Studies on Miscibility of Blends of Poly (Ethylene Acrylic Acid) and Ethylene-*co*-Vinyl Acetate by Melt Rheology

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ABSTRACT: Rheological behavior of blends of poly (ethylene-acrylic acid) (EAA) and ethylene vinyl acetate (EVA) copolymer have been carried out at various temperatures, namely, 100, 110, and 120°C, and different shear rates from 61.33 to 613.30 s^{-1} using a Monsanto Processability Tester. The melt viscosity of the blends shows synergism during processing. The activation energy of the blends is in the range 20.7–44.6 kJ/mol. Highest activation energy was observed for the blends containing 40–60% of EVA by weight. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1947–1954, 2005

Key words: blend; EAA; EVA; melt rheology; miscibility

INTRODUCTION

In recent years polymer blends have gained considerable attention due to their cost effectiveness and the relative ease with which new tailor-made materials can be produced to meet specific applications. Extensive studies on the miscibility of polymer blends by different techniques have been reported earlier by several researchers.[1–8] The miscibility has been attributed to either specific interaction or chemical reaction between the blend constituents causing an increase in density of the blend above that calculated from the additivity rule. In most of the cases, this has been reflected in the rheological response of the blends, showing a higher melt viscosity as compared to that obtained by the log-additivity rule.

Uttracki and Kamal[9] have reviewed in detail the subject of melt rheology of polymer blends and have compared the rheological properties of polymer blends with those of emulsions, block copolymers, and homologous polymer blends. They have been able to categorize the polymer blends into three groups, namely: (i) positively deviated blends (PDB), that is, those having higher value of viscosity than that predicted by the log additivity rule; (ii) negatively deviated blends (NDB), that is, those having a lower value of viscosity than that predicted by the log additivity rule; and (iii) positive-negative deviation blends (PNDB), that is, those where both these characteristics are present.

Nando et al.[10,11] have demonstrated that the blends of EMA/PDMS are miscible throughout the composition range. This miscibility has been assigned to the chemical reaction between PDMS and EMA. Blends of EVA are extensively used in packaging industries because of its easy availability, processability, and excellent optical and physicomechanical properties. Lee et al.[12] have investigated the miscibility of LDPE/LLDPE blends. Recently, Song and Baker[13] reported the *in situ* compatibilization of PS/PE blends using amino methacrylate-grafted polyethylene as the compatibilizer. Nando et al.[14] also investigated the *in situ* compatibilization of EVA/PDMS using EMA copolymer as a compatibilizer.

Normally, shear rates encountered in a Brabender Plasticorder range from 10 to 100 s^{-1}. Many of the processing operations[15] involving polymer melts, such as extrusion and injection molding, encompass a much higher shear rate ranging from 100 to 10,000 s^{-1}. Hence, to make reasonable and valid predictions on the processability of these materials on the aforesaid equipment, it is absolutely essential to carry out the tests under similar conditions of shear rate and temperature as those of production machines. Capillary rheometers, such as the Instron capillary rheometer and the Monsanto Processability Tester (MPT), have been found to be highly useful in this regard.[13–21] Since both EAA and EVA are polar polymers, we expected some kind of chemical interactions that would influence the mechanical performance. From a thorough literature survey, it was noticed that there was no report on the blends of these. In the present work, the melt rheological characteristics of poly (ethylene acrylic acid) (EAA) and ethylene-*co*-vinyl acetate (EVA) blends have been studied using a Monsanto

Processability Tester under various shear rates (61.33 to 613.30 s^{-1}) and at three different temperatures, namely, 100, 110, and 120°C. The present work is an attempt to correlate the melt viscosity of the EAA/EVA blends with their miscibility characteristics.

EXPERIMENTAL

Materials

Poly (ethylene acrylic acid) copolymer (EAA) (Escor 5001) was supplied by M/s Exxon Chemicals Eastern Inc., Mumbai, India, with the following specifications: acrylic acid content 6.2 wt %, density 0.931 g/cc, MFI 2 g/10 min, and mp 99 to 100°C. Ethylene vinyl acetate (EVA) copolymer was obtained from Polyolefin Industries Ltd., India, with the specifications: vinyl acetate content 18%, MFI 2 g/min, density 0.937 g/cc, tensile strength 14 MPa, percentage elongation 780, and surface hardness 92 shore A.

Preparation of the blend

Melt blending of the constituents in various proportions was carried out in a Brabender Plasticorder (mold PLE-330) at 150°C with 80 rpm rotor speed and for 6 min. The molten mass was then taken out from the plasticorder and sheeted out immediately in a laboratory open two-roll mixing mill (150 mm × 300 mm) at room temperature.

Measurement of flow properties

The rheological characteristics were measured on a Monsanto Processability Tester (MPT), which is a micro-processor-controlled programmable capillary rheometer having an L/D ratio of 20. The extrusion studies were carried out at three different temperatures (100, 110, and 120°C) and at four different shear rates (61.33, 122.66, 245.32, and 613.3 s^{-1}).

The apparent shear rate (γ_a), apparent shear stress (τ_a), and apparent viscosity (η_a) were calculated using the following relations:

$$\gamma_a = 32Q/\pi d_c^3 \qquad (1)$$

$$\tau_a = \Delta P/4(L_c/d_c) \qquad (2)$$

$$\eta_a = \tau_a/\gamma_a \qquad (3)$$

where Q = volumetric flow rate of melt; m^3/s (= barrel cross section area × plunger velocity); d_c = capillary diameter; L_c = capillary length; and ΔP = pressure drip across the capillary, Pa. The flow behavior or pseudoplasticity index, n, and consistency index, K, were determined from the power law expression:

TABLE I
Flow Behavior Index (n) and Consistency Index (K) of EAA, EVA, and Their Blends at Different Temperatures

Sample (EAA/EVA)	Temperature (°C)	n	K (Pa s^n)
	100	0.2699	2.043
100/0	110	0.3230	1.729
	120	0.3536	1.582
	100	0.2857	1.978
80/20	110	0.3481	1.639
	120	0.369	1.509
	100	0.3453	1.821
60/40	110	0.3596	1.558
	120	0.3637	1.489
	100	0.2940	1.815
40/60	110	0.3594	1.556
	120	0.3666	1.472
	100	0.3212	1.728
20/80	110	0.3605	1.529
	120	0.3645	1.459
	100	0.3279	1.658
0/100	110	0.3476	1.554
	120	0.3653	1.459

$$\tau_a = K(\gamma_a)^n \qquad (4)$$

Logarithmic plots of τ_a and γ_a were found to be linear over the experimental shear rate range, from the slope and intercept of which the parameters n and K were estimated.

RESULTS AND DISCUSSION

Flow behavior

The calculated flow behavior index (n) and consistency index (K) of the EAA/EVA blends and pure components at three different flow temperatures are given in Table I. It is observed from Table I that the flow behavior index, n, lies in the range 0.2699–0.3653. The results show a progressive increase in the pseudoplasticity index with temperature from 100 to 120°C. Thus, the systems become less shear thinning as temperature is increased. It is known that as the behavior departs more from Newtonian (with lower values of n), the melt flow becomes more plug like, with high shear rates being concentrated near the surface of the wall leading to a low shear within the main body of the melt. In other words, increase in the flow behavior index of the blend systems with temperature is expected to result in better distribution of shear rate in the bulk of the polymer melt, leading to better mixing. The value of n < 1 is the pseudoplastic or shear thinning behavior of the system. The consistency index (K) decreases after incorporation of EVA, and decreases with an increase in flow temperature. The blends occupy intermediate positions depending on the composition. As the temperature increases, the
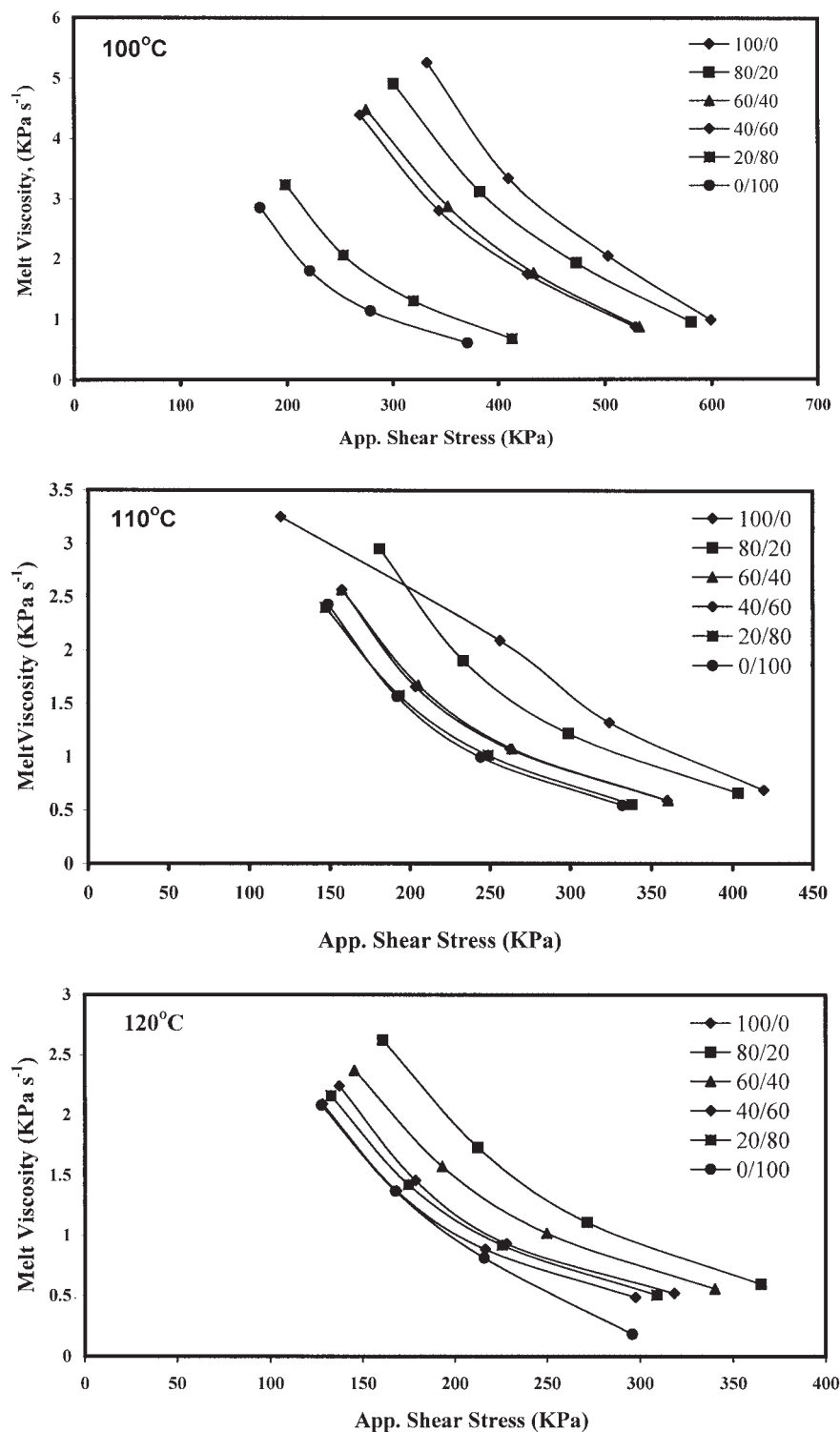
Figure 1 Plot of melt viscosity of the pure components and their blends against true shear stress at: (a) 100, (b) 110, and (c) 120°C.

molecular motion within the system increases, giving rise to higher kinetic energy. Thus, a reduced tendency is observed in molecular orientation, which, in turn, ensures the descending trend of the consistency index K value.

Both these parameters (n and K) vary with the blend composition for different blends, but n does not seem to give any definite trend. In the whole, the blends are more pseudoplastic in nature than the pure components.
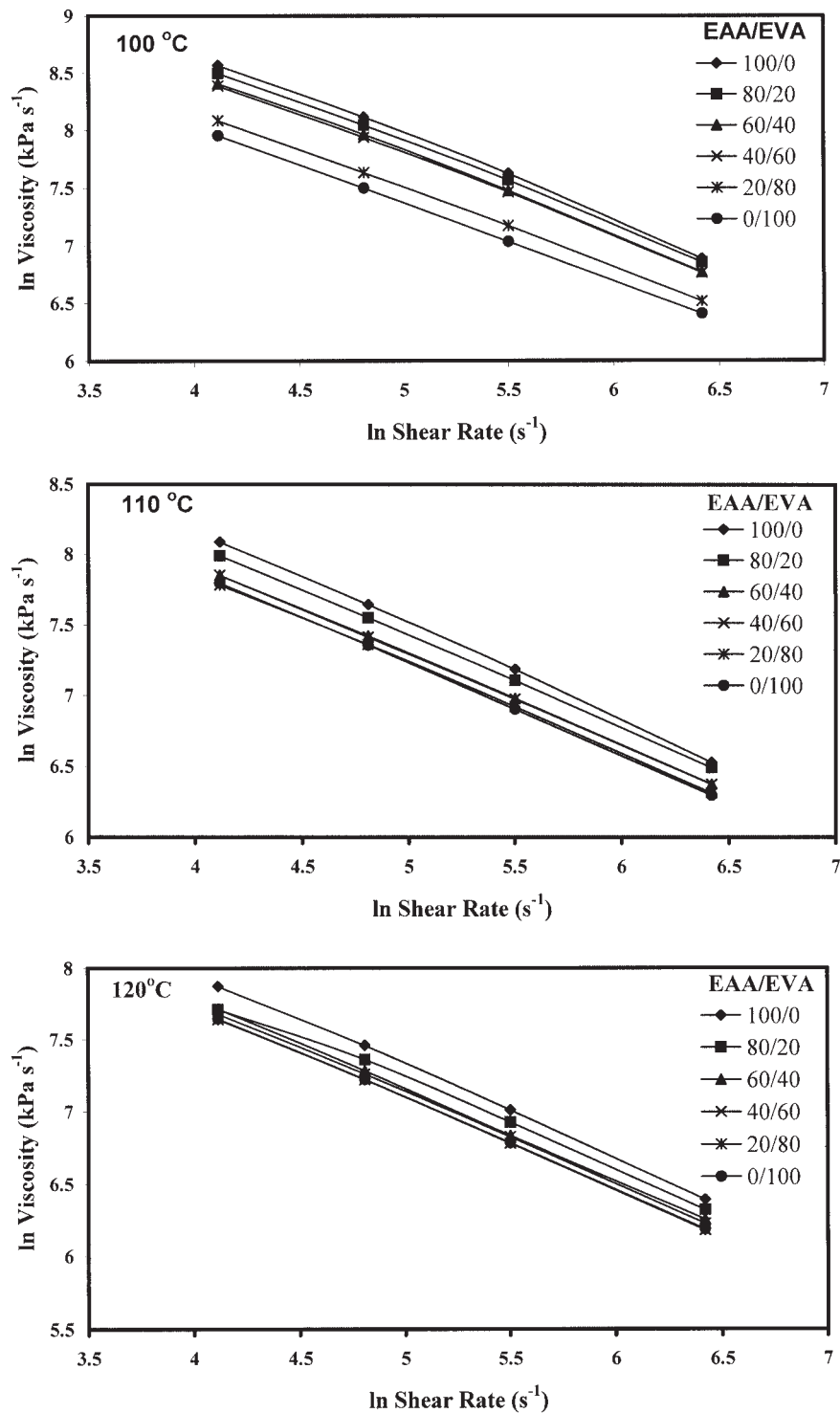
Figure 2 Plot of ln melt viscosity of the pure components and their blends against ln shear stress rate at: (a) 100, (b) 110, and (c) 120°C.

Melt viscosity

The melt viscosity of the pure components and the blends are plotted against the shear stress at three different temperatures, namely, 100, 110, and 120°C, as depicted in Figures 1(a–c). It is observed in general that at all temperatures of capillary flow, the shear viscosity decreases with an increase in shear stress, an indication of shear thinning or pseudoplastic nature of the blends. However, at all three different processing temperatures, the reduction in melt viscosity of EAA is more drastic at higher shear stresses than that ob-
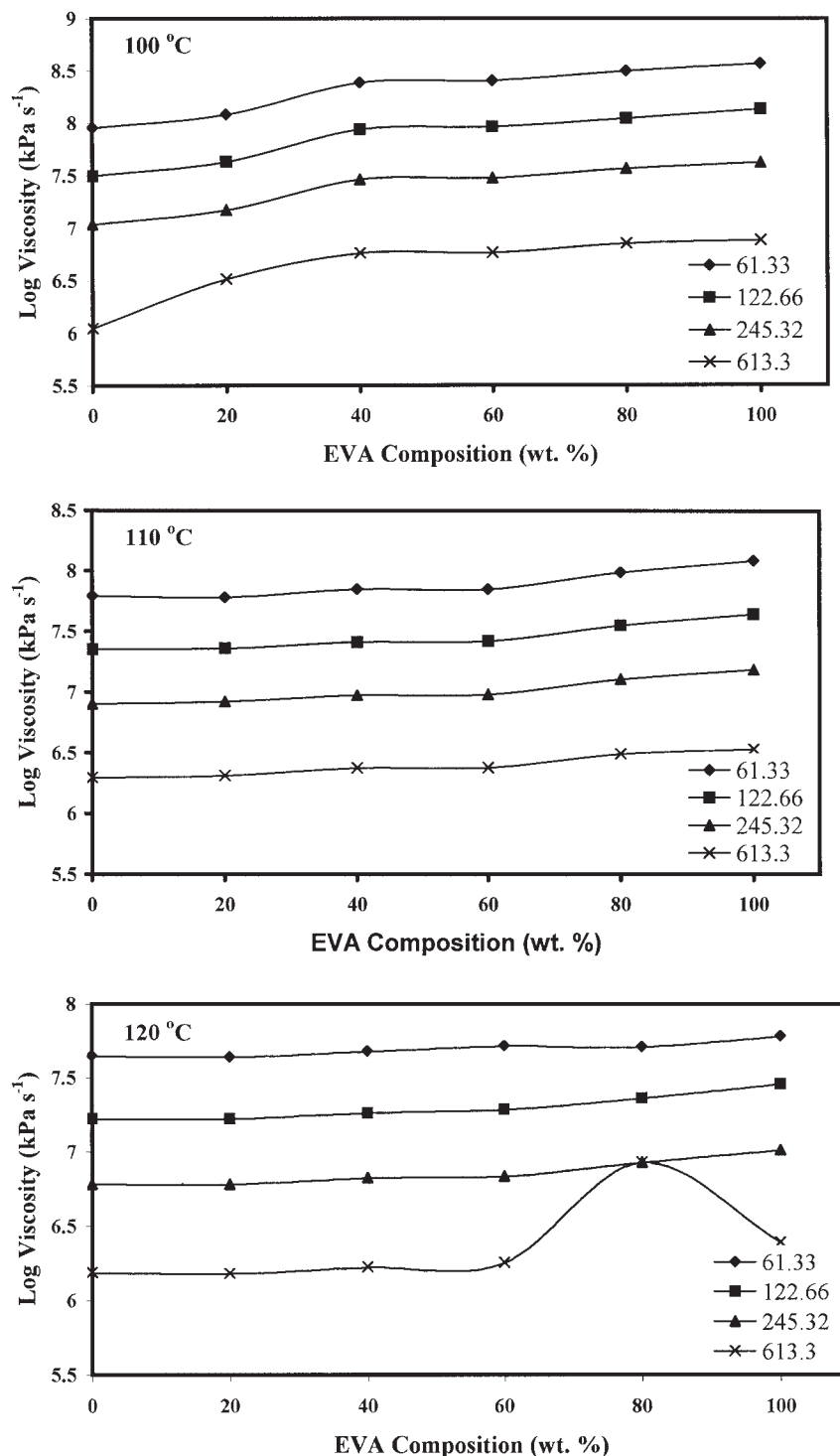
Figure 3 Plot of log viscosity versus EVA compositions of the blends at: (a) 100, (b) 110, and (c) 120°C.

served for EVA, in which case the reduction in melt viscosity is minimum at all three temperatures. As the capillary used in these experiments had an L/D = 20 and as the Bagley Corrections for shear stress were not estimated, the data is presented on the basis of apparent shear stress and apparent rate of shear.

Figures 2(a–c) give the variations in ln viscosity with ln shear rate of all the EAA/EVA blends at 100,

110, and 120°C. It is evident from these Figures that an increase in the shear rate decreases the melt viscosity of all the blends and the pure components invariably at all the temperatures studied because of shear thinning effects of the materials. With an increase in concentration of EVA in the EAA matrix, the shear viscosity decreases in all the proportions may be due to the low melting point of EVA. The viscosity values of
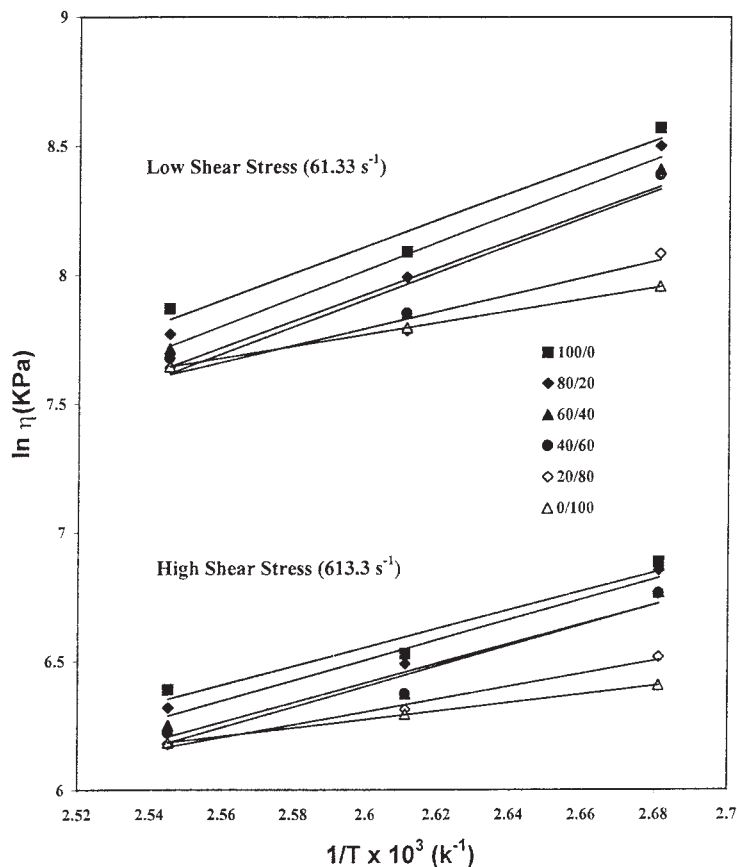
Figure 4 Plot of melt viscosity versus reciprocal of temperature for the pure components and the blends at low (61.33 s^{-1}) and high (613.3 s^{-1}) shear rates.

the blends lie in between those of the pure components. This may be explained as due to higher wall slip at higher shear rates, as suggested by Tuner and Moore.[20] It has also been observed that on increasing the temperature of shear flow from 100 to 120°C, that the shear viscosity decreases nonuniformly for all the blends and pure components, only varying in degree. The reduction in viscosity is more drastic for EAA and marginal for EVA at lower shear rates; whereas in the case of the blends, the reduction is intermediate depending upon the blend composition. Also at higher shear rate (>613.3 s^{-1}), the decrease in viscosity is marginal for EAA/EVA blends. This may be explained as due to increase in the free volume at higher temperatures.

It is interesting to note that the viscosity of EAA is higher than that of EVA at the same processing temperature. The melt viscosity of EAA reduces steadily with the increase in shear stress, which may be due to higher intermolecular force of interactions between the chain segments due to the presence of polar acrylic units, resulting in comparatively lesser extent of orientation under high shear stress. The viscosity of the blends follows an intermediate path depending on the composition. The shear thinning characteristics of the

blends and the pure components at different temperatures are depicted in Figures 1–3.

Plots of log of viscosity versus blend composition at four different shear rates and at three temperatures, namely, 100, 110, and 120°C, are shown in Figures 3(a–c), respectively. These Figures show a increase in viscosity with an increase in EVA content in the blend. These Figures also reveal that the experimental melt viscosities are higher than the theoretical ones for the blends showing a positive deviation from the additivity rule.[9,15] This trend of positive deviation in melt viscosity is observed at all the processing temperatures for all the blends, which is a characteristic property of miscible and homologous polymer blends. Therefore, it is inferred that the blends of EAA and EVA are miscible throughout the composition range. This is due to the fact that EAA and EVA are polar in nature and are also copolymers of ethylene.

Activation energy of flow

The activation energy of viscous flow derived from the Arrhenius type of relation is valid for the power law of fluids[21] and is calculated by using the following equation:
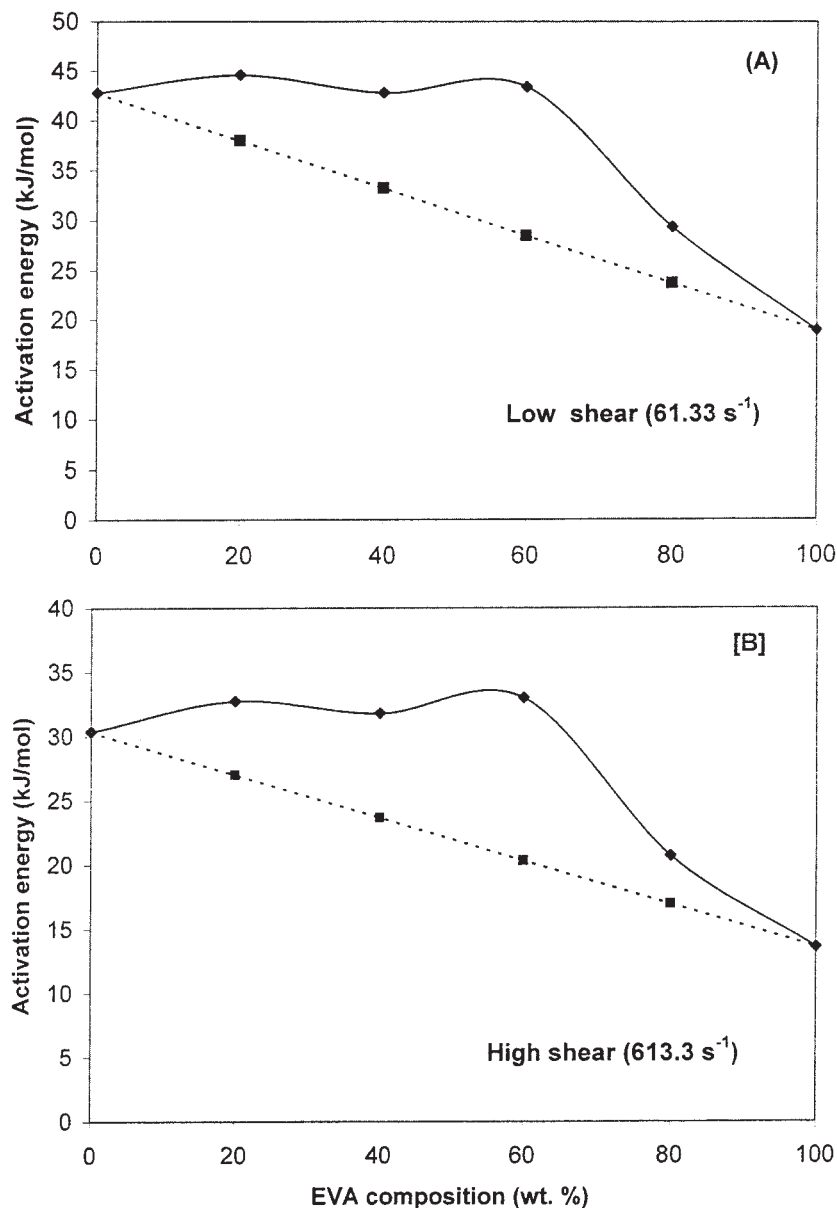
Figure 5 Plot of activation energy versus EAA/EVA blend composition at: (A) low shear rate (61.33 s^{-1}) and (B) high shear rate (613.3 s^{-1}).

$$\eta = Ae^{Ea/RT} \qquad (5)$$

where A is constant, E_a is the activation energy of viscous flow, R is the gas constant, and T is the absolute temperature.

Plots of melt viscosity against reciprocal of temperature at low shear rate (61.33 s^{-1}) and at higher shear rate (613.30 s^{-1}) for all the blends and individual components are depicted in Figure 4. The plots are linear, and their slopes are equal to E_a/R. Plots of activation energy versus blend composition at both low and high shear rates, that is, 61.33 and 613.30 s^{-1}, respectively, are shown in Figures 5(a,b). It is observed that the activation energy of flow is less at high shear rates than at lower shear rates for all the blends and pure components. However, at both lower and higher shear rates (61.33 and 613.3 s^{-1}), EAA has higher activation energy of flow than EVA. This implies that EVA is less temperature sensitive. This is attributed to its typical structure and lower intermolecular forces of attraction.[22] The activation energies of the blends shows a positive deviation from the additivity rule.

Figures 5(a,b) show a reduction in the activation energy of flow with an increase in shear rate so as to exhibit a positive deviation from the obtained by the additivity rule. Thus, the EAA/EVA blends require higher activation energy of flow than that calculated as per the additivity rule. Maximum deviation of E_a

values from the additive rule was observed when the EVA content lies in the range of 60–40% by weight ratio of the blend. This has been attributed to the high degree of miscibility between EAA and EVA. This type of synergism is maximum in the range 40/60–60/40 EAA/EVA blends at both the shear rates. Similar observations have been made earlier for the EMA/PDMS system.[14]

CONCLUSIONS

The following conclusions may be drawn from the present investigation:

1. On increasing shear rate and temperature of shear flow, the melt viscosity decreases for all the blends and pure components concurring with the shear thinning effect of the materials.
2. The melt viscosity of EAA is higher than that of EVA for all shear rates and temperatures.
3. The melt viscosities of the blends fall in between those of the pure components at all shear stresses.
4. The melt viscosity of the blends at all shear stresses is found to be less than that calculated as per the additivity rule. This result implies that the blend viscosity shows negative deviation from that of the additivity rule, a clear indication of miscibility of the polymer blends in the entire composition range.
5. The activation energy (E_a) of flow for EAA is higher than that of EVA at all shear rates. E_a values decrease with increase in shear rate. When EVA composition lies between 60 and 40% by weight, maximum activation energy of viscous flow was observed. This is due to maximum miscibility in this composition range.

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