

# Effect of Rheological Parameters on the Miscibility and Polymer-Filler Interactions of the Black-Filled Blends of Polyethylene-Vinyl Acetate and Polychloroprene

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## SYNOPSIS

Miscibility of 30 phr loaded black-filled (N110) blends of polyethylene-vinyl acetate (EVAc, VAc content 28%) and polychloroprene (CR) are investigated through shear and dynamic deformations. Both shear ( $\eta_a$ ) and dynamic elongational ( $\eta'_E$ ) viscosities are conducive to their miscibility as both show positive deviation for all blends, though dynamic out-of-phase ( $\eta''_E$ ) viscosity shows negative-positive deviation. Both  $\eta_a$  and  $\eta'_E$  follow the power law relationship with shear rate ( $\dot{\gamma}_{wa}$ ) and frequency ( $\omega$ ), respectively. Both storage ( $E'$ ) and loss ( $E''$ ) moduli increases with frequency. The higher dissipative energy at around 11 Hz may be due to its synchronization with molecular vibrations of the polymer segments. The effect of rheological parameters like strain rate and temperature on the relative change in shear ( $RV_S$ ) and dynamic elongational ( $RV_D$ ) viscosities is reported for the variation of blend composition with 30 phr loaded black-filled compounds. The variation of both  $RV_S$  and  $RV_D$  follows a third order polynomial equation with carbon black loading in 50/50 EVAc/CR blend; all the polynomial constants are function of temperature and strain rate.

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## INTRODUCTION

During processing, polymers are blended with other additives like filler to improve the properties of the finished product. The rheological behavior of individual gum rubbers and blends play an important role in the quality of mixing of polymers and fillers. The completeness of the mixing consequently influences the final product quality. The rheological parameters like shear stress ( $\tau$ ) and rate of shear ( $\dot{\gamma}$ ) follow the power law relationship,

$$\tau = K \cdot \dot{\gamma}^n \quad (1)$$

where  $K$  and  $n$  are constants known as the consistency index and non-Newtonian index, respectively.

Viscosity of a blend can be related to its component viscosities as<sup>1</sup>

$$\ln \eta_B = \sum w_i \ln \eta_i \quad (2)$$

where  $\eta_B$  is the viscosity of the blend and  $\eta_i$  and  $w_i$  are the viscosity and weight fraction of  $i$ th component. When the experimentally observed viscosity of a blend exceeds the calculated one [eq. (2)], it is called a positively deviating blend (PDB).<sup>1</sup> The specific interactions (polar-polar, H-bonding, etc.) lead to the volume contraction, thereby causing the higher viscosity of the blend.

The incorporation of filler to polymeric blends has a major influence on the rheological properties.<sup>2</sup> Filler and polymer interact with each other in a very complex fashion involving filler-polymer, filler-filler, and polymer-polymer interactions. Generally, filler reinforced polymer melts exhibit an increase in viscosity, an apparent decrease in elastic memory, and development of thixotropy at very high filler loadings.<sup>3</sup> These properties of filled polymeric melts can be explained by the hydrodynamic theory of Einstein<sup>4</sup> and Guth.<sup>5</sup> They represented the viscosity,  $\eta_f$ , of filled system as a function of  $\eta_o$ , the polymer viscosity, and  $\phi$ , the

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**Table I Materials Used**

Material	Specification	Producer
Polyethylene-vinyl acetate (Pilene-2806)	Vinylacetate content: 28 wt % Density: 0.96 g/cm <sup>3</sup> M.F.I.: 6 g/10 min	Polyolefin Industries Limited, India
Polychloroprene (Neoprene WM1)	Specific gravity: 1.23 Mooney viscosity: 40 (ML <sub>1+4</sub> , 100°C)	du Pont, USA
Carbon black (N110)	CTAB, m <sup>2</sup> /g: 127 BET (N <sub>2</sub> ) m <sup>2</sup> /g: 140 DBPA, cm <sup>3</sup> /100 g: 93 S <sub>f</sub> of acetonitrile at 150°C: 1.64	Degussa AG
Dicumyl peroxide, DCP (PERCITOL-40)	Purity: 60%	Peroxide India Limited
Triallyl cyanurate	Purity: 97% Fusion point: > 100°C	Aldrich Chemicals

volume fraction of filler in a blend containing inert filler at room temperature, as

$$\eta_f = \eta_o[1 + C_1\phi + C_2\phi^2 + C_3\phi^3 + \dots] \quad (3)$$

where the coefficients  $C_1$ ,  $C_2$ , and  $C_3$  depend on particle shape and orientation. For inactive spherical particles,  $C_1$  is 2.5;  $C_2$  is reported to be in the range of 10–14; and  $C_3$ , etc., are zero. Theories of concentrated suspensions have been developed by Simha.<sup>6</sup>

Filled polymeric blends exhibit very unusual change in viscosity with shear rate. At low filler loading, the behavior is similar to that of the pure polymer melt; whereas Bingham plastic flow is observed at moderate to high solid content, and even thixotropic behavior is observed at very high filler loading.<sup>7</sup> Earlier, we have reported<sup>8</sup> that both cap-

illary and dynamic viscosities are conducive to the miscibility of EVAc and CR blends. This paper reports in details the effect of rheological parameters on the miscibility and filler-polymer interaction of the black filled blends of EVAc and CR.

## EXPERIMENTAL

### Materials Used

The details of the materials used are given in Table I.

### Sample Preparation

The polymers and their additives were mixed as per the formulation given in Table II in a Brabender

**Table II Compound Formulations (phr)**

	Compound Number						
	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	B <sub>7</sub>
EVAc	100	70	50	30	0	50	50
CR	0	30	50	70	100	50	50
Filler (N110)	30	30	30	30	30	10	50
DCP (60%)	3	3	3	3	3	3	3
Triallyl cyanurate	1	1	1	1	1	1	1

Table III  $n'$  and  $K'$  Values

Compound Number	Temperature					
	80°C		100°C		120°C	
	$n'$	$K'$	$n'$	$K'$	$n'$	$K'$
B <sub>1</sub>	0.18	165.9	0.31	68.4	0.36	40.6
B <sub>2</sub>	0.19	216.1	0.29	82.6	0.33	53.9
B <sub>3</sub>	0.20	184.7	0.22	129.5	0.27	78.3
B <sub>4</sub>	0.21	183.4	0.21	142.3	0.28	86.0
B <sub>5</sub>	0.28	169.2	0.12	278.6	0.11	163.0
B <sub>6</sub>	0.20	153.6	0.26	81.6	0.32	47.6
B <sub>7</sub>	0.28	210.1	0.17	302.6	0.28	84.3

Plasticorder (PLE-330) having cam type rotors. The thermoplastic EVAc was first melted at 100°C and 60 rpm rotor speed for 2 min. The premasticated CR was added with subsequent incorporation of black to ensure proper mixing, and the mixing was allowed to continue for another 5 min. DCP and TAC was added at a lower rotor speed (30 rpm) at 100°C to avoid dynamic vulcanization caused by decomposition of DCP at higher temperature (>110°C) due to excess heat generation by shearing at higher rotor speed. The hot mix was taken out and passed through a tight (low nip gap) two-roll mill to get a sheet.

Rheological properties of the samples were studied with the help of Monsanto Processability Tester (MPT, No. 83077). The capillary used was of 1 mm diameter, having a length to diameter ratio ( $L/D$ ) equal to 30. The test sample was charged into the barrel and preheated for about 5 min for uniform temperature and then extruded at the piston rates of 0.042, 0.085, 0.169, and 0.254 mm/s (100–750 s<sup>-1</sup>), which corresponds to the apparent rate of shear of 122.6, 245.2, 490.4, and 735.6 s<sup>-1</sup>.

The cure characteristics of the Brabender mixed compounds was tested by a Monsanto Rheometer (R100S) and the MPT at 100 and 120°C. As the compound gets cured during testing, extra energy is required to flow the material. This extra energy gave rise to an increase in torque for rheometric test or an increase in the wall pressure in the capillary, leading to an increase in shearing force for capillary test in Monsanto processability tester. There was no change in torque and wall pressure at the piston rate of 0.0042 mm/s for all compounds at 100°C in the rheometer and the MPT, respectively. But these parameters increased considerably at 120°C after 35 and 20 min in the rheometer and the MPT, respectively, for black-

filled CR. The response time increased with the increase in EVAc in the blends. Thus, compounds under rheological study in the MPT were completely devoid of curing during processing up to 100°C, beyond which there is a possibility of curing at higher piston rates.

For the measurement of dynamic flow of the filled polymers, a dynamic viscoelastometer (Rheovibron DDV-III-EP) was used. The measurements were carried out using 3.5, 11, 35, and 110 Hz frequencies and a temperature range of 30–200°C, with a heating rate of 1°C/min. The test samples of 70 × 10 × 5 mm were punched out from the sheets cured at a temperature of 170°C and a pressure of 10 MPa for 15 min.

## THEORY

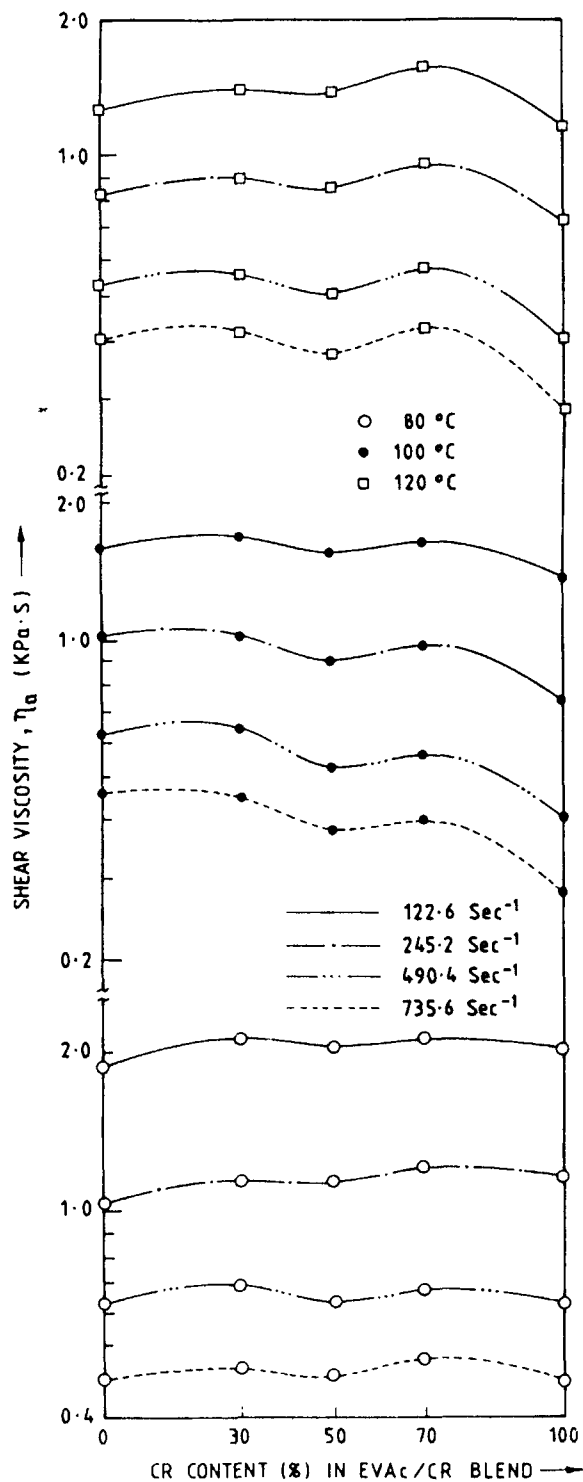
The apparent wall shear rate,  $\dot{\gamma}_{wa}$  and shear stress,  $\tau_w$  can be estimated from the knowledge of the barrel diameter, piston speed, length and diameter of capillary, and pressure drop through the capillary. These are expressed as

$$\tau_w = \frac{d_c \Delta P}{4l_c} \quad (4)$$

$$\dot{\gamma}_{wa} = \frac{32Q}{\pi d_c^3} \quad (5)$$

The true wall shear rate is obtained by applying Rabinowitsch correction<sup>9</sup>

$$\dot{\gamma}_w = \frac{3n' + 1}{4n'} \cdot \dot{\gamma}_{wa} \quad (6)$$



**Figure 1** Variation of shear viscosity with CR content (wt %) in the EVA/CR blend at temperatures of 80, 100, and 120°C and shear rates of 122.6, 245.2, 490.7, and 735.6 s<sup>-1</sup>.

where  $\tau_w$  is the shear stress at the wall;  $d_c$ , capillary diameter;  $l_c$ , capillary length;  $\Delta P$ , pressure drop over the capillary length measured as pressure gauge reading at the inlet of capillary;  $\dot{\gamma}_{wa}$ ,

apparent rate of shear at the wall;  $Q$ , volumetric flow rate of the melt;  $\dot{\gamma}_w$ , true rate of shear at wall; and

$$n' = \left( \frac{d \ln \tau_w}{d \ln \dot{\gamma}_{wa}} \right)$$

= slope of the line obtained

by plotting  $\ln \tau_w$  versus  $\ln \dot{\gamma}_{wa}$

As the capillary used has conical entry with multiple angles, the entry losses can be considered negligible as compared to the pressure drop in the capillary and the wall shear stress.  $\tau_w$ , given by eq. (4) can be considered as the true shear stress. The apparent shear viscosity is given by

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \quad (7)$$

The shear stress and shear rate can be correlated by the power-law model [eq. (1)].

The sample was also subjected to dynamic deformation under tension mode with a sinusoidal frequency. The dynamic response is expressed in terms of in-phase or storage modulus,  $E'$ , and 90° out-of-phase or loss modulus,  $E''$ .

The total energy input due to the deforming frequency has two components. One part, which causes flow of the material and is dissipated as heat, is defined as the dissipative energy ( $W_D$ ) per unit volume, which is related to  $E''$  as<sup>10</sup>

$$W_D = \gamma_o^2 \cdot \omega \cdot E''/2 \quad (8)$$

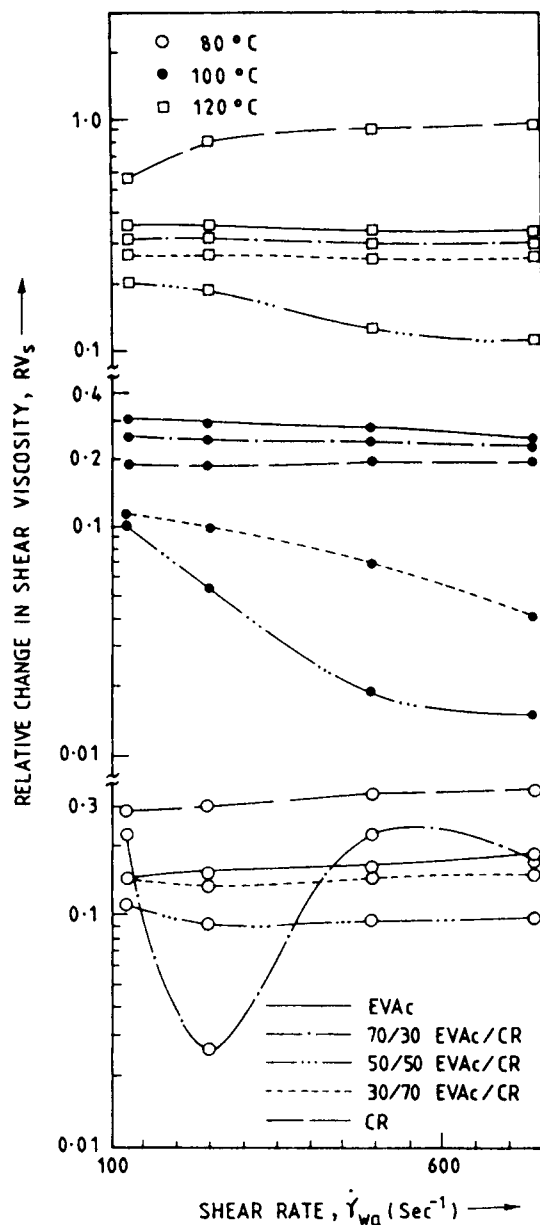
where  $\gamma_o$  is the strain amplitude of the input frequency,  $\omega$ . Other part of input energy is stored in the material in first fourth of the cycle and is used up in the next fourth cycle. This energy is defined as storage energy ( $W_S$ ) per unit volume, which is related to  $E'$  as

$$W_S = \frac{\omega \gamma_o^2}{\pi 2} \cdot E' \quad (9)$$

The fraction of dissipative energy ( $f_D$ ) is given by

$$f_D = W_D/(W_S + W_D) \quad (10)$$

In line with the definition of dynamic out-of-phase viscosity,<sup>11</sup> the dynamic elongational viscosity ( $\eta_E'$ ) and out of phase elongational viscosity ( $\eta_E''$ ) are defined as



**Figure 2** Variation of the relative change in shear viscosity with rate of shear at temperatures of 80, 100, and 120°C for all blends.

$$\eta'_E = E''/\omega \quad \text{and} \quad \eta''_E = E'/\omega. \quad (11)$$

## RESULTS AND DISCUSSION

### Capillary Flow

From the experimental data, the wall shear stress ( $\tau_w$ ), shear rate ( $\dot{\gamma}_{wa}$ ), and the constants  $n'$  and  $K'$  are calculated by the statistical method (Table III). The value of  $n'$  is found to be constant over the range of  $\dot{\gamma}_{wa}$  studied; hence, it can be taken as the flow

behavior index,  $n$ , in the power law [eq. (1)]. For all blends,  $n' < 1$ , which indicates pseudoplastic or shear thinning nature of the blends. The values of  $\zeta'_w$  and  $\eta_a$  are calculated using eqs. (6) and (7).

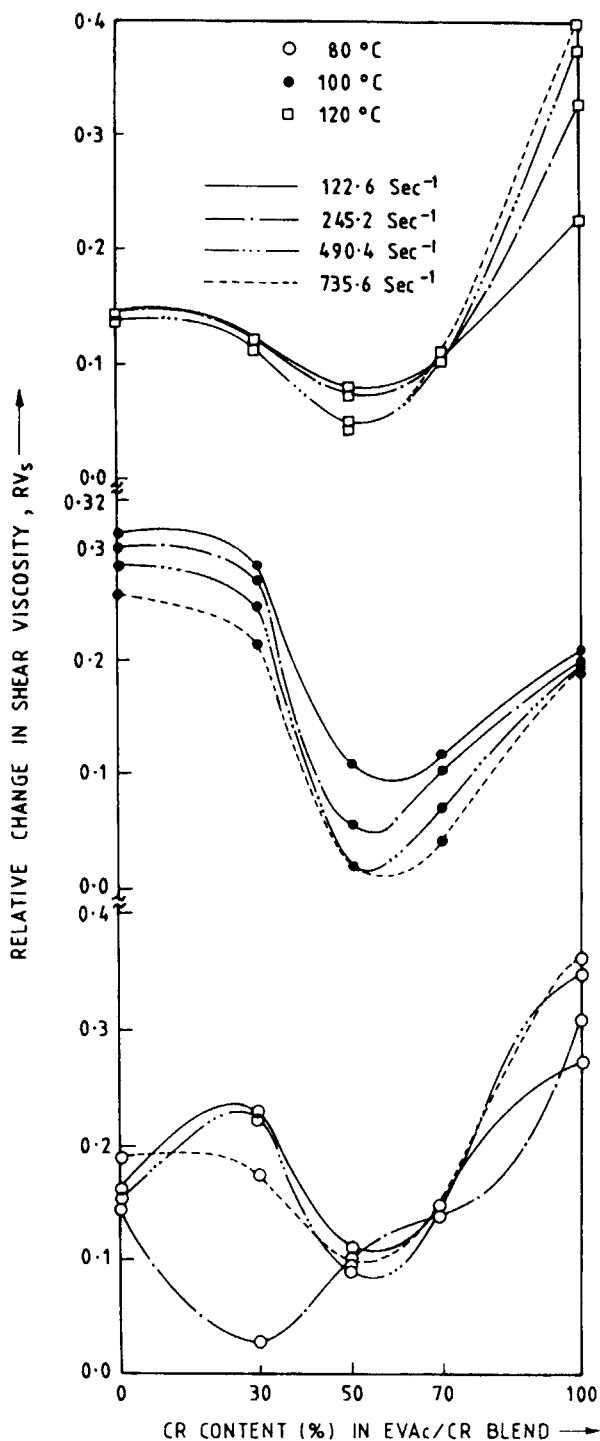
Shear viscosity ( $\eta_a$ ) at 80, 100, and 120°C is plotted against blend composition on a semilog scale in Figure 1. All the plots show positive deviation in  $\eta_a$  with respect to the additive values of blended polymer [eq. (2)]. The positive deviation is minimum for 50/50 blend. The viscosity for all samples decreases with increase in temperature as expected. It also decreases with shear rate, indicating the shear thinning or pseudoplastic rheological behavior. The interaction parameter between the polymer and filler can be calculated from the relative shear viscosity ( $RV_S$ ) of the filled polymers. For this purpose, the 30 phr black-filled system has been studied. The relative change in shear viscosity,  $RV_S$ , is defined as

$$RV_S = \frac{\eta_f - \eta_o}{\eta_o} \quad (12)$$

where  $\eta_f$  and  $\eta_o$  are the apparent viscosity of filled and gum systems. The values of  $\eta_a$  for gum system have been reported in our earlier publication.<sup>8</sup>

The relative change in shear viscosity calculated from eq. (12) at 80, 100, and 120°C are plotted against shear rate in Figure 2.  $RV_S$  of CR at all temperatures shows increasing trend, which is more so at a higher temperature (120°C) than at a lower temperature. This is because of the formation of more chemical bonds between CR and black due to the generation of free radicals from the decomposition of dicumyl peroxide<sup>12</sup> at higher shear rates. Most of the systems either show practically no change in  $RV_S$  with rate of shear or show only marginal increase (pure CR) at different temperature, except for 30/70 and 50/50 blends at 100°C, which show decreasing trend. The 70/30 blend at 80°C shows erratic behavior.

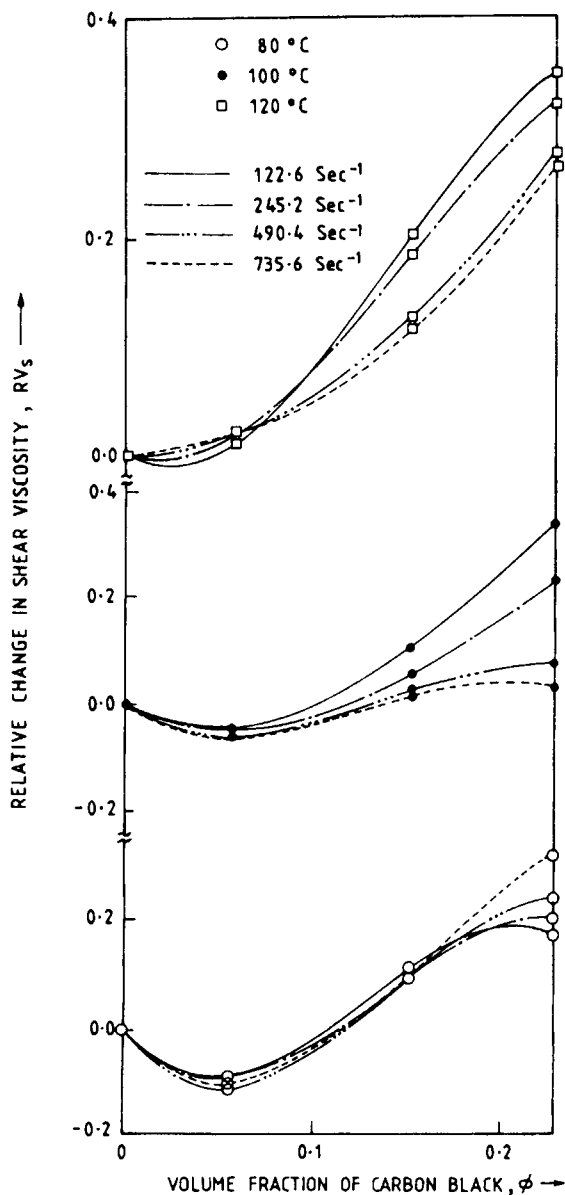
The small amount of crystallites present in EVAc at 80°C and active olefinic double bonds of CR act as the anchoring site between the polymer and solid black filler. Higher shear rate can force proper alignment of the filler-anchored polymer in the direction of force and thus facilitates proper filler-polymer interaction at the interface. That is the reason for increasing tendency of  $RV_S$  for EVAc at 80°C and CR at all temperatures. The crystals of EVAc melted at higher temperatures and higher shear rates enable fillers to slip at polymer-filler interface, causing a lower relative viscosity. The erratic behavior of 70/30 blend at 80°C may be due to the instabilities caused by the softening of crystallites of EVAc around this temperature.



**Figure 3** Variation of the relative change in shear viscosity with CR content (wt %) in the EVAc/CR blend at temperatures of 80, 100, and 120°C and shear rates of 122.6, 245.2, 490.4, and 735.6  $s^{-1}$ .

The variation of  $RV_S$  with weight percent of CR in EVAc/CR blends at 80, 100, and 120°C is shown in Figure 3. Filler-polymer interaction of the blends depends primarily on the relative dispersion of filler,

the viscosity gradient<sup>2</sup> between blended polymers, and the relative activity to form physical or physicochemical bonds between the filler and polymers. All these factors control the relative change in viscosity ( $RV_S$ ) of blended polymers with filler. Due to presence of active olefinic double bonds and chloro groups, the filler interaction is expected to be higher for CR as compared to EVAc.<sup>12</sup> Thus, as the amount of CR increases in the blend, the  $RV_S$  should increase; but at up to 50% CR, the  $RV_S$  shows decreasing trend, except for 70/30 blend at 80°C. In



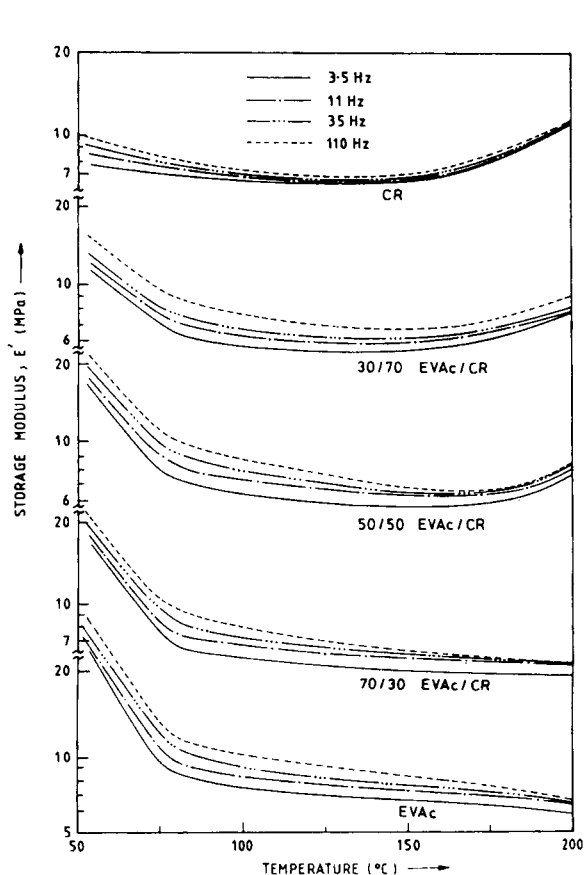
**Figure 4** Variation of the relative change in shear viscosity with volume fraction of carbon black  $\phi$  at temperatures of 80, 100, and 120°C and shear rates of 122.6, 245.2, 490.4, and 735.6  $s^{-1}$ .

**Table IV Polynomial Constants for the Plots of Relative Change in Shear Viscosity Versus Volume Fraction of Carbon Black in 50/50 EVAc/CR Blend**

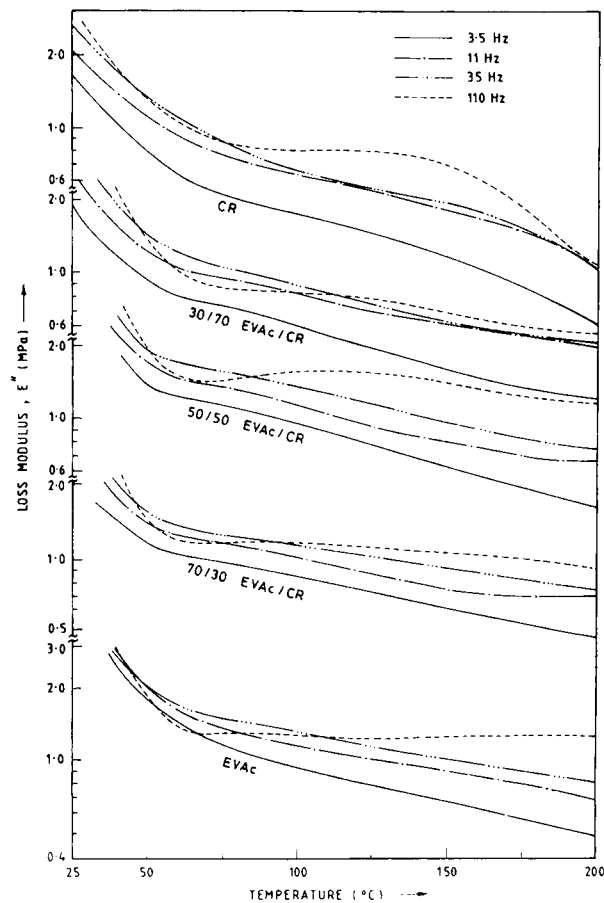
Rate of Shear (s <sup>-1</sup> )	Temperature (°C)	Polynomial Constants		
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
122.6	80	-4.15	53.58	-139.96
	100	-1.92	22.03	-30.79
	120	-0.99	23.82	-56.01
245.2	80	-3.81	46.15	-111.40
	100	-1.57	15.75	-19.11
	120	-0.57	18.15	-41.62
490.4	80	-4.59	54.03	-128.13
	100	-2.16	23.54	-55.23
	120	-0.10	7.06	-5.73
735.6	80	-3.96	44.21	-89.68
	100	-2.32	26.56	-69.37
	120	0.19	2.76	6.60

this region, the crystallinity of EVAc gets lowered,<sup>13</sup> which causes lowering in the entrapment of the filler particle. Beyond 50% CR blending, the chemical interaction between the olefinic double bond of CR

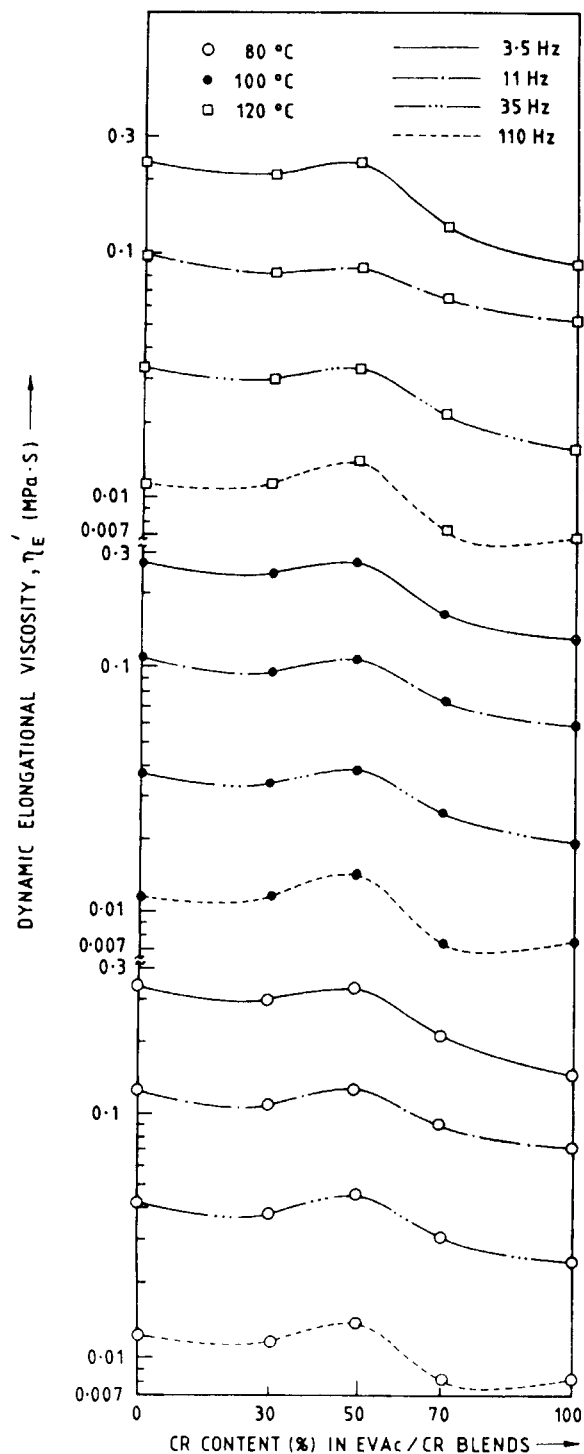
and the surface active filler is predominant over physical entrapment or entanglement. This leads to an increase in  $RV_S$  beyond 50% CR in the blends.



**Figure 5** Variation of the storage modulus with temperature at frequencies of 3.5, 11, 35, and 110 Hz for all blends.



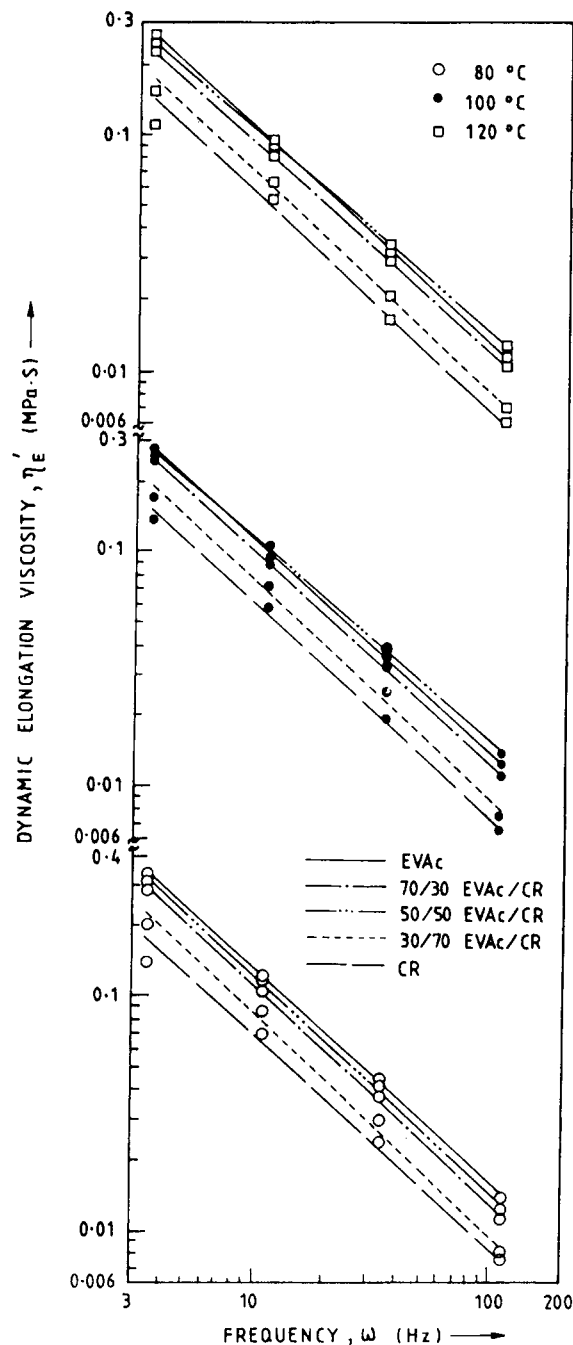
**Figure 6** Variation of the loss modulus with temperature at frequencies of 3.5, 11, 35, and 110 Hz for all blends.



**Figure 7** Variation of dynamic elongational viscosity with CR content (wt %) in EVAc/CR blends at temperatures of 80, 100, and 120°C and frequencies of 3.5, 11, 35, and 110 Hz.

The relative change in shear viscosity is also calculated for 10, 20, and 30 phr carbon black loaded 50/50 EVAc/CR compounds. The variation of  $RV_S$  at 80, 100, and 120°C with volume fraction

( $\phi$ ) of carbon black in 50/50 blend is shown in Figure 4. The variation of  $RV_S$  with the volume fraction of filler has been fitted with a three-degree polynomial equation [eq. (12)]. The constants of the equation are functions of temperature and rate of shear and are reported in Table IV. The inclu-



**Figure 8** Variation of dynamic elongational viscosity with frequency at temperatures of 80, 100, and 120°C for all blends.



Table V  $n_1$  and  $K_1$  Values [eq. (13)]

Compound Number	Temperature					
	80°C		100°C		120°C	
	$n_1$	$K_1$	$n_1$	$K_1$	$n_1$	$K_1$
B <sub>1</sub>	0.96	11.7	0.91	9.1	0.88	7.5
B <sub>2</sub>	0.93	9.7	0.89	7.7	0.85	6.2
B <sub>3</sub>	0.92	10.7	0.85	8.0	0.82	6.4
B <sub>4</sub>	0.85	12.3	0.81	11.5	0.78	11.0
B <sub>5</sub>	0.91	11.0	0.83	10.5	0.76	10.0

sions of filler in the polymer reduces the free movement of polymers as well as enhances its mastication due to generation of a higher shearing force during mixing. The decrease in viscosity up to 10 phr carbon black loading, which gives negative values of  $C_1$ , may be due to the mastication of polymers, which reduces the molecular weight and, hence, the viscosity.

### Dynamic Flow

The variation of storage ( $E'$ ) and loss modulus ( $E''$ ) for all samples with temperature is shown in Figures 5 and 6, respectively. The steep fall of both storage and loss modulus at around 50°C for all blends is due to the termination of  $\beta$ -relaxation of the excited molecules and initiation of  $\alpha$ -transition (melting) of EVAc and its blends. The EVAc and the 70/30 EVAc/CR blend show decrease in both  $E'$  and  $E''$  throughout the entire temperature range, whereas the CR and the other two blends (50 : 50 and 30 : 70 EVAc/CR) show a decrease in  $E''$  but an increase in  $E'$  after certain temperature. Throughout the entire temperature range beyond 50°C, both  $E'$  and  $E''$  increase with increase in frequency. The increase in storage modulus at higher temperatures (>150°C) for CR and its blends is due to high temperature hardening of CR.<sup>14</sup>

The dynamic out-of-phase ( $\eta_E''$ ) and dynamic elongational ( $\eta_E'$ ) viscosities are calculated from  $E'$  and  $E''$  using eq. (11).

In Figure 7, the dynamic elongational viscosities at 80, 100, and 120°C are plotted against CR content (%) in the blends. All of the blends show positive deviation in  $\eta_E'$  with respect to that of pure polymers at all temperatures and frequencies, except 110 Hz, at which the 30 : 70 blend shows negative deviation. The log-log variation of  $\eta_E'$  with frequency at 80,

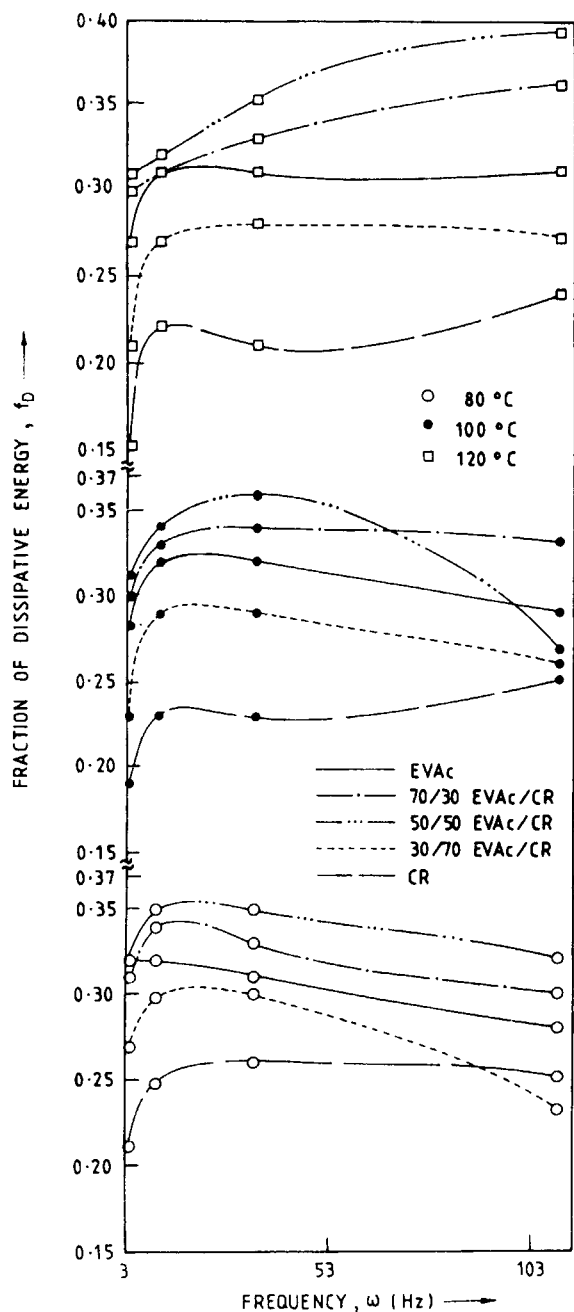
100, and 120°C is shown in Figure 8. All the plots are straight lines, indicating the Power Law relationship.

$$\eta_E' = K_1 \cdot \omega^{-n_1} \quad (13)$$

where,  $n_1$  and  $K_1$  are constants which are reported in Table V.

The change in the fraction of dissipative energy ( $f_D$ ) with frequency is shown in Figure 9. The fraction of dissipative energy shows a sharp increase with frequency in the low frequency region (3–11 Hz) at all temperatures except 120°C for 50/50 and 70/30 EVAc/CR blends, where it slowly increases with frequency. In the higher frequency region, the dissipative energy shows a decreasing trend at the lower temperatures (80 and 100°C), except for CR, which maintains its increasing trend; whereas at higher temperature (120°C), all blends except the 50/50 blend show an increasing trend. The probable reason for an increase in the dissipative energy at the higher temperature is that the effect of increase in temperature, which causes randomization of molecular motion, appears to be dominating over the effect of an increase in frequency, which tends to freeze the molecular motion. At around 100°C, however, both these effects balance each other; whereas, at 80°C, the effect of frequency variation is predominant over temperature.

The variation of out-of-phase viscosities ( $\eta_E''$ ) with %CR in EVAc/CR blends at all temperatures is shown in Figure 10. All plots show negative deviation except at the low temperature (80°C) and high frequency (110 Hz) with high CR content, where the blend shows a marginal positive deviation. For all frequencies, the 50/50 blends show minimum negative deviation, indicating better in-

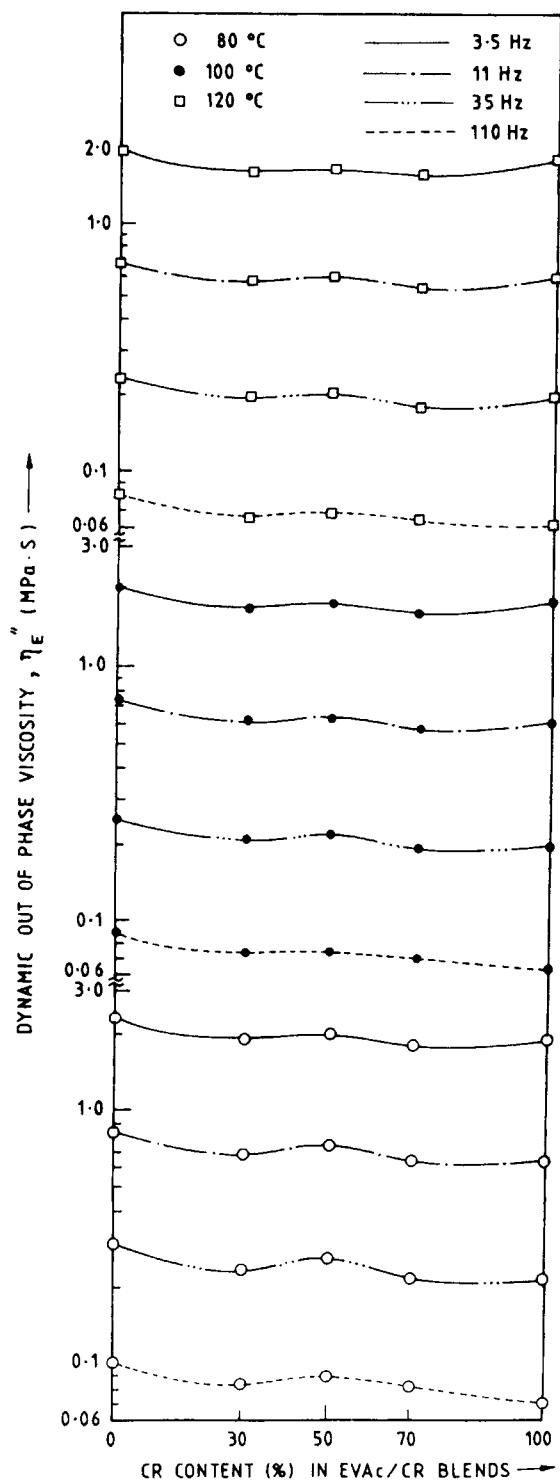


**Figure 9** Variation of the fraction of dissipative energy with frequency at temperatures of 80, 100, and 120°C for all blends.

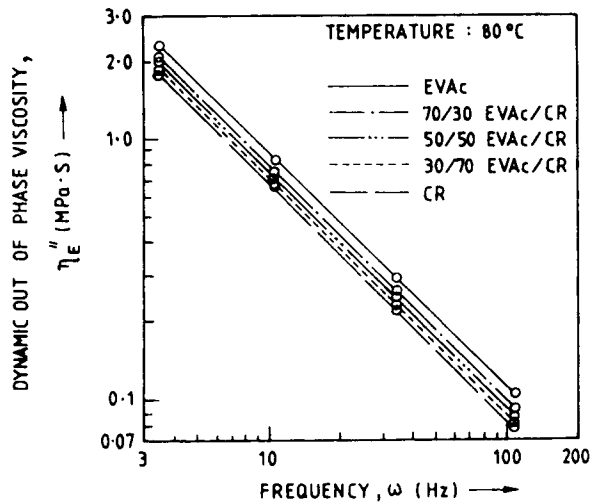
terphasial compatibility. The out-of-phase viscosity is a consequence of the capacity of the viscoelastic systems to store energy due to its elastic nature. The negative deviation in the blends may be due to the intersegmental slip between the two components. This slip between the segments reduces at high frequency and low temperature (both

of which tend to reduce the segmental motion), resulting in the negligible negative deviation under these conditions.

The log-log variation of  $\eta''_E$  with frequency at 80°C



**Figure 10** Variation of dynamic out-of-phase viscosity with CR content (wt %) in EVAc/CR blends at temperatures of 80, 100, and 120°C and frequencies of 3.5, 11, 35, and 110 Hz.



**Figure 11** Variation of dynamic out-of-phase viscosity with frequency at a temperature of 80°C for all blends.

is shown in Figure 11. All plots are straight lines, indicating the power law relationship of  $\eta''_E$  with frequency

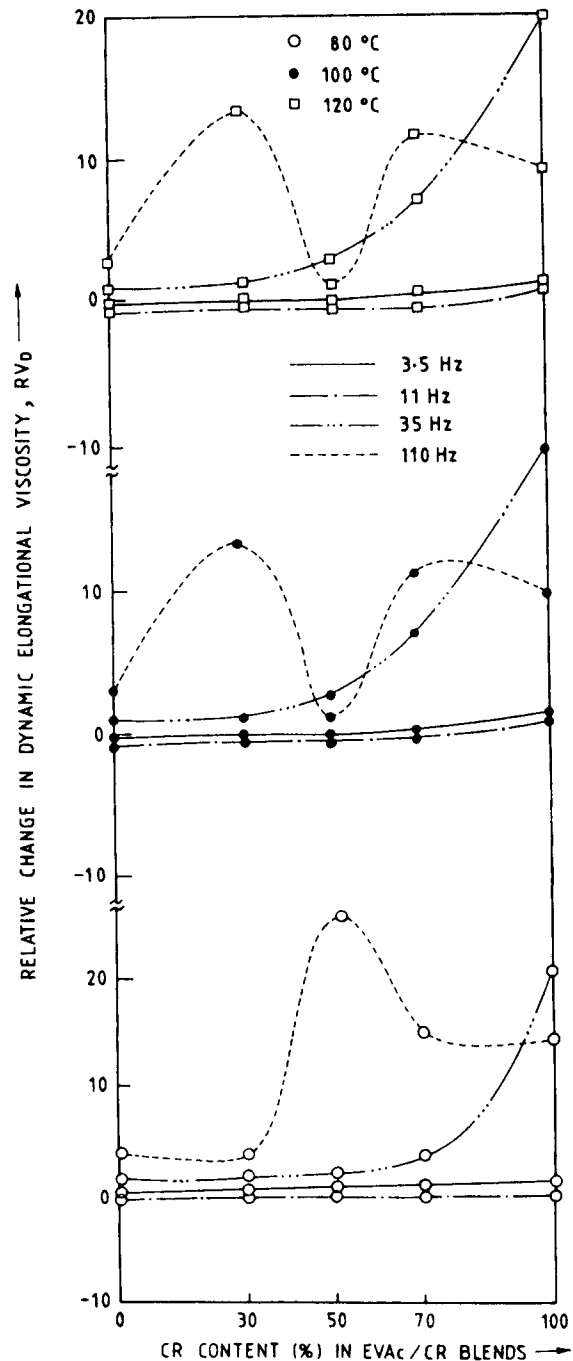
$$\eta''_E = K_2 \cdot \omega^{-n_2} \quad (14)$$

where  $n_2$  and  $K_2$  are constants given in Table VI.

The relative change in the dynamic viscosity ( $RV_D$ ) of filled polymers can be obtained from dynamic elongational viscosities ( $\eta'_E$ ) of filled and gum compounds as

$$RV_D = \frac{\eta'_{E, \text{filled}} - \eta'_{E, \text{gum}}}{\eta'_{E, \text{gum}}} = \frac{E''_{\text{filled}} - E''_{\text{gum}}}{E''_{\text{gum}}} \quad (15)$$

The variation of  $RV_D$  at 80, 100, and 120°C with wt % CR in EVAc/CR blend is shown in Figure 12.  $RV_D$  at a lower frequency (3.5 and 11 Hz) shows almost constant values with a slight increasing trend. At 35 Hz frequency,  $RV_D$  is almost constant,

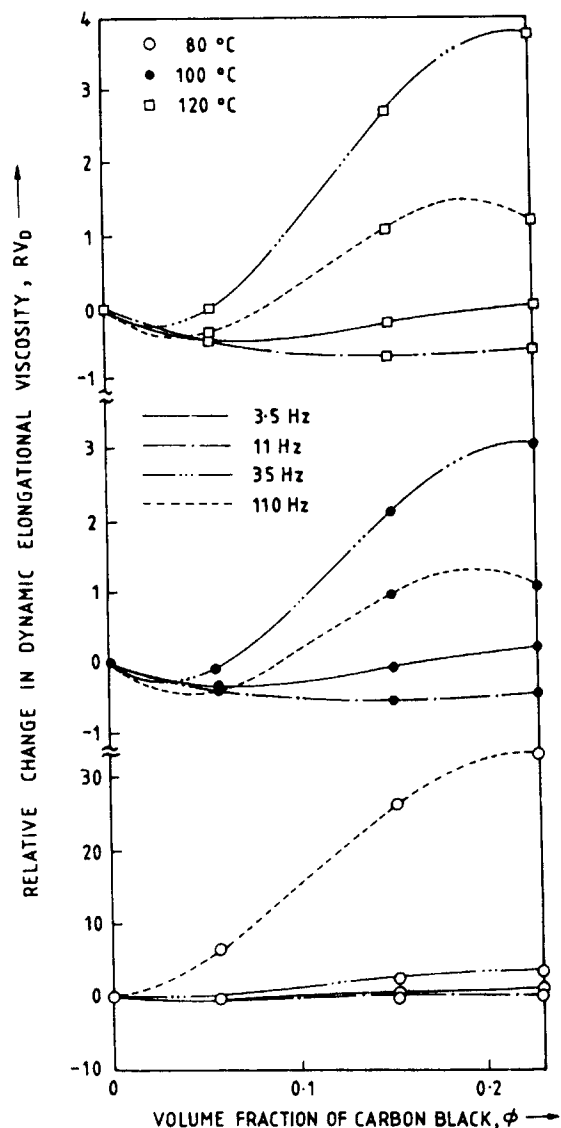


**Figure 12** Variation of the relative change in dynamic elongational viscosity with CR content (wt %) in EVAc/CR blends at temperatures of 80, 100, and 120°C and frequencies of 3.5, 11, 35, and 110 Hz.

**Table VI**  $n_2$  and  $K_2$  Values [eq. (14)] at 80°C

Compound Number	$n_2$	$K_2$
B <sub>1</sub>	0.91	73.6
B <sub>2</sub>	0.91	60.4
B <sub>3</sub>	0.91	63.9
B <sub>4</sub>	0.90	55.9
B <sub>5</sub>	0.95	63.5

up to 30% CR, beyond which it starts increasing and the rate of increase becomes faster with the higher content of CR. The plots at 110 Hz for all temperatures show erratic variation. Dynamic



**Figure 13** Variation of the relative change in dynamic elongational viscosity with the volume fraction of carbon black at temperatures of 80, 100, and 120°C and frequencies of 3.5, 11, 35, and 110 Hz.

elongational viscosities of polymeric samples at higher temperatures are reduced considerably due to factors like intersegmental slippage,<sup>11</sup> slippage at black-polymer interface,<sup>15,16</sup> reduction in the molecular chain length due to enhanced mastication of carbon black loaded compounds<sup>17</sup> and synchronization of employed frequency with that of polymeric chain vibration frequency.<sup>8</sup> The cured samples under dynamic tests should show an increase in  $RV_D$  with an increase in CR content in the blends as CR is more actively involved in filler polymer interactions compared to EVAc<sup>12</sup>,

whereas carbon black inclusions can reduce the effective chain length, and, hence, the synchronization effect at a lower frequency region (3.5–11 Hz) gets minimized, which leads to the lower dynamic elongational viscosity of filled compounds. The nearly constant or slightly increasing trend of  $RV_D$  at 3.5–11 Hz and at all temperatures is explained by these two opposing factors. As the synchronization effect does not exist at 35 Hz, it shows an increasing trend of  $RV_D$  with an increasing amount of CR in the blends; and the rate of increment is higher beyond 50% CR due to increased filler-polymer interactions. The maximum and minimum relative changes in the dynamic elongational viscosity at lower (80°C) and higher (100–120°C) temperatures and at 110 Hz frequency for 50 : 50 EVAc/CR blend may be due to lower and higher interchain and black filler interface slippage. The decreasing trend at 110 Hz in 50–100% CR at 80°C and 30–50% and 70–100% CR at 100–120°C can be explained by these slip factors.

The variation of relative change in dynamic viscosities with the volume fraction ( $\phi$ ) of carbon black in the 50 : 50 EVAc/CR blends is shown in Figure 13. All plots generate a third-order polynomial equation quite similar to Equation 3. All the polynomial constants are reported in Table VII. The explanation for negative values of the first polynomial constants ( $C_1$ ) at all temperatures and frequencies is the same as that for relative shear viscosities. Here, intersegmental slippage predominates at lower (10 phr) black loading, whereas enhanced cross-link network predominates at higher filler loading, causing higher negative and positive values of  $C_1$  and  $C_2$ , respectively, compared to those obtained from relative shear viscosities.

## CONCLUSIONS

The following conclusions can be drawn from the above studies.

1. All EVAc/CR blends show positive deviation in both shear and dynamic elongational viscosities irrespective of shear rates and frequencies, except for 110 Hz, which shows negative deviation at the 30/70 blend. This positive deviation indicates miscibility of the blends in the filled system.
2. Both storage and loss modulus increases with frequency for pure polymers and their blends.
3. The filled system shows the power law rela-

**Table VII Polynomial Constants for the Plots of Relative Change in Dynamic Viscosity Versus Volume Fraction of Carbon Black in 50/50 EVAc/CR Blend**

Frequency (Hz)	Temperature (°C)	Polynomial Constants		
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
3.5	80	-9.20	101.67	-230.13
	100	-11.56	106.99	-234.04
	120	-14.21	125.45	-278.51
11	80	-5.93	19.64	5.47
	100	-8.71	36.59	-35.01
	120	-10.54	45.96	-50.97
35	80	-19.29	382.30	-1043.97
	100	-20.45	380.90	-1027.98
	120	-21.46	440.39	-1203.96
110	80	27.45	1803.39	-5653.47
	100	-23.66	342.77	-961.57
	120	-22.04	335.69	-949.37

tionship of both shear and dynamic elongational viscosities.

- The plot of fraction of dissipative energy ( $f_D$ ) with frequency shows a peak at around 11 Hz, which indicates synchronization of this frequency with the molecular vibrations.
- Relative change in viscosity measured from both shear ( $RV_S$ ) and dynamic elongational ( $RV_D$ ) viscosities are functions of blend composition.
- Both  $RV_S$  and  $RV_D$  are functions of volume fraction of carbon black. Both generate a polynomial equation that is quite similar to the Guth-Gold equation but with different polynomial coefficients. These coefficients are functions of both strain rate (shear rate and frequency) and temperature.

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