

Rheological Properties of the Blends of Polychloroprene with Poly[ethylene(vinyl acetate)]

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ABSTRACT: Blends of poly[ethylene(vinylacetate)] (EVAc-45; 45% VAc content) and polychloroprene (CR) have been studied with respect to capillary and dynamic flow. It is found that EVAc-45, CR, and their blends are shear thinning (pseudoplastic) in nature. Though shear viscosity (η_a) and dynamic out-of-phase viscosity (η_E') obeys power law, dynamic elongational viscosity (η_E'') does not follow it due to the synchronization of molecular vibration with the applied frequency at around 11 Hz. Both η_a and η_E' of the blends show positive deviation with respect to their additive values. The relative positive deviation (RPD) in shear flow increases with increasing temperature and shear rate. In the case of dynamic flow, RPD increases with increasing temperature but exhibits a decreasing trend with increasing frequency. RPD can be fitted well into a fifth-order equation with a weight fraction of CR (W_{CR}) in EVAc-45–CR blends. From rheological point of view, this relative positive deviation indicates blend compatibility between EVAc-45 and CR. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1759–1765, 1997

Key words: shear and dynamic extensional viscosity; relative positive deviation; blend compatibility

INTRODUCTION

Polymeric materials are viscoelastic materials; i.e., the stress depends on the history of the deformation. Rheology is related to the mechanical properties of polymers under different deformation conditions when they simultaneously exhibit the ability to flow and accumulate recoverable deformations.

According to the basic principle of rheology, the flow behavior of a material can be expressed by the power law equation,¹ as follows:

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

where τ and $\dot{\gamma}$ are true shear stress and shear rate, K is the consistency index, and n is the flow

behavior index. When $n = 1$, the material is Newtonian in nature ($\tau \propto \dot{\gamma}$). For a non-Newtonian system, when $n > 1$, the material is dilatant (shear thickening) as viscosity (η_a) increases with shear rate ($\dot{\gamma}$); when $n < 1$, it is called pseudoplastic in nature (i.e., η_a decreases with $\dot{\gamma}$). Most of the polymeric systems are pseudoplastic character.

In a blend, the constituent polymers may be either thermodynamically compatible or incompatible, depending on whether their enthalpy of mixing (ΔH_m) is positive or negative. The polymeric blends with specific interactions should have a negative heat of mixing.² Also, the viscosity of the polymeric blend follows the following log additivity rule³:

$$\log \eta_B = \sum W_i \log \eta_i \quad (2)$$

where η_i and η_B are the true viscosity of the component and its blend at a shear rate, which tends to zero, and W_i is the weight fraction of i th compo-

This study is based on a 45% vinyl acetate content.
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Table I Blend Composition in Wt %

Blend Code	A	B	C	D	E
EVAc-45 ^a	100	70	50	30	0
CR ^b	0	30	50	70	100

^a Leavaprene-450: VAc content, 45%; sp. gravity, 0.98; producer, Bayer A. G., Germany.

^b Neoprene WM1: sp. gravity, 1.23; producer, Du Pont, U.S.A.

ment. Compatible blends lead to the positive deviation in rheological properties, such as viscosity, die swell, etc., and are termed as positively deviating blends (PDB).^{4–5} On the other hand, for incompatible blends, rheological properties generally show a negative deviation from their additive values. These blends are termed as negatively deviating blends (NDB).^{6–7}

It is reported elsewhere^{8–9} that the blends of poly[ethylene(vinylacetate)] having 28 and 45% vinylacetate and polychloroprene are miscible in all blend compositions. The polar–polar interactions between the blended components is the main reason for their miscibility.¹⁰ The blend compatibility of poly[ethylene(vinylacetate)] having 28% vinylacetate and polychloroprene has also been studied through capillary and dynamic flow.¹¹ In this article, the flow behavior of the miscible elastomeric blends of EVAc-45 and CR has been studied at higher temperatures and at varying strain rates under capillary and dynamic flows.

EXPERIMENTAL

The polymers were mixed in a Brabender Plasticorder (PLE-330) as per the formulations given in Table I. EVAc-45 was first mixed in the chamber at 100°C and 60 rpm for about 2 min, followed by the addition of premasticated CR. The mixing was allowed to continue for another 5 min at 100°C and 100 rpm to get a better mix.

Rheological properties were studied with the help of a Monsanto Processability Tester (MPT 83077) using a fixed die (length to diameter = 30 : 1 with multiple cone angle entry of 45 and 60°) and at the piston speeds of 0.042, 0.085, 0.169, and 0.254 mm s. The material was initially preheated in the barrel for 5 min at 6 MPa to get a compact mass, then the excess material was purged at a rate of 0.169 mm s and extruded at different rates of shear (in the range of 100 to 750 s⁻¹) and temperatures of 80, 100, and 120°C in a programmed way using a microprocessor.

A dynamic viscoelastometer (Rheovibron,

DDV-III-EP) of Orientec Corporation, Japan, was used for measurement of dynamic flow of the polymers and their blends. Four frequencies (3.5, 11, 35, and 110 Hz) were used with a programmed heating rate of 1°C min. The study was carried out at a temperature range of 20–200°C. As the uncured samples cannot withstand high temperature and are likely to flow during sinusoidal deformation, the samples were partially cured. Samples were cut in the size of 70 × 10 × 5 mm for dynamic testing.

CAPILLARY FLOW

Apparent shear stress (τ_{wa}) and shear rate ($\dot{\gamma}_{wa}$) are calculated from the experimental data using standard rheological equations.¹² The plots of apparent shear stress versus shear rate (γ_{wa}) at different temperatures are straight lines (not shown here), whose intercept K' and slope n' of the plots are given in Table II. Slope n' , taken as the flow behavior index, and n , taken as the Bagley correction factor, is negligible for the die used for processability studies. The n values are less than one (<1), which indicate the pseudoplastic behavior of EVAc-45, CR, and their blends. Pseudoplasticity is lowest for CR and increases with increasing content of EVAc-45 in the blends.

Considering the multichannel flow in the die, apparent shear stress is taken as true shear stress (τ_w). True shear rate ($\dot{\gamma}_w$) is calculated from apparent shear rate ($\dot{\gamma}_{wa}$) by applying the Rabinowitsch correction.¹³ Shear viscosity (η_a) can be calculated from true shear stress and shear rate.

Shear viscosity at all temperatures and shear rates are plotted against content of CR (%) for EVAc-45–CR blends in Figure 1. Shear viscosity of the blends at 80°C shows negative deviation with respect to their additive values; whereas at higher temperatures (100 and 120°C), they show positive deviation. With the increase in temperature, this positive deviation increases. For interactive blends, it is expected that the density will increase on mixing, leading to the positive devia-

Table II Flow Behavior Index (n) and Consistency of Flow (K)

Blend Code	Temperature					
	80°C		100°C		120°C	
	n'	K'	n'	K'	n'	K'
A	0.26	88.6	0.29	53.4	0.32	32.3
B	0.21	115.6	0.24	77.9	0.29	43.8
C	0.18	145.2	0.20	109.2	0.24	72.0
D	0.16	172.5	0.16	150.9	0.25	75.5
E	0.15	225.1	0.11	257.6	0.07	279.6

tion in the rheological functions like viscosity.³ Thus, positive deviation in viscosity is an indication of blend compatibility between EVAc-45 and CR. The relative positive deviation calculated from positive deviation is defined as follows. The positive deviation $\Delta\eta_a$ due to blending is expressed as

$$\Delta\eta_a = \eta_{a,\text{Exp}} - \sum w_i \log \eta_{a,i} = \eta_{a,\text{Exp}} - \eta_{a,\text{add}} \quad (3)$$

where $\eta_{a,\text{Exp}}$ is the viscosity of the blend calculated from experimental measurements, and $\eta_{a,\text{add}}$ is its log-additive value. From eq. (3),

$$\Delta\eta_a/\eta_{a,\text{Exp}} = 1 - \eta_{a,\text{add}}/\eta_{a,\text{Exp}} \quad (4)$$

The variation RPD at 100 and 120°C with the weight fraction of CR (W_{CR}) in the EVAc-45–CR blend is shown in Figure 2. Irrespective of shear rates, at 100°C, RPD is maximum for 50 : 50 blend; whereas at 120°C, it is maximum for 30 : 70 blend. The plots of RPD with W_{CR} can be fitted to a fifth-order polynomial equation, as follows:

$$\text{RPD} = C_0 + C_1 W_{\text{CR}} + C_2 W_{\text{CR}}^2 + C_3 W_{\text{CR}}^3 + C_4 W_{\text{CR}}^4 \quad (5)$$

where C_0 and C_1 – C_4 are constants, as reported in Table III. At 100°C, the polynomial plots for all shear rates show negative deviation at both lower and higher CR contents corresponding to the negative values of C_1 and C_3 . This indicates that this polynomial equation does not hold good at 100°C.

DYNAMIC FLOW

The dynamic elongation viscosity (η'_E) and out-of-phase viscosity (η''_E) at 80, 100, and 120°C are calculated from loss (E'') and storage (E') modu-

lus, respectively, as stated in our previous publication.¹²

The log–log variation of η''_E with frequency (ω) is shown in Figure 3. η''_E decreases linearly with frequency and follows a general relationship similar to that of shear viscosity and shear rate, as follows:

$$\eta''_E = C_1 \cdot \omega^{-d_1} \quad (6)$$

where C_1 and d_1 are constants whose values are 3.33, 4.34, 2.83, 2.64, and 3.00 and 1.07, 0.99, 1.00, and 1.00 for EVAc-45, 70 : 30, 50 : 50, and 30 : 70 blends and CR, respectively.

The log–log variations of η'_E with frequency at 80°C are shown in Figure 4. Pure EVAc-45, CR, and their blends show a decrease in dynamic elongational viscosities with increasing frequency. But the rate of decrease in η'_E in the region of 11 to 35 Hz frequency is found to be maximum, beyond which η'_E either increases or shows a plateau behavior. The peak or hump at around 11 Hz, caused due to a sudden fall in η'_E , may be explained as synchronization of molecular vibration with the applied frequency.^{11,12} Thus, 11 Hz is a critical frequency where maximum viscous absorption takes place and molecules reach their maximum excited state, which is in resemblance with the temperature effect during any transitions (glass transition or crystalline melting).¹²

Figure 5 shows the variation of dynamic elongational viscosities with CR content (%) in EVAc-45–CR blends at temperatures of 80, 100, and 120°C and at frequencies of 3.5, 11, 35, and 110 Hz. At all temperatures and frequencies, η'_E of the blends show positive deviation with respect to their additive values. Positive deviation is maximum for the 70 : 30 EVAc-45–CR blend at all temperatures and frequencies except at 80°C for 11 Hz, in the case of which the 50 : 50 blend shows

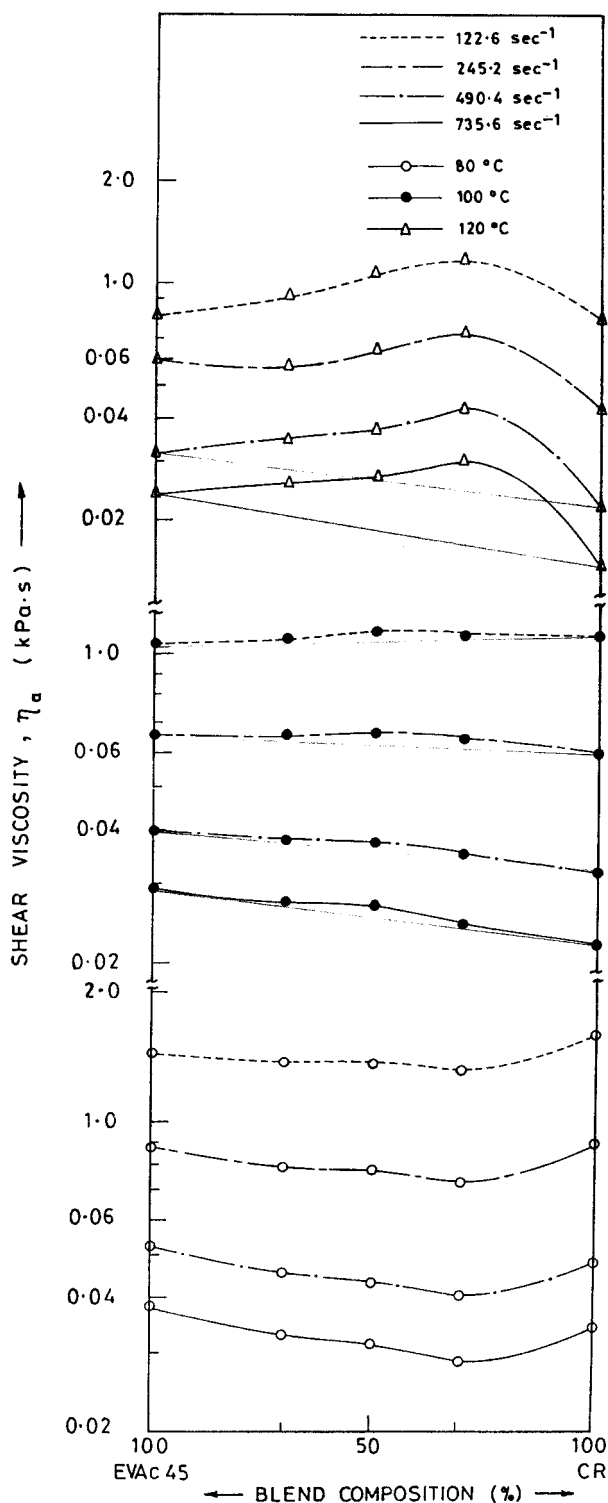


Figure 1 Variation of shear viscosity with wt % CR content in the EVAc-45-CR blends at the temperatures of 80, 100, and 120°C and shear rates of 122.6, 245.2, 490.4, and 735.6 s^{-1} .

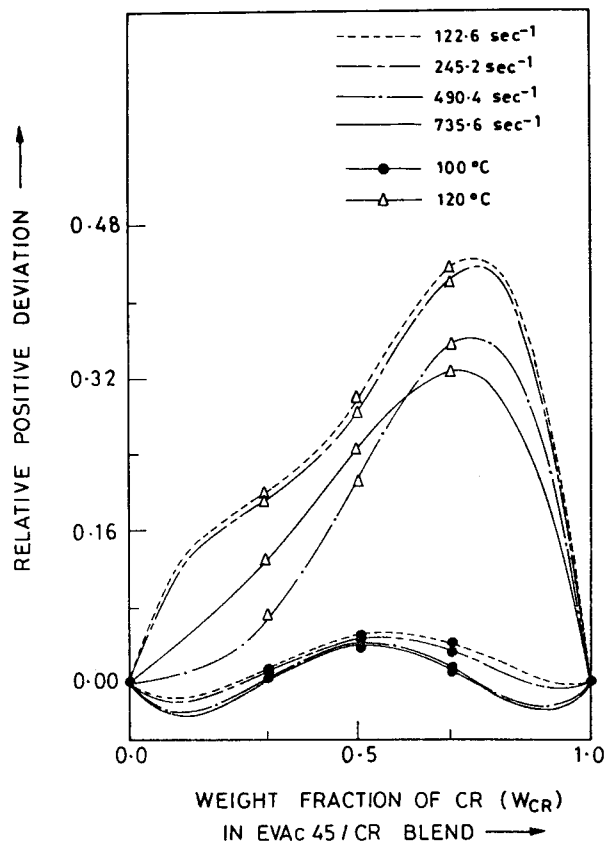


Figure 2 Variation of RPD of viscosity with the weight fraction of CR content (W_{CR}) in the EVAc-45-CR blends at temperatures of 100 and 120°C and at shear rates of 122.6, 245.2, 490.4, and 735.6 s^{-1} .

maximum positive deviation. At 80°C, the 70 : 30 blend and CR show higher η'_E values at 110 Hz compared to those at 35 Hz; whereas at 100°C, for both polymers and their blends, higher η'_E is observed at 110 Hz compared to 35 Hz. This may be due to maximum extent of intermolecular slippage at 35 Hz for these blends at the above-mentioned temperatures.

Following the definition of relative positive deviation (RPD) of shear viscosity, the RPD of dynamic elongational viscosity has been defined as

$$\Delta\eta'_E/\eta'_E = (\eta'_E - \eta'_{E,add})/\eta'_E \quad (7)$$

The variation of RPD with weight fraction of CR (W_{CR}) in EVAc-45-CR blend is shown in Figure 6. The experimental points can be fitted into a fifth-order polynomial equation (similar to eq. 5). The values of all the polynomial constants are reported in Table IV. The nature of the polynomial plots at 3.5 and 35 Hz frequencies are elliptical at all temperatures except at 120°C for 35 Hz,

Table III Polynomial Constants

Temp (°C)	Shear Rate (s ⁻¹)	Polynomial Constants			
		C ₁	C ₂	C ₃	C ₄
100	122.6	-0.65	3.70	-6.00	2.95
100	245.2	-0.39	2.43	-3.79	1.75
100	490.4	-0.34	2.27	-3.69	1.76
100	735.6	-0.57	3.45	-5.70	2.83
120	122.6	0.44	-0.32	3.87	-3.62
120	245.2	0.77	-0.32	3.87	-3.62
120	490.4	1.62	-6.23	12.02	-7.41
120	735.6	1.67	-6.40	12.25	-7.52

which shows a truncated ellipsoid generating double peaks at the 70/30 and 30/70 blends. This type of truncated ellipsoid plots are generated at 110 Hz frequency at all temperatures. Also, for all temperatures, the fifth-order polynomial at 11 Hz generates negative relative deviation at lower and higher CR contents, corresponding to the negative values of C_1 and C_3 . It indicates that this polynomial equation does not hold good at 11 Hz.

CONCLUSION

EVAc-45, CR, and their blends are pseudoplastic in nature both in capillary and dynamic flow. Cap-

illary viscosity (η_a), dynamic out-of-phase viscosity (η_E''), and dynamic elongation viscosity (η_E') decreases with an increase in shear rate and frequency, respectively. The abnormally higher η_E' at around 11 Hz is due to the synchronization of molecular vibration, whereas the decrease in shear viscosity with shear rate is governed by the power law. All the blends show positive deviation in both η_a and η_E' with respect to their additive values at all shear rates, frequencies, and temperatures, except for η_a at 80°C, where all blends show negative deviation. RPD increases with increasing temperature in the case of both capillary and dynamic flow. RPD in both η_a and η_E' are func-

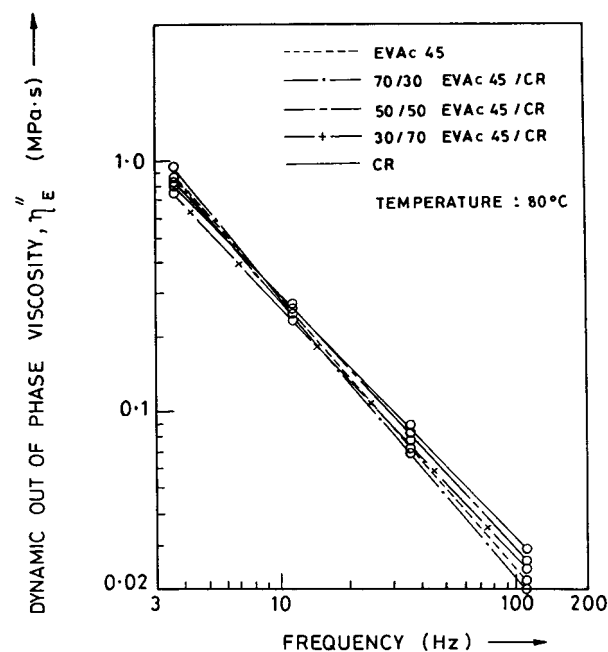


Figure 3 Variation of out-of-phase viscosity (η_E'') with frequency at the temperature of 80°C.

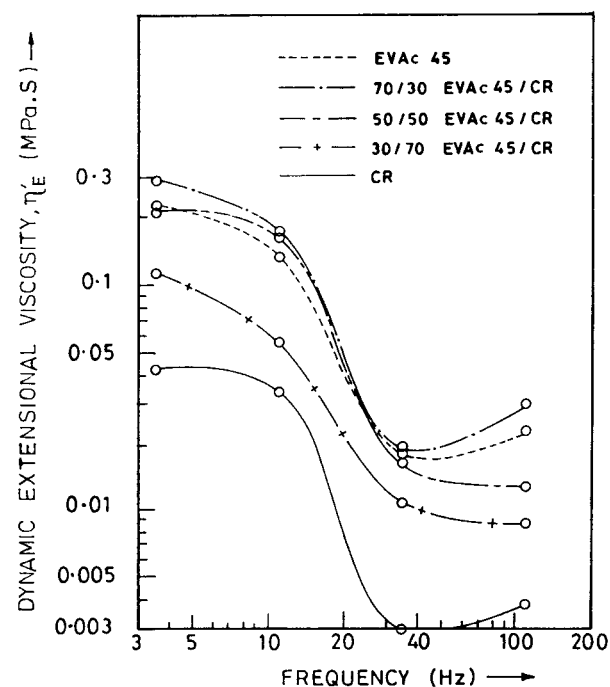


Figure 4 Variation of dynamic elongational viscosity (η_E') with frequency at the temperature of 80°C.

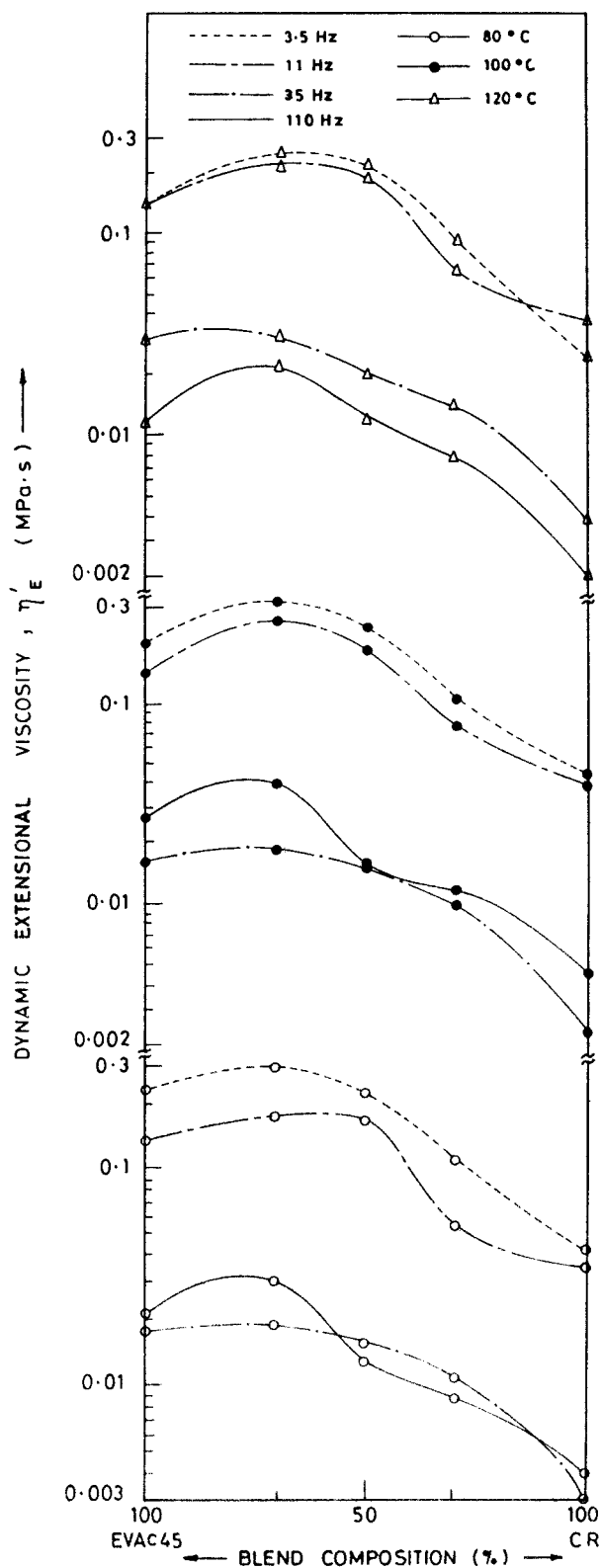


Figure 5 Variation of dynamic elongational viscosity with wt % CR content in EVAc-45/CR blend at the temperatures of 80, 100, and 120°C and the frequencies of 3.5, 11, 35, and 110 Hz.

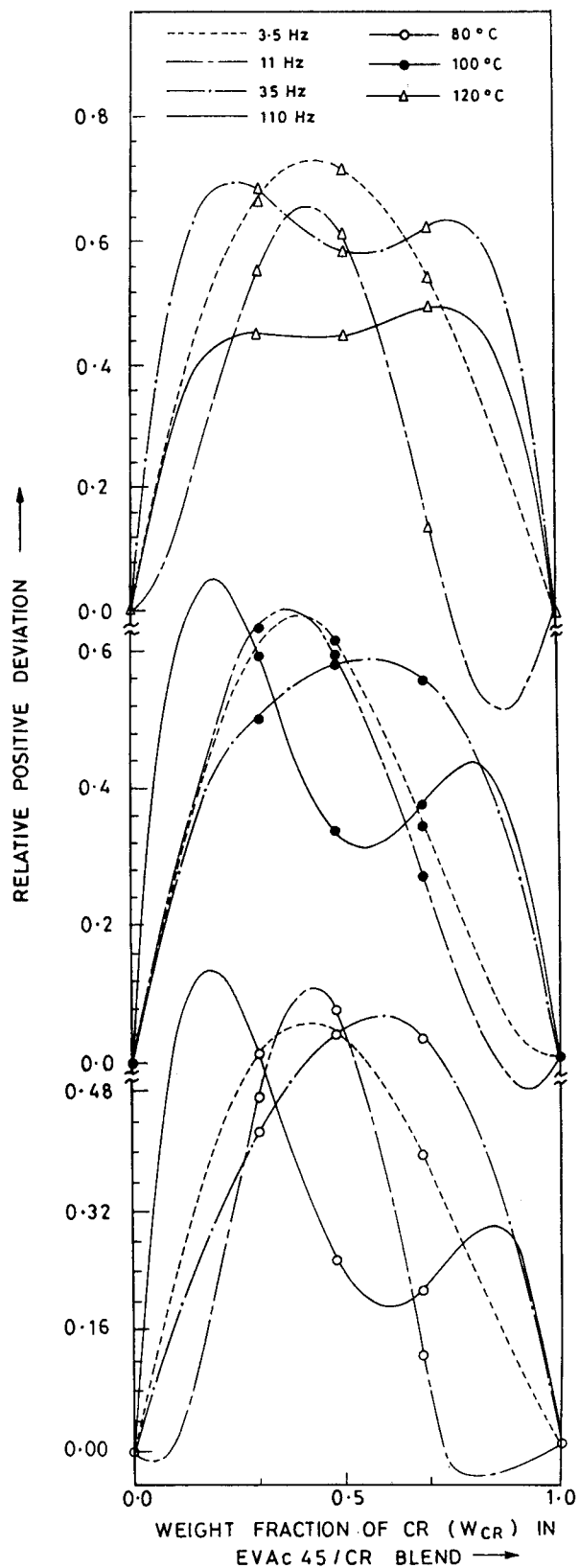


Figure 6 Variation of RPD of dynamic elongational viscosity with weight fraction of CR in the EVAc-45-CR blends at the frequencies of 3.5 and 35 Hz.

Table IV Polynomial Constants

Temp (°C)	Frequency (Hz)	Polynomial Constants			
		C ₁	C ₂	C ₃	C ₄
80	110	8.24	-33.77	47.38	-21.84
80	35	1.81	-1.54	0.92	-1.20
80	11	-1.72	22.73	-46.82	25.82
80	3.5	2.71	-2.85	-1.53	1.67
100	110	8.86	-36.11	51.63	-24.38
100	35	3.39	-8.48	10.85	-5.76
100	11	2.85	-0.23	-9.64	7.02
100	3.5	2.73	-0.83	-6.80	4.89
120	110	4.43	-15.53	22.76	-11.67
120	35	7.55	-27.72	39.67	-19.50
120	11	0.002	14.60	-34.03	19.43
120	3.5	3.60	-5.06	1.45	—

tions of blend composition, and they can be fitted into a fifth-order polynomial equation, except for η_a at 100°C for all shear rates and η'_E at 11 Hz for all temperatures. RPD in capillary flow is maximum for the 50/50 blend at 100°C and for the 30/70 blend at 120°C; whereas, in dynamic flow, it is maximum for the 50/50 blend. Positive deviation in η_a and η'_E for the blends of EVAc-45 and CR indicates their compatibility in a rheological sense.

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