Rheology and phase behaviour of blends of poly(ethylene oxide) with poly(vinyl acetate) and with poly(vinyl acetate-*ran*-ethylene)

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The dynamic viscoelastic properties of blends of poly(ethylene oxide) (PEO) with poly(vinyl acetate) (PVAc) and with poly(vinyl acetate-*ran*-ethylene) (PVAE) were measured, using a cone-and-plate rheometer in the oscillatory shear mode. For the study, two grades of PEO, one with weight-average molecular weight $M_w = 20000$ (PEO20) and the other with $M_w = 100000$ (PEO100), were used. The PVAE used was found to be amorphous, as determined by differential scanning calorimetry, and it had $M_w = 12600$, as determined by gel permeation chromatography, and 73.4 wt% vinyl acetate, as determined by elemental analysis. It was found that the amorphous phase of the PEO20/PVAc blend system has one glass transition temperature T_g over the entire range of blend compositions, whereas the amorphous phase of the PEO100/PVAc blend system has one T_g for blend compositions up to 50 wt% PVAc, but two T_g values for blends with greater amounts of PVAc. Melting-point depression measurements were conducted to determine the Flory interaction parameter χ to be: (a) -0.211 for PEO20/PVAc pair; (b) -0.069 for PEO100/PVAc pair; (c) -0.027 for PEO20/PVAE pair; and (d) -0.024 for PEO100/PVAE pair. Our experimental results show that plots of the logarithm of zero-shear viscosity *versus* blend composition at constant temperature exhibit *negative* deviations from linearity for the PEO20/PVAc blend system, but *positive* deviations from linearity for both PEO20/PVAE and PEO100/PVAE blend systems. These experimental observations are interpreted using a molecular viscoelasticity theory recently developed by Han and Kim.

(Keywords: rheology; phase behaviour; blends; poly(ethylene oxide); poly(vinyl acetate); poly(vinyl acetate-*ran*-ethylene))

INTRODUCTION

Poly(vinyl acetate) (PVAc) is one of the most important synthetic polymers in wide use for industrial applications, such as adhesives and coatings for papers and textiles. In order to improve flexibility of PVAc, two approaches have been taken[1]. One approach is to prepare copolymers of vinyl acetate and ethylene, and another approach is to prepare blends of PVAc with other flexible polymer(s), such as poly(ethylene oxide) (PEO). In the preparation of copolymers consisting of vinyl acetate and ethylene, one can produce either *crystalline* random copolymers, poly(ethylene-*ran*-vinyl acetate) (PEVA), in which ethylene is the major component, or *amorphous* random copolymers, poly(vinyl acetate-*ran*-ethylene) (PVAE), in which vinyl acetate is the major component. PEVA is widely used in extrusion applications and hot melt adhesives, while PVAE is used in adhesives and paper coatings.

It has been reported[2–5] that blends of PEO and PVAc are miscible in the molten state at temperatures above the melting temperature of PEO. According to Sanchez[6], the solubility parameters for PEO and PVAc are very close to each other, with a difference of only 0.02 $\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$.

Martuscelli *et al.*[7] reported viscosity measurements for blends of PEO having weight-average molecular weight $M_w = 20000$ with PVAc having $M_w = 64000$ and 316000, respectively. They reported that plots of the logarithm of zero-shear viscosity (η_{0b}) *versus* blend composition at constant temperature exhibit *positive* deviations from linearity for blends containing less than about 30 wt% PVAc, but *negative* deviations from linearity for blends containing greater than 30 wt% PVAc.

Very recently we have conducted an experimental investigation on the rheological behaviour of blends of PEO and PVAc, and blends of PEO and PVAE. We have observed that plots of log η_{0b} *versus* blend composition at a constant temperature exhibit *negative* deviations from linearity for the PEO/PVAc blend system over the entire range of blend compositions, and *positive* deviations from linearity for the PEO/PVAE blend system over the entire range of blend compositions. In this paper we shall first present our experimental results for the linear dynamic viscoelastic properties of the two blend systems investigated, and then interpret the results using a molecular viscoelasticity theory recently developed by Han and Kim[8,9].

EXPERIMENTAL

Materials

The materials used in the present study, together with information on molecular weight, are summarized in *Table 1*. Using the polymers given in *Table 1*, four blend

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Table 1 Molecular characteristics of the polymers investigated

Sample code	Polymer	M_w	Source
PEO20	Poly(ethylene oxide)	20000	Fluka
PEO100	Poly(ethylene oxide)	100000	Aldrich Chemicals
PVAc	Poly(vinyl acetate)	45000	Air Products
PVAE[a]	Poly(vinyl acetate-*ran*-ethylene)	12600	Quantum Chemicals

[a] Contains 73.4 wt% vinyl acetate

systems, (a) PEO20/PVAc, (b) PEO100/PVAc, (c) PEO20/PVAE and (d) PEO100/PVAE, each with 10/90, 20/80, 40/60, 50/50, 60/40, 80/20 and 90/10 blend compositions (by weight per cent), were prepared by solvent casting from chloroform. Specifically, for each blend, a pair of polymers were dissolved in chloroform at room temperature with frequent agitation and then the solvent was evaporated very slowly under atmospheric conditions for a week. Thin films of about 0.3 mm (or sheets of about 2 mm) in thickness, formed by solvent casting, were dried under vacuum at 50°C for about one week, until there was no change in weight.

Measurement of glass transition temperature and melting-point depression

The glass transition temperature (T_g) of samples, and melting-point depression of PEO in a blend sample, were determined using differential scanning calorimetry (d.s.c.) (duPont 1090 Thermal Analyzer). About 10 mg of the dried sample were used for d.s.c. measurements. The temperature reading of d.s.c. was calibrated with indium. Prior to d.s.c. measurement, the samples were first annealed for about 10 min at a temperature about 30°C above the melting point of the crystalline PEO in order to remove their previous thermal histories, and then quenched to a temperature below their T_g value. A heating rate of $10°C\,min^{-1}$ was used for all blend samples.

Rheological measurement

Before rheological measurements, thin sheets of samples prepared by solvent casting were further dried in a vacuum oven at 50°C for 24 h to remove any moisture and to relieve residual stress. The dried samples were then kept in a desiccator. A cone-and-plate rheometer (model R16 Weissenberg Rheogoniometer) was used in the oscillatory shear mode to measure the dynamic storage modulus (G') and dynamic loss modulus (G''), as functions of angular frequency (ω). Rheological measurements were made at 100, 110 and 120°C for all blend samples as well as their constituent components. The reason for the rather narrow range of temperature chosen lies in the fact that PEO was found to be thermally unstable at temperatures above 130°C.

RESULTS AND DISCUSSION

Miscibility of the PEO/PVAc and PEO/PVAE blend systems as determined by d.s.c. measurement

Figure 1 gives plots of T_g *versus* blend composition for the amorphous phase of the PEO20/PVAc and PEO100/PVAc blend systems. It should be pointed out that PEO is a crystalline polymer while PVAc is an amorphous polymer. It can be seen in *Figure 1* that the amorphous phase of the PEO20/PVAc blend system has only one T_g over the entire range of blend compositions, but the amorphous phase of the PEO100/PVAc blend system has one T_g for blend composition only up to 50 wt% PVAc. This then suggests that, as the molecular weight of PEO is increased, the PEO100/PVAc blend system is miscible only over a limited range of blend composition. For the reason of partial miscibility of the PEO100/PVAc blends, their rheological properties will not be discussed further.

Figure 2 gives plots of T_g *versus* blend composition for the amorphous phase of the PEO20/PVAE and PEO100/PVAE blend systems. It can be seen in *Figure 2*

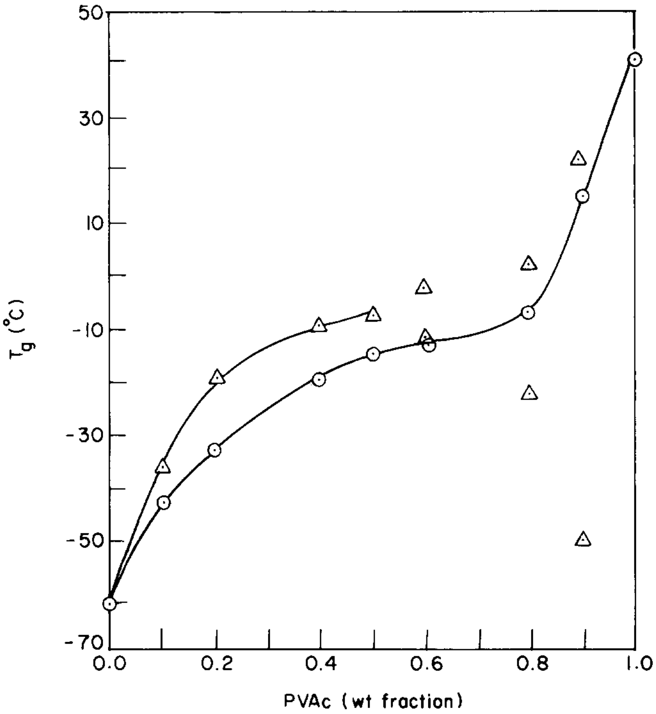

Figure 1 Plots of glass transition temperature for the amorphous phase *versus* blend composition for: (○) PEO20/PVAc blends; (△) PEO100/PVAc blends

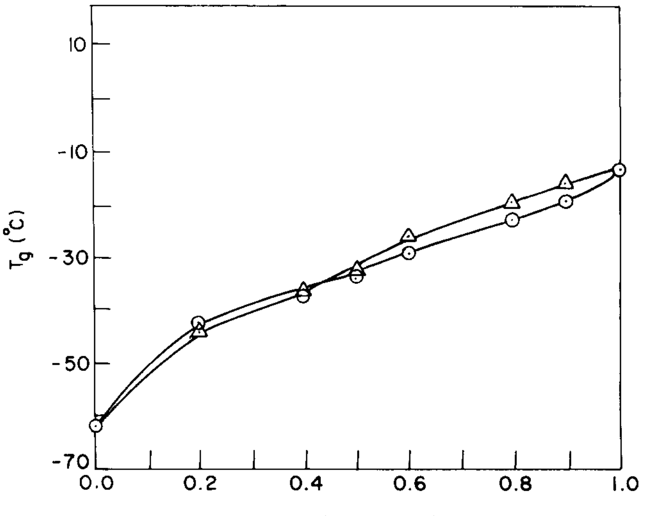

Figure 2 Plots of glass transition temperature for the amorphous phase *versus* blend composition for: (○) PEO20/PVAE blends; (△) PEO100/PVAE blends

Table 2 Summary of PEO melting-point measurements for the PEO/PVAc blend system

PVAc (wt%)	Melting point for PEO20/PVAc blends (°C)	Melting point for PEO100/PVAc blends (°C)
0	64.6	62.4
10	64.2	60.5
20	63.7	60.3
40	61.9	59.5
50	59.4	59.1
60	58.4	58.9
80	–	–
90	–	–
100	–	–

Table 3 Summary of PEO melting-point measurements for the PEO/PVAE blend system

PVAE (wt%)	Melting point for PEO20/PVAE blends (°C)	Melting point for PEO100/PVAE blends (°C)
0	64.6	62.6
10	64.3	62.3
20	63.9	61.9
40	63.2	61.1
50	62.7	60.6
60	62.1	60.3
80	60.9	58.8
90	59.3	57.0
100	–	–

Table 4 Summary of the interaction parameter values determined from melting-point depression

Blend system	Interaction parameter χ
PEO20/PVAc	−0.211
PEO100/PVAc	−0.069
PEO20/PVAE	−0.027
PEO100/PVAE	−0.024

that the amorphous phase in both blend systems has only one T_g over the entire range of blend compositions and T_g varies little as the molecular weight of PEO increases from 20000 to 100000.

The interaction parameter χ as determined by melting-point depression

It has long been recognized that the melting point of a crystalline polymer is depressed when it is mixed with an amorphous polymer[10], and this observation has been used to determine the interaction parameter χ of a polymer pair[10,11]. *Table 2* gives a summary of melting-point measurements for the PEO20/PVAc and PEO100/PVAc blend systems, and *Table 3* gives a summary of melting-point measurements for the PEO20/PVAE and PEO100/PVAE blend systems. It can be seen in *Tables 2* and *3* that melting-point depression increases with increasing amount of PVAc or PVAE. Owing to an insufficient amount of crystalline PEO present, it was not possible to measure melting points of the PEO20/PVAc blends containing more than 60 wt% PVAc, and melting points of the PEO100/PVAc blends containing more than 70 wt% PVAc.

The melting-point measurements were used to determine the Flory interaction parameter χ, on the basis of the expression[10,11]:

$$(1/T_m - 1/T_m^\circ)/V_1 = (-BV_{2u}/\Delta H_{2u})(V_1/T_m) \quad (1)$$

where V_1 is the volume fraction of the amorphous component in the mixture, V_{2u} is the molar volume of the repeat unit of the crystalline component, ΔH_{2u} is the enthalpy of fusion per mole of the repeat unit of the crystalline component, T_m° is the melting point of the undiluted crystalline component, T_m is the melting point of the blend, and B is the interaction energy density of the polymer pair, which is related to χ by $B = \chi RT/V_{1u}$, where R is the universal gas constant, T is the absolute temperature and V_{1u} is the molar volume of the repeat unit of the amorphous component.

From the slope of $(1/T_m - T_m^\circ)/V_1$ *versus* V_1/T_m plots we have determined values of χ for each blend system investigated, and they are summarized in *Table 4*. In determining values of χ from equation (1), we used the following values of the various parameters involved: $V_{1u} = 72.4\ \mathrm{cm^3\ mol^{-1}}$ for PVAc, $V_{2u} = 39.2\ \mathrm{cm^3\ mol^{-1}}$ for PEO and $\Delta H_{2u} = 2.02\ \mathrm{kcal\ mol^{-1}}$ for PEO[12].

The following observations are worth noting in *Table 4*: (1) The absolute value of χ for the PEO100/PVAc pair is much smaller than that of the PEO20/PVAc pair, indicating that, at temperatures above the melting point of PEO, the miscibility of PEO with PVAc decreases as the molecular weight of PEO increases from 20000 to 100000. The observation is consistent with that made above based on T_g measurements. (2) The absolute value of χ for the PEO/PVAE pair is changed little as the molecular weight of PEO is increased from 20000 to 100000. (3) The absolute value of χ for the PEO20/PVAE pair is smaller than that for the PEO20/PVAc. This is not surprising in light of the fact that polyethylene is not miscible with PEO and, consequently, when part of the vinyl acetate in PVAc is replaced by ethylene, the resultant polymer, PVAE, will become less miscible with PEO, as compared to the miscibility between PVAc and PEO. As a matter of fact, in the present study we have found that a PVAE containing about 40 wt% vinyl acetate was not miscible with PEO over the entire range of blend compositions.

Viscosity of PEO/PVAc and PEO/PVAE blends

Figure 3 gives logarithmic plots of dynamic viscosity η'_b *versus* angular frequency ω for PEO20/PVAc blends at 100 and 120°C. It can be seen in *Figure 3* that, for the blends as well as the constituent components, η'_b approaches a constant value, the zero-shear viscosity η_{0b}, as ω approaches zero. Plots of $\log \eta_{0b}$ *versus* blend composition are given in *Figure 4* for the PEO20/PVAc blend system at 100, 110 and 120°C. It can be seen in *Figure 4* that plots of $\log \eta_{0b}$ *versus* blend composition at constant temperature show *negative* deviations from linearity over the entire range of blend compositions. *Figure 5* gives plots of $\log \eta'_b$ *versus* $\log \omega$ for the PEO20/PVAE blend system at 100 and 120°C. Cross-plotting η_{0b} against blend composition on semi-logarithmic coordinates, we obtain the results given in *Figure 6*. Similar plots are given in *Figure 7* for the PEO100/PVAE blend system. It is of interest to observe in *Figures 6* and *7* that plots of $\log \eta_{0b}$ *versus* blend composition at a constant temperature show *positive* deviations from linearity over the entire range of blend compositions in both PEO20/PVAE and PEO100/PVAE blend systems.

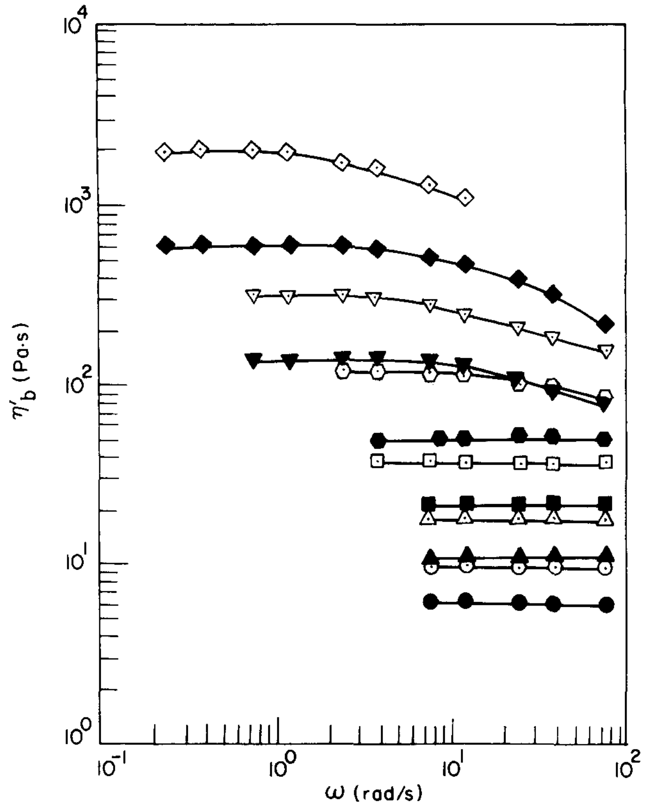

Figure 3 Plots of log η'_b *versus* log ω for the PEO20/PVAc blend system: (⊙, ●) PEO20; (◇, ◆) PVAc; (△, ▲) 80/20 PEO20/PVAc; (⊡, ■) 60/40 PEO20/PVAc; (⊙, ●) 40/60 PEO20/PVAc; (▽, ▼) 20/80 PEO20/PVAc. Open symbols are for 100°C and full symbols are for 120°C

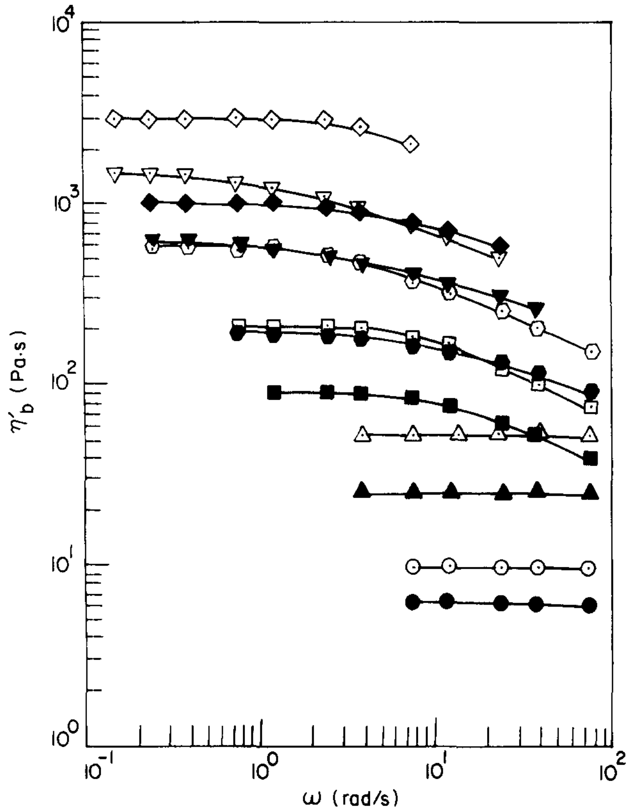

Figure 5 Plots of log η'_b *versus* log ω for the PEO20/PVAE blend system: (⊙, ●) PEO20; (◇, ◆) PVAE; (△, ▲) 80/20 PEO20/PVAE; (⊡, ■) 60/40 PEO20/PVAE; (⊙, ●) 40/60 PEO20/PVAE; (▽, ▼) 20/80 PEO20/PVAE. Open symbols are for 100°C and full symbols are for 120°C

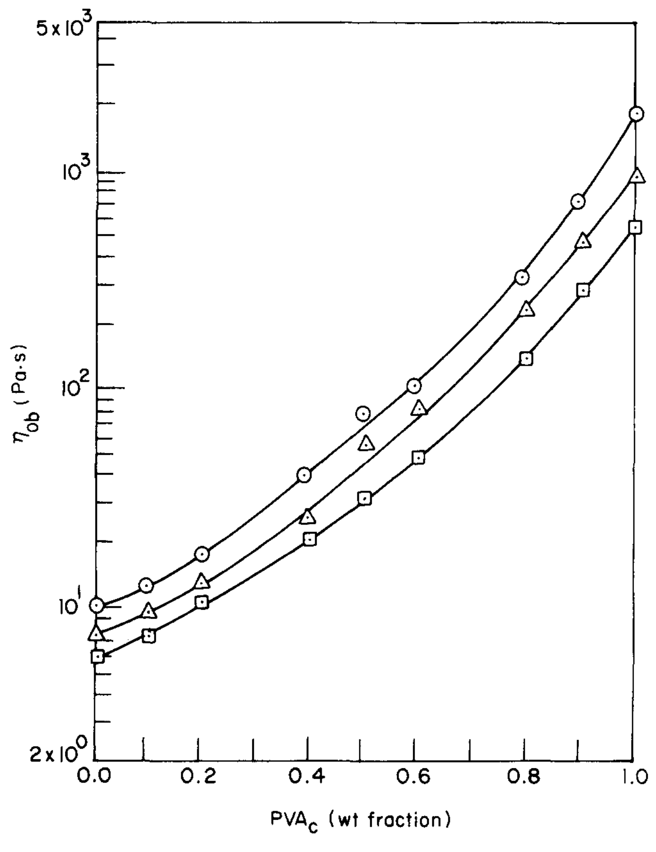

Figure 4 Plots of log η_{0b} *versus* blend composition for the PEO20/PVAc blend system at three temperatures: (⊙) 100°C; (△) 110°C; (⊡) 120°C

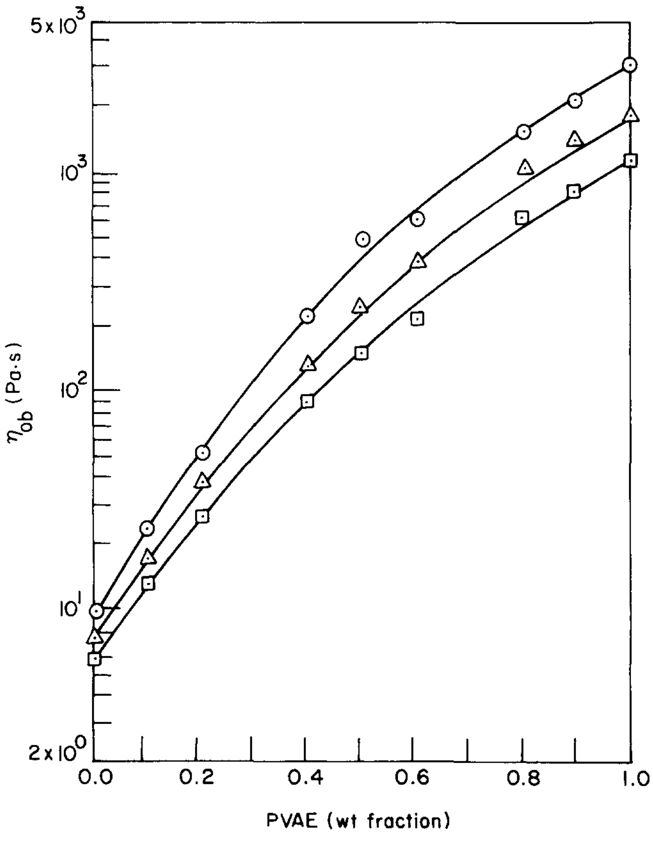

Figure 6 Plots of log η_{0b} *versus* blend composition for the PEO20/PVAE blend system at three temperatures: (⊙) 100°C; (△) 110°C; (⊡) 120°C

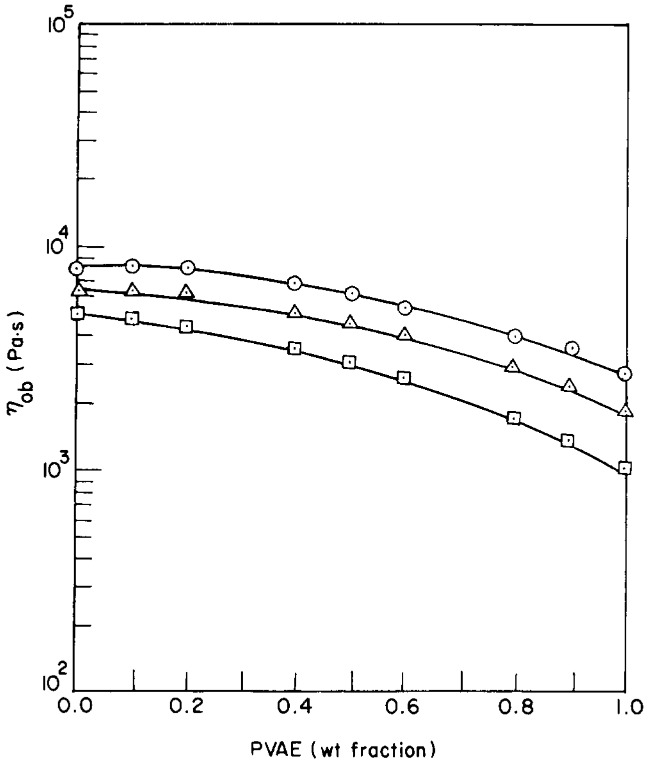

Figure 7 Plots of log η_{0b} *versus* blend composition for the PEO100/PVAE blend system at three temperatures: (○) 100°C; (△) 110°C; (□) 120°C

Earlier, using PEO ($M_w = 20000$) and PVAc with two different molecular weights ($M_w = 64000$ and 316000) Martuscelli *et al.*[7] observed that (a) in the PEO20/PVAc64 blend system plots of log η_{0b} *versus* blend composition at constant temperature exhibited positive deviations from linearity for blends containing less than 50 wt% PVAc and then negative deviations from linearity for blends containing more than 50 wt% PVAc, and (b) in the PEO20/PVAc316 blend system plots of log η_{0b} *versus* blend composition at constant temperature exhibited positive deviations from linearity for blends containing less than 20 wt% PVAc and then negative deviations from linearity for blends containing more than 20 wt% PVAc. In other words, they obtained sigmoidal curves in log η_{0b} *versus* blend composition plots for both PEO20/PVAc64 and PEO20/PVAc316 blend systems.

Both positive and negative deviations from linearity in the plot of log η_{0b} *versus* blend composition have been observed for other miscible polymer blend systems[8,9,13–19]. According to Han and Kim[8,9], the interaction parameter χ plays an important role in determining the shape of the log η_{0b} *versus* blend composition plots in miscible polymer blend systems. More of this will be discussed below when we compare theoretical predictions with experimental results.

It should be pointed out at this juncture that attempts[17–19] were made to observe the effect of blend composition on log η_0 for miscible polymer blends consisting of two *amorphous* polymers, at an iso-free-volume condition, or at a temperature T_1 for component 1 and at a temperature T_2 for component 2, so as to satisfy the relationship $T_1 - T_{g1} = T_2 - T_{g2}$, where T_{g1} and T_{g2} are the glass transition temperatures for components 1 and 2, respectively. For instance, Aoki[18] reported that, for miscible blends of poly(styrene-*co*-*N*-phenylmaleimide) and poly(acrylonitrile-*co*-styrene), plots of log η_{0b} *versus* blend composition exhibited negative deviations from linearity at an isothermal condition, but positive deviations from linearity at an iso-free-volume condition. However, when one of the constituent components in a miscible blend is crystalline, as is the case in the PEO/PVAc and PEO/PVAE blends investigated in this study, the use of the iso-free-volume condition is not straightforward. We are of the opinion that, in dealing with miscible polymer blends containing a crystalline component(s), the melting temperature plays a more important role than T_g, and thus plots of log η_0 *versus* blend composition at isothermal conditions may be justified.

Melt elasticity of PEO/PVAc and PEO/PVAE blends

It should be remembered that the dynamic storage modulus G' represents the energy stored in the fluid (thus an elastic property) and the dynamic loss modulus G'' represents the energy lost (thus a viscous property) during oscillatory shear flow[20]. Plots of log G' *versus* log G'' are given in *Figure 8* for PEO20 and PEO100 at various temperatures, and in *Figure 9* for PVAc and PVAE at various temperatures. It can be seen in *Figure 8* that both PEO20 and PEO100 give rise to a single correlation, which becomes independent of molecular weight and also *virtually* independent of temperature. Similar observations were made earlier for other homopolymers[21–25]. In light of the fact that the entanglement molecular weight (M_e) of PEO is about 2000, the PEO20 and PEO100 used in this study must be regarded as entangled macromolecules in the molten state. On the basis of the tube model[26], Han and Jhon[23] offered a molecular interpretation of the observation that we have made from *Figure 8*. We can conclude from *Figure 9* that PVAE is more elastic than the PVAc. It should be emphasized that, when using log G' *versus* log G'' plots

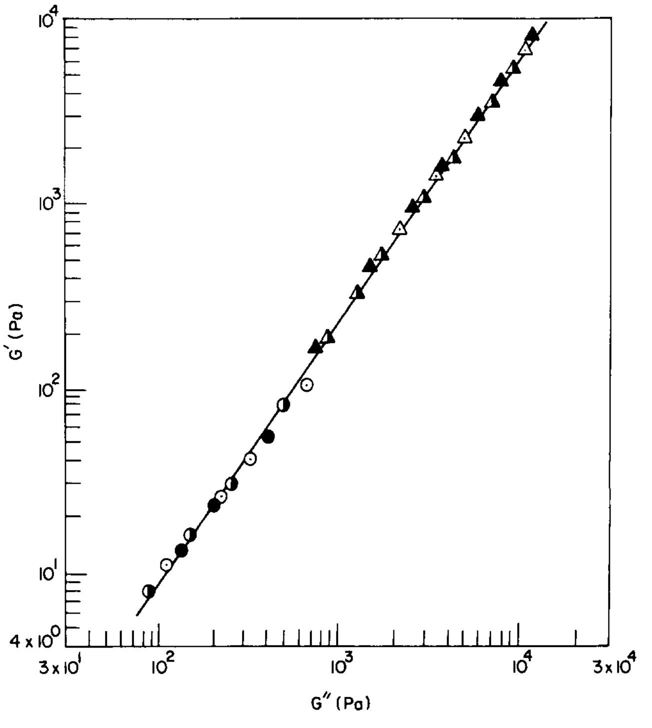

Figure 8 Plots of log G' *versus* log G'' for: PEO20 at 100°C (○), 110°C (◑) and 120°C (●); PEO100 at 100°C (△), 110°C (▲) and 120°C (▲)

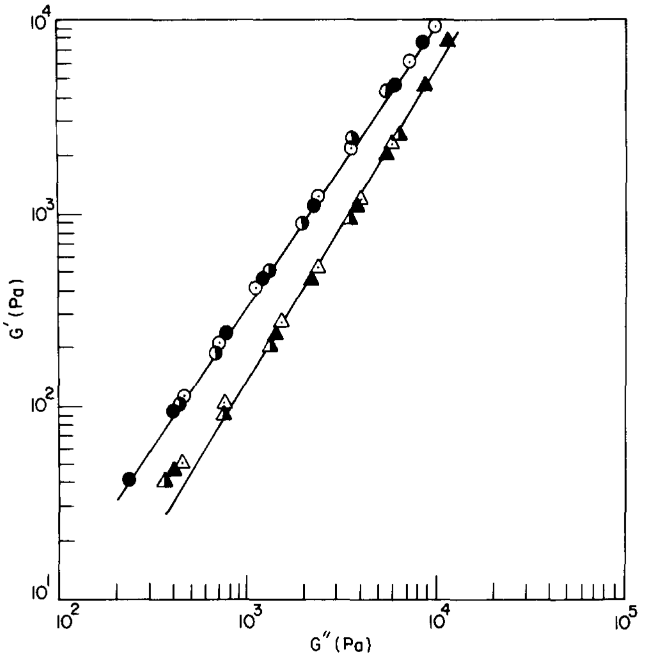

Figure 9 Plots of log G' *versus* log G'' for: PVAc at 100°C (△), 110°C (◭) and 120°C (▲); PVAE at 100°C (○), 110°C (◑) and 120°C (●)

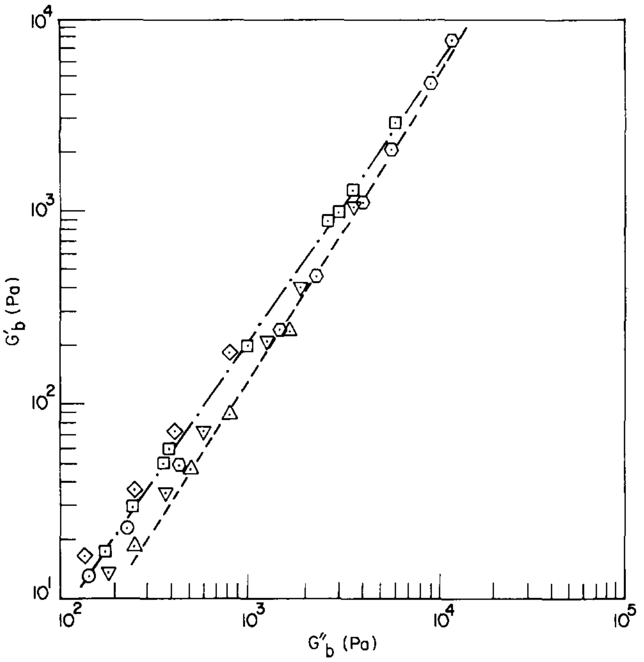

Figure 10 Plots of log G'_b *versus* log G''_b for the PEO20/PVAc blend system at 120°C: (⊙) PEO20; (○) PVAc; (◇) 80/20 PEO20/PVAc; (△) 60/40 PEO20/PVAc; (▽) 40/60 PEO20/PVAc; (⊡) 20/80 PEO20/PVAc

to assess and/or to compare the elastic properties of homopolymers or miscible polymer blends, temperature does not come into the picture (see *Figures 8* and *9*). However, such an observation will not be true for microphase-separated block copolymers[27–29].

Let us now examine the effect of blend composition on the elastic properties of PEO/PVAc and PEO/PVAE blends. For this, plots of log G'_b *versus* log G''_b are given in *Figure 10* for the PEO20/PVAc blend system, in *Figure 11* for the PEO20/PVAE blend system and in *Figure 12* for the PEO100/PVAE blend system. Notice in these figures the following points: (a) In *Figure 10*, the upper chain curve represents a correlation for PEO20 (see *Figure 8*), and the lower broken curve represents a correlation for PVAc (see *Figure 9*). (b) In *Figure 11*, the upper broken curve represents a correlation for PVAE (see *Figure 9*) and the lower chain curve represents a correlation for PEO20. (c) In *Figure 12*, the upper broken curve represents a correlation for PVAE and the lower chain curve represents a correlation for PEO100. We can conclude from *Figures 10–12* that the PEO is more elastic than the PVAc, and that the PVAE is more elastic than the PEO and PVAc.

Earlier, Han[25] reported that, for binary blends consisting of nearly monodisperse, entangled homopolymers

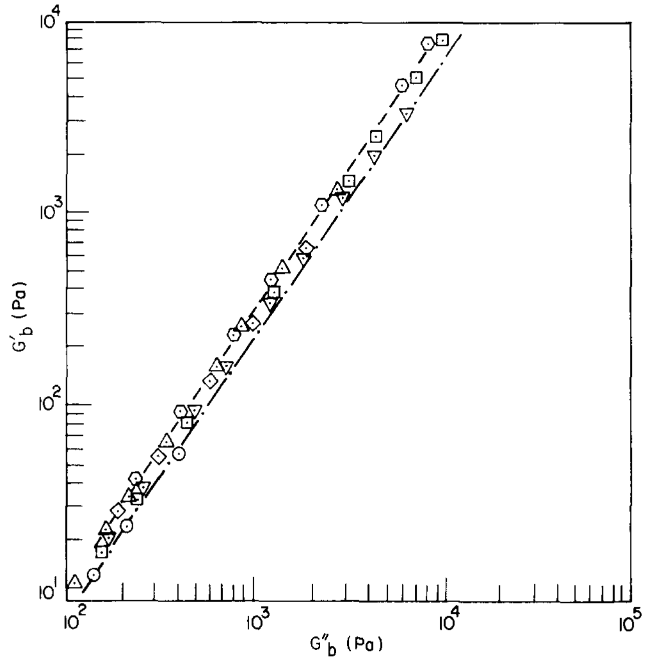

Figure 11 Plots of log G'_b *versus* log G''_b for the PEO20/PVAE blend system at 120°C: (⊙) PEO20; (○) PVAE; (◇) 80/20 PEO20/PVAE; (△) 60/40 PEO20/PVAE; (▽) 40/60 PEO20/PVAE; (⊡) 20/80 PEO20/PVAE

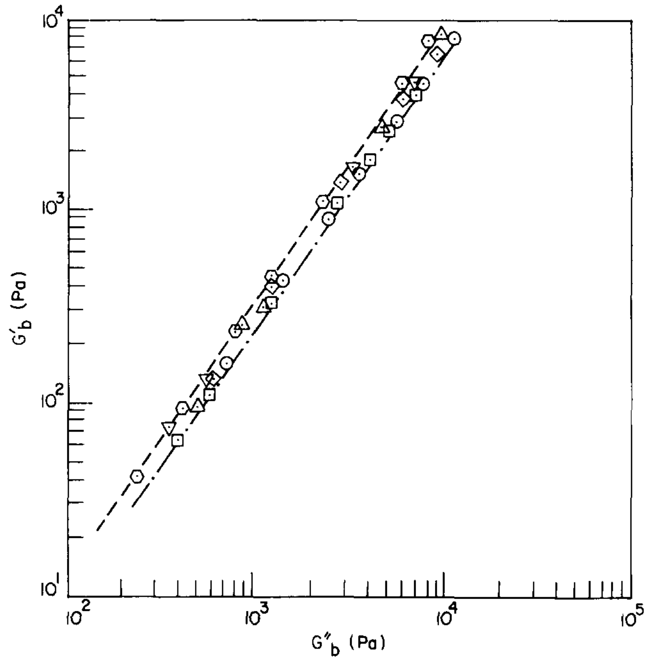

Figure 12 Plots of log G'_b *versus* log G''_b for the PEO100/PVAE blend system at 120°C: (⊙) PEO100; (○) PVAE; (◇) 80/20 PEO100/PVAE; (△) 60/40 PEO100/PVAE; (▽) 40/60 PEO100/PVAE; (⊡) 20/80 PEO100/PVAE

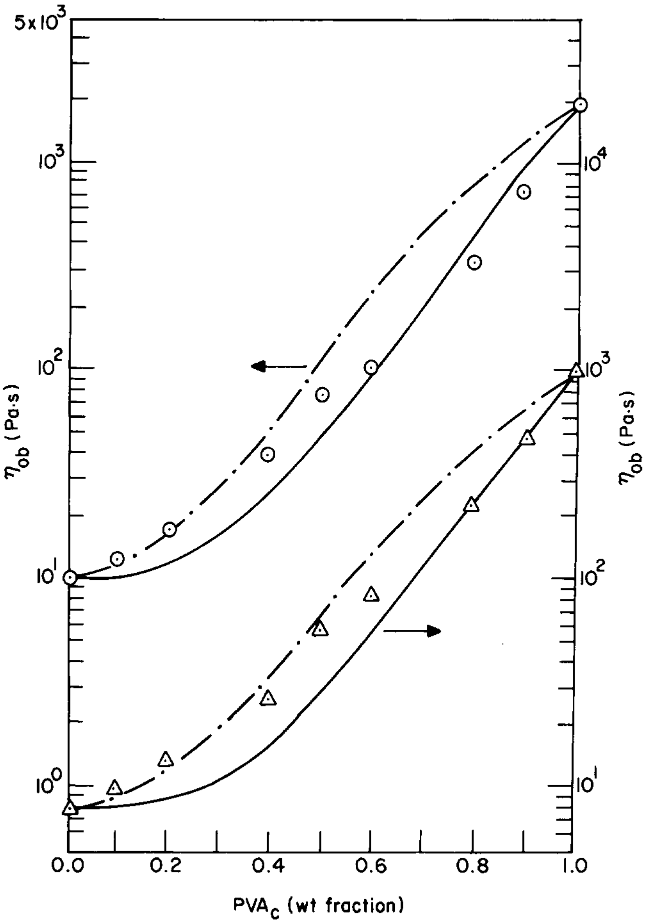

Figure 13 Theoretically predicted dependence of log η_0 on blend composition for the PEO20/PVAc blends. The predictions are based on the Han–Kim theory[9] with $z = 6$ (——) and with $z = 4$ (—·—), in which $\chi = -0.211$ was used. Symbols are experimental data at 100°C (⊙) and at 110°C (△)

with identical chemical structure, plots of log G'_b *versus* log G''_b for certain blend compositions may lie above those for the constituent components. It should be pointed out that log G'_b *versus* log G''_b plots for such constituent components become identical. Han noted further that, when the constituent components have molecular-weight distributions with considerable overlap, the dependence of log G'_b *versus* log G''_b plots on blend composition diminishes, giving rise to a single curve. Such an observation is relevant here, because the PEO, PVAc and PVAE used in this study are polydisperse. In other words, the spread of log G'_b *versus* log G''_b plots in miscible blends would depend on the polydispersity of the constituent components.

Theoretical interpretation of experimental results

In order to offer a theoretical interpretation of the different shapes of log η_{0b} *versus* blend composition plots obtained experimentally, as displayed in *Figures 4*, *6* and *7*, using the Han–Kim theory[9] we have calculated zero-shear viscosities for each of the blend systems. The theoretically predicted dependence of log η_{0b} on blend composition, along with experimental data, is given in *Figure 13* for the PEO20/PVAc blend system, in *Figure 14* for the PEO20/PVAE blend system and in *Figure 15* for the PEO100/PVAE blend system. In the calculations, we have used experimentally measured zero-shear viscosities (η_0) for the constituent components, the values of the interaction parameter χ given in *Table 4*, and the following numerical values for plateau modulus G^0_N: (a) 1.8×10^6 Pa for PEO[16], (b) 2.65×10^5 Pa for PVAc[30] and (c) 3.93×10^5 Pa for PVAE*. The details of the computational procedures employed are given in a paper by Han and Kim[9].

In the use of the Han–Kim theory, there is one adjustable parameter, referred to as the constraint release parameter z. It has been reported in the literature[9,31,32] that the value of z varies from one blend system to another, say from 3 to 20. It appears from *Figure 13* that for the PEO20/PVAc blend system the prediction with $z = 4$ fits better to experimental data for blend compositions with less than 50 wt% PVAc, whereas the prediction with $z = 6$ fits better to experimental data for blend compositions with greater than 50 wt% PVAc, although a single value of z, either $z = 4$ or $z = 6$, over the entire blend compositions, may be equally acceptable. A similar conclusion can be drawn from *Figure 14* for the PEO20/PVAE blend system. On the other hand, as can be seen in *Figure 15*, we were able to obtain a very good agreement between prediction and experiment for the PEO100/PVAE blend system using a value of z ranging from 2 to 6. In other words, predicted values of η_{0b} for the PEO100/PVAE blend system were found to be less sensitive to the choice of z, as compared to the other two blend systems.

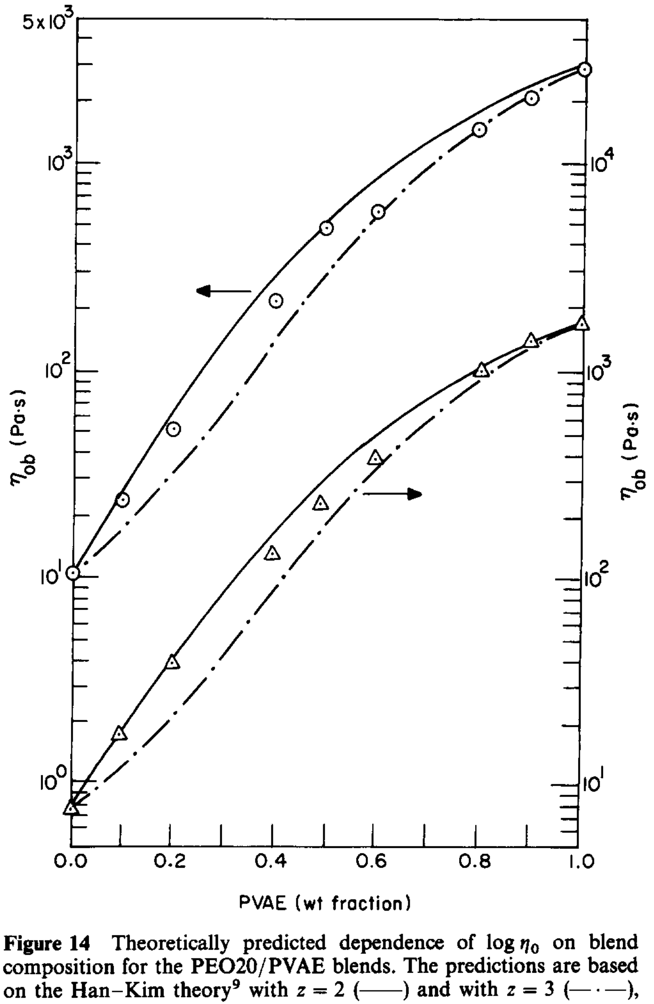

Figure 14 Theoretically predicted dependence of log η_0 on blend composition for the PEO20/PVAE blends. The predictions are based on the Han–Kim theory[9] with $z = 2$ (——) and with $z = 3$ (—·—), in which $\chi = -0.027$ was used. Symbols are experimental data at 100°C (⊙) and at 110°C (△)

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* This value was obtained by $G^0_N \approx 3.56 G''_m$, where G''_m was obtained from the plot of G'' *versus* ω at 60°C

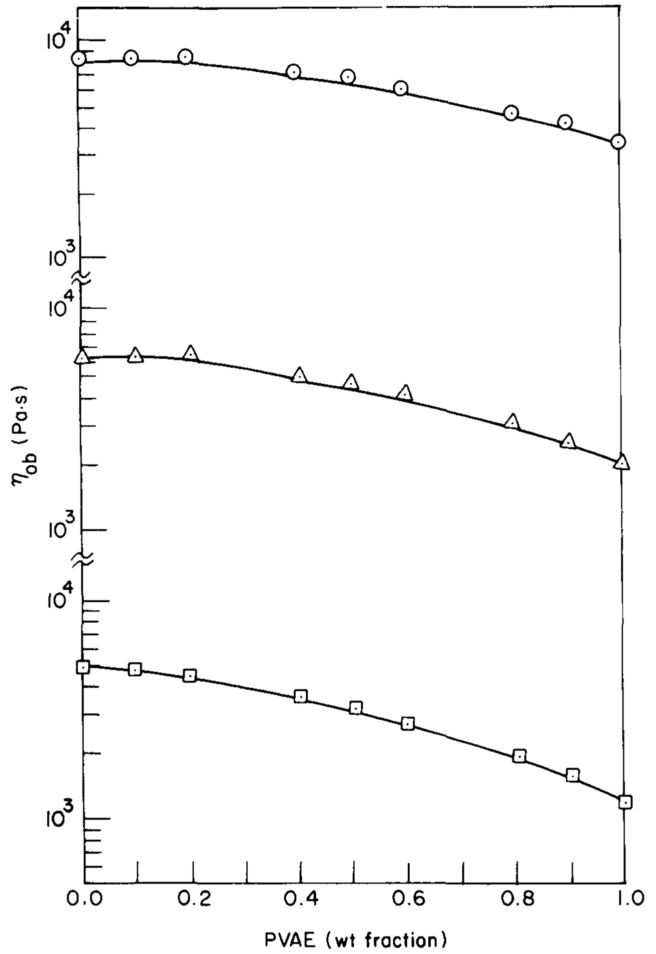

Figure 15 Theoretically predicted dependence of $\log \eta_0$ on blend composition for the PEO100/PVAE blend. The predictions are based on the Han–Kim theory[9] in which $\chi = -0.024$ was used. The prediction was found to be insensitive to the value of z ranging from 2 to 6. Symbols are experimental data at 100°C (○), 110°C (△) and 120°C (□)

What comes out of the theoretical calculations presented above is that the interaction parameter χ plays an important role in determining the shape of the plot of $\log \eta_{0b}$ *versus* blend composition. Specifically, the Han–Kim theory predicts that plots of $\log \eta_{0b}$ *versus* blend composition exhibit negative deviations from linearity for $|\chi| = 0.211$, but positive deviations from linearity for $|\chi| = 0.027$. Similar observations were reported earlier by Han and Kim[8,9] who observed in the plots of $\log \eta_{0b}$ *versus* blend composition negative deviations from linearity for blends of poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVDF) that have $|\chi| = 0.3$, but positive deviations from linearity for blends of PMMA with poly(styrene-*stat*-acrylonitrile) (PSAN) that have $|\chi| = 0.01$. It should be pointed out that, in the present study, the decrease in $|\chi|$ from 0.211 to 0.027 was due to the replacing of part of the vinyl acetate, originally present in PVAc, with ethylene, which then resulted in PVAE.

CONCLUSIONS

In this study we have shown experimentally that plots of $\log \eta_{0b}$ *versus* blend composition at constant temperature show negative deviations from linearity for the PEO/PVAc blend system, but positive deviations from linearity for the PEO/PVAE blend system. We were able to explain the experimental results using the molecular viscoelasticity theory by Han and Kim[8,9]. Specifically, according to this theory, the negative deviation observed in the plot of $\log \eta_{0b}$ *versus* blend composition for the PEO/PVAc blend system is attributed to a sufficiently large value of the interaction parameter $|\chi|$, 0.211, of the PEO/PVAc pair, and the positive deviations observed in the plot of $\log \eta_{0b}$ *versus* blend composition for the PEO/PVAE blend system is attributed to a very small value of $|\chi|$, 0.027, of the PEO/PVAE pair. We have explained the origin of the observed decrease in $|\chi|$ when part of the vinyl acetate originally present in PVAc is replaced by ethylene, giving rise to PEVA or PVAE depending upon the amount of ethylene content in the resultant polymer.

In the present study we have determined values of the interaction parameter χ by melting-point depression. We are well aware of the fact that the accuracy of the values of χ determined by melting-point depression may not be as good as that which can be obtained by more sophisticated experimental techniques. The subject of determining more accurate values of χ is a separate issue, which must be addressed in future study. Nevertheless, we believe that the theoretical interpretation of the experimental results offered here is valid.

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