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Dynamic rheological analysis of a miscible blend showing strong interactions

Haijun Cai[a], Abdellatif Ait-Kadi[b], Josée Brisson[a,*]

[a]*Département de chimie, Faculté des sciences et de génie, Centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval, Québec, Que., Canada G1K 7P4*

[b]*Département de génie chimique, Faculté des sciences et de génie, Centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval, Québec, Que., Canada G1K 7P4*

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Abstract

The rheological behavior of miscible blends was studied through oscillatory shear measurements. Two miscible blends were selected to compare with athermal blending cases, i.e. the hydrogen bonding poly(4-vinyl phenol)/poly(ethylene oxide) (PVPh/PEO) blend and the weakly interacting polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPO) blend. The homopolymers and the blends were characterized over a wide experimental window using the time–temperature superposition principle.

The horizontal shift factor, a_T, does not vary appreciably with composition for PS/PPO, whereas a strong compositional dependence is observed for the PVPh/PEO blends. Additions of up to 30 wt% of PEO to PVPh produce only minor changes in the value of rubber plateau modulus (G_N^0), while G_N^0 increases steadily after this concentration. The G_N^0 values follow athermal blending models [J. Polym. Sci., Part B: Polym. Phys. 25 (1987) 2511; J. Polym. Sci., Part B: Polym. Phys. 26 (1988) 2329] in the case of PS/PPO but not of PVPh/PEO. Values of η_{0b} for PVPh/PEO blends were estimated from weighed relaxation spectra. The three measured parameters, a_T, G_N^0 and η_0 show a turning point around 20–30 wt% of PEO, which corresponds to a 41–54 mol% of PEO, in correlation with the previously reported observation of a maximum in the deformation-induced uniaxial orientation behavior of PEO component near this composition [Macromolecules 32 (1999) 8509].

Keywords: Poly(4-vinyl phenol) blend; Rheology; Hydrogen bonds

1. Introduction

In the past years, our group has studied orientation behavior upon deformation of miscible blends containing poly(4-vinyl phenol) (PVPh) [1–3]. PVPh can be described as a polystyrene with a hydroxyl function attached on the *para* position of each aromatic group. It has been reported to form miscible blends with other polymers that contain accessible 'proton-acceptor' groups, such as carbonyl, ester and ether groups, through the formation of hydrogen bond interactions [4,5]. For blends with polyethylene oxide (PEO), a maximum in deformation-induced uniaxial orientation of the PEO component was observed for 30 wt% PEO [3]. This unusual behavior promoted the choice of the PVPh/PEO blend for the present study.

To better understand the influence of hydrogen bonds on the rheological behavior of PVPh/PEO blends, it was decided to compare the PVPh/PEO blend with predictions using the athermal blending cases reported by Wu [6] and Tsenoglou [7], which suppose that interactions do not modify the entanglement probability with respect to the case of the pure polymers. In order to further verify the effect of interactions, a miscible, weakly interacting blend was also selected to compare with PVPh/PEO. Because of the strong structural similarity between polystyrene (PS) and PVPh, which differs only by the presence of a *para*-substitution with a hydroxyl function in PVPh, miscible blends based on PS were sought. Unfortunately, PS/PEO blends are immiscible. The main miscible blend over a large temperature window with PS reported in the literature is with poly(phenylene oxide)(PPO) [8,9]. Prest and Porter [9] have previously reported rheological characterization of PS/PPO blends. In their work, the rubbery plateau modulus

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* Corresponding author. Tel.: +1-418-656-3536; fax: +1-418-656-7916. *E-mail address:* jbrisson@chm.ulaval.ca (J. Brisson).

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and the WLF parameters at T_g were determined. Therefore, as the rheological behavior of this system is already well known, only a few compositions were measured in the present work.

On the other hand, little is known on rheology of PVPh-based blends. The only work reported in the literature is that of Akiba and Akiyama [10]. They have shown that, for PS and PVPh of relatively low molecular weights, compositional dependence and magnitude of zero-shear viscosity of miscible PVPh/PVME blends are almost same as those of PS/PVME blends under iso-free volume conditions. The fact that viscoelastic properties between the two blends varied negligibly indicated that, for the molecular weights studied, hydrogen bonds present in PVPh/PVME induced little influence on long time scale rheological properties, such as zero-shear viscosity (η_0).

In order to shed light on the origin of the peculiar behavior upon deformation of the PVPh/PEO blend, the objective of the present paper is to contribute to the understanding of the effect of hydrogen bonding on the overall behavior of PVPh/PEO blends. To enlighten the effect of hydrogen bonds on rheology, dynamic rheological data in the linear viscoelastic regime (LVE) were obtained and compared to those of athermal blending cases that show no effect of interactions on entanglement probability. Changes in G_N^0, η_0 and horizontal shift factor (a_T) were compared for both studied systems. A forthcoming paper will discuss specifically the determination of molecular weight between chain entanglements (M_e) and interchain friction coefficients (ξ).

2. Experimental

2.1. Materials and characterization

Molecular weights, polydispersities and sources of selected polymers are listed in Table 1. Molecular weight and polydispersity of the pure constituents were determined by gel permeation chromatography (GPC) using a Waters HPLC pump model 515, a Rheodyne Injector model 7125, several separated Styragel columns, a light scattering Dawn DSPF detector and a refractive detector Optilab 903 from Wyatt. HPLC grade tetrahydrofuran (THF) filtered through 0.2 μm filters was used as a solvent.

Prior to all other measurements (e.g. differential scanning calorimetry DSC and rheological characterization), samples were thoroughly dried under dynamic vacuum for at least 2 weeks.

The glass transition temperature (T_g) was determined by DSC (Perkin–Elmer DSC-7). DSC scans were recorded using a heating rate of 20 °C/min and a sample capsule of 15–25 mg after calibration with indium. T_g is taken as the midpoint of the transition. The occurrence of a single T_g was taken as confirmation of miscibility.

PVPh and PEO were blended at a concentration of 2–4% in THF at approximately 60 °C. PVPh/PEO blends were obtained by evaporating the solvent in a fume hood, followed by further drying for 2–4 weeks in a vacuum oven at a temperature close to T_g of each blend.

PS and PPO were blended at a concentration of 2.5% in benzene. The solution was subsequently frozen in liquid nitrogen and placed in a FTS system freeze-dryer (Model #FD-3-85A-MP) at − 80 °C under a pressure of 200 Torr for several hours, allowing the complete sublimation of the solvent. The resulting white powder blend was subsequently broken down into finer particles with a mortar and pestle, and further dried for several days in a vacuum oven at a temperature in the vicinity of T_g to remove any residual solvent.

2.2. Rheological measurements

Rheological measurements were carried out on a Rheometric Scientific ARES-II rheometer and a Bohlin CS and CVO rheometer using parallel plate geometry. Disk-shaped samples having 25 mm diameter and 1.5 mm thickness were pressed using a Carver laboratory press. Strain sweep tests were performed first to determine the linear viscoelastic zone for each blend at very low strain (0.5–20%). All experiments were carried out under dry nitrogen atmosphere. Test temperature was varied from $T_g + 10$ to $T_g + 100$ °C for all blends. Storage modulus, G', loss modulus, G'', and loss tangent, tan δ as a function of frequency were obtained by performing frequency sweep tests at each temperature. For each blend, tests under the same experimental conditions were repeated two to three times in order to confirm reproducibility.

Master curves for G', G'' and tan δ were obtained using the time–temperature superposition principle at a reference temperature $T_{ref} = T_g + 15$ °C for pure polymers and blends.

Relaxation spectra, $H(\tau)$, were calculated from the shifted data, i.e. $G'(a_T\omega)$ and $G''(a_T\omega)$, where a_T is the

Table 1
Selected polymers

Polymer	M_w (g/mol)	M_w/M_n	Sourcem
Poly(4-vinyl phenol)	78,900	2.5–2.8	TriQuest, Corpus Christi
Poly(ethylene oxide)	6600	1.24	Aldrich Chemical
Polystyrene	276,000	2.01	Dow Chemical
Poly(2,6-dimethyl 1,4-phenylene oxide)	40,000	2.19	General Electric

horizontal shift factor, using a neural network program (NNSPEC software) developed by Grandjean, Ait-Kadi and Coté [11]. For PVPh-rich blend compositions, samples were brittle and T_g higher, which forced us to use high temperatures where sample degradation was fast even under dry nitrogen atmosphere. Thus, rheological measurements were limited and the zero-shear viscosity, η_0, was calculated from the following equation [11]

$$\eta_0 = \int_{-\infty}^{+\infty} \tau H(\tau) \mathrm{d}(\ln \tau) \quad (1)$$

where $H(\tau)$ is calculated from the limited and discrete linear viscoelastic data, e.g. $G'(\omega)$ and $G''(\omega)$, using a software based on neural network models.

3. Results and discussion

3.1. Selected blend systems

As mentioned in Section 1, one of the aims of this work was to shed light on the peculiar behavior upon deformation-induced orientation of PVPh/PEO blends. In order to better understand the influence of hydrogen bond interactions, a comparison with athermal models and with a weakly interacting blend was sought. This posed the problem of choosing which weakly interacting miscible blend could better serve this purpose, while being sufficiently similar, chemically, to offer a sensible comparison with the PVPh/PEO blend. In the case of weak interactions, the number of miscible blends is limited. PEO-based blends were rejected, as polymers miscible with PEO (polyacrylic acid, polymethacrylic acid, polyurea, arboxymethyl dextran) form hydrogen bonds, and complexation of the two polymers is often observed [12]. Miscible PVPh-based blends, likewise, form hydrogen bonds. Therefore, because of its chemical similarity to PVPh, PS-based blends were sought. PS is known to form miscible blends with PPO and with poly(vinyl methyl ether) (PVME). The PS/PVME blend system presents a lower critical solution temperature (LCST), which limits the experimental temperature window in which the system is miscible, and was also rejected [12]. PS/PPO was therefore selected. Unfortunately, on a thermal point of view, it is not ideal, as T_gs of the pure polymers are quite different, T_g of PPO being higher than that of PS, whereas the reverse is observed for PEO and PVPh.

Once the blend systems are selected, a choice must be made in terms of molecular weight. In this specific instance, this choice was made with respect to number of entanglements in the polymer chain. It has been shown by Aoki and Tanaka [13] that, when the difference in the number of entanglement couplings ($n_e = M_w/M_e$) is very large between the two components of a miscible blend, the plateau modulus (G_N^0) of the blend cannot be determined by conventional methods, i.e. from the storage modulus at the frequency where tan δ is a minimum. Further, we also aimed at choosing molecular weights for which the polymers were in an entangled state. Therefore, from the polymers available commercially, we selected a PVPh of $n_e = 2.7$ and a PEO of $n_e = 2.6$, while for PS we used $n_e = 10$ and for PPO $n_e = 11$. Molecular weights, polymer source and polydispersities are reported in Table 1.

3.2. Rheological behavior of the blends

It has been reported that PVPh and PEO form miscible blends exhibiting strong interactions, i.e. hydrogen bonds between the hydroxyl proton of PVPh and the accessible ether oxygen of PEO [14].

In a previous study on molecular orientation upon uniaxial deformation [3], a maximum in deformation-induced orientation of the PEO component was observed. Only compositions in which PEO crystallization was absent were studied. The blends therefore formed a single amorphous phase, as attested by the presence of a single T_g transition and the absence of a melt endothermic peak in DSC. The same PVPh/PEO blend compositions are used in the present study for comparison purposes. The T_gs of pure polymers and blends are reported in Table 2.

Figs. 1 and 2 show typical storage and loss moduli master curves at $T_g + 15$ for representative PS/PPO and PVPh/PEO blend, respectively. The behavior is found to be thermorheologically simple in all cases, and the empirical time–temperature superposition (tTS) principle applies to all the studied pure polymers and blends. For the pure PS and the PS/PPO (60/40, wt) blend, the minimum in loss tangent (tan δ) and plateau are clearly detected. PVPh and most PVPh/PEO compositions display a minimum in loss tangent (tan δ), but no clear plateau modulus is observed. The plateau modulus was therefore determined as an instantaneous point, i.e. the storage modulus at the minimum of tan δ [15]. In Fig. 2(a) is reported the PVPh/PEO (60/40) blend. For this specific composition, no minimum in tan δ could be detected.

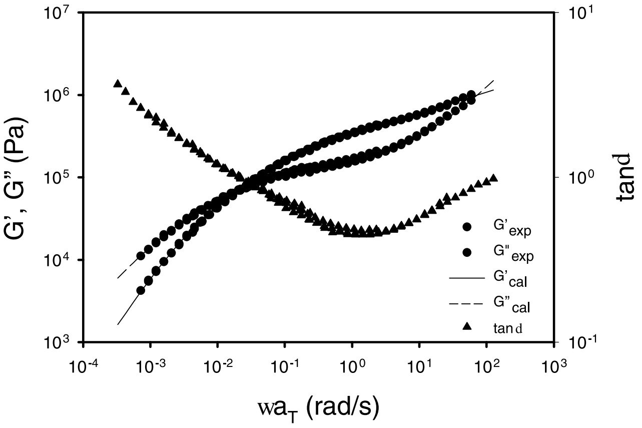

Fig. 1. Storage and Loss Moduli (G' and G'') of PS/PPO (60/40, wt) at $T_g + 15$.

Table 2
T_g, G_N^0 and η_0 values of PS/PPO and PVPh/PEO blends

Sample ID	PEO (mol%)	T_g (°C)	G_N^0(MPa) ⇒ $(G')_{\tan\,\delta\to\mathrm{minimum}}$	G_N^0(MPa) ⇒ G_c	η_0 at $T_g + 15$ (Pa s)
PS		98	0.151 ± 0.001	0.149 ± 0.008	6.82×10^4
PS/PPO (60/40, wt)		143	0.400 ± 0.008	0.403 ± 0.007	2.26×10^7
PS/PPO (50/50, wt)		151	0.455 ± 0.005	0.449 ± 0.013	3.19×10^7
PPO		217	1.190 ± 0.006	1.187 ± 0.005	$3.07 \times 10^{+11}$
PVPh	0	177	0.148 ± 0.006	0.140 ± 0.049	6.33×10^6
PVPh/PEO (95/5, wt)	13	154	0.147 ± 0.009	0.143 ± 0.033	3.56×10^7
PVPh/PEO (85/15, wt)	32	131	0.153 ± 0.006	0.150 ± 0.008	4.17×10^7
PVPh/PEO (82/18, wt)	37	120	0.157 ± 0.004	0.153 ± 0.003	1.24×10^8
PVPh/PEO (80/20, wt)	41	115	0.160 ± 0.005	0.154 ± 0.020	1.70×10^8
PVPh/PEO (77/23, wt)	45	101	0.168 ± 0.013	0.166 ± 0.009	2.49×10^7
PVPh/PEO (75/25, wt)	48	92	0.172 ± 0.009	0.175 ± 0.004	1.50×10^7
PVPh/PEO (70/30, wt)	54	88	0.194 ± 0.018	0.198 ± 0.013	2.12×10^7
PVPh/PEO (65/35, wt)	59	67	0.227 ± 0.016	0.224 ± 0.023	6.72×10^7
PVPh/PEO (60/40, wt)	65	33		0.326 ± 0.007	1.10×10^8
PEO	100	−61		0.907 ± 0.043	

In the terminal region, the rheological behavior of PS and PS/PPO is close to what is normally expected at the low frequencies, i.e. $G' \propto \omega^2$ and $G'' \propto \omega$. However, the rheological window is more limited for PVPh and for PVPh/PEO blends due to thermal degradation at high temperature and to brittleness of these blends. Some sets of rheological data cannot be extended to the terminal zone where $G' \propto \omega^2$ and $G'' \propto \omega$, in particular for the PVPh-rich blends with PEO compositions up to 20 wt%.

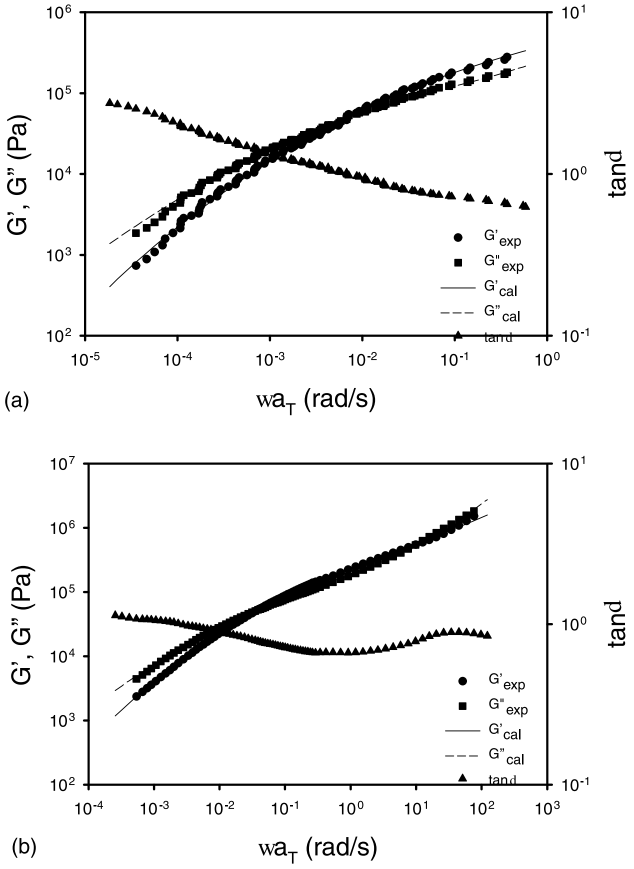

Fig. 2. Storage and loss Moduli (G' and G'') of PVPh/PEO blends at $T_g + 15$ (a) PVPh/PEO (60/40, wt), (b) PVPh/PEO (70/30, wt).

3.3. Determination of G_N^0

G_N^0 is a key parameter to determine M_e [16]. Usually, for amorphous polymers, G_N^0 can be estimated from the storage modulus at the frequency where a minimum of the loss tangent (tan δ) occurs. In the present work, except for the PVPh/PEO (60/40, wt) blend, the plateau modulus for all other blends (PS/PPO, PVPh/PEO) was obtained by $G_N^0 = (G')_{\tan\,\delta\to\mathrm{minimum}}$. For the PVPh/PEO (60/40, wt) blend, no minimum in tan δ was observed. This is attributed to the limited temperature range accessible for this blend composition whose $T_g = 33$ °C. Test temperature was varied from 43 °C ($T_g + 10$) to 133 °C ($T_g + 100$ °C) in order to be within the applicability range of the WLF equation, and thus far away from the low frequency terminal zone. Therefore, the plateau modulus was deduced from the crossover modulus, G_c, using the following semi-empirical equation [17]

$$\log(G_N^0/G_c) = 0.380 + \frac{2.63(\log p)}{1 + 2.45(\log p)} \tag{2}$$

where p is the polydispersity ($p < 3$), and $G_c = G'(\omega_c) = G''(\omega_c)$. This equation was proposed by Wu [17], taking into account the effects of molecular weight distribution. The validity of the equation was confirmed theoretically and experimentally for several amorphous and crystalline polymers [17]. Wu [6,17] and Tsenoglou [7] indicated that the above techniques for measuring G_N^0 are also applicable for a binary miscible blend. The polydispersity of the PVPh/PEO blend as estimated using the polydispersities of the pure polymers is 2.6 ± 0.1. It must be noted that as reported in Table 2, this approach yielded, within experimental error, similar values to those of the minimum in tan δ for compositions where the latter were observed, thus confirming the validity of the approach for the PVPh/PEO blend studied here.

The plateau moduli G_N^0 for PVPh/PEO blends are also shown in Fig. 3, with respect to weight fraction. As can be seen, G_N^0 is almost insensitive to blend composition up to 30 wt% of PEO. Above this concentration, G_N^0 appreciably increases with PEO concentration.

Wu [6] proposed an athermal blending model for miscible blends, as expressed by

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 \tag{3}$$

where G_{Nj}^0 is the plateau modulus of the blend ($j = b$) or the constituent ($j = 1$ or 2), and ϕ_i ($i = 1$ or 2) the volume fraction. In the athermal blending case, specific interchain interactions exert little influence on entanglement probability, which is unperturbed with respect to individual components.

Tsenoglou [7], on the other hand, proposed a random formation of chain entanglement between chains of the two components in a miscible blend. The blending rule for the athermal case is then given by

$$(G_{Nb}^0)^{1/2} = \phi_1 (G_{N1}^0)^{1/2} + \phi_2 (G_{N2}^0)^{1/2} \tag{4}$$

which is based on the fact that entanglement probability between dissimilar chains is proportional to the geometric average of the entanglement probability between similar chains.

Lomellini [18] has already compared the weakly interacting PS/PPO blends with the mentioned two athermal blending cases. G_N^0 values of PS/PPO were reasonably close to the model predictions using Tsenoglou's athermal case blending rule. On the other hand, Wu's model showed an increased entanglement probability with reference to Tsenoglou's athermal case. Lomellini proposed that the weak interactions in PS/PPO blends exert little influence on the entanglement probability, and thus result in an athermal case described by the above-mentioned equations. Further, Aoki and Tanaka [13] showed, for PMMA/SAN blends, that variations in the Flory–Huggins interaction parameter (χ) did not change the linearity of G_N^0 vs. blend composition curves. However, although the specific values of χ were not determined, it is known from small-angle neutron scattering that the PMMA/SAN blends are weakly interacting with χ values averaging -0.011 [19]. Whereas small variations in χ may not affect G_N^0 and entanglements markedly, strong interchain interactions are proposed to have a stronger influence. In the present case, the experimentally determined G_N^0 values of PVPh/PEO are significantly lower than both the Wu and the Tsenoglou model predictions, up to a concentration of 40 wt% PEO, as seen in Fig. 3. This is attributed to the presence of stronger interchain interactions, which may exert a repulsive effect on the entanglement probability of the PVPh/PEO blends. Therefore, a PVPh/PEO blend is not athermally entangled according to neither Wu's model nor Tsenoglou's model.

G_N^0 values deviate significantly from those calculated by the athermal case blending rules, and the rheology of PVPh/PEO differs significantly from that of the weakly interacting PS/PPO. This is mainly attributed to the formation of strong hydrogen bonds in PVPh/PEO mixtures, which are not accounted for by the athermal models.

3.4. Determination of η_0

Zero-shear viscosity of a miscible blend, η_{0b}, is directly related to global interchain friction coefficient (ξ) [16]. The zero-shear viscosity (η_0) can be either directly obtained by inspection of the experimental data or else estimated from the relaxation spectrum, $H(\tau)$, using Eq. (1).

As seen in Figs. 4 and 5, rheological windows of $G'(\omega)$ and $G''(\omega)$ are limited to the range of $10^{-5}-10^5$ for PS/PPO and $10^{-3}-10^5$ for PVPh/PEO. As for PVPh/PEO blends, the experimental window is not large enough to reach the low frequency terminal zone where the zero-shear viscosity could be deduced. More specifically, for the PVPh/PEO blends of composition ranging from 0 to 20 wt% of PEO, thermal degradation limited rheological measurements at higher temperatures, therefore limiting the experimental window. Using conventional techniques to estimate η_0 could lead to errors of the order of 50% in the case of PVPh/PEO blends. Consequently, conventional ways to determine

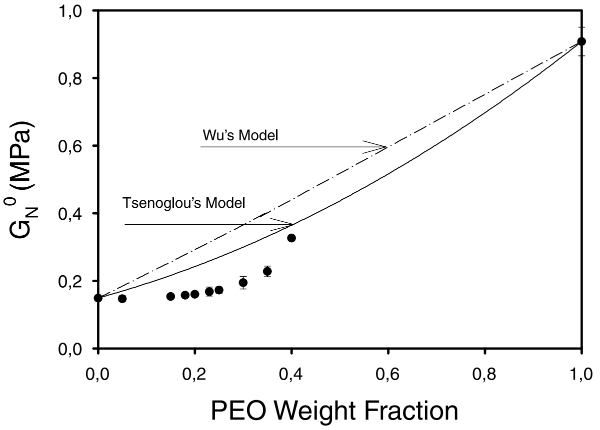

Fig. 3. Plateau modulus (G_N^0) vs. blend composition for PVPh/PEO blends.

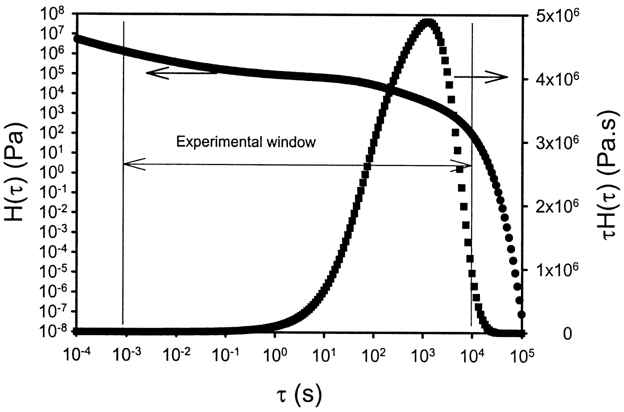

Fig. 4. Relaxation spectrum of PS/PPO (60/40, wt).

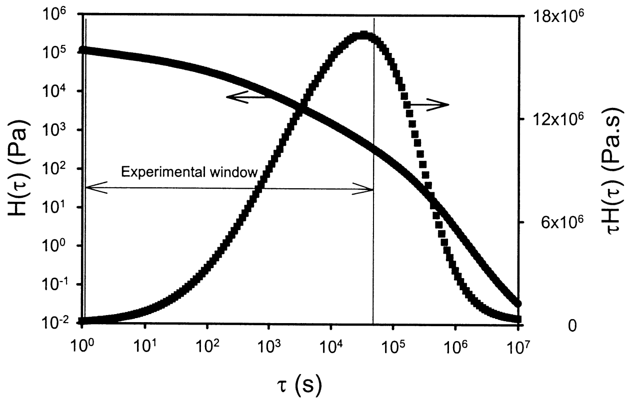

Fig. 5. Relaxation spectrum of PVPh/PEO (60/40, wt).

η_0, such as $\eta_0 = \lim_{\omega\to0} G''(\omega)/\omega$, are not applicable to the PVPh/PEO system.

Based on these rheological data, however, the relaxation spectra determined by the neutral network model can be extended to a larger range, as shown in Figs. 4 and 5 for typical relaxation spectra of PS/PPO and PVPh/PEO blends, respectively. This has been done following the approach developed by Grandjean, Ait-Kadi and Coté [11]. The relaxation spectrum reflects the response of the polymer to a given deformation history by considering the weighted contributions of each relaxation mode. The relatively large range can be viewed as an extrapolation of the experimental data to the lower and higher frequencies. In the case of PS/PPO blends, as seen in Fig. 4, this extrapolation is limited. For PVPh/PEO blends, it encompassed an important section of the peak. Care was therefore taken to fit as accurately as possible for the experimental section of the curve, as well as to verify the initial model settings and optimization parameters, which can affect the resultant relaxation spectra. Typical relaxation spectra are obtained when the spectrum is Gaussian-shaped. The relaxation spectra of PVPh and PVPh/PEO are broader than those of PS and PS/PPO. Similar results were obtained by Stadler et al. [20–23], who reported that hydrogen bond formation in the functionalized polybutadienes results in a broadened relaxation time spectrum and an increase in zero-shear viscosity. Further, G' and G'' curves were recalculated from the relaxation spectra deduced by the neural network model using the following equations [11,16]

$$G'(\omega) = \int_{-\infty}^{+\infty} \frac{\omega^2\tau^2}{1+\omega^2\tau^2} H(\tau)\mathrm{d}(\ln\tau) \tag{5}$$

$$G''(\omega) = \int_{-\infty}^{+\infty} \frac{\omega\tau}{1+\omega^2\tau^2} H(\tau)\mathrm{d}(\ln\tau) \tag{6}$$

Results appear as a solid line for G' and a dotted line for G'' in Figs. 1 and 2. The excellent fit between the calculated and experimental G' and G'' data guarantees in part the correctness of the calculated relaxation spectra, at least within the experimental window explored for each sample.

Until now η_0 values of PS/PPO at T_g or at temperatures equally distant from the T_g have not been reported in the literature. For the PS/PPO blends, for which limited compositions have been studied, η_0 values always increases with PPO composition at $T_g + 15$ as reported in Table 2. On the other hand, as can be seen in Fig. 6, for the PVPh/PEO blends at $T_g + 15$, η_0 increases upon addition of PEO to PVPh up to a composition of 20 wt% of PEO, drops at 30 wt% of PEO, and then starts increasing again. In order to verify that the maximum in η_0 values around 0.2 PEO weight fraction was not an artefact, two blend compositions were specially introduced in the neighborhood of this concentration, i.e. 0.18 and 0.23 PEO weight fractions. The η_0 values of these two blend compositions confirm the presence of the maximum.

This discontinuous behavior in η_0 was unexpected. It could stem from improper extrapolation, although this seems improbable in view of the fact that the value reported here is the average over 2–3 distinct experiments. η_0 is related to friction coefficient, ξ_0, and is also correlated to variations in free volume caused by interchain interactions [24,25]. The 30 wt% PEO composition corresponds to a 54 mol% PEO composition. This suggests that a change in the polymer forming major entanglement network, at a concentration where the dominant network forming chains shift from the PVPh-based type to a PEO-based one, exerts an influence on interchain interactions in terms of friction or free volume. For the PVPh-based network, PEO chains tend to form hydrogen bonds with rigid PVPh chains. The portion of PEO that binds to PVPh is rigidified and adopts almost the same type of entanglements as that of PVPh–PVPh chains. Upon changing the network type to a PEO-based one, PEO chain entanglement will now revert to that of pure PEO, albeit with a rigidification proportional to the number of PVPh chains present. Further work on quantification of hydrogen bond formation will be necessary to clarify this point. The fact that a switch in regime occurs at relatively low weight percentage can be attributed to the presence of a bulky side group on the PVPh chains, and

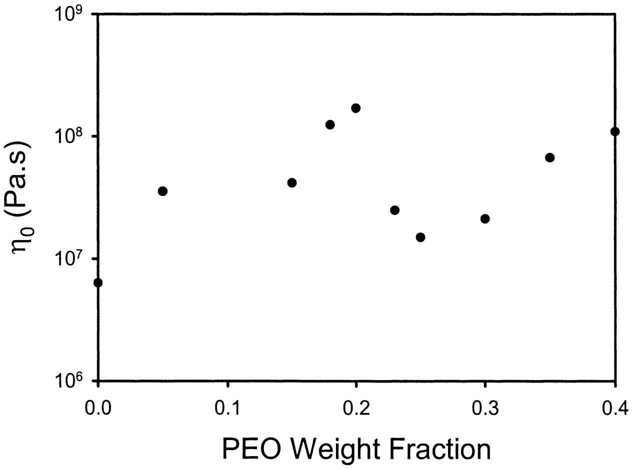

Fig. 6. Zero-shear viscosity (η_0) values of PVPh/PEO blends at $T_g + 15$.

therefore molar percentages describe more aptly the network state.

3.5. Determination of WLF parameters

For all studied polymers and blends, master curves have been obtained at $T_{ref} = T_g + 15$ °C. It can be recalled that one of the major aims of this study was to shed light on the specific orientation behavior of the PVPh/PEO system [3]. As deformation is normally conducted at a constant temperature vs. T_g, it was imperative to select such a reference temperature for the determination of the rheological parameters. The horizontal shift factors (a_T) as a function of temperature for both PS/PPO and PVPh/PEO samples is represented by the WLF equation

$$\log a_T = \log \frac{\eta_0(T)}{\eta_0(T_0)} = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \tag{7}$$

where $C_1^0 = 8.86$, $C_2^0 = 101.6$. An adjustable parameter, T_0 is generally found to be about 50 °C above T_g for various polymer systems [13,26]. At T_0, the rheological behavior of different blend compositions can be compared under iso-free volume conditions [8]. For the PS/PPO blends, $T_0 - T_g \cong 66.5$, and T_0 for the two blend compositions studied follows a linear relationship with the weight fraction of PPO, as is the case for most miscible blends having negligible thermodynamic interactions reported in the literature [13,26]. Both Wu [7] and Aoki [13] mentioned that the free volume of miscible blends tends to be linearly additive, and the free volume additivity results in a decrease in melt viscosity.

Doolittle [27] proposed that the melt viscosity was related to the fractional free volume, f, as expressed by

$$\ln \eta = \ln A + \frac{B}{f} \tag{8}$$

where A and B are constants. Therefore, the maximum in η_0 observed in Fig. 6 indicates a minimum in free volume, which could be due to a decrease in average distances between interacting groups upon hydrogen bond formation. This may also be responsible for the observed non-linearity in T_0 in Fig. 7, as in the presence of a decrease in free volume, a higher temperature may be needed to reach iso-free volume conditions. Further, in Fig. 7, a discontinuity in T_0 is observed at 30 wt% of PEO or 70 wt% of PVPh. This composition is close to that of the discontinuity in η_0 and of the maximum in orientation previously observed in uniaxial deformation studies [3], and therefore further points to the close relationship between rheological behavior and orientation in this blend.

As mentioned earlier, it is often of interest to compare rheological behavior of miscible blends under iso-free volume conditions. When $T_0 = T_g + 15$ °C is selected as an adjustable parameter for all PVPh/PEO blends, the obtained horizontal shift factor variables with temperatures (a_T) are shown in Fig. 8. Some rheological data fits extend up to $T_g + 200$ °C, far beyond the limit of applicability of the WLF equation. In these cases, the Arrhenius equation was used to estimate a_T as a function of T

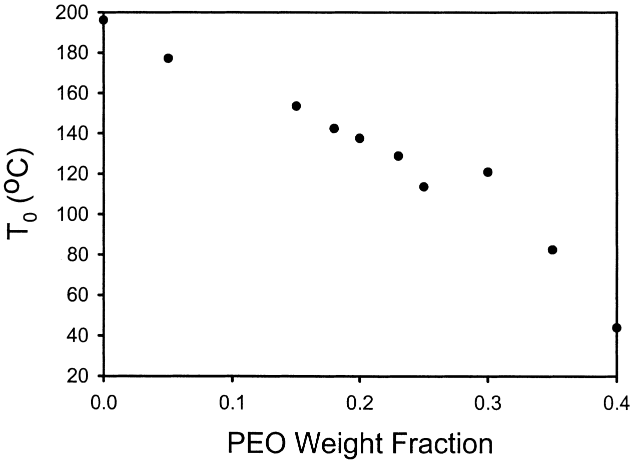

Fig. 7. T_0 values of PVPh/PEO blends.

$$\ln a_T = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{9}$$

where E_a is the flow activation energy, and R is the universal gas constant. The Doolittle equation relates the WLF parameters, C_1^0 and C_2^0, to the fractional free volume (f_0) and the thermal expansion coefficient of free volume (α_f) at T_0, i.e. $f_0 = B/2.303C_1^0$ and $\alpha_f = B/2.303C_1^0C_2^0 = f_0/C_2^0$, where B is assigned a value of unity [25].

A more useful reference temperature for our purpose is T_g or $T_g + x$, which is the reference temperature normally used for deformation-induced orientation studies. It is also the reference temperature used for PS/PPO by Prest and Porter [9], who showed that a_T is comparable, within experimental error, for all PS/PPO compositions. In other words, the fractional free volume at the reference temperature of T_g, f_g, is nearly invariant with composition for PS/PPO, and α_f slightly decreases

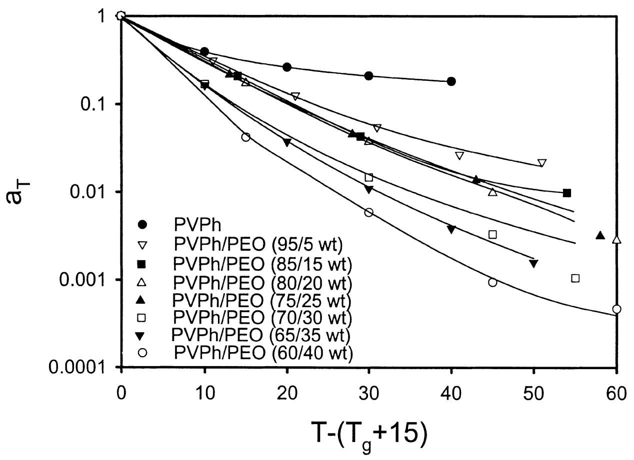

Fig. 8. Horizontal shift factors (a_T) with temperatures in PVPh/PEO blends.

with PPO weight fraction. These results showed that, for PS/PPO, iso-free volume conditions are observed at T_g. On the other hand, the a_Ts of PVPh/PEO samples show a compositional dependence. Fig. 8 shows that there are no universal WLF parameters for the PVPh/PEO system at $T_{ref} = T_g + 15$, and that the difference in temperature dependence of viscosity between PVPh and PEO is large.

Many factors have been reported to affect the WLF parameters, such as polydispersity and crystallinity [28, 29]. When one of the constituents in a miscible blend is crystalline, e.g. the PEO component in a PVPh/PEO blend, the melting point of the crystalline component plays a more important role than the glass transition temperature in determining the rheological window regarding viscoelastic properties. According to Yang, Han and Kim [28], when a miscible blend shows thermodynamic interactions, as was the case for the PVDF component in a PMMA/PVDF blend ($\chi = -0.5$), different behaviors are observed when varying blend composition for the a_T vs. T curves. Pathak and Colby [30] also observed similar behaviors. As reported in the literature [20–23,31], formation of hydrogen-bonding networks in polybutadienes and ureidopyrimidone leads to higher WLF parameters. For miscible blends consisting of two amorphous constituents showing weak interactions ($\chi \approx -0.01$), such as PMMA/SAN blends, there is little change in the a_T value for each blend composition [26,28]. Moskala and Coleman [32] indicated that hydrogen bonds form the dominant interactions in PVPh blends, and the strength or number of the interactions is clearly a function of temperature. As temperature increases, the extent of the interaction term decreases while that of the free volume term increases. Although many factors cause variations in WLF parameters of the PVPh/PEO blends, it is proposed that, in this case, the most probable cause for the observed behavior is hydrogen bond formation and its temperature dependence.

4. Conclusion

Rheology of hydrogen bond forming PVPh/PEO blends differs significantly from that of weakly interacting PS/PPO blends. This is mainly attributed to formation of strong hydrogen bonds in PVPh/PEO mixtures. G_N^0, η_0 and T_0 show a discontinuity around 30 wt% of PEO, i.e. approximately 50 mol% of PEO. This can be correlated to the occurrence of a maximum in orientation upon uniaxial deformation near this concentration, as previously observed [3].

Although a correlation between G_N^0, η_0 and deformation-induced uniaxial orientation was expected, it is the first occurrence in the literature, to our knowledge, where it is as striking. This is proposed to be due to a change in entanglement network formation when the dominant polymer, as determined by mol% and not wt%, attains approximately 50%, therefore provoking a change in entanglement network type in the system.

According to Ferry, G_N^0 is related to M_e and η_0 to ξ [16]. Both M_e and ξ have been proposed to be related to post-deformation relaxation in oriented polymer via Doi and Edwards theory [4]. Therefore, it was expected that the behavior of G_N^0 and η_0 could relate to that of deformation-induced orientation. However, in this particular case, the correlation is even more evident as it is expressed by an important discontinuity in the rheological behavior of the blends.

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