

Blends of Poly[ethylene(vinyl acetate)] and Polychloroprene: Studies on Capillary and Dynamic Flows

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SYNOPSIS

Rheological properties of the blends of poly[ethylene(vinylacetate)] (EVAc; vinylacetate content 28%) and polychloroprene (CR) have been measured through capillary and dynamic uniaxial elongational flows. Capillary flow indicates their shear thinning behavior. The decrease in the out of phase viscosities with increasing frequency is in accordance with the power law equation, whereas dynamic elongational viscosities follow nonlinear relationship in log-log plot with an initial increase at 11 Hz, followed by a very sharp drop. With an increase in temperature, the viscosity for capillary flow of all blends goes down due to their positive activation energy of flow but for dynamic elongational flow of EVAc blended with CR, viscosity increases, except for 30/70 blend and pure CR, in which case the dynamic elongational viscosity decreases with an increase in temperature. This abnormal behavior in dynamic elongational viscosity is due to the process of melting and recrystallization of EVAc at low heating rate (1°C/min) beyond the melting temperature. Capillary viscosities of all blends show positive deviation from the log additive values of pure polymers. But in the case of dynamic elongational flow, all blends show positive deviation at frequencies of 3.5 and 35 Hz and at higher temperatures (80–120°C). © 1997 John Wiley & Sons, Inc.

INTRODUCTION

As polymer blends find increasing industrial applications, the study of their rheological properties has gained considerable importance. In a blend, the two polymers may either be thermodynamically miscible or immiscible, 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.¹ It is expected that the density will increase on mixing leading to the positive deviation in the rheological functions.²

Viscosity of polymeric blends follow the log-additivity rule²⁻³:

$$\log \eta_B = \sum w_i \log \eta_i \quad (1)$$

where η_i and η_B are the true viscosity of *i*th component and its blend, respectively, and w_i is the weight fraction of *i*th component. It is reported⁴⁻⁹

that the miscible blends leading to positive deviation in rheological properties, such as viscosity, die swell, etc., are called positively deviating blends (PDB). In the case of immiscible blends,¹⁰⁻¹⁵ rheological properties generally show negative deviation from their additive values. These are termed as negatively deviating blends (NDB).

Viscosity is a function of temperature that follows the Arrhenius-type relation¹⁶

$$\eta = A \cdot e^{E_a/RT} \quad (2)$$

where *A* is the proportionality constant; E_a , the activation energy of flow; *T*, the temperature of the material; and *R*, the universal gas constant.

We have already reported¹⁷ that the blends of poly[ethylene(vinylacetate)] (EVAc having VAc content 28%) and polychloroprene (CR) are miscible in all blend compositions. The polar-polar interaction between the two components is the main reason for their miscibility.¹⁸ The aim of the present paper is to investigate the effect of blend compositions, temperature, and strain rate on the rheological

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Table I Blend Composition in Weight Percent

Blend Code	A	B	C	D	E
EVAc-28 ^a	100	70	50	30	0
CR ^b	0	30	50	70	100

^a PILENE-2806; VAc content, 28%; sp. gravity, 0.95; producer, Polyolefin Industries Ltd., India.

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

parameters of the blends of EVAc and CR under capillary and dynamic flow.

EXPERIMENTAL

The polymers were mixed in a Brabender Plastocorder (PLE-330) as per the formulations given in Table I. Thermoplastic EVAc was first melted 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 Processibility Tester (MPT 83077) using a fixed die (length/diameter = 30/1 with multiple cone angle entry of 45 and 60 degrees) 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 to 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.

RESULTS AND DISCUSSION

Capillary Flow

From the experimental data, the wall shear stress (τ_w) and shear rate ($\dot{\gamma}_{wa}$) are calculated using stan-

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	0.20	164.9	0.28	169.3	0.37	27.7
B	0.21	152.1	0.33	44.7	0.33	39.8
C	0.21	155.7	0.29	65.1	0.31	48.4
D	0.21	163.7	0.27	79.7	0.28	67.4
E	0.15	225.1	0.11	257.6	0.07	279.6

dard rheological equations.¹⁹ From their linear plot in log-log scale (not shown here), one can get the slope (n') and intercept (K'), which are given in

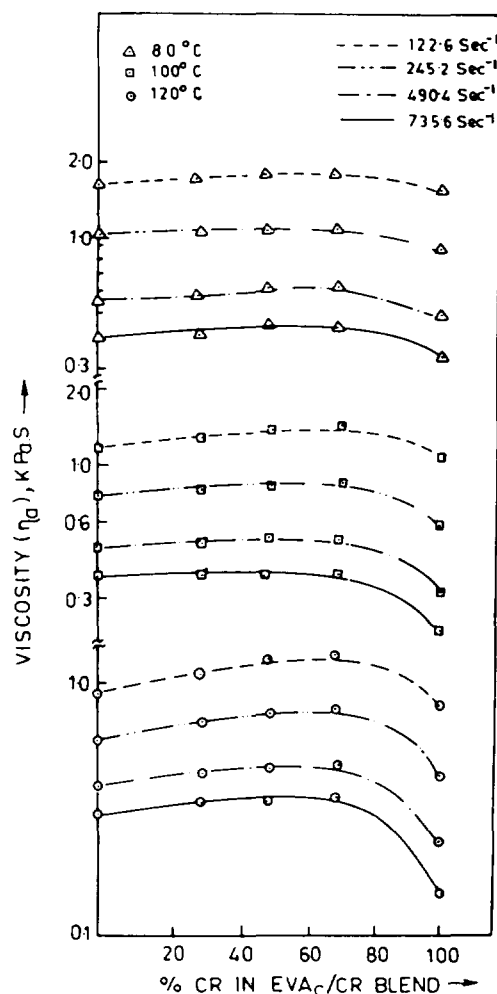


Figure 1 Variation of viscosity with %CR content in EVAc/CR blends at the temperatures of 80, 100, and 120°C and shear rates of 122.6, 245.2, 490.4, 735.6 s⁻¹.

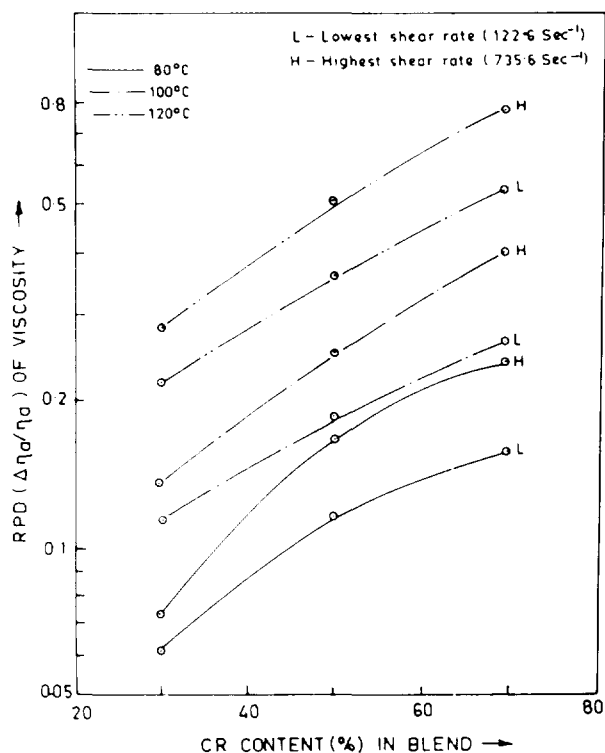


Figure 2 Variation of relative positive deviation (RPD) of viscosity with CR content in EVA_c/CR blends at the lowest (122.6 s⁻¹) and highest (735.6 s⁻¹) shear rates.

Table II. 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 equation. For all blends, $n' < 1$, which indicates pseudoplastic or shear thinning nature of the blends. By applying Rabinowitsch correction, true wall shear rate $\dot{\gamma}_w$ and, hence, apparent viscosity η_a are calculated.

The plots of viscosity versus blend composition at 80, 100, and 120°C and at different rates of shear are shown in Figure 1. At all temperatures and shear rates, the EVA_c-CR blends show positive deviation from their additivity values [eq. (1)] because of the

Table III A_1 and B_1 Values*

Temperature (°C)	Shear Rate ($\dot{\gamma}_w$)			
	122.6 s ⁻¹		735.6 s ⁻¹	
	A_1	B_1	A_1	B_1
80	0.023	0.032	0.029	0.033
100	0.021	0.062	0.028	0.061
120	0.023	0.112	0.026	0.133

* See eq. (5).

Table IV Activation Energy for Shear (η_a) and Dynamic Elongational (η_E) Viscosity

Blend Code	Activation Energy (E_a) in kJ/mol	
	η_a	η_E
A	16.32	-2.99
B	13.69	-4.49
C	12.73	-2.88
D	11.22	3.76
E	4.32	13.96

specific polar-polar interactions, which results in volume contraction of the system. The existence of the polar-polar interaction has been confirmed through Fourier transform infrared (FT IR) studies.¹⁸ The positive deviation $\Delta\eta_a$ due to blending is expressed as follows:

$$\Delta\eta_a = \eta_{a,exp} - \sum w_i \log \eta_i = \eta_{a,exp} - \eta_{a,add} \quad (3)$$

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

$$\frac{\Delta\eta_a}{\eta_{a,exp}} = 1 - \frac{\eta_{a,add}}{\eta_{a,exp}} \quad (4)$$

$\Delta\eta_a / \eta_{a,exp}$ can be defined as relative positive deviation (RPD).

The semilog variation of RPD with blend composition at 80, 100, and 120°C and at lowest and highest shear rates (122.6 and 745.6 sec⁻¹) are

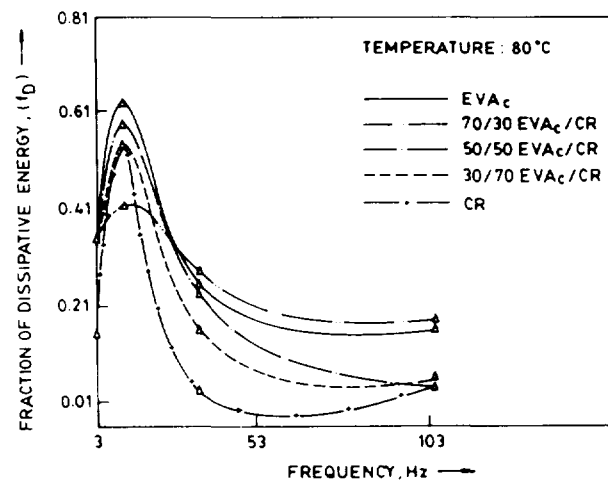


Figure 3 Variation of fraction of dissipative energy (f_d) with frequency (Hz) at the temperature of 80°C.

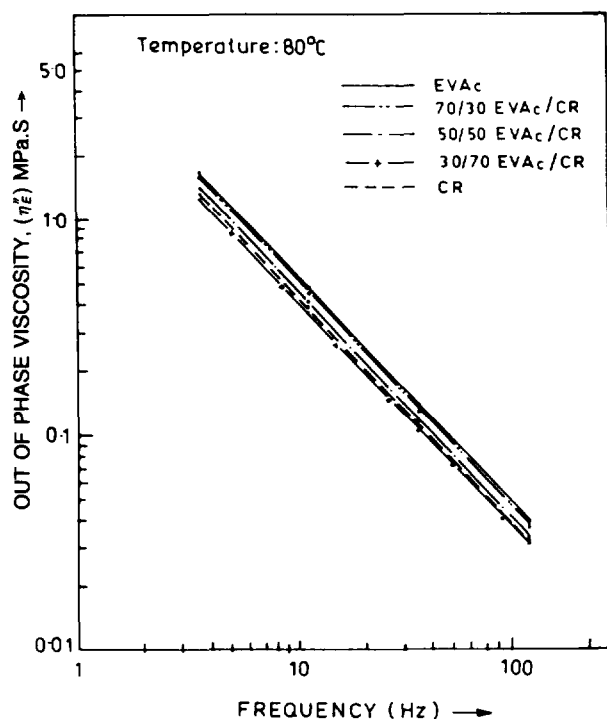


Figure 4 Variation of out-of-phase viscosity (η''_E) with frequency at the temperature of 80°C.

shown in Figure 2. At temperatures of 100 and 120°C, RPD increases with increase in CR content in the blends, which is represented in the form of the following empirical relationship:

$$\text{RPD} = B_1 e^{A_1 W_{CR}} \quad (5)$$

where W_{CR} is the content of CR in the blends in wt %, and A_1 and B_1 are constants given in Table III.

Viscosity of all polymeric samples studied decreases with the temperature in accordance with eq. (2). The activation energy of flow E_a has been calculated from eq. (2) for EVAc, CR, and their blends and are reported in Table IV.

Dynamic Flow

The fraction of dissipative energy (f_D) at 80, 100, and 120°C is calculated from storage modulus (E') and loss modulus (E'').¹⁹ The variation of fraction of dissipative energy (f_D) at 80°C with frequency (ω) is shown in Figure 3. It is observed that f_D increases with frequency for all blends with a maximum at 11 Hz, beyond which it falls sharply. It may be hypothesized that the molecular segmental motion and imposed frequency of 11 Hz synchronize

Table V C_1 and d_1 Values at 80°C

Blend Code	d_1	C_1
A	1.086	64.94
B	1.099	54.54
C	1.082	63.03
D	1.079	51.04
E	1.064	49.03

to give enhanced intermolecular interaction, resulting in the maximum dissipation of energy.

The dynamic elongational viscosities (η'_E) and out of phase viscosities (η''_E) at 80, 100, and 120°C

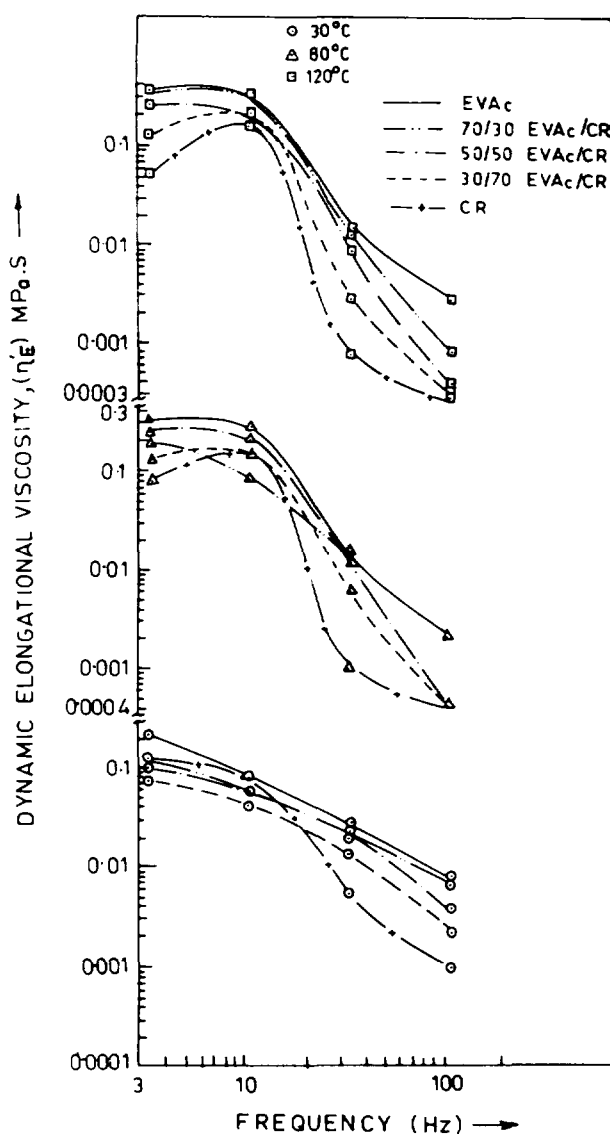


Figure 5 Variation of dynamic elongational viscosity (η'_E) with frequency at the temperatures of 30, 80, and 120°C.

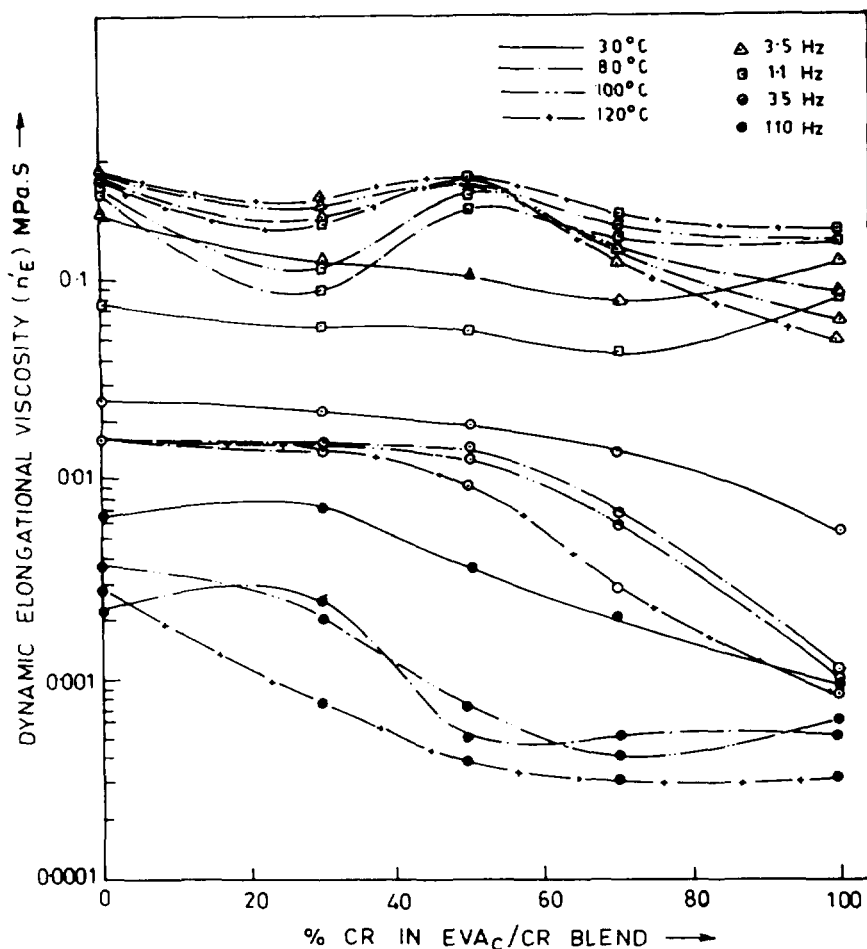


Figure 6 Variation of dynamic elongational viscosity with %CR content in EVA_c/CR blend at the temperatures of 30, 80, 100, and 120°C and the frequencies of 3.5, 11, 35, and 110 Hz.

are calculated from E'' and E' .¹⁹ The log-log variation of η''_E with frequency (ω) is shown in Figure 4. It decreases linearly with frequency in the log-log plot and follows a general relation, as follows:

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

where C_1 and d_1 are constants given in Table V.

The log-log variation of η'_E with frequency at 30, 80, and 120°C are shown in Figure 5. The variation of η'_E is similar to that of f_D showing weak maxima at 11 Hz, except at 30°C, where it gradually falls. This variation of the dynamic viscosity is in conformity with the variational dissipative energy. Thus, it can be said that 11 Hz frequency acts as a critical frequency where maximum viscous absorption is taking place and molecules reach their maximum excited state, which is in resemblance with

the temperature effect during any transitions (glass transition or crystalline melting).

The variation of η'_E with %CR in the blend at 30, 80, 100, and 120°C are shown in Figure 6. It is interesting to note that at a lower temperature (30°C), both higher frequencies of 35 and 110 Hz show positive deviation with respect to their additive values, whereas lower frequencies of 3.5 and 11 Hz show negative deviation. All the plots at 80, 100, and 120°C for 3.5 and 35 Hz frequencies shows positive deviation, whereas 11 Hz frequency shows negative-positive deviation. The plot for 110 Hz at 80°C shows positive-negative deviation; on the other hand, the plots at 120°C for 110 Hz show negative deviation throughout the entire blend composition.

In line with the definition of relative positive deviation (RPD) in shear viscosity, the RPD in dynamic elongational viscosity has been defined as follows:

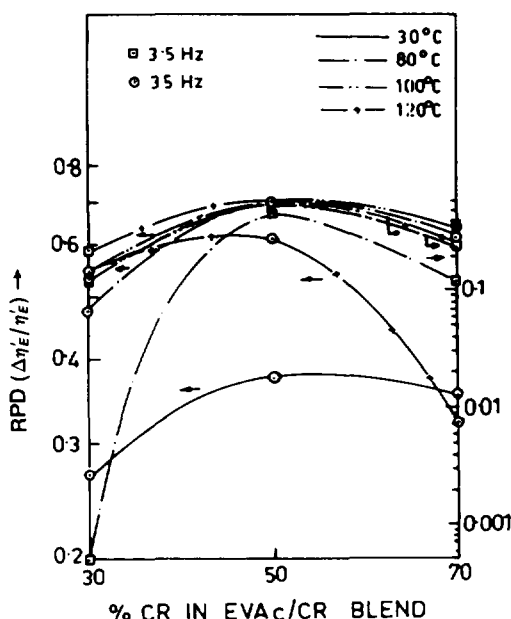


Figure 7 Variation of relative positive deviation (RPD) of dynamic elongational viscosity with %CR in EVAc/CR blends at the frequencies of 3.5 and 35 Hz.

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

The semilog variation of RPD with blend composition for 3.5 and 35 Hz frequencies at 80, 100, and 120°C are shown in Figure 7. RPD initially increases up to 50% CR in blends; then it decreases, giving a maximum value for the 50 : 50 blend, showing the maximum interaction or maximum compatibility between the two blend constituents.

The semilog plot of η'_E with inverse temperature in K^{-1} at 3.5 Hz is shown in Figure 8. With the lowering of temperature, the dynamic elongational viscosity (η'_E) decreases in case of EVAc and 50/50 and 70/30 EVAc/CR blends (negative slope); whereas for CR and the 30/70 EVAc/CR blend, it increases (positive slope). The activation energy calculated from the slopes of straight lines is reported in Table IV. The abnormal behavior of EVAc and its blends with CR can be explained by the process of melting and recrystallization of EVAc above 80°C.²⁰⁻²¹ It has already been reported in our earlier publication¹⁷ that at the high heating rate of 20°C, the DSC thermogram shows completion of melting of EVAc at around 75°C. But at the very low heating rate of 1°C/min used during dynamic measurements, the crystals of EVAc show extended melting above 80°C due to the process of recrystallization. This recrystallization effect is observed in all blends

of EVAc/CR, except that of 30/70, where crystallinity of EVAc goes down to a minimum.¹⁷ During this melting transition, the loss modulus and, hence, η'_E goes on increasing with increasing temperature, which leads to the negative values of activation energy for EVAc and 70/30 and 50/50 EVAc/CR blends. The positive activation energy for 30/70 EVAc/CR and CR is due to the absence of recrystallization effect.

CONCLUSION

It can be concluded that all the blends of EVAc and CR are pseudoplastic in nature, i.e., shear thinning of viscosity both in capillary and dynamic flow. The dynamic out-of-phase viscosity decreases linearly with frequency (log-log plot), whereas dynamic elongational viscosity shows non-linear variation due possibly to synchronization of molecular vibration with the applied frequency of 11 Hz. The activation energy of capillary flow of the blends has been calculated to be positive; whereas, in dynamic flow, it is found to be negative for EVAc and 70/30, 50/50 EVAc/CR blends and positive for the 30/70 blend and CR. All blends of EVAc/CR show positive deviation of viscosity in capillary flow. In the case of dynamic flow, dynamic elongational viscosity (η'_E) shows only positive deviation at higher temperatures (80–120°C) and 3.5 and 35 Hz frequencies. Whereas for other frequencies (11 and 110

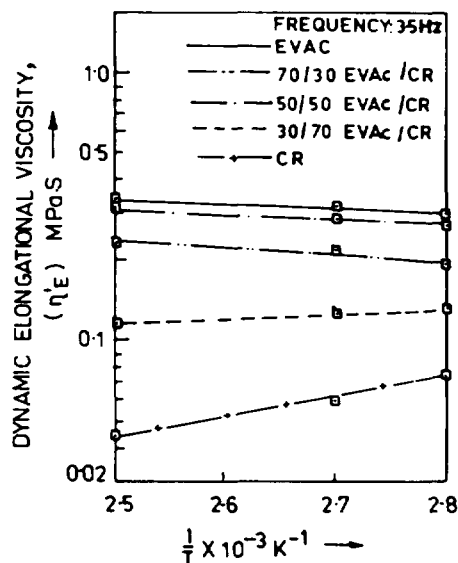


Figure 8 Variation of dynamic elongational viscosity with inverse temperature ($1/T$) in K^{-1} at the frequency of 3.5 Hz.

Hz), it shows positive deviation at 30°C and negative-positive deviation at higher (80–120°C) temperatures. Considering all the blends, relative positive deviation is higher for the 70/30 and 50/50 blends in case of capillary (η_a) and dynamic flows (η'_E), respectively.

One of the authors (P.P.K.) is grateful to Council for Scientific & Industrial Research for providing financial assistance to carry out this work.

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Received August 29, 1995

Accepted July 23, 1996