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Composition-dependent dynamics in miscible polymer blends: influence of intermolecular hydrogen bonding

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Abstract

Dynamics of the miscible blend of poly(vinyl methyl ether) and poly(4-vinylphenol) [PVME/PVPh] have been studied using broadband dielectric relaxation spectroscopy (DRS). The results are compared with those reported for PVME/polystyrene [PS] and PVME/poly(2-chlorostyrene) [P2CS] blends to examine the effect of intermolecular hydrogen bonding. These blends have similar chemical structures, with the exception that strong intermolecular hydrogen bonds are formed between PVME and PVPh. Whereas PVME and P2CS (or PS) relax individually in their blends due to intrinsic mobility differences and the absence of strong intermolecular interactions, the segmental relaxations of PVPh and PVME are coupled in the blends controlled by intermolecular hydrogen bonding. Dynamic heterogeneity was observed in PVPh/PVME blends with PVPh concentration higher than 50%. This is due to the decoupling arising from the strong intramolecular hydrogen bonding between PVPh segments. Finally, in the blend, the secondary relaxation processes of both components occur at approximately the same temperature-frequency location as those in corresponding neat polymers, but with much lower intensity, suggesting suppression by the intermolecular hydrogen bonding. Our results suggest that the composition-dependent dynamics in PVPh/PVME are even more complicated than that observed in blends without strong intermolecular interactions.

Keywords: Dynamics; Hydrogen bonding; Dielectric spectroscopy

1. Introduction

A classical and simple experimental criterion for determining miscibility in polymer blends is based on the measurement of the calorimetric glass transition temperature [T_g] by differential scanning calorimetry [DSC], and a single T_g is anticipated if the component polymers are thermodynamically miscible [1]. Another general method is to evaluate the dynamic segmental (α) relaxation process(es) of a blend, either dielectrically [DRS] or mechanically [DMA]; a single α process, located between those of the neat components, also indicates miscibility [2]. However, since these methods interrogate blends at different length scales, apparently contradictory conclusions are sometimes arrived at for the same blend, based on results from different experimental techniques.

One of the most well-studied blend systems is polystyrene [PS]—poly(vinyl methyl ether) [PVME]. The miscibility of PS/PVME has been confirmed by DSC measurements, in which a single T_g is observed in blends with different compositions and different component molecular weights. Although no strong specific interactions exist between PS and PVME, small-angle neutron scattering [SANS] measurements have established a marginally negative χ (~ -0.01, depending on temperature and composition), which is attributed to the interaction between the aromatic ring in PS and the ether oxygen in PVME [3]. In apparent contrast however, dielectric relaxation spectroscopy, DMA, thermal stimulated depolarization current [TSDC], FTIR, and NMR results demonstrate that segments of PS and PVME have very different relaxation rates, even at temperatures far above the blend T_g [3–11].The relaxation of the lower T_g PVME is found to be much faster (>3 decades) than that of PS segments, close to the blend T_g.

Whereas, only the segmental relaxation of PVME can be dielectrically observed due to the small dipole moment of the PS repeat unit, in PVME/poly(2-chlorostyrene) [P2CS] blends both components are dielectrically active. In a DRS

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study of the P2CS/PVME blend, Urakawa and co-workers clearly observed two segmental relaxation processes, although these polymers are miscible [12]. They attributed this to the large intrinsic mobility difference between P2CS and PVME, as inferred from the large difference in their T_g's($\Delta T_g \sim 130$ K). Even in the miscible blend environment, the two polymers still relax individually. This was later confirmed by a TSDC study, in which it was again found that P2CS and PVME have different effective local glass transition temperatures [T_g^{eff}] [13]. The TSDC results were quantitatively interpreted using the self-concentration model of Lodge and McLeish [14]. It was proposed that P2CS and PVME experience different local concentrations due to chain connectivity effects and their effective T_g's are consequently different.

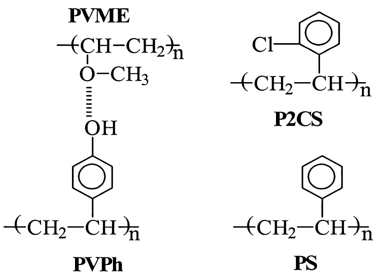
Although similar dynamic heterogeneity has also been observed in other miscible polymer blends with large ΔT_g, a common feature of them is the absence of any specific intermolecular interactions between the corresponding component polymers, e.g. only van der Waals interactions between PS and PVME and polar–polar interactions between P2CS and PVME. In this paper we present a study on a chemically similar blend, PVME with poly-(4-vinylphenol) [PVPh] (Scheme 1), in which strong intermolecular hydrogen bonds can form between the phenolic –OH groups and the ether groups in PVME. Therefore, the influence of intermolecular hydrogen bonding on the segmental dynamics and miscibility can be examined by comparing the present findings with those on PS/PVME and P2CS/PVME blends.

2. Experimental

2.1. Materials and sample preparation

PVME was purchased from Scientific Polymer Products Inc. and has $M_w = 46{,}000$ and $M_n = 8{,}400$. PVPh (Aldrich, Inc.) has $M_n = 21{,}000$ and $M_w/M_n = 2.5$. Molecular weights of both polymers were determined by gel permeation chromatography using tetrahydrofuran as the mobile phase and narrow molecular weight distribution polystyrene standards.

Blends with PVPh concentrations ranging from 10 through 80 wt% were prepared by solution casting. 5 wt% methyl ethyl ketone solutions of the neat polymers were mixed and stirred for at least 30 min before being cast into Teflon-coated foil dishes. The solvent was removed in a vacuum oven while gradually increasing temperature at ~5 K/12 h up to $T_g + 20$ K. All films were ~200 μm in thickness. For DRS studies of samples with T_g above room temperature, gold was sputtered on both sides in an argon atmosphere. For neat PVME, and the 10–30% PVME blends (whose T_g's are well below ambient), gold sputtering was not attempted; these samples were sandwiched between two electrodes and a polypropylene spacer was used to control the thickness.



Scheme 1. Chemical structures of polymers.

Samples for DSC analysis were prepared by directly cutting specimens from the corresponding DRS samples before the dielectric experiment, with weight approximately 10 mg.

2.2. Characterization

2.2.1. DRS Experiments

The dielectric spectra $\varepsilon^*(f, T)$ were collected isothermally using a Novocontrol GmbH Concept 40 broad-band dielectric spectrometer in the frequency domain [0.01 Hz–10 MHz], on cooling from $\sim T_g + 80$ K to T_g. For PVME, the 30, 50, and 80% PVEE blends, dielectric spectra at temperatures from −160 °C to T_g were also collected to study the local relaxation process(es). Sample films were held between two parallel gold-sputtered steel electrodes, having a diameter of 20 mm. Temperature was controlled by a Novocontrol Quatro Cryosystem, which uses N_2 to heat and cool the sample and has a stability of ±0.1 K.

2.2.2. Glass transition

DSC experiments were performed using a Seiko SSC 5200 DSC. The samples were first heated to 50 K above the expected T_g, held for 3 min and then cooled at a rate of 20 K/min. After soaking at a minimum temperature [$T_g - 40$ K] for 5 min, the sample was heated again at a rate of 10 K/min. T_g was taken as the midpoint of the heat capacity change in the second heating run.

2.2.3. Hydrogen bonding

A Bio-Rad FTS-6 spectrometer was used to collect FTIR spectra of the blends and PVPh, with a resolution of 2 cm^{-1} by averaging 64 scans. Sample solutions were dropped onto KBr windows and the solvent removed in a heated vacuum oven, following the same procedure as that for DRS samples.

3. Results

3.1. Miscibility in PVPh/PVME blends

The miscibility between PVME and PVPh has been studied previously using DSC and FTIR spectroscopy

[15–17]. It was found that miscibility can be achieved across the entire composition range, due to the strong intermolecular hydrogen bonding. Since polymers with different molecular weights were used in these previous studies, we confirmed the miscibility for the polymers used here from their DSC thermograms (Fig. 1). It is worth noting that the glass transition interval of the blends is significantly broadened to about 20–30 °C, compared with ~8 °C for neat component polymers. However, in general, the broadening is somewhat smaller than in the corresponding PS/PVME blend (breadth up to ~45 °C, for blends with 50–80% PS) [5].

Inter- and intramolecular hydrogen bonding in the component polymers and blends can be examined by assessing the phenolic hydroxyl stretching in FTIR spectra. In the spectra of PVPh/PVME blends, there are three principle bands arising from the phenolic –OH: 'free', intramolecularly hydrogen-bonded, and intermolecularly hydrogen-bonded with the ether oxygen in PVME, progressing from high to low wavenumber (Fig. 2). The larger wavenumber shift of the intermolecularly H-bonded –OH confirms that intermolecular hydrogen bonding between PVME and PVPh is stronger than that among PVPh repeat units themselves.

3.2. Dielectric segmental relaxation

The segmental relaxation (α) of PVME occurs above its T_g and involves the cooperative relaxation of a few repeat units. As shown in Fig. 3, the relaxation time distribution of the α process in PVME is relatively narrow, with a full width at half-maximum [FWHM] of ~2.5 decades. The FWHM essentially does not change with temperature, indicating that time–temperature supposition [TTS] principle is valid for this process. The maximum height of the loss spectra is ~0.6, which is quantitatively consistent with the value reported by Cendoya et al. [6]. The α process follows the well-known Vogel–Fulcher–Tammann [VFT] equation [18]:

$$\tau = \tau_0 \exp[B/(T - T_0)] \quad (1)$$

in which τ is the segmental relaxation time, τ_0 is a prefactor correlated to the time scale at which the molecules are attempting to overcome some energy barrier. B is a parameter related to strength for glass-forming. T_0 is a temperature at which the segments are frozen. For the PVME used in the present study, VFT fitting leads to $\tau_0 = 4 \times 10^{-13}$ s, $B = 0.116$ ev = 1346 K, and $T_0 = 203$ K.

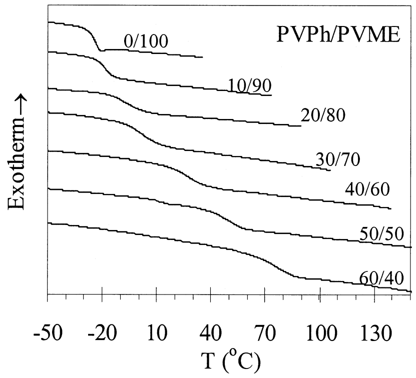


Fig. 1. DSC thermograms of PVPh/PVME blends: second heating run, heating rate = 10 K/min.

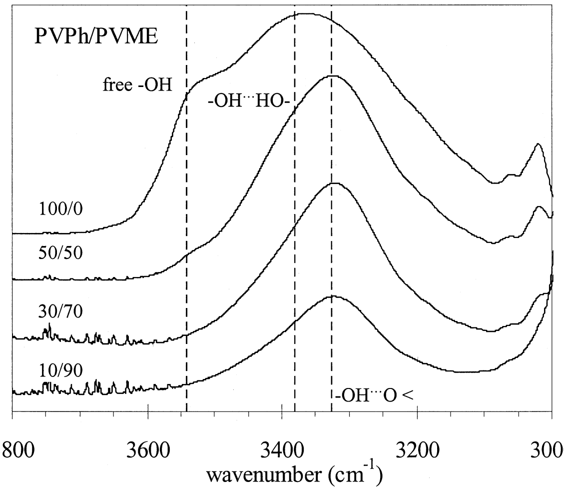


Fig. 2. FTIR spectra of PVPh/PVME blends at room temperature.

3.2.1. Relaxation in blends with low PVPh concentration

For blends with PVPh concentrations ≤50%, although the segmental relaxation time distribution has been broadened considerably, only a single α process is observed (Fig. 4). This is a quite significant finding considering the relaxation behavior observed for PS/PVME and P2CS/PVME blends and the very large ΔT_g for PVPh/PVME. Since both PVPh and PVME have comparable dipole moments, the α process of the blends will include contributions from both polymers, just as in P2CS/PVME. The observation of one α process immediately suggests that PVME and PVPh have similar relaxation rates in blends

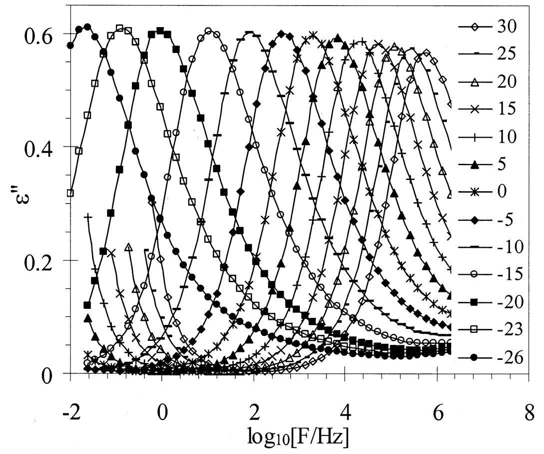


Fig. 3. DRS loss spectra of PVME. The labels inside each figure give corresponding temperatures in °C.

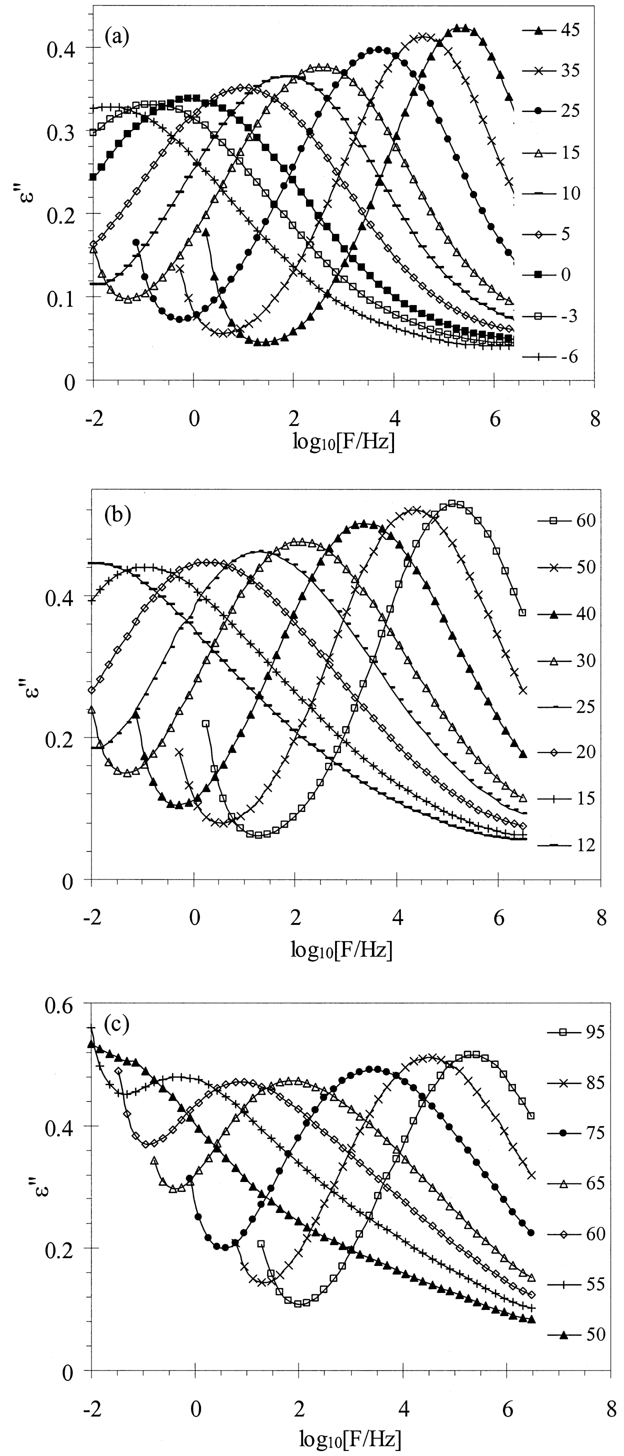


Fig. 4. DRS loss spectra of PVPh/PVME blends with PVPh concentration of (a) 20%, (b) 30%, and (c) 50%. The labels inside each figure give corresponding temperatures in °C.

with [PVPh] ≤50%, despite their large intrinsic mobility difference. In PS/PVME, only PVME contributes to the dielectric α process, and the broadening of relaxation time distribution was attributed to concentrations fluctuations (CF) [4]. Strong intermolecular interactions are believed to be able to damp CF, thus this will not be considered further here. Because the primary difference between the present blend and P2CS/PVME (and PS/PVME) lies in the existence of strong intermolecular hydrogen bonding in PVPh/PVME, the different segmental relaxation behaviors can be rationalized by invoking the coupling effect of the intermolecular hydrogen bonding, as proposed in our previous studies on blends of poly(vinyl ethyl ether) [PVEE] with PVPh [19] and a styrene-*co*-*p*-hydroxystyrene random copolymer [SHS] [20]. Strong intermolecular associations like hydrogen bonding are capable of coupling components' segmental relaxations in polymer blends with large mobility difference.

Close inspection of the dielectric spectra reveals further evidence for intermolecular coupling. For blends with 10 and 20% PVPh (Fig. 4a—for clarity, the spectra of the 10% blend is not shown), the segmental relaxation time distributions exhibit clear low frequency broadening. This can be interpreted by the co-existence of hydrogen-bonded and non-associated PVME segments in these blends, as a result of low PVPh content. The hydrogen bonded PVME and PVPh segments contribute to the slow relaxation portion, and the 'free' PVME to the faster part of the spectra. However, it should be pointed out that the low-frequency broadening in 20/80 PVPh/PVME is less significant than that observed in similar PVPh/PVEE blend; in the latter a visible shoulder developed at the low frequency side of the main process [19]. This difference can be rationalized by considering the effect of the more bulky ethyl species in the PVEE side groups. The ethyl group is considerably larger than the methyl of PVME and it can shield the ether oxygen from forming hydrogen bonds with PVPh. This leads to more and stronger intermolecular hydrogen bonds in PVME/PVPh than in PVEE/PVPh blends, that is, a stronger coupling in the former. In fact, it has been observed that the miscibility of poly(vinyl alkyl ether)s with PVPh deteriorates as the alkyl side group becomes larger [15].

Following the same stoichiometric argument for hydrogen bonding, the low frequency shoulder should disappear if all PVME segments are hydrogen-bonded with PVPh. This expectation is in fact confirmed in blends with higher PVPh concentrations, i.e. 30–50%, in which a single segmental relaxation process is observed (Fig. 4, spectra of 40% not included for clarity). Although the fraction of hydrogen bonds between hydroxyl and ether groups cannot be experimentally measured by FTIR, due to serious band overlap in the hydroxyl stretching region, it can be theoretically calculated using the association constant between these two groups in small molecular analogs [16,21]. The validity of this approach has been confirmed in previous studies. Our calculations indicate that about 40–55% of the PVME ether groups, i.e. one out of every two or three, are associated with PVPh in these blends. Considering that one independent relaxing segment may include several repeat units, the results of the above calculation suggest that nearly every segment of PVME interacts via at least one intermolecular hydrogen bond with PVPh, and unassociated PVME segments essentially disappear in blends with high PVPh content. Note that if one repeat unit of the relaxing segment is hydrogen-bonded, the entire segment will likely be coupled with the relaxation of PVPh to some degree. Similar behavior has also been observed in our DRS studies of PVEE/PVPh and PVEE/SHS blends and explained by the same stoichiometric model for intermolecular hydrogen bonding [19,20].

However, it should be noted that the coupling does not necessarily establish that PVME and PVPh segments are relaxing simultaneously, although a single α process is dielectrically observed. Two relaxing segments may have different mean relaxation times (i.e. dynamical heterogeneity still exists), but these may not be as widely separated (and hence observable) as in blends without strong intermolecular interactions (e.g. PS/PVME, P2CS/PVME). The intermolecular hydrogen bonding influences the dynamics by significantly increasing the monomer friction coefficient of PVME and decreasing that of PVPh, therefore minimizing the difference to a degree that only one peak can be observed in the dielectric loss spectra. It is reasonable to expect that stronger intermolecular interactions would lead to a narrower relaxation time distribution in polymer blends and a truly single segmental relaxation process can be achieved, if the interaction is as strong as a covalent bond. The degree of coupling between different segments depends on how effectively the stress is transferred from one segment (low T_g) to its neighbor (high T_g). In an ideal network, if the crosslink density is sufficiently high, all segments must move cooperatively due to the constraint from the crosslink junctions, whereas in polymer blends one segment can move with little or no co-operativity with its partner if the frictional force between them is too weak to support the stress. Hydrogen bonding enhances the friction between different segments, and the degree of coupling is therefore generally higher than that in blends without strong intermolecular interactions.

Three additional features of the segmental relaxation of the PVME/PVPh blends deserve comment. First, the peak location at constant temperature gradually shifts to lower frequency with increasing PVPh concentration, since the T_g of PVPh is much higher than PVME. Secondly, the relaxation time distribution becomes significantly broader compared with that of neat PVME, demonstrating that dynamic heterogeneity exists even though all segmental relaxations are coupled. Finally the dielectric loss peak for a particular blend clearly narrows with increasing temperature, as a result of weakened dynamical heterogeneity at higher temperatures.

The most probable segmental relaxation time ($\tau_{\max}$) can be determined by fitting the measured dielectric loss spectra in the frequency domain with the phenomenological Havriliak–Negami (HN) equation [22,23]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega) = \varepsilon_\infty - \mathrm{i}\frac{\sigma_0}{(\varepsilon_v\omega)^s} + \frac{\Delta\varepsilon}{[1+(\mathrm{i}\tau_{HN}\omega)^m]^n} \qquad (2)$$

in which σ_0, s, τ_{HN}, $\Delta\varepsilon$, m, and n are free variables in fitting the DRS loss spectra, ε''. $\tau_{\max}$ can be calculated from the fitted τ_{HN} following the procedure described in Ref. [24], together with the physical significance of the different parameters in the HN equation.

Fig. 5 contains the fitted relaxation times of blends with PVPh concentrations up to 50%. In the plot it is clear that all segmental relaxations follow the VFT equation and the relaxation time increases with increasing PVPh concentration. It is common practice to normalize the temperature with a reference temperature T_{ref} to compare the glass transition behavior of materials with different T_gs. We define T_{ref} as a temperature at which $\tau_{\max} = 1$ s, the same definition used in our previous work on PVPh/PVEE and

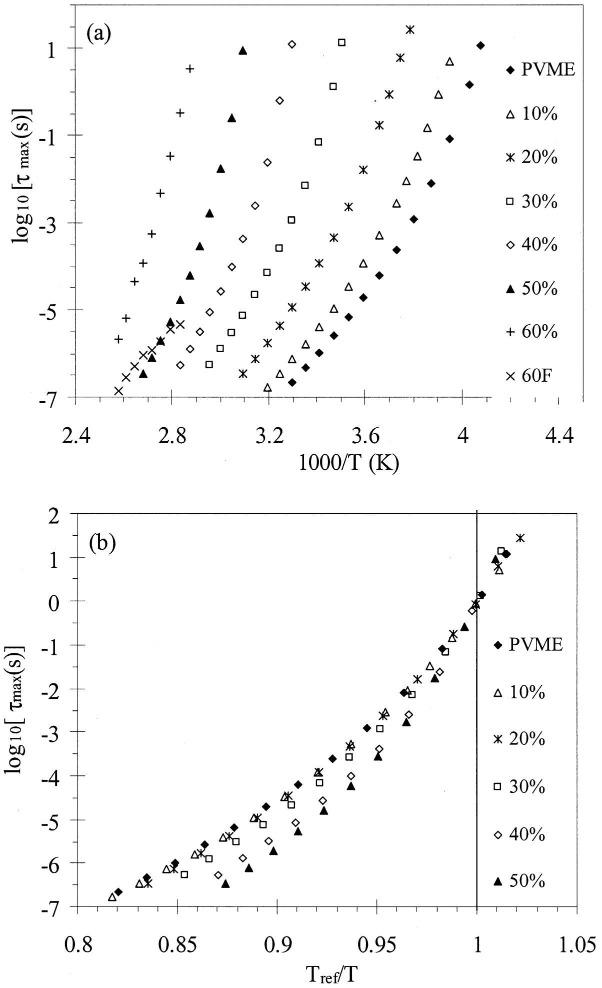


Fig. 5. Segmental relaxation time of PVPh/PVME blends: (a) VFT plot, (b) fragility plot. The percentage in the label indicates the weight concentration of PVPh. '60F' in (a) is the relaxation time of the fast process in 60% blend. T_{ref} was defined as the temperature at which $\tau_{\max} = 1$ s.

SHS/PVEE blends. The normalized Arrhenius plot, i.e. the so-called fragility plot, is also shown in Fig. 5. The fragility is defined as the slope at T_{ref} and it reflects the temperature sensitivity of the segmental relaxation time [25,26]; larger fragility has been correlated with stronger intermolecular coupling or larger segmental size [27,28]. Although $\tau_{\max}$ for PVME and its blends with 10 and 20% PVPh are indistinguishable, the fragility increases with increasing PVPh concentration in the other blends. Quantitatively, the fragility F can be calculated using the VFT parameters [27]:

$$F = \frac{B/T_{\mathrm{ref}}}{(\ln 10)(1 - T_0/T_{\mathrm{ref}})^2} \tag{3}$$

The calculated fragilities are list in Table 1, together with the VFT parameters and other characteristic temperatures. The fragility increases from 66 for PVME to 97 for the 50% PVPh blend, an even more significant increase than what we have observed for other intermolecularly hydrogen-bonded blends, likely a result of stronger interactions involved between PVPh and PVME. It is also worth noting that $T_{\mathrm{ref}}(\tau_{\max} = 1\ \mathrm{s})$ is very close to the T_g measured by DSC with heating rate of 10 K/min when the latter is defined as the midpoint of heat capacity jump.

Although PVPh/PVME blends exhibit relaxation behavior similar to that of PVPh/PVEE and SHS/PVEE blends, the former polymers' chemical structures are closer to those of PS/PVME and P2CS/PVME blends, and the observed coupling can be unequivocally attributed to the effect of intermolecular hydrogen bonding.

3.2.2. Relaxation in blends with high PVPh concentration

The segmental relaxation time distribution for the 50% blend is broadened slightly at high frequency (Fig. 4). This trend becomes more noticeable with increasing PVPh concentration and a faster shoulder is clearly visible in the spectra of the 60 and 80% PVPh blends (Fig. 6). This is not what is anticipated from coupling via hydrogen bonding, which predicts that unassociated PVME segments should have disappeared in these blends. There are several possible origins for this high-frequency shoulder, as discussed below.

The first possibility is that a local relaxation of PVPh is responsible. At least two dielectric local relaxation processes have been observed for PVPh and their loss spectra are shown in Fig. 7(a). The γ process occurs at very low temperature and can be ruled out from consideration. Although the PVPh β process is observed at temperatures slightly lower than the location of the shoulder in the blends, its relaxation strength is too small ($\Delta\varepsilon \sim 0.15$) when compared with the shoulder at constant temperature

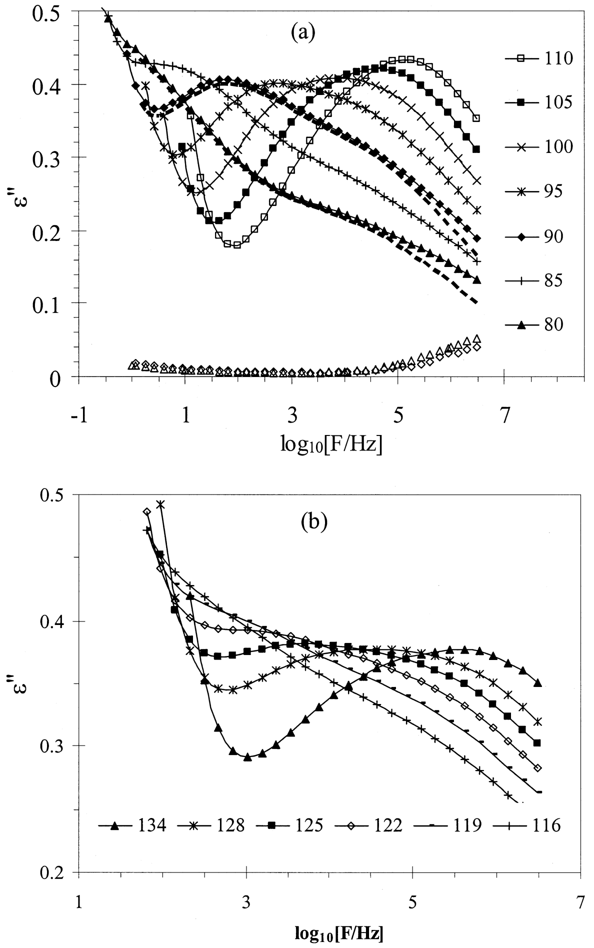


Fig. 6. DRS loss spectra of PVPh/PVME blends with PVPh concentration of (a) 60% and (b) 80%. The labels inside each figure give corresponding temperatures in °C. In (a), the dashed lines are the spectra of the blend minus the relaxation of PVPh at the same temperature. Empty triangles and diamonds represent the dielectric spectra of PVPh at 80 and 90 °C, respectively.

Table 1
VFT fitting parameters, reference temperatures, and fragility of the blends

PVPh/PVME	0/100	10/90	20/80	30/70	40/60	50/50	60/40[a]
T_g (K)	248	255	266	284	300	323	349
τ_0 (s)	4.2×10^{-13}	3.5×10^{-13}	3.3×10^{-13}	3.5×10^{-12}	1.4×10^{-12}	1.4×10^{-12}	6.6×10^{-16}
T_0 (K)	203	207	219	247	265	286	288
B (eV)	0.116	0.120	0.126	0.0956	0.0986	0.0940	0.191
T_{ref}[b] (K)	250	256	270	289	307	326	351
F[c]	66	65	66	79	87	97	84

[a] The segmental relaxations of this blend are fitted with two processes and the data presented here are those from the slow process.

[b] Defined as $\tau_{\max}(T_{\mathrm{ref}}) = 1$ s.

[c] Calculated using Eq. (3).

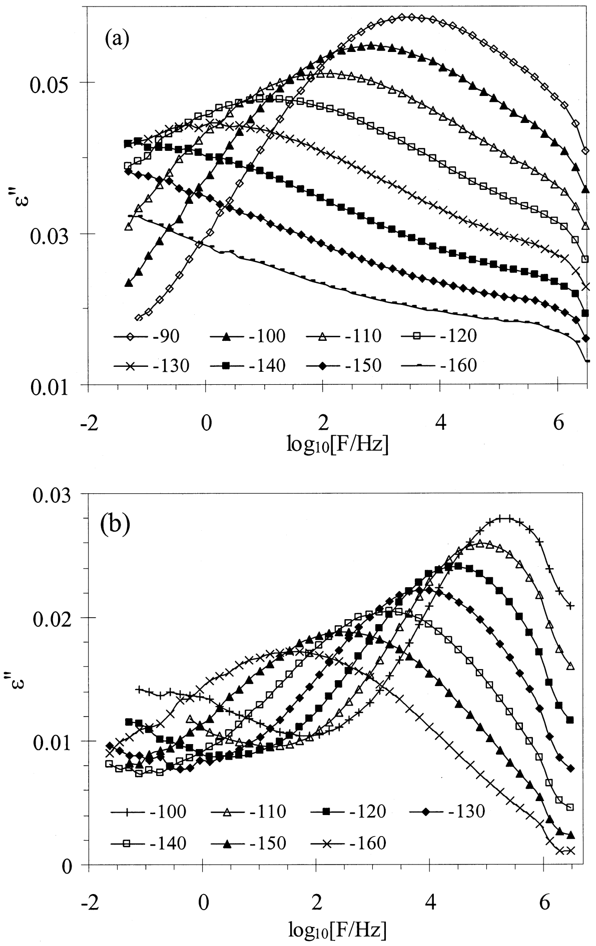


Fig. 7. Secondary relaxation processes of (a) PVPh and (b) PVME at selected temperatures.

($\Delta\varepsilon \sim 1.0$). If we assume to a first approximation that blending does not influence the β process of PVPh, as observed in PVPh/poly(ethyl methacrylate) [PEMA] blends [29], the contribution of the β (PVPh) can be removed from the segmental relaxation of the blend. This is achieved by subtracting the loss spectrum of neat PVPh normalized by its concentration in the blend from the corresponding loss spectrum of the blend at the same temperature. As can be seen from Fig. 6 (dashed lines), although the high frequency shoulder becomes somewhat weaker after this operation (this is a lower bound for the intensity, as discussed later), the shoulder remains. This therefore excludes the PVPh β process as the origin of the higher frequency shoulder.

It is appealing to attribute this shoulder to the relaxation of hydrogen bonded PVPh-PVME segments, and the lower frequency, more intense peak to relaxation of neat PVPh segments. PVPh is the main component in these blends and a considerable portion of PVPh segments are intramolecularly hydrogen bonded, rather than intermolecularly hydrogen bonded with PVME. The self-associated PVPh segments will relax slower than the coupled PVPh-PVME segments. However, comparison of the dielectric spectra of the 50–80% PVPh blends shows that the high frequency shoulder becomes stronger with increasing PVPh concentration. This is clearly contrary to the fact that intermolecularly hydrogen-bonded PVME-PVPh concentration should be lower in blends with high PVPh content ($\geq 50\%$). Therefore, this possibility is also rejected.

Approximate curve fitting of the spectrum of the 60% PVPh/PVME blend at temperatures where the slow and fast processes are clearly separated yields a ratio of the relaxation strength of the low frequency peak to the high frequency shoulder of about 1.8:1. This value is much larger than the ratio of the dipole moment concentrations in this blend, $\sim 1{:}1$ (this was calculated by multiplying the molar concentration of the dipole and its dipole moment, ignoring any difference in the correlation parameter) [30]. Since there is no reason to expect that the high T_g PVPh participates in the fast relaxation process, this suggests that a portion of the PVME segments ($\sim 30\%$) contribute to the slow relaxation, and the remainders contribute to the fast process.

We propose that the segmental relaxations in blends with high PVPh concentrations result from enhanced intramolecular association of PVPh segments. In blends with 60% or more PVPh, calculations reveal that more than half of the phenolic hydroxyl groups participate in intramolecular hydrogen bonds. In this situation, although PVME segments attempt to couple with the relaxation of PVPh segments through intermolecular hydrogen bonding, competitive intramolecular associations between PVPh segments retard this process since the temperature is still well below the intrinsic PVPh T_g. In blends with lower PVPh concentrations, a majority of the phenolic hydroxyl groups are associated with PVME, the intramolecular constraints are very weak and inter-component coupling is achieved. Strong coupling of component dynamics can only be achieved in a blend controlled by inter-component associations.

PVME segments with lower intermolecular hydrogen bonding are embedded in the matrix of PVPh (or the ‘continuous phase’, far above the percolation concentration) in blends with high PVPh concentration. Since PVPh has a T_g 195 K higher than PVME, even at the blend’s T_g (348 K for the 60% PVPh blend, vs. $T_g = 443$ K for neat PVPh), the mobility of PVPh segments is relatively low, although not completely frozen due to dilution from PVME. Therefore, the PVPh matrix is relatively rigid and applies considerable confinement on PVME segments. This leads to a much slower segmental relaxation of PVME as compared to the neat state.

Finally, with increasing temperature, the mobility of PVPh segments is significantly increased and their confinement upon PVME is therefore gradually released. A single α process is indeed observed at ~ 30 °C above the blend T_g.

3.2.3. *Comparison with other studies*

In previous studies on blends of PVEE/PVPh and PVPh with an ethylene-*co*-vinylacetate random copolymer [EVA], generally similar coupling effects were observed [19,24].

However, only blends with PVPh concentrations of ≤50% were studied, and a high frequency shoulder was not observed. Inspired by the results in the previous subsection, we recently investigated PVPh/PVEE and EVA blends with PVPh content ≥50%, as well as amorphous blends of a relatively high T_g styrene–hydroxystyrene [SHS] random copolymer with poly(ethylene oxide) [PEO]. In all of these systems a similar fast process at high PVPh or SHS content was observed [31]. A fast process was also observed in PVEE/SHS blends, but it is more apparent than in PVME/PVPh, even in the blend with 40% SHS, in which the SHS concentration is too low to invoke domination by intramolecular hydrogen bonding or confinement. We interpreted this latter dynamic heterogeneity by considering the repulsion between the styrene repeating units and PVEE [20]. Strong intramolecular interactions between PVPh, along with confinement, undoubtedly contribute to the fast process in blends with higher SHS contents.

It should be noted that similar dynamic heterogeneity has also been observed in a recent NMR study of poly(methyl methacrylate) [PMMA]/PEO blends, in which PMMA has a $T_g \sim 180$ K higher than PEO [32]. For blends with PEO concentrations ≤30%, it was found that the segmental relaxation of PEO is about 12 decades faster than that of PMMA at the blend's T_g, although this is a miscible blend. This was interpreted by considering PMMA as rigid cage and PEO segments as relaxing individually.

In summary, the segmental relaxations in PVPh/PVME blends are composition-dependent and the dynamics are not as thermorheologically simple as observed in PVPh/PVEE blends in a particular composition range and as predicted by theory [33]. Similar behavior has also been observed in a recent NMR study of PVAc/PMAA blends [34].

3.3. Secondary relaxations

A secondary β process is observed in neat PVME below −80 °C (Fig. 7), and it has been attributed to relaxation of the side groups. This relaxation was found to be essentially unmodified by blending with PS [6]. PVPh has two secondary relaxation processes, namely β and γ, from high to low temperature [29], both of which are relatively weak (i.e. lower than about 10% of the relaxation strength of the α process of the blends). The PVPh β process occurs above 0 °C and partially overlaps with the segmental relaxations in the blends, and therefore it is difficult to define. The PVPh γ process is slightly faster than β (PVME), and these consequently merge in the blends.

The low temperature relaxation behavior of blends with 30, 50, and 80% PVPh was also measured. In the blends, a similar secondary relaxation occurs below −100 °C in the frequency window of our instrument, but significantly broadened. Close examination of Fig. 8 suggests that this process in blends includes contributions from both component polymers and the low frequency broadening should arise from the relaxation of PVPh. Although quantitative information on the relaxation strength (Δε) can provide insight into their molecular origins, no curve fitting was attempted since their relaxation times are too close to one another. Synthesized dielectric loss spectra of 30 and 80% blends are also provided in Fig. 8 (dotted lines) to facilitate comparison. These spectra are obtained by adding the spectra of neat PVPh and PVME, normalized by concentration, at the specified temperature, with the assumption that these secondary relaxations are not influenced by blending. Qualitatively, the synthesized spectrum is much stronger than that observed for the corresponding blend, particularly at lower frequencies and in blends with high PVPh concentration. Although the low frequency tail becomes relatively stronger with increasing PVPh concentration, compared with the high frequency side, the increase is not proportional to PVPh content. This is in contrast to the behavior observed for PS/PVME blends, in which the β relaxation strength of PVME in the blends is proportional to PVME concentration [6]. Our findings strongly suggest that the relaxation of some side groups of both polymers (and

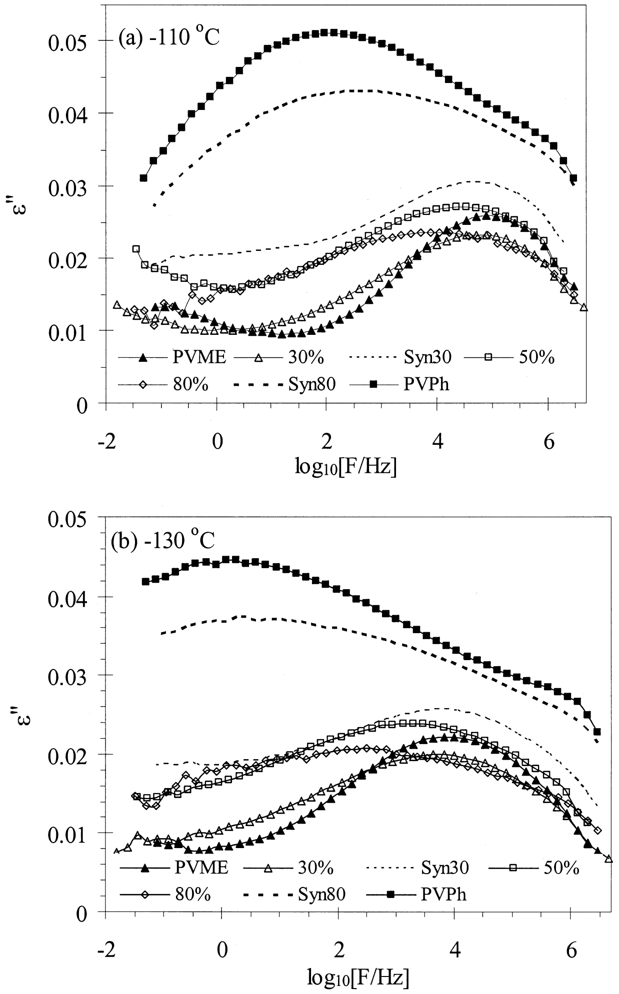


Fig. 8. Low temperature relaxation of PVPh/PVME blends at (a) −110 °C and (b) −130 °C. The number represents the percentage of PVPh. Thin and thick dotted lines are synthesized spectra for blends with 30 and 80% PVPh concentration, respectively.

particularly those of PVPh) is suppressed by blending, and these groups are likely those constrained by intermolecular hydrogen bonding. The unassociated groups will maintain mobility at these temperatures and contribute to the observed low temperature relaxation.

In a previous study on poly(ethyl methacrylate)/PVPh blends, we found that the relaxation time of the PEMA β process is unaffected by blending [29]. However, since the β process in PEMA is believed to involve accompanying main chain rocking, that is, having a larger relaxation size and higher activation energy (~70 kJ/mol), the hydrogen bonding (~16 kJ/mol) is probably not sufficiently strong to retard this secondary relaxation. The β process of PVME is much faster than PEMA and has an activation energy of only 22 kJ/mol, which is comparable to the strength of hydrogen bonding between PVME and PVPh (stronger than that between PEMA and PVPh), therefore hydrogen bonding should be capable of damping this secondary relaxation. The ability of hydrogen bonding to modify the secondary relaxation of the associated functional groups was also observed in our recent studies on several other systems and the β relaxation can be completely suppressed in blends with sufficiently strong hydrogen bonding [35–37]. However, we currently cannot explain why the local relaxation of PVPh is weakened more significantly than that of PVME considering an activation energy of 39 kJ/mol for γ(PVPh).

4. Summary

In order to examine the influence of strong intermolecular hydrogen bonding on the dynamics of polymer blends, we studied miscible PVPh/PVME mixtures with PVPh concentrations up to 80%. Different relaxation behaviors were observed for blends with different compositions, and thermorheological simplicity does not exist in this dynamically asymmetric blend, despite the presence of strong intermolecular interactions.

For blends with 10 and 20% PVPh content, two segmental relaxations were observed. The slow process was attributed to the relaxation of intermolecularly hydrogen-bonded PVPh-PVME segments, and the fast to 'free' PVME segments. A single dielectric α process was observed in blends with somewhat higher PVPh content, in which all PVME and PVPh segments have been intermolecularly coupled through hydrogen bonding. These results are consistent with those of our previous studies of PVPh/PVEE and SHS/PVEE blends, but the chemical structures of the component polymers used in present blends are more akin to those of the well-studied PS/PVME and P2CS/PVME blends, in which significant dynamical heterogeneity has been observed as a result of their large T_g difference. Because the only difference between these blends and PVPh/PVME is the presence of intermolecular hydrogen bonding in the latter, the results confirm that hydrogen bonds are capable of coupling components' segmental relaxations in blends with very large ΔT_g.

A second segmental relaxation was also observed in blends with 60 and 80% PVPh. This process is proposed to arise from the relaxation of a portion of PVME confined in a relatively rigid matrix of PVPh, whose segments are relaxing much slower than PVME segments due to the presence of considerable intramolecular hydrogen bonding. The low temperature relaxations of the component polymers are partially suppressed in the blends since their relaxations involve hydrogen-bonded side groups.

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