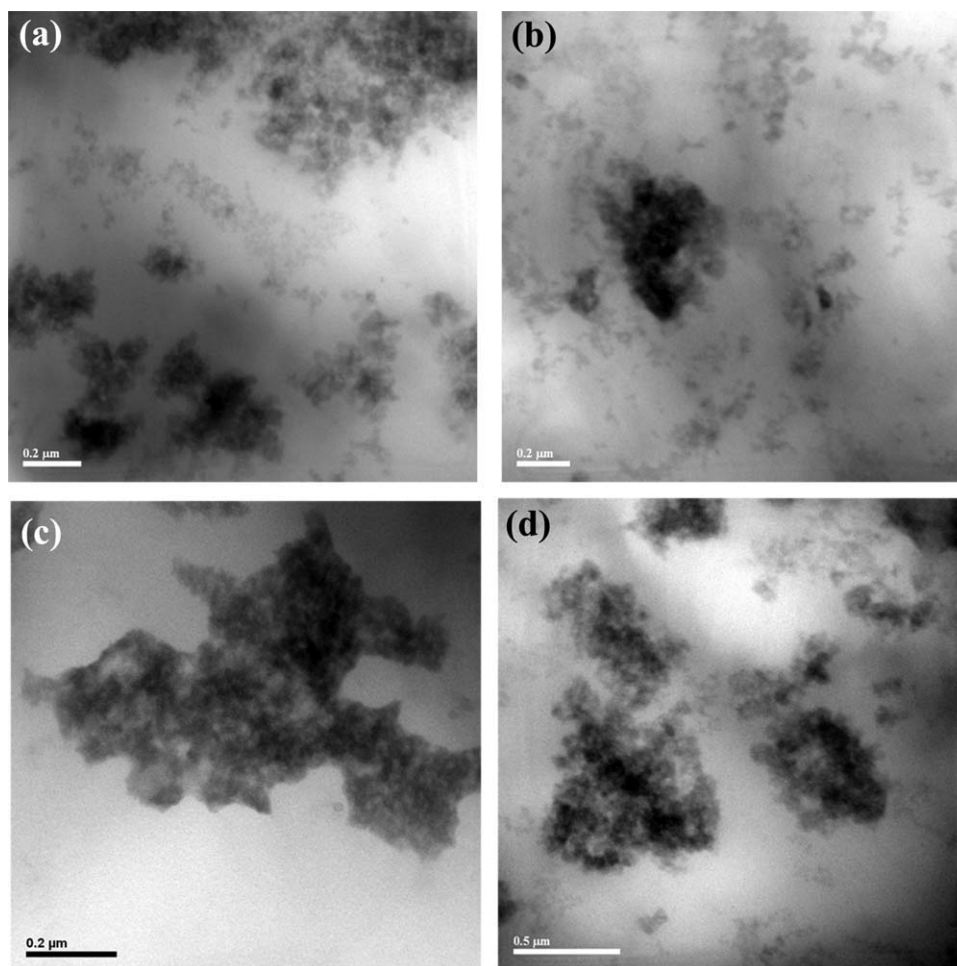


Figure 8 Transmission electron photomicrographs of samples extruded at 612.5 s^{-1} : (a) extruded CS/3-1/2R at 12 k magnification, (b) extruded CS/1.5-2/2R at 10 k magnification, (c) extruded CS/3-2/2R at 20 k magnification, (d) extruded CS/5-2/2R at 8 k magnification.

wt % and 5 wt % loadings [Fig. 7(b,c)]. The aggregation tendency of silica particles increases with increase in silica loading.

The analyses of the extrudate structures (both at low and high shear rates) are achieved by TEM on ultramicrotomic slices cut in the direction of the extrudate axis (parallel to the flow direction and normal to the momentum transfer direction). The representative morphology is shown in Figure 8. On the micrograph of extruded (at 612.5 s^{-1}) CS/3-1/2R [Fig. 8(a)], most of the silica particles are distributed randomly in both LDPE matrix and dispersed EVA phase as well as in the interface. It further proves the occurrence of intermixing of EVA and LDPE that becomes more significant after extrusion. Ultimately, this type of morphology affects the viscosity of this particular sample. In case of extruded (at 612.5 s^{-1}) CS/1.5-2/2R [Fig. 8(b)], the morphology exhibits similarity with CS/3-1/2R. In case of unirradiated CS/3-2, large numbers of silica particles are distributed randomly in the continuous LDPE matrix after extrusion at higher shear rate. But interestingly,

after irradiation, the extruded (at 612.5 s^{-1}) CS/3-2/2R exhibits a completely different morphology [Fig. 8(c)]. The EVA domains retain almost all silica particles. However, the spherical shape of domains gets distorted due to faster quenching as it escapes the die. In case of extruded (at 612.5 s^{-1}) CS/5-2/2R [Fig. 8(d)], disintegration of silica-filled EVA domain occurs and some particles are distributed randomly in the polymer matrix. This is also reflected in the sudden drop of viscosity value, which is mentioned in the earlier section (MPT).

Field Emission scanning electron microscopy (FESEM)

FESEM experiments were carried out on extruded samples at a high shear rate (1225.0 s^{-1}) to observe the ultimate dispersion of silica aggregates. From FESEM photomicrographs [Fig. 9(a,d)], it can be clearly visualized that in case of all extruded samples, the particle diameter ranges from 30 to 443 nm. In case of CS/3-1/2R [Fig. 9(a)] and CS/3-

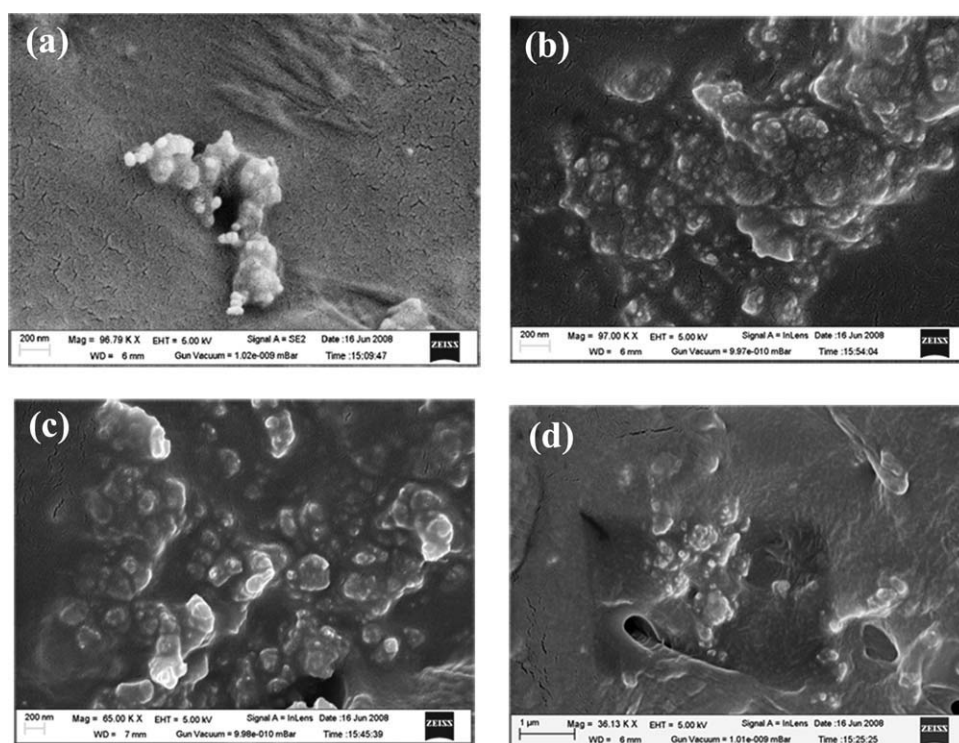


Figure 9 FESEM photomicrographs of the microtome surface of samples extruded at 1225.0 s^{-1} : (a) CS/3-1/2R extruded at 96.8 k magnification, (b) CS/3-2/4R extruded at 97.00 k magnification, (c) CS/5-2/2R extruded at 65.0 k magnification, and (d) CS/3-Si69-2/4R extruded at 36.00 k magnification.

Si69-2/4R [Fig. 9(d)], silica particles are well dispersed in the polymeric matrix. At 1225.0 s^{-1} shear rate, rupture of rigid EVA domain occurs in CS/5-2/2R [Fig. 9(c)] and some silica particles are distributed in the polymeric matrix. But interestingly, at the same shear rate, in case of CS/3-2/4R [Fig. 9(b)], EVA domains retain the finer dispersion of nano-silica particles.

CONCLUSIONS

The silica-filled irradiated TPE systems with controlled irradiation show higher melt viscosity when compared with that of unirradiated filled systems. The variation of viscosity with temperature can be explained on the basis of residual crystallinity, radiation-induced crosslinking, rolling effect, and improvements in interfacial bonding. At higher dose, the radiation sensitizing effect of silica particles becomes marginal. Thus, the viscosity of all the samples merges over the range of frequency studied here. All filled TPE systems represent an increase in elastic modulus (G') with increasing frequency and with increase in radiation dose. The increase in elastic modulus with the increase in irradiation dose is attributed to the radiation-induced crosslinking of the silica-filled TPE systems. Because of the strengthened interface, G' value of CS/3-1/2R

is higher than that of CS/3-2/2R. This is also substantiated with dynamic strain sweep results. The dynamic and steady shear viscosity cannot be superimposed. Extrudate swell and stress relaxation parameters register good correlation in terms of difference in number of crosslinks present in the system. Radiation sensitizing and scavenging activity of nanosilica and Si69, respectively, are reflected from the capillary and the dynamic rheological data. The extrudate morphology correlates well with the aforesaid rheological behaviors.

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