

Rheological properties of poly[ethylene co-(methylacrylate)], polychloroprene and their blends

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Rheological properties of blends of poly[ethylene-co-(methylacrylate)] (PEMA, methyl acrylate content 22%) and polychloroprene (CR) have been studied through capillary and dynamic elongational flow. Both capillary and dynamic out of phase viscosity (η'_{E}) decreases with increased shear rate and frequency in accordance with the power law. On the other hand dynamic extensional viscosity (η''_{E}) shows a non-linear relationship with frequency with an initial increase followed by a sharp drop at around 11 Hz. The positive activation energy of shear flow indicates lowering of viscosity at higher temperature. 30/70 and 70/30 PEMA/CR blends show maximum relative positive deviation (RPD) in case of shear and dynamic flow respectively. RPD increases linearly with shear rate for capillary flow whereas for dynamic flow, RPD shows non-linear relationship with frequency. The increase of RPD with temperature for both capillary and dynamic flows indicates better interaction between PEMA and CR in their blends. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymeric materials are viscoelastic materials i.e. the stress depends on the history of the deformation. Efficient production of polymeric products requires that fillers be easily incorporated into polymers and that the resulting compounds be smoothly extruded or calendered. The flow behaviour of a material can be studied by a power equation

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

where τ and $\dot{\gamma}$ are the true shear stress and shear rate, k is the consistency index and n the flow behaviour index. When $n = 1$, the material behaviour is Newtonian ($\tau \propto \dot{\gamma}$). For non-Newtonian system, when $n > 1$, the material is shear thickening (dilatant) as the viscosity (η) increases with $\dot{\gamma}$ and when $n < 1$, it is called shear thinning (pseudoplastic) material i.e. η decreases with $\dot{\gamma}$. Almost all polymeric systems are pseudoplastic in nature.

Polymeric blends now find wide application in industry because of their superior properties compared to the constituent polymers. 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 negative heat of mixing¹. The problems associated during processing of polymers and their blends can be studied through rheological properties.

Viscosity of polymeric blends followed by log-additivity rule^{2,3} is given by:

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

where η_i and η_B , are the true viscosity of the i -th component and its blend and w_i , the weight fraction of the i -th component. It is reported^{4,5} that the miscible blends

having positive deviation from their additive values of rheological properties such as viscosity, die swell etc. are called positively deviating blends (PDB). In case of immiscible blends^{6,7}, generally rheological properties show negative deviation from their additive values. Such blends are called negatively deviating blends (NDB).

Study of the temperature dependence of viscosity of polymers help in understanding the mechanism of their flow process and in elucidation of the structural relationship of the polymers and their behaviour on deformations. The temperature dependence of the viscosity of polymers has a substantial effect on their processability since the sensitivity of viscosity towards a change in temperature governs the choice of the processing conditions.

Arrhenius, Frenkel and Eyring proposed a mathematical relation for the temperature dependence of viscosity (η)⁸:

$$\eta = A \cdot e^{E_a/RT} \quad (3)$$

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

We have already reported that the blends of poly[ethylene co-(methylacrylate)] (PEMA having methylacrylate content 21%) and polychloroprene are miscible in all blend composition⁹. The polar-polar interaction between the two components is the main reason for their miscibility⁹. The aim of the present paper is to investigate the effect of blend compositions, temperature and strain rate on the rheological parameters of the blends of PEMA and CR under capillary and dynamic flow.

EXPERIMENTAL

Sample preparation

The polymers were mixed as per the formulations given in Table 1 in a Brabender Plasticorder (PLE-330).

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Table 1 Blend composition

Component	A	B	C	D	E
PEMA (Wt. %)	100	70	50	30	0
CR (Wt. %)	0	30	50	70	100

Poly[ethylene co-(methylacrylate)], methylacrylate content 22 wt%, density = 940 kg.m, melting point = 81 C, Producer: Exxon Chemicals, U.S.A.

Neoprene WM1, Sp. gravity: 1.23, Producer: Dupont, U.S.A.

Thermoplastic PEMA was first melted at 100°C and at 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 at 100 rpm to get a homogeneous mix.

Rheological properties were studied with the help of a Monsanto Processibility Tester (MPT 83077) using a fixed die (Diameter = 1 mm, Length/Diameter = 30/1 and multiple cone angle entry of 45° and 60°) and at piston speeds of 0.042, 0.085, 0.169 and 0.254 mm/sec. 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/sec and extruded at different rates of shear (in the range of 100–750 sec) and temperatures of 80, 100 and 120°C in a programmed way using a microprocessor.

A dynamic viscoelastometer (Rheovibron, DDV-111-EP) of Orientec Corporation, Japan was used for measurement of dynamic flow of the polymers and their blends under tension mode. 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 with a temperature range of 20–200°C. As the uncured samples cannot withstand high temperatures 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.

THEORY

Monsanto Processibility Tester is a high pressure capillary rheometer, the basic principle of which is to correlate the pressure loss during the extrusion through a capillary tube with wall shear stress and the volumetric flow rate to the rate of shear at the wall.

The apparent wall shear rate and shear stress can be estimated from the knowledge of the barrel diameter, piston speed, capillary length and diameter and pressure at the inlet of the capillary. These are expressed as:

$$\tau_w = \frac{d_c \Delta P}{4l_c} \tag{4}$$

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

The true wall shear rate is obtained by applying Rabinowitsch correction:

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

where τ_w is the shear stress at the wall; d_c , capillary diameter; l_c , capillary length; ΔP , 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 material; γ_w , true rate of shear at wall. $n' + \frac{d \ln \tau_w}{d \ln \dot{\gamma}_{wa}}$ = slope of the line obtained by plotting $\ln \tau_w$ vs $\ln \dot{\gamma}_w$

Dies of very low diameter (1 mm) with their 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, τ_w , as given by equation (4), can be considered as the true shear stress. Also high L/D dies are usually preferred for viscosity measurements, since Bagley correction is smaller. As the L/D ratio of the die used is 30:1 (dia. 1 mm), the correction is negligible¹⁰. The apparent shear viscosity is given by:

$$\eta_a = \tau_w / \dot{\gamma}_w \tag{7}$$

The shear stress and shear rate can be correlated by the power law model (equation (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 of the deforming frequency has two components. One part, which causes flow of the material and is dissipated as heat is defined as dissipative energy (W_D) per unit volume and is related to E'' as¹¹:

$$W_D = \gamma_0^2 \cdot \omega \cdot E'' / 2 \tag{8}$$

where γ_0 is the strain amplitude of the input frequency, ω . The other part of the input energy is stored in the material in the 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:

$$W_s = \gamma_0^2 \cdot E' \cdot \omega / 2\pi \tag{9}$$

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

$$f_D = W_D / (W_s + W_D) \tag{10}$$

In line with the definition of dynamic viscosity the dynamic extensional viscosity¹² (η_E') and out of phase extensional viscosity (η_E'') are defined as:

$$\eta_E' = E' / \omega \text{ and } \eta_E'' = E'' / \omega \tag{11}$$

RESULTS AND DISCUSSIONS

Capillary flow

Wall shear stress (τ_w) and shear rate ($\dot{\gamma}_{wa}$) are calculated from experimental data using a statistical method. From their linear plot in log–log scale, we can get slope (n') and intercept (k' at $\dot{\gamma}_{wa} = 1 \text{ sec}^{-1}$) which are given in Table 2. The raw data error in log of shear stress is also given in Table 2 as standard deviation (SD). It is found that the SD values are within the range of 5% of original values. The value of n' is found to be constant over the range of $\dot{\gamma}_{wa}$ studied (122.6–735.6 sec^{-1}), and hence, it can be taken as the flow behaviour index, n , in the power law (equation (1)).

Table 2 Flow behaviour index (n'), consistency index (k') and standard deviation (SD)

Blend code	Temperatures of								
	80°C			100°C			120°C		
	n'	k'	SD	n'	k'	SD	n'	k'	SD
A	0.22	130.7	0.148	0.35	33.4	0.243	0.40	20.2	0.272
B	0.22	128.3	0.150	0.33	42.4	0.225	0.37	26.8	0.252
C	0.25	114.1	0.168	0.30	56.0	0.204	0.34	35.4	0.229
D	0.24	128.5	0.163	0.27	73.2	0.183	0.31	49.3	0.210
E	0.15	225.1	0.102	0.11	257.6	0.075	0.07	279.6	0.050

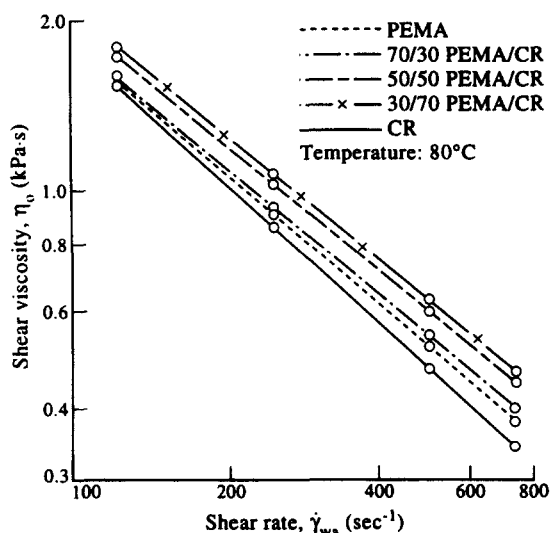


Figure 1 Variation of shear viscosity, η_a with shear rate, $\dot{\gamma}_{wa}$ at a temperature of 80°C.

For all blends with $n' < 1$ pseudoplastic or shear thinning nature of blend is indicated. The intercept gives consistency index, k' of the fluid, and η_a values are calculated using equations (6) and (7).

The viscosity, η_a is plotted against rate of shear, $\dot{\gamma}_{wa}$ at 80°C on a log–log scale in *Figure 1*. Viscosity decreases with increase in shear rate. This is due to the shear thinning or pseudoplastic behaviour of the systems. The flow process requires a certain activation energy which aligns the macromolecules in the direction of applied shearing force. The activation energy in terms of shearing energy is lower at low shear rate and higher at high shear rate which leads to higher and lower viscosity of the macromolecules. The viscosities of the pure components (PEMA and CR) are lower than that of the blends at a particular rate of shear. Amongst the blends the viscosity increases with increase in CR content. The plots show the relationship of η_a with $\dot{\gamma}_{wa}$:

$$\eta_a = A' \cdot \dot{\gamma}_{wa}^{n'-1} \quad (12)$$

where $n' - 1$ and A' are constants which are functions of the blend composition (*Table 2*). A' is related to k' as:

$$k' = A'(3n' + 1)/4n' \quad (13)$$

equations (12) and (13) also hold good at higher temperatures (100 and 120°C).

The plots of η_a , versus blend composition (weight fraction) at 80, 100 and 120°C and at all shear rates are shown in *Figure 2*. All the blends show positive deviation in η_a from their log additive values (equation (2)) at all temperatures and shear rates. The blends of PEMA and CR are miscible at all compositions due to the specific interactions (polar–polar)⁹ which results in some volume contraction during their mixing process leading to positive deviation in viscosity².

The positive deviation $\Delta\eta_a$ due to blending is expressed as:

$$\Delta\eta_a = \eta_{a, \text{Exp}} - \eta_{a, \text{add}} \quad (14)$$

where $\eta_{a, \text{Exp}}$ is the apparent viscosity of the blend calculated from experimental measurements and $\eta_{a, \text{add}}$ is its log additive value. $\Delta\eta_a/\eta_{a, \text{Exp}}$ can be calculated from equation (14) and is defined as relative positive deviation (RPD).

The variation of RPD with shear rate at 80, 100 and 120°C are shown in *Figure 3* in the log–log scale. RPD shows

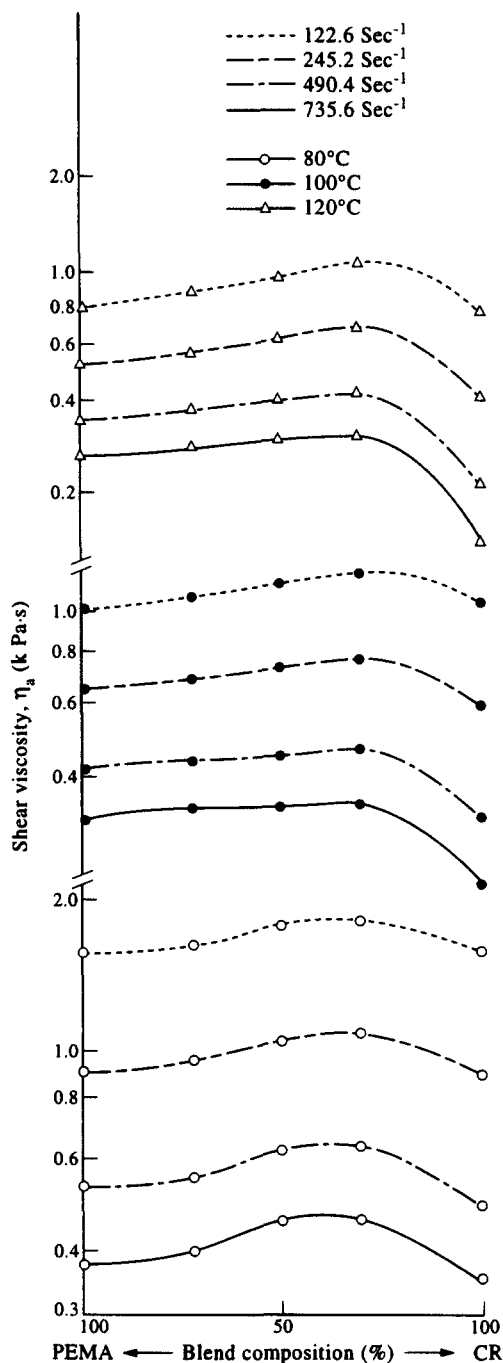


Figure 2 Variation of shear viscosity, η_a with % blend compositions at temperatures of 80, 100 and 120°C and shear rates of 122.6, 245.2, 490.4 and 735.6 sec^{-1}

linear increase with increase in $\dot{\gamma}_{wa}$ and can be co-related in the following equation.

$$\text{RPD} = B_1 \gamma_{wa}^{A_1} \quad (15)$$

where A_1 and B_1 are constants given in *Table 3*.

Figure 4 shows the semi-log plot of viscosity with inverse temperature for all blends at lowest and highest shear rates. Viscosity decreases linearly with increase in temperature and follows Arrhenius, Frenkel and Eyring equation (equation (3)). From the slope of the lines, the activation energy of flow, E_a has been calculated using equation (3) for PEMA and its blends. The calculated values of E_a are 19.5, 16.9, 14.2, 4.2 and 9.9, 9.2, 12.2, 10.5, 3.9 corresponding to the shear rate of 122.6 and 735.6 sec^{-1} for PEMA, 70/30, 50/50, 30/70 PEMA/CR blends and CR. The blends show

Table 3 Values of constants A_1 and B_1 (equation (15))

Temperature	Blend code	A_1	B_1
80°C	B	0.521	0.003
	C	0.338	0.024
	D	0.330	0.027
100°C	B	0.409	0.010
	C	0.362	0.020
	D	0.316	0.036
120°C	B	0.320	0.028
	C	0.266	0.062
	D	0.224	0.105

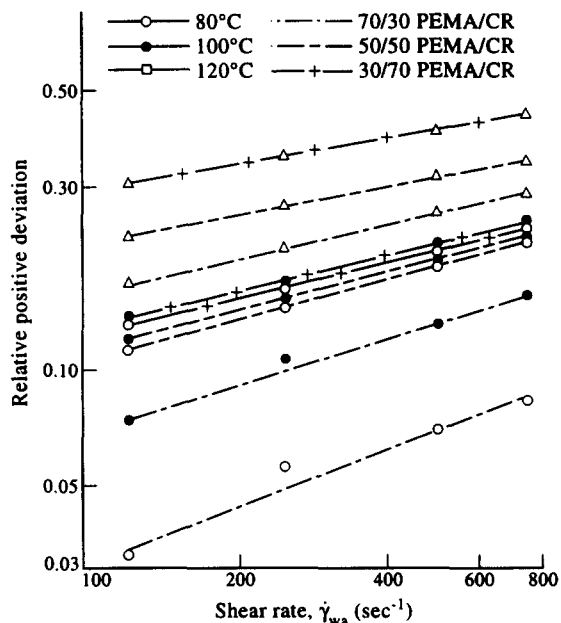


Figure 3 Variation of relative positive deviation (RPD) with rate of shear, $\dot{\gamma}_{wa}$ at temperatures of 80, 100 and 120°C for 70/30, 50/50 and 30/70 PEMA/CR blends.

much higher activation energy compared to their additive values.

Dynamic flow

The dynamic extensional viscosity (η_E') and the out of phase viscosities (η_E'') are calculated from E'' and E' (equation (11)) at 80, 100 and 120°C. Fraction of dissipative energy (f_D) at 80, 100 and 120°C are calculated from equation (10). The log-log variation of dynamic out of phase viscosity (η_E'') and frequency (ω) is shown in Figure 5. η_E'' decreases linearly with frequency and follows a general relationship as in the case of shear viscosity and shear rate:

$$\eta_E'' = c_1 \cdot \omega^{-d_1} \tag{16}$$

where c_1 and d_1 are constants whose values at 80°C are reported as: 0.990, 0.955, 0.960, 1.004 and 2.045, 2.181, 2.438, 2.185, 2.995 for PEMA; 70/30, 50/50, 30/70 PEMA/CR blends and CR.

The log-log plots of dynamic extensional viscosity (η_E'), $\tan \delta$ and fraction of dissipative energy with frequency for all samples at 80°C are shown in Figure 6. Trends in the variation of η_E' with ω for the blends vary from that of the pure polymers. For blends, η_E' decreases with frequency, the decrease being more prominent at around 11 Hz. With

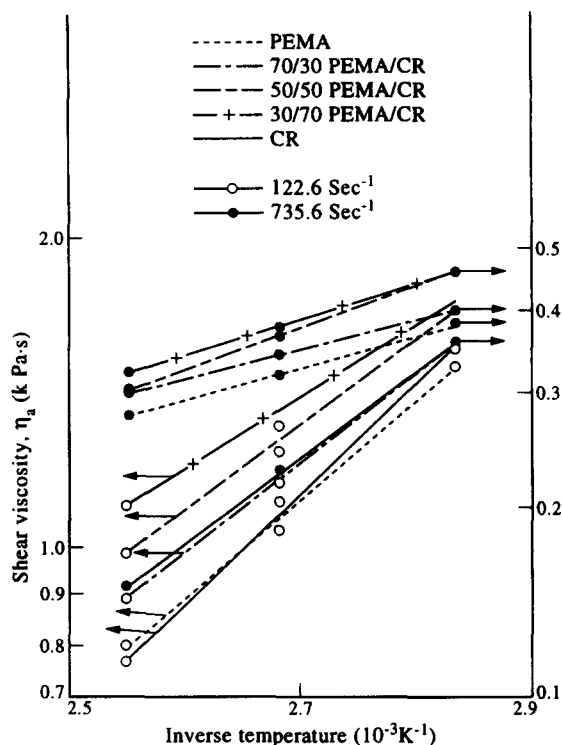


Figure 4 Variation of shear viscosity, η_a with inverse temperature (K^{-1}) at lowest (122.6 sec^{-1}) and highest (735.6 sec^{-1}) shear rates.

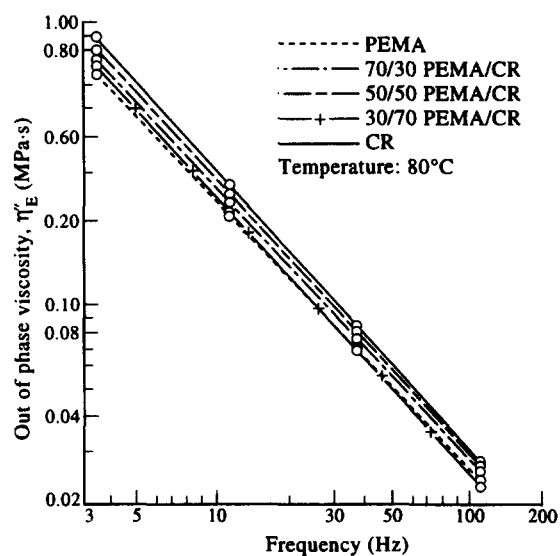


Figure 5 Variation of dynamic out of phase viscosity (η_E'') with frequency at a temperature of 80°C.

increase in frequency, PEMA shows almost a linear decrease in η_E' whereas CR shows drastic fall between 11 to 35 Hz beyond which η_E' increases. Plots for f_D and $\tan \delta$ show a clear peak (maximum) at 11 Hz for all samples except for pure PEMA. These indicate that higher fraction of input energy is lost as dissipative energy at 11 Hz compared to other frequencies except for PEMA which shows minimum loss in energy at this frequency. At 11 Hz frequency, it may be hypothesised that the molecular segmental motion and imposed frequency synchronises to give enhanced intermolecular interaction resulting in the maximum dissipation of energy. The behaviour of pure PEMA is opposite to CR and its blends with PEMA particularly at 11 Hz frequency. The trends in the variation

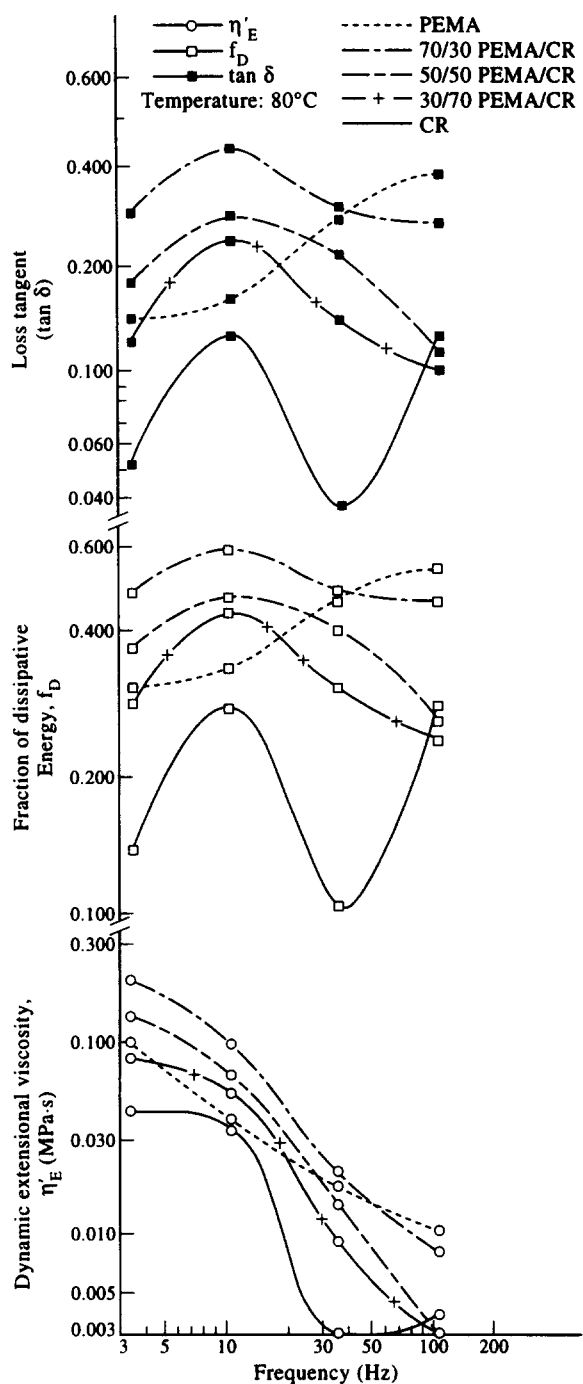


Figure 6 Variation of dynamic extensional viscosity (η_E'), fraction of dissipative energy (f_D), and $\tan \delta$ with frequency at a temperature of 80°C.

of η_E'' , $\tan \delta$ and f_D with frequency remains almost unaltered at other temperatures (100 and 120°C). At higher temperatures, the rate of fall of η_E' at 11 Hz becomes higher and the peaks become more prominent.

The variation of η_E' with weight percent of CR in PEMA/CR blends at 80, 100 and 120°C are shown in *Figure 7* for all frequencies. Positive deviation in η_E' is observed for all blends with respect to their additive values at all temperatures and frequencies except at 110 Hz where positive–negative deviation is observed. The negative deviation of the blends containing more than 50% CR at 110 Hz frequency may be due to intermolecular slippage occurring at this higher frequency. The positive deviating character of the blends at lower strain rate (frequency) confirms the finding at higher strain rate (shear rate) for capillary flow.

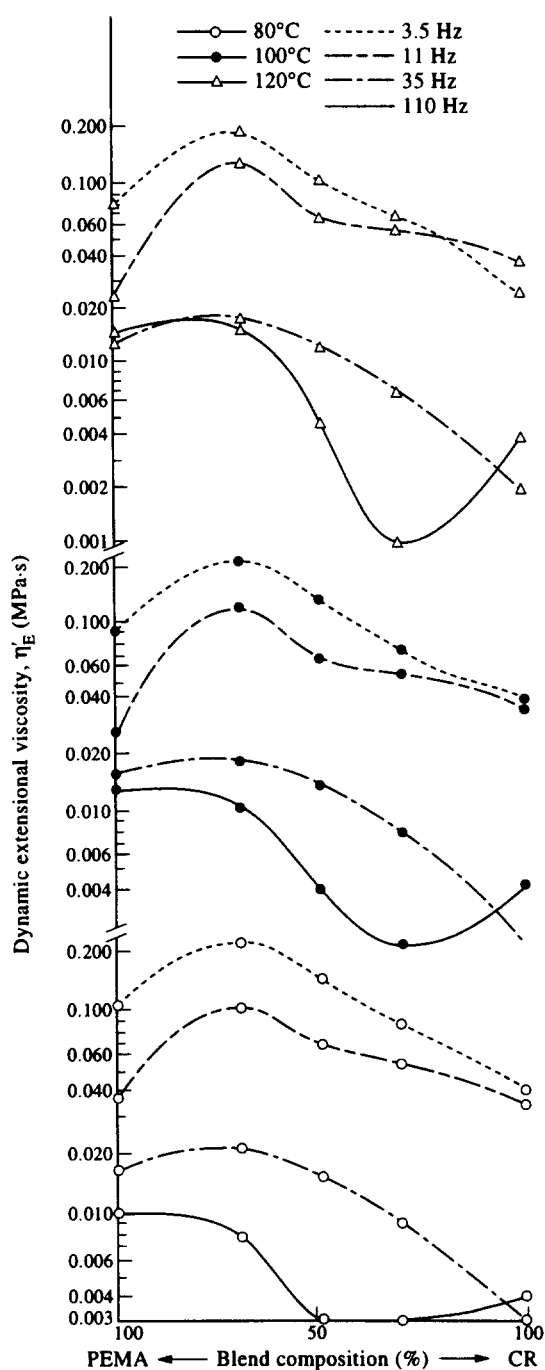


Figure 7 Variation of dynamic extensional viscosity (η_E') with % blend composition at temperatures of 80, 100 and 120°C and frequencies of 3.5, 11, 35 and 110 Hz.

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

$$\Delta\eta_E'/\eta_E' = (\eta_E' - \eta_{E,\text{add.}}')/\eta_E' \quad (17)$$

Figure 8 shows the variation of RPD with frequency at temperatures of 80, 100 and 120°C. Both 30/70 and 50/50 blend shows decrease in RPD with increasing frequency except for 30/70 both at 100°C which shows increasing trend in RPD. 70/30 blend shows initial increase in RPD in the region of 3.5–11 Hz frequency beyond which the trend is reversed.

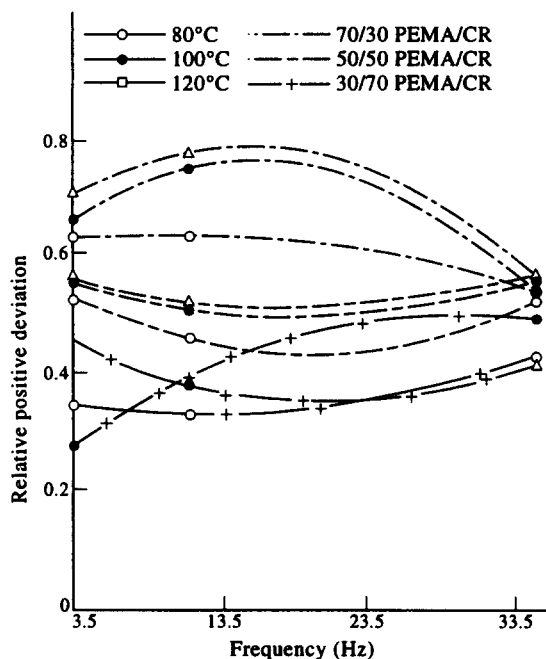


Figure 8 Variation of relative positive deviation (RPD) with frequency at temperatures of 80, 100 and 120°C for 70/30, 50/50 and 30/70 PEMA/CR blends.

CONCLUSIONS

From the above studies, it can be concluded that all blends of PEMA and CR are pseudoplastic in nature i.e. their viscosities are shear thinning both under capillary and dynamic shear. Both capillary and dynamic out of phase viscosities decrease with increase in shear rate and frequency. The individual polymers and their blends flow in the capillary with a positive activation energy and thus viscoisty decreases with increase in temperature. All the blends of PEMA/CR show positive deviation of viscosity

both in capillary and dynamic flows at all temperatures and strain rates except for higher frequency (110 Hz) in dynamic flow. Relative positive deviation (RPD) is maximum for 30/70 and 70/30 PEMA/CR blends in case of shear and dynamic extensional viscosities respectively. RPD of blends in capillary flow increases linearly with increasing rate of shear whereas in case of dynamic flow, RPD shows non-linear relationship with frequency due to the synchronisation of molecular vibration at around 11 Hz. The increase in RPD with increasing temperature for both capillary and dynamic flow indicates better interaction between the blended components at higher temperatures.

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