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Coupling of Component Segmental Relaxations in a Polymer Blend Containing Intermolecular Hydrogen Bonds

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ABSTRACT: The segmental relaxations of poly(4-vinylphenol)/poly(vinyl ethyl ether) [PVPh/PVEE] blends, with PVPh content from 10 to 50 wt % and having a very large T_g difference between the components, have been investigated using broadband dielectric spectroscopy. Although a single T_g was observed for all compositions in DSC measurements, two segmental α processes for blends with low PVPh concentration are highly probable. The slow process is attributed to the relaxation of intermolecular hydrogen-bonded PVPh and PVEE segments, while the fast one is assigned to unassociated PVEE segments. However, at PVPh concentrations ≥30 wt %, most PVEE segments are hydrogen-bonded to PVPh and the blends exhibit a single α relaxation. This behavior is compared to that of other miscible blends with large T_g contrast but having weak intermolecular interactions. The observed behavior is explained by the role of intermolecular hydrogen bonding, which is believed to be capable of coupling the segmental relaxations of PVEE and PVPh, which would otherwise exhibit two distinct segmental relaxation processes due to their large intrinsic mobility difference. The time−temperature superposition principle, which fails for many polymer blends, is successful in blends with higher PVPh content, indicating thermorheological simplicity of this dynamically asymmetric blend. Finally, increases in both the fragility and the coupling parameter are clearly observed in the blends compared to neat PVEE, confirming that intermolecular coupling is enhanced by hydrogen bonding.

Introduction

As blending of two or more polymers has became an economical route to develop new materials to meet the challenging requirements for industrial applications, understanding miscibility is of critical importance. One of the conventional probes for ascertaining component miscibility is the number and location of glass transition temperature(s) [T_g], as determined by differential scanning calorimetry [DSC]. Equivalently, the cooperative segmental relaxation [α process] is closely related to the glass transition; thus, it is generally believed that only one α process should be observed in dynamic mechanical or dielectric relaxation spectroscopy [DRS] experiments of a miscible polymer blend.[1]

However, this criterion has been questioned by recent studies of miscible polymer blends with a large T_g contrast and weak intermolecular interactions, e.g., polyisoprene/poly(vinylethylene) [PIP/PVE],[2−10] polystyrene/poly(vinyl methyl ether) [PS/PVME],[11−17] PS/poly(methylphenylsiloxane) [PMPS],[18,19] and poly(2-chlorostyrene)/PVME [P2CS/PVME].[20] Although a single calorimetric T_g was observed in the above blends, nuclear magnetic resonance [NMR], dynamic mechanical analysis [DMA], and/or DRS studies clearly indicate that the two components have different segmental relaxation times. In PIP/PVE and P2CS/PVME, two dielectric α processes have been observed: the fast process originates from the low-T_g component [i.e., PIP or PVME], and its relaxation rate is very close to that of the corresponding neat polymer. The slow process is related to the high-T_g polymer [i.e., PVE or P2CS] and is much faster than the α relaxation of the corresponding homopolymer in the unblended state. In PS/PVME and PS/PMPS, although only one component [PVME or PMPS] is dielectrically active, two dielectric segmental relaxations were observed: the fast process is believed to originate from the relaxation of PVME or PMPS surrounded by like segments, whereas the slow one originates from the modified relaxation of the same polymer segments in the blend (mixed) environment.

Two possible mechanisms have been proposed to explain the above observations: concentration fluctuations [CF] or intrinsic mobility difference between the two components. Concentration fluctuations are inherent to polymer blends, and dynamically heterogeneous environments exist in macroscopically homogeneous systems. These heterogeneous nanodomains have different compositions, thus different T_g's.[21−23] Roland and Ngai[4] modeled the dynamics of PIP/PVE blends by assuming that concentration fluctuations lead to normally distributed coupling parameters for each component, and the observed relaxation time distribution is a summation of all of these compositions. In the CF model of Fischer and co-workers,[21,22] it was assumed that there are many dynamically heterogeneous domains in polymer blends and different domains have different compositions, which follow a Gaussian distribution centered around the global composition. In this early CF model, all heterogeneous domains assume the same size, equal to Donth's cooperatively rearranging region [CRR] at the global DSC T_g.[24] This model successfully reproduced the broadening of segmental relaxations in certain polymer blends. However, it cannot explain the existence of two segmental relaxations in PS/PVE and PS/PMPS blends. Kumar, Colby, and co-workers[23] modified Fischer's CF model by correlating the size of heterogeneous nanodomains with their local composition. This model qualitatively predicts the bimodal relaxation behavior in blends that exhibit weak intermolecular interactions and a relatively large

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T_g contrast [ΔT_g] between the component polymers. The low-T_g polymer is more likely to aggregate than the other because it requires a smaller cooperative relaxation volume; thus, a dynamic low-T_g rich domain can be observed experimentally. More recently, this bimodal relaxation behavior and the broadening of the glass transition have also been interpreted by a self-concentration model, in which a Kuhn segment is regarded as an independent relaxation unit and chain connectivity is taken into consideration.[25]

On the other hand, the dielectric behavior of PIP/PVE and P2CS/PVME blends has been attributed to the intrinsic mobility difference between the component polymers, which is suggested by the fact that their T_g's are very different. Although concentration fluctuations are undoubtedly important for understanding segmental relaxations, NMR studies indicate that the intrinsic mobility difference between components plays a key role in determining this unusual behavior. In a two-dimensional deuteron NMR study of PIP/PVE blends, Chung et al. could not explain the large difference between the fast and slow segmental relaxation rates by considering only the role of concentration fluctuations. They argued that PIP and PVE feel distinct effective T_g's, and the intrinsic mobility difference between PIP and PVE should also contribute to the observed difference in motional rates.[10]

The apparently contradictory DSC and NMR/DRS results can be understood by considering the different experimental probe sizes. NMR and DRS are capable of interrogating compositional heterogeneity at the ~3 nm size scale, and the blends discussed above are therefore dynamically heterogeneous on a similar length scale. However, DSC is sensitive to heterogeneity larger than ~10 nm, and heterogeneities smaller than this will be averaged out by this larger probe size. Thus, a single calorimetric T_g is observed, although the transition generally becomes broader for blends compared to the component polymers.[26,27]

It is worth mentioning that the intermolecular interactions in PIP/PVE, P2CS/PVME, and PVME/PS blends are very weak; their interaction parameters χ are only marginally negative [e.g., $\chi \sim -0.01$ for PS/PVME and $\chi \sim -0.002$ for PIP/PVE].[11,23,28,29] Investigating the segmental dynamics in blends with strong intermolecular interactions, such as intermolecular hydrogen bonding, is helpful for understanding the nature of segmental relaxation in polymer blends. It is now well-known that hydrogen bonding is capable of promoting miscibility in otherwise immiscible polymer blends.[30]

Recently, we investigated the dynamics of hydrogen-bonded poly(4-vinylphenol)−poly(ethyl methacrylate) [PVPh/PEMA] blends, with PVPh concentrations ranging from 10 to 40 wt % by DRS.[31] This system was found to be miscible across the entire composition range by DSC and Fourier transform infrared [FTIR] spectroscopy measurements. In this previous study, a single segmental relaxation process was observed for all blend compositions, although the ΔT_g is ~100 K, while $\Delta T_g \sim$ 60, 135, 150, and 190 K for the PIP/PVE, PVME/PS, P2CS/PVME, and PS/PMPS blends, respectively. The α process of PVPh/PEMA blends involves the relaxation of both PVPh and PEMA; i.e., the two polymers relax at similar rates. Concentration fluctuations are insignificant in PEMA/PVPh, and this is attributed to the presence of intermolecular hydrogen bonding.

In the present study, we increase the hydrogen-bonding strength by choosing a different proton acceptor, poly(vinyl ethyl ether) [PVEE], to blend with PVPh. We demonstrate the ability of intermolecular hydrogen bonding to couple the segmental relaxations of PVEE and PVPh. This blend has a chemical structure similar to PS/PVME and P2CS/PVME and a larger ΔT_g [~186 K] and should exhibit two segmental relaxations in the absence of strong intermolecular interactions. Therefore, by comparing our results with those of PS/PVME and P2CS/PVME, the effect of hydrogen bonding on segmental dynamics can be determined. Another advantage of using PVEE over PEMA in the blends lies in its well-defined α process: the α and β relaxations are very close in PVPh/PEMA, and a complicated curve-fitting scheme has to be used to resolve them.

Experimental Section

A. Materials and Sample Preparation. PVPh was purchased from Polysciences, Inc., and has $M_w = 41\,000$ and $M_w/M_n = 6.8$. PVEE is the product of Monomer-Polymer & DAJAC Laboratories, Inc., with $M_w = 27\,000$ and $M_w/M_n = 2.1$. Molecular weights of both polymers were determined by gel permeation chromatography using dimethylformamide as the mobile phase and narrow molecular weight distribution poly(ethylene oxide) standards. All polymers were used as purchased without further purification.

Blends with PVPh concentrations from 5 to 50 wt % [designated as PE05 through PE50, where the number denotes the weight percentage of PVPh in the blend] were prepared by solution casting. Initially, 5 wt % solutions of the neat polymers in methyl ethyl ketone were prepared, and then the appropriate amounts of each were mixed to provide the desired blend composition. The mixed solutions were stirred for at least 30 min before being cast into Teflon-coated foil dishes. The solvent was removed in a vacuum oven with gradually increasing temperature up to $T_g + 20$ K for at least 1 week. All films were 200−300 μm in thickness. For DRS studies, gold was sputtered on both sides of the samples in an argon atmosphere for samples with T_g above room temperature. For PVEE, PE05, PE10, and PE20, whose T_g's are well below ambient temperature, gold sputtering was not attempted; these samples were sandwiched between two electrodes, and a polypropylene spacer was used to control the thickness. Because of the strong dc conduction of PVPh, the α process of blends with more than 50% PVPh cannot be reliably resolved.

Samples for DSC were prepared by slowly dropping the mixed solutions into individual aluminum DSC pans, following the same thermal procedure as in the DRS study.

B. DRS Experiments. The dielectric relaxation spectra $\epsilon^*(f,T)$ were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency domain [0.01 Hz−4 MHz], on cooling from $T_g + 60$ K to T_g. 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.

C. DRS Curve Fitting. The phenomenological Havriliak−Negami [HN] equation[32] was employed to describe the dielectric relaxation spectra. A dc conduction contribution is observed at high temperatures due to impurity ions and is removed by a simple power law. Curve fitting was performed using the WinFit program (Novocontrol). The HN[32] function reads

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty - i\frac{\sigma_0}{(\epsilon_0\omega)^s} + \frac{\Delta\epsilon}{[1 + (i\tau_{HN}\omega)^m]^n} \quad (1)$$

in which $\omega = 2\pi f$, ϵ_∞ and ϵ_R are the unrelaxed and relaxed dielectric constants [ϵ'] at very high and low frequency, respectively, and $\Delta\epsilon$ is the dielectric strength, $\epsilon_\infty - \epsilon_R$. σ_0, s,

Table 1. Glass Transition Temperatures and Transition Breadths of PVPh/PVEE Blends

		PE10		PE20					
	PVEE	fast	slow	fast	slow	PE30	PE40	PE50	PVPh
T_g (°C)	−28	−20		−3		25	44	75	158
ΔT (°C)[a]	8	15		40		36	35	33	15
T_g^{eff} (°C)[b]	−14	−10	4	1	23	34	59	96	N/A
$T_g^{eff} - T_g$ (°C)	14	10	24	4	26	9	15	21	N/A

[a] Defined as the difference between the onset and completion of the glass transition. [b] Defined as the temperature at which the relaxation time $\tau_{max} = 0.01$ s.

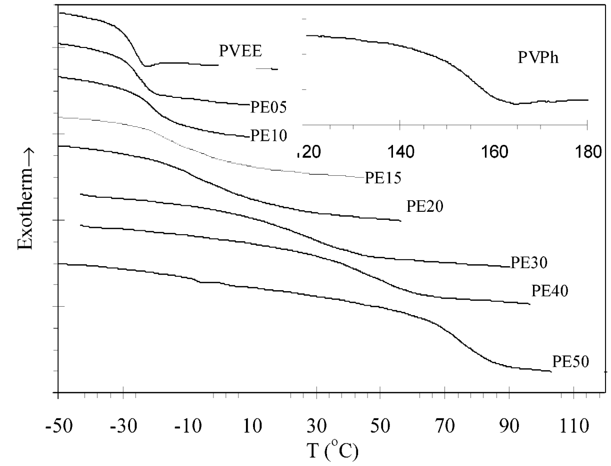

Figure 1. DSC curves of PVPh/PVEE blends: second heating run, heating rate = 10 K/min.

τ_{HN}, $\Delta\epsilon$, m, and n are fitting parameters, while ϵ_0 is the vacuum permittivity. The exponents m and n [$0 < m, mn \leq 1$] are shape constants. σ_0 is the dc conductivity constant with units of S/cm; the exponent s [$0 < s \leq 1$] characterizes the conduction process and is close to 1 in the systems studied herein. τ_{HN} is related to the peak location τ_{max} by eq 2:[33]

$$\tau_{max} = \tau_{HN}\left[\sin\frac{\pi m n}{2(n+1)}/\sin\frac{\pi m}{2(n+1)}\right]^{1/m} \qquad (2)$$

In this paper, τ_{max} is used to compare the blends' relaxation behavior.

D. DSC. DSC experiments were performed using a Seiko SSC 5200 DSC with sample weight ~10 mg. 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 [$T_g - 20$ 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. Each sample was measured three times, and the average value is reported.

E. FTIR. FTIR spectra were recorded on a Bio-Rad FTS-6 spectrometer with a resolution of 2 cm^{-1} by averaging 64 scans. Sample solutions were coated onto KBr windows, and the solvent was removed in a heated vacuum oven.

Results

A. Miscibility of PVPh/PVEE. A previous FTIR study of PVEE/PVPh blends showed that strong hydrogen bonds are formed between the ether oxygen atoms in PVEE and the hydroxyl groups of PVPh, immediately suggesting they may be miscible.[34] This is confirmed by our DSC results, in which a single T_g was observed for each blend (Figure 1). However, the glass transition is broadened considerably in the blends compared with the component polymers, indicating local heterogeneity. Careful inspection of the DSC curves reveals that broadening reaches a maximum at PE20 (see Table 1), and then the transition becomes somewhat narrower with increasing PVPh concentration. This is rather unusual behavior, because the glass transition is generally broader in blends with larger high-T_g component concentration, compared to those rich in the low-T_g component.[25] As to be discussed later together with similar broadening of the corresponding DRS spectra, we attributed this unusual behavior to the existence of two different relaxing segments in blends with low PVPh content, that is, intermolecularly hydrogen-bonded PVEE−PVPh and nonassociated PVEE, due to the stoichiometric effect in forming hydrogen bonds.

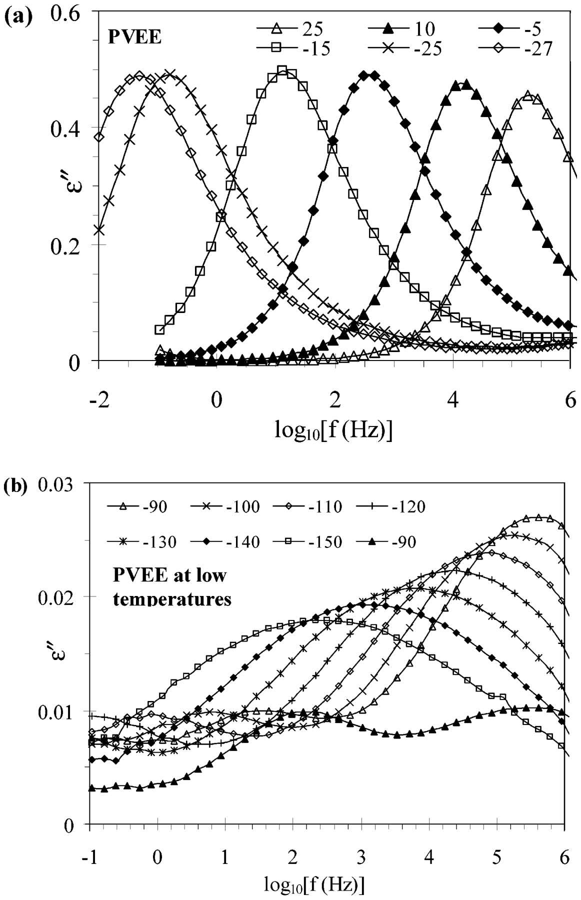

Figure 2. DRS loss spectra of neat PVEE: (a) segmental and (b) local relaxation processes. The solid triangles are data for a moisture-equilibrated PVEE sample at −90 °C.

B. Dielectric Relaxation of Component Polymers. To clearly interpret the DRS spectra of the blends, it is essential to understand the dielectric behavior of the component polymers. To the best of our knowledge, although there have been a number of dynamics studies on PVME, no investigation of PVEE has been reported in the literature. Three dielectric relaxation processes are observed for PVEE, namely α, β', and β with decreasing temperature (Figure 2). As usually observed in other homopolymers, the α process in PVEE occurs above T_g and is broadened slightly

Table 2. VFT Fit Parameters and Fragility of PVPh/PVEE Blends

	PVEE	PE30	PE40	PE50
τ_0 (10^{-14} s)	15.3	7.74	5.90	2.74
B (eV)	0.140	0.159	0.160	0.149
T_0 (K)	194	235	260	304
T_{ref} (K)[a]	249	296	321	359
F[b]	58	63	70	88

[a] Defined as temperature at which $\tau_{\max} = 1$ s. [b] Calculated using eq 6.

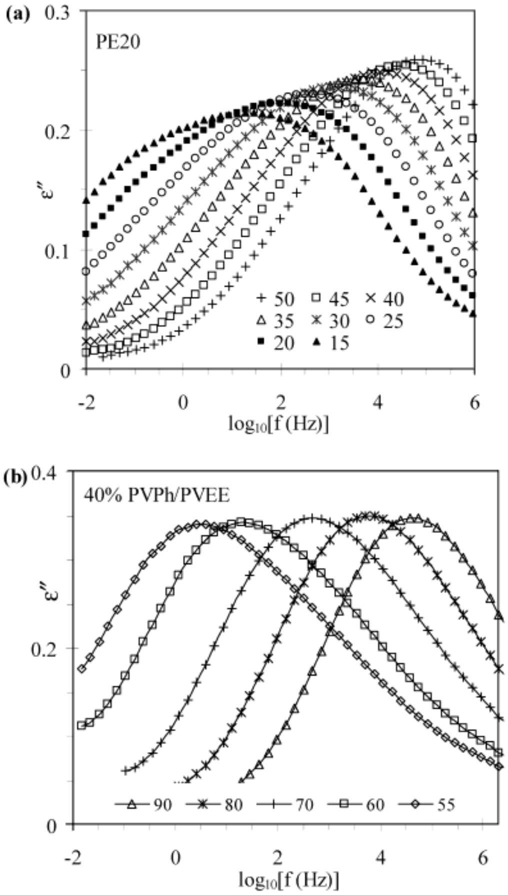

Figure 3. Dielectric segmental relaxation spectra of (a) PE20 and (b) PE40. For clarity, only spectra at representative temperatures are displayed. The dc conduction has been removed as described in the text.

toward high frequencies. As a cooperative process, it follows the well-known Vogel−Fulcher−Tammann (VFT) equation[35]

$$\tau = \tau_0 \exp[B/(T - T_0)] \tag{3}$$

in which τ_0, B, and T_0 are fitting parameters and have different physical significance. Curve-fitted values of these parameters are listed in Table 2.

On the other hand, the β relaxation as a secondary process and is thus relatively weak. It has an Arrhenius temperature dependence with an activation energy of 20 kJ/mol, which is the same as found for the β process of PVME.[13] The strength of the β' process increases rapidly after equilibrating with water at room temperature for 2 days, while no change was observed for the other two processes. It is therefore attributed to the relaxation of residual moisture. A similar relaxation process due to moisture has also been observed for PVME.[20]

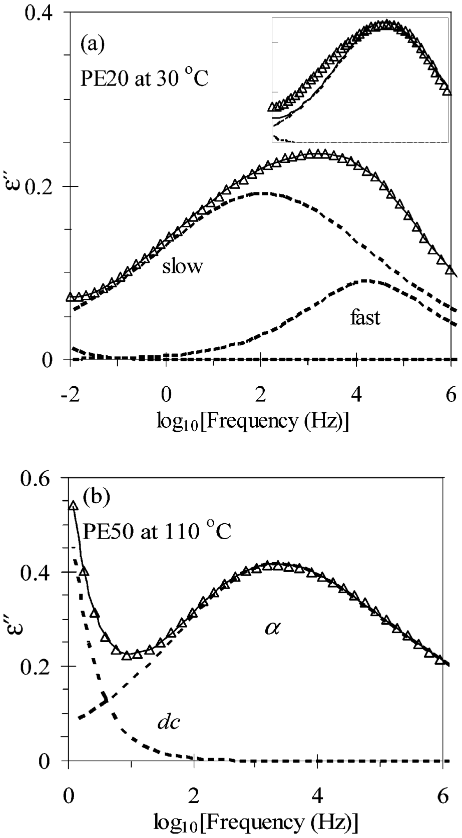

Figure 4. (a) Curve fitting of DRS spectra of PE20 at 30 °C by two HN relaxations and (b) PE50 at 110 °C by one HN relaxation. Fitting results of PE20 with one HN process are also presented as an inset in (a). The triangles are experimental data; the dotted lines are HN curve fitting results, and the solid line is the sum of fitted components.

Because of its strong dc conductivity, the α relaxation of neat PVPh cannot be resolved dielectrically. At lower temperatures, it exhibits two local processes, β and γ from high to low temperature. These processes also follow the Arrhenius equation with activation energies of 56 and 39 kJ/mol, respectively. The PVPh γ process occurs at much lower temperatures than the segmental relaxation of PVEE; the β transition is located near the glass transition region of PVPh/PVEE blends but with very low intensity, due to its local character, compared with the cooperative relaxation.[31] Therefore, it was unnecessary to take the PVPh local processes into consideration during HN curve fitting of the blends' α processes.

C. Segmental Relaxation of Blends. Figure 3 presents the DRS spectra of two blends with different PVPh concentrations [i.e., 20 and 40%] above their glass transition temperatures. By comparing their spectra with that of PVEE, it is immediately apparent that the blends have a much broader distribution of relaxation times, although the broadness has different characteristics for different compositions.

At low PVPh concentrations, i.e., PE05, PE10, and PE20, DRS spectra are asymmetrically broadened on the low-frequency side. This broadening is so significant that two HN functions must be used to model these spectra, whereas the result of fitting with only one HN function is rather poor (Figure 4). This suggests that there are two segmental relaxation processes, even though these blends are miscible as determined in DSC

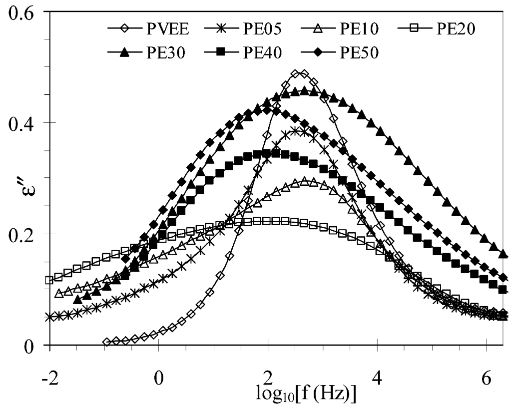

Figure 5. Comparison of dielectric loss spectra of PVPh/PVEE blends at $\sim T_g + 23$ K. The dc conduction has been subtracted.

experiments. DRS spectra of PE30−PE50, however, can be fitted with a single HN function.

The observed dielectric segmental relaxation of PVPh/PVEE blends includes contributions from both PVPh and PVEE. Both components are dielectrically active with comparable dipole moments. The dipole moment of ethyl ethyl ether, a small molecule analogue of the PVEE repeat unit, is 1.25 D in benzene, while that of *p*-ethylphenol, a model for the PVPh repeat unit, is 1.61 D in benzene.[36] For blends with two segmental processes, although the intensity of the high-frequency peak decreases with PVPh concentration, the low-frequency shoulder correspondingly becomes stronger; thus, the dielectric relaxation strength $\Delta\epsilon$, the area under the $\epsilon''-\ln f$ curve, is approximately the same for different blends (Figure 5). This supports the proposition that PVPh participates in the observed broad dielectric α process.

The most intriguing problem is the origin of the extraordinary broadening of the DRS loss spectra of blends with low PVPh concentrations. Although concentration fluctuations usually broaden relaxation spectra and sometimes two segmental relaxations may be observed, concentration fluctuations are likely damped in PVPh/PVEE blends because of strong intermolecular hydrogen bonding. The CF model of Kumar and Colby et al.[11,23,29] proposes that concentration fluctuation is a dynamic process, and the local compositions in different cooperatively rearranging regions follow a Gaussian distribution with the probability $P_{\mathrm{dynamic}}(\phi)$ of finding a composition ϕ:

$$P_{\mathrm{dynamic}}(\phi) \sim \exp\left[\frac{-(\phi - \phi_0)^2 b^2 d^3 T_0^{\,2}}{24\xi^2 \phi_0 (1 - \phi_0)(T - T_0)^2}\right] \qquad (4)$$

In this expression, ϕ_0 is the bulk composition, b the monomer size, d a material-specific dimensionless constant, and T_0 the Vogel temperature [same as in eq 3, but composition-dependent], and the correlation length ξ can be estimated by[11]

$$\frac{\xi}{b} = \left(12\left[-2\chi\phi_0(1 - \phi_0) + \frac{1}{N}\right]\right)^{-1/2} \qquad (5)$$

where χ is the interaction parameter and N is the degree of polymerization.

For the PS/PVME blend, $\chi \sim -0.01$, which leads to a relatively large ξ. The occurrence of a dynamically PVME-rich phase is therefore highly probable, since $T - T_0$ is maximized and T_0 is concurrently minimized at a particular temperature.[11] For blends with strong intermolecular interactions, the effective χ is large and negative, and the correlation length approaches zero; large-scale concentration fluctuations become energetically unfavorable. Applying this model to miscible blends of poly(hexyl methacrylate) [PhMA, $T_g = 268$ K] and poly(styrene-*co*-vinylphenol) [SHS50, $T_g = 400$ K], Kumar et al. predict the concentration distribution to be unimodal and very sharp around the global average composition.[23] In such blends, the presence of low-T_g component-rich domains, i.e., PhMA or PVEE-rich, is thermodynamically unfavorable. Although ΔT_g is larger for PVPh/PVEE than the SHS50/PhMA blend, the hydrogen-bonded fraction (of −C═O or O⟨), at the same composition, is much higher in the former, since more hydroxyl groups are available in PVPh than in SHS50. Furthermore, the hydrogen bond between ether oxygen atoms and phenolic −OH is stronger than that between −C═O and phenol. Delocalization of free electrons between the carbonyl oxygen atom and the ester oxygen atom [O═C−O] reduces its ability to associate with the hydroxyl group. Therefore, the unusual DRS low-frequency shoulder in PVPh/PVEE blends is not a consequence of concentration fluctuations, as in PS/PVME and PS/PMPS blends.

The suppression of concentration fluctuations in hydrogen-bonded polymer blends was also found in a previous small-angle neutron scattering [SANS] experiment on a similar system, the blend of SHS50 and deuterated poly(tetrahydrofuran) [d-PTHF]. This can be regarded as a quasi-analogue system of PVPh/PVEE. No scattering features were observed in the q range 0.12−0.27 nm^{-1}, although the blend has a $\Delta T_g \sim 225$ K.[37] Strong scattering was observed, however, in an analogous blend *without* strong intermolecular interactions, d-PS/poly(*n*-butyl methacrylate), at a similar composition and temperature. Taken together, these results strongly indicate that intermolecular hydrogen bonding is capable of damping concentration fluctuations.

We therefore arrive at the conclusion that the bimodal relaxation behavior in blends with low PVPh concentrations originates from the intrinsic mobility difference between PVPh and PVEE. This is a reasonable explanation, considering the very large T_g contrast [186 K] and similar chemical structure compared with the P2CS/PVME blend. However, we argue below that the intrinsic mobility difference has been reduced by intermolecular hydrogen bonds. The presence of two segmental relaxations in PVPh/PVEE is only observed for blends low in PVPh, whereas two segmental processes are more evident at 50/50 compositions for PS/PVME or P2CS/PVME blends than for low-T_g component rich compositions.[8,11,20] The different composition dependences for blends with and without strong intermolecular hydrogen bonding suggest that there is a different mechanism for the bimodal behavior in these two types of mixed systems.

HN curve fitting of PE10 and PE20 spectra indicates that there are possibly two distinct segmental processes; the fast one has a relaxation rate very near that of neat PVEE and thus represents the relaxation of PVEE segments. The other is much slower and involves the relaxation of not only PVPh but also PVEE (Figure 4a). The latter argument is supported by comparing the relaxation strengths $\Delta\epsilon$ (fast) and $\Delta\epsilon$ (slow). Their ratio

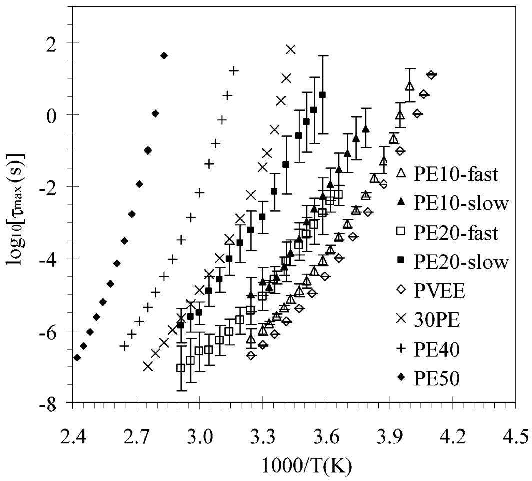

Figure 6. Arrhenius plots of the segmental relaxations in PVPh/PVEE blends. The error bars in PE10 and PE20 were obtained by fitting the corresponding dielectric spectra with the Havriliak–Negami equation using a Gaussian nonlinear regression algorithm.

is in the range of 2–3, much smaller than the mole ratio of PVEE to PVPh (e.g., 20:3 for PE20), even after taking into account their slightly different dipole moments. This supports the participation of PVEE in the slow segmental relaxation process and is in contrast to P2CS/PVME and PIP/PVE blends, in which the slow relaxation process mainly stems from the high-T_g component.[8,20] The reason for this difference in behavior will be discussed in detail in the next section.

To further explore the origin of the slow process, we define an effective glass transition temperature T_g^{eff} for each component, at which the dielectric relaxation time $\tau_{max} = 0.01$ s. This is common practice in characterizing the mobility difference in calorimetrically miscible polymer blends.[25] The reason for choosing this short time, not 1 or 100 s as conventionally used, is that the fast and slow processes are relatively well resolved at this T_g^{eff}. This characteristic temperature is an approximation to the T_g determined by DSC, and the existence of two T_g^{eff}'s indicates that the two component polymers experience distinct effective microscopic glass transition temperatures, although a single macroscopic T_g was observed. The mean relaxation time of a given process was obtained through HN curve fitting of the DRS spectra, and the Arrhenius plot is presented in Figure 6. The deviations of T_g^{eff}(slow) from T_g(DSC) are much larger for PE10 and PE20 than for neat PVEE (Table 1). Since T_g(DSC) is proportional to the overall blend composition, the larger departure of T_g^{eff}(slow) from T_g(DSC) indicates that the slow dielectric process in PE10 and PE20 originates from the relaxation of a nanodomain with higher PVPh concentration than the average composition of the parent blend. This is reasonable considering the existence of the fast process, which arises from neat PVEE. The increase of τ_{max}(fast) from τ_{max}(PVEE) can be explained by constraints imposed by neighboring hydrogen-bonded segments.

D. Coupling of Component Segmental Relaxations. The influence of intermolecular hydrogen bonding is not limited to suppression of concentration fluctuations. The difference in the dependence of the relaxation behavior on composition for the PIP/PVE (and also P2CS/PVME) and PVPh/PVEE blends is difficult to explain by considering only intrinsic mobility differences and concentration fluctuations. To reiterate, two segmental relaxations have been clearly observed in DRS spectra [even for a 50/50 composition] in PIP/PVE and P2CS/PVME blends, whereas only one can be resolved in PVPh/PVEE blends with PVPh concentrations ≥ 30%. This contradiction can only be resolved by considering the effect of hydrogen bonding.

Blending clearly changes the relaxation environment and the dynamics of the two components can be coupled to a certain degree, depending on their ΔT_g and intermolecular interactions. However, it is very difficult, if not impossible, for two polymers in a blend to relax at nearly the same rate if their T_g's are far from each other. In blends with a small T_g contrast, these two processes can be completely coupled, and only one dielectric α relaxation observed.[1] Relaxation broadening can also be minimized or eliminated if the two components have closely matched T_g's or T_0's.[38] Returning to the PVPh/PVEE blends, despite the much larger ΔT_g, the intermolecular hydrogen bonding, if sufficiently strong, should be capable of reducing the mobility difference between PVPh and PVEE and coupling their segmental motions. To imagine this in an intuitive way, the hydrogen bond “sticks” the segments of PVPh and PVEE together for a certain time period above T_g, and they must consequently relax cooperatively and simultaneously. This is demonstrated by the presence of a single α process in PE30 through PE50.

The difference in the broadening behavior of low and higher PVPh content blends can be explained by a simple difference in the stoichiometry of hydrogen bonding. For blends with low PVPh concentration, the fraction of hydrogen-bonded PVEE repeat units is relatively low, and many are able to relax freely, without restriction from PVPh. Using equilibrium constants for $-$OH$\cdots$HO$-$ hydrogen bonds and $-$OH$\cdots$O$\langle$ hydrogen bonds previously employed in the study of phase behavior of PVPh/polyether blends, it is possible to calculate the fraction of hydrogen-bonded and nonbonded phenolic hydroxyl and ether oxygen groups.[30] In a blend containing 20% PVPh, approximately 10–15% of the ether oxygen atoms are calculated to be hydrogen-bonded to PVPh $-$OH groups. Accordingly, only one or two PVEE repeat units are associated with PVPh, out of every 10 PVEE chemical repeat units. This indicates nanoheterogeneity on the scale of about 10 repeat units, i.e., ~2 nm. Although the size of the cooperative segment, the unit that can relax independently, is still an open question, it is generally believed that it involves several to several tens of monomer units. This would correspond to a scale of ~1–3.5 nm at T_g, with this size decreasing with increasing temperature following the scaling relationship $\xi \propto [T_0/(T - T_0)]^{0.69}$.[24,39–41] The above two values, the nanoheterogeneity scale and cooperative relaxation unit size, are comparable. As a consequence, some PVEE segments are free from hydrogen bonding and can more or less relax as in the neat environment, while others are coupled with PVPh segments and can relax only through cooperative motion with PVPh. On the other hand, for the PE20 blend, about 90% of the PVPh units are hydrogen-bonded to PVEE units and are therefore coupled to PVEE segments. This indicates that the low-frequency shoulder observed in PE05, PE10, and PE20 arises from the coupled relaxation of hydrogen-bonded PVPh and PVEE segments. The high-frequency peak represents the relaxation of “free” PVEE only, and it slows down

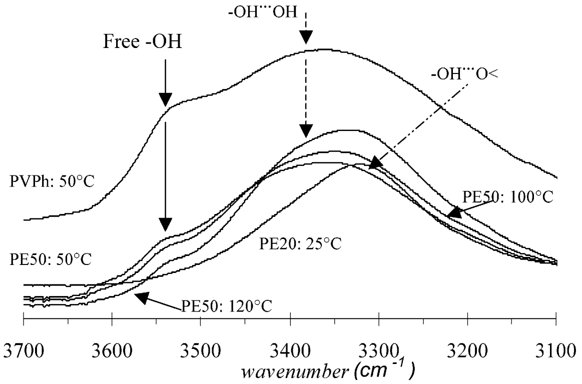

Figure 7. FTIR spectra of PVPh/PVEE blends at different temperatures (in °C).

somewhat due to the indirect influence of PVPh units that are hydrogen-bonded to neighboring segments.

This interpretation is confirmed by careful inspection of the DRS spectra of PE05, PE10, and PE20 at $T_g + 23$ K (Figure 5). The strength of the high-frequency peak decreases faster than the reduction in overall PVEE concentration, indicating that progressively more PVEE segments relax together with PVPh, because the hydrogen-bonded fraction of PVEE segments increases with PVPh concentration. Furthermore, by comparing the DRS loss spectra at different temperatures, it is found that the relaxation strength increases with increasing temperature in PE20 (Figure 3), which contrasts to the generally observed trend for segmental relaxations.[42] Nevertheless, this agrees well with the proposed nanoheterogeneity concept. The infrared peak at 3325 cm^{-1}, corresponding to intermolecular hydrogen-bonded −OH, becomes weaker with increasing temperature, indicating the usual decrease in the fraction of hydrogen-bonded groups with increasing temperature (Figure 7). Accordingly, more PVEE segments are free from the restrictions imposed by hydrogen bonds to PVPh at higher temperatures, and the high-frequency process is intensified. In blends with higher PVPh concentrations, the relaxation of all PVEE segments is coupled with PVPh because of the relatively high hydrogen-bonded fraction. For example, for PE50 blends we calculate that about 45% of the PVEE units are hydrogen-bonded to PVPh; thus, only one α process is observed.

It should be noted that hydrogen bonding is a dynamic process, and hydrogen bonds are in equilibrium between breaking and reassociating. If this occurred at a faster rate than segmental relaxation, we would presumably see a single α relaxation in low PVPh content blends, as the effect of hydrogen bonding would be “averaged out”. However, if the lifetime of a hydrogen bond is longer than the segmental relaxation, the blend behaves like a physically cross-linked network in the time frame of the experiment, and heterogeneity is a natural consequence.

E. Time−Temperature Superposition (TTS). For neat amorphous polymers, it is usually possible to construct a master curve by superposing dynamic data at different temperatures based on the TTS principle. However, TTS fails for many miscible polymer blends, since the relaxations or diffusion friction coefficients of the two components have different temperature dependences, even in the same blend.[43,44] Pathak and coworkers found that it was possible to build a master curve for styrene-*co*-acrylonitrile copolymer/poly(methyl methacrylate) [SAN/PMMA] blends, which has a $\Delta T_g \sim 20$ K,[45] but not possible for PVME/PS blends with $\Delta T_g \sim 125$ K.[11,46] These authors proposed that TTS is only possibly valid either for blends that have a small ΔT_g, such as SAN/PMMA[45] and poly(epichlorohydrin) [PECH]/PVME,[38] or for those blends exhibiting strong intermolecular interactions.

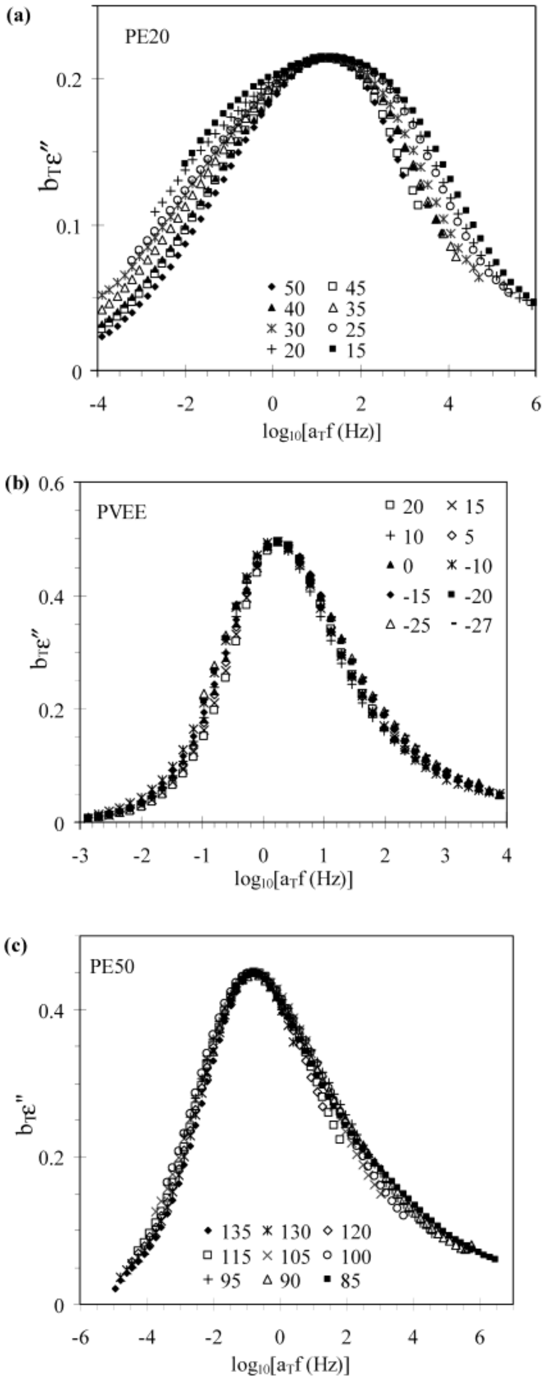

Figure 8. (a) Normalized DRS spectra of PE20 and dielectric master curves of (b) PVEE and (c) PE50 with $T \cong T_g + 10$ K as the reference temperature (the curve presented with filled squares).

As discussed earlier, there are two types of relaxing segments in PE10 and PE20, and their relaxations have different temperature dependences; i.e., τ_{max}(slow)/τ_{max}(fast) changes continuously with temperature. Accordingly, the DRS spectra of these two blends change shape dramatically with temperature (Figure 8a), and TTS clearly fails. However, for blends with higher PVPh concentration the motions of the different chemical units are highly coupled by hydrogen bonding. As a result, we do not need to consider the issue of temperature dependence, and the TTS principle should be obeyed. In fact, we find that TTS provides reasonable master curves, comparable with neat PVEE (Figure 8). This indicates that these blends are thermorheologically simple.

The applicability of TTS to polymer blends with strong interactions has also been investigated in a DMA study of blends of the lithium salt of lightly sulfonated PS ionomers (Li−SPS) and N-methylated nylon-2,10 (mPA).[47] Master curves of the storage (G') and loss (G'') moduli were constructed using DMA data from 95 to 185 °C. The authors concluded that the strong complexation between the metal sulfonate and amide groups could couple the relaxation of Li−SPS and mPA, and TTS was therefore successful.

It is worth noting that TTS is valid for segmental relaxations in polymer blends if (i) the two components have close-matched WLF parameters and (ii) concentration fluctuations are insignificant. While condition (i) suggests the same temperature dependencies for the two components' relaxations, as proposed by Pathak et al.,[43−45] (ii) is an important issue for most polymer blends without strong interactions. Generally speaking, large-scale concentration fluctuations, if they exist, are gradually weakened with increasing temperature (if no phase separation occurs), and the dielectric segmental relaxation distribution will be much narrower; thus, TTS is consequently invalid for most blends. That is, the suppression of concentration fluctuations is another indispensable prerequisite for applying TTS. This is the case in polymer blends with strong intermolecular interactions. For PE30−PE50, although the relaxation time distribution is much broader than neat PVEE, the relaxation width changes only by a small amount with temperature and is independent of composition in this range. This again supports the idea that concentration fluctuations are damped in PVPh/PVEE blends as a result of strong intermolecular hydrogen bonding. Similar behavior was also observed in our previous study of the PVPh/PEMA system.[31] Finally, although the fraction of intermolecular hydrogen bonds is lower at higher temperatures, it appears that the residual hydrogen-bonded fraction is still sufficient to couple the segmental relaxations of the two components.

F. Fragility of PVPh/PVEE Blends. Fragility plots are often used to compare the relaxation behavior of systems with different T_g's. Fragility, F, is defined by eq 6:[48,49]

$$F = \frac{\mathrm{d}\log \tau_{\max}}{\mathrm{d}T_{\mathrm{ref}}/T}\Big|_{T=T_{\mathrm{ref}}} \tag{6}$$

in which T_{ref} is a reference temperature correlated with the glass transition. Conventionally, T_{ref} is defined as the temperature at which $\tau_{\max} = 1$ s and is slightly higher than T_g. The fragility can be calculated from the VFT equation:[50]

$$F = \frac{B/T_{\mathrm{ref}}}{(\ln 10)(1 - T_0/T_{\mathrm{ref}})^2} \tag{7}$$

Fragility reflects how rapidly $\tau_{\max}$ changes with temperature and is generally correlated with the degree of intermolecular coupling or the topology of the potential energy hypersurface.[48,49,51] It is believed that as intermolecular coupling becomes stronger (or, in other words, as intermolecular cooperativity increases), the material becomes more fragile. This is because the coupling will be gradually reduced with increasing temperature, and segmental relaxations become faster than would be expected on the basis of increased free volume and mobility effects alone.

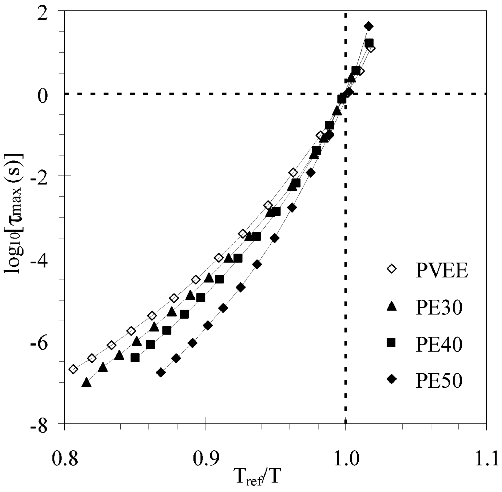

Figure 9. Fragility plots of PVPh/PVEE blends. T_{ref} is defined in Table 1.

The fragility of PVPh/PVEE blends increases with increasing PVPh content (Figure 9). This is likely to be a consequence of the strong intermolecular hydrogen bonding, which couples the relaxation of PVPh and PVEE segments. At the same $T - T_g$, a larger cooperative volume is expected to be involved in PVPh/PVEE blends, compared with neat PVEE in which the coupling is certainly weak due to the lack of strong interactions. PVEE is a fairly "strong" glass-former, with a fragility of ∼58, whereas PVPh is relatively "fragile". Although it is difficult to capture the α relaxation of PVPh by DRS or DMA, a dielectric study of styrene-*co*-4-vinylphenol [STVPh] random copolymers with up to 18 mol % VPh found a fragility of 92, independent of VPh content.[51] An increase in fragility has also been observed in other hydrogen-bonded polymer blends compared to their non-hydrogen-bonded counterparts, e.g., poly(methyl acrylate)/PVPh,[52] poly(vinyl acetate)/PVPh, and PVPh/poly(ethylene-*co*-vinyl acetate) with vinyl acetate content of 70 wt % [EVA70].[53] However, we did not observe any significant change in fragility for PEMA/PVPh blends with PVPh concentration up to 40%, which we attributed to the relatively high fragility of PEMA (∼84).[31]

The fragility of PVPh/PVEE blends is similar to chemically cross-linked polymers. In a dielectric study of model heterocyclic polymer networks, Kramarenko and co-workers found that F increased with increasing cross-linking density, and this was attributed to increased intermolecular coupling from the network constraints.[54] Similar behavior has also been observed for cross-linked PVE[55] and styrene−butyl acrylate copolymers.[56] Thus, intermolecular hydrogen bonds have an effect on the segmental dynamics analogous to chemical cross-linking, which demonstrates again that the strength of intermolecular hydrogen bonding in PVPh/PVEE blends is sufficient to couple component segmental relaxations.

G. KWW Coupling Parameters of PVPh/PVEE Blends. Intermolecular cooperativity in polymer

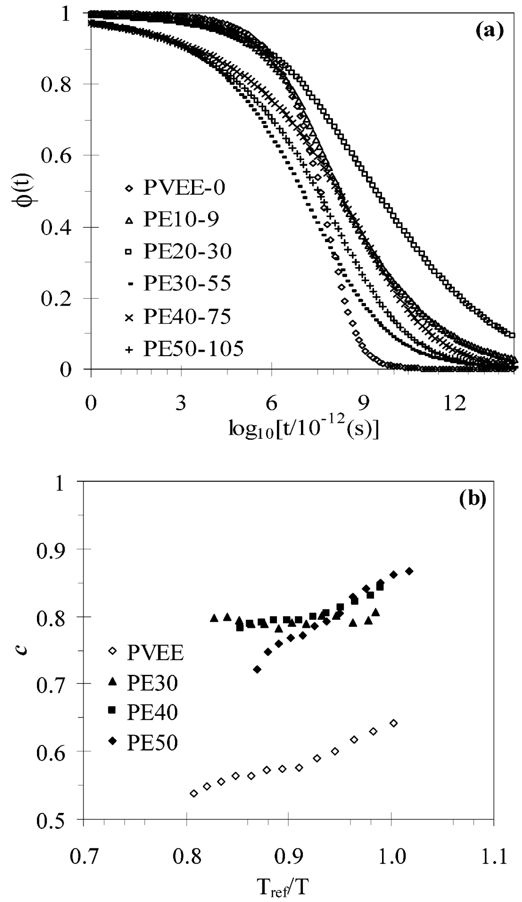

Figure 10. (a) KWW plots at $\sim T_g + 30$ K and (b) coupling parameters of PVPh/PVEE blends.

blends can also be evaluated by comparing their coupling parameters, *c*, with that of the neat components using[57,58]

$$\phi(t) = \phi_0 \exp[-(t/\tau^*)^{1-c}] \tag{8}$$

Equation 8 is the well-known Kohlrausch−Williams−Watts [KWW] expression, characterizing the nonexponential [stretched] relaxation behavior in the time domain. The quantities $\phi(t)$ and ϕ_0 are the dynamic response at time *t* and 0, respectively, after a perturbation, while τ^* is a characteristic time. For Debye relaxation behavior, the response is an exponential function and $c = 0$. According to the cooperativity concept,[58] *c* increases with intermolecular coupling. Transforming dielectric spectra from the frequency domain to the time domain requires a Laplace operation:[59]

$$\phi(t) = \frac{2}{\pi}\int_0^\infty \frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} \cos(\omega t)\, \frac{\mathrm{d}\omega}{\omega} \tag{9}$$

This is performed using the WinFit software [Novcontrol], after fitting the original DRS spectra with the HN model.

The resulting time-domain spectra exhibit clear nonexponential behavior for PVPh/PVEE blends at a normalized temperature (Figure 10). In particular, PE10 and PE20 blends include a fast and a slow relaxation processes and cannot be fitted with one KWW function, which agrees with the frequency spectra. Furthermore, the coupling parameters of the blends, ~0.8, are not only much larger than that of neat PVEE [~0.6] but also larger than those of other blends without strong intermolecular coupling.[58] This strongly supports the conclusion that there is strong intermolecular coupling between PVPh and PVEE.

Discussion

Blending modifies the segmental dynamics of miscible polymers, since they experience a different relaxation environment in the blended state and the fractional free volume is different compared to that of the neat polymers, even at the same temperature. Blending is sufficient to couple the segmental relaxations in polymer blends in which the component polymers have a small T_g difference, as in PECH/PVME blends,[38] even though they do not have strong intermolecular interactions. The nearly coincident T_g's of PECH and PVME lead not only to a single dielectric α relaxation process but also to anomalous dynamic homogeneity. In EVA70/poly(vinyl chloride) [PVC] blends, whose ΔT_g is relatively large (~90 K), one segmental relaxation has also been observed, but it is much broader than that found for either neat polymer, as a result of concentration fluctuations.[60,61] The importance of hydrogen bonding is demonstrated in blends with very large ΔT_g, for example, in PVPh/PEMA[31] and the present PVPh/PVEE blends, which would no doubt otherwise exhibit two segmental relaxation processes if there were no strong intermolecular interactions.

Coupling occurs between segments through the influence of intermolecular hydrogen-bonded repeat units; it does not require an equal molar ratio of segments. Although the presence of more than one hydrogen bond between a PVEE segment (consisting of a number of repeat units) and a PVPh segment will undoubtedly couple their relaxations more effectively, a single hydrogen bond between segments should also influence the segmental relaxation. In the latter case, one intermolecularly associated PVPh hydroxyl group is capable of modifying the relaxation of a corresponding repeat unit of PVEE, which in turn will restrict the relaxation of its neighboring repeat units. In other words, the coupling effect is magnified. This explains the single dielectric α relaxation in PE30 in which, although only a small fraction of PVEE repeat units [~25%] are associated with PVPh, the motions of all PVEE segments are coupled to those of PVPh. Recalling that $\Delta\epsilon(\text{slow})/\Delta\epsilon(\text{fast}) \sim 2$ for PE10, we estimate that only ~35% PVEE repeat units are involved in the fast process, which is much lower than the fraction of unassociated PVEE repeat units [~75%]. This confirms the "magnification" effect of hydrogen bonds on coupling segmental relaxations.

The stoichiometry of hydrogen bonding requires further comment. If hydrogen bonding is completely uniform and segmental relaxation involves more than 10 repeat units at $T_g + 20$ K, the 20% PVPh blend would be expected to be homogeneous on the cooperatively rearranging region (CRR) scale, and there would only be a single α process at $T_g + 20$ K. Hydrogen bonding is a statistical process, and there is a spatial distribution of hydrogen bonds, enhanced by chain connectivity effects, which result in more same-chain contacts than would be expected on the basis of random mixing of segments.[62,63] For some PVEE−PVPh segments, there might be only one intermolecular hydrogen bond, while others may possess two or more, depending on concentration and temperature. This leads to a broad

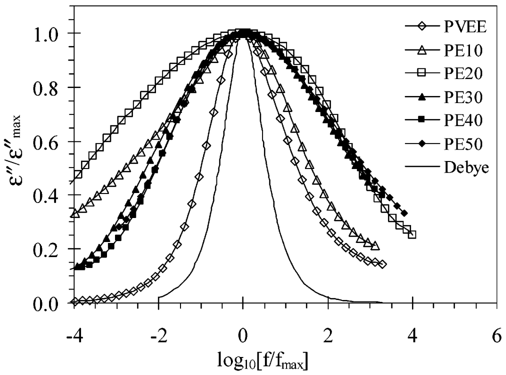

Figure 11. Dielectric broadening of PVPh/PVEE blends at $T_g + 30$ K. The loss spectra have been normalized by f_{max} and ϵ''_{max}, and the dc contribution has been subtracted. Temperatures are the same as the corresponding sample in Figure 10a.

distribution of dielectric relaxation times. Although the relaxation time distribution of PE50 exhibits only a small increase with decreasing temperature, the α relaxation of PE50 is much wider than that of neat PVEE (Figure 11). The full width at half-peak height is ~4.5 decades for PE30−PE50, whereas it is only ~2.5 decades for neat PVEE. This is a direct consequence of the distribution of intermolecular hydrogen bonds between PVEE and PVPh segments. Surprisingly, however, PE30, PE40, and PE50 have the same extent of relaxation time broadening [narrower than PE10 and PE20], whereas in other blends without strong interactions this distribution generally becomes broader with an increase in the high-T_g component concentration. This supports our stoichiometric explanation of the segmental relaxation behavior in PVPh/PVEE blends and the lack of concentration fluctuations in hydrogen-bonded polymer blends.

The existence of both free and hydrogen-bonded segments in blends with PVPh content ≤20% suggests that homogeneity at a scale smaller than the segment size is impossible in blends with low PVPh concentration. In light of the previous discussion, the following question arises: why is only one segmental relaxation observed in other polymer blends rich in one component and without specific interactions, in which there are also some segments surrounded by like segments and some in contact with unlike segments, because of similar stoichiometric effects? This can be explained by considering concentration fluctuations, which are dynamic and may be very fast in blends without strong interactions. Such fluctuations can rapidly change the segmental environment and therefore average segmental heterogeneity. In PVPh/PVEE, however, concentration fluctuations are suppressed and become very slow. The blend segments are transiently linked in a quasi-cross-linked network, and their motions can be resolved in DRS spectra in the segmental relaxation time scale.

The influence of hydrogen bonding on relaxation behavior was also clearly observed in DRS and DMA studies of urazole-modified polybutadienes (PBD) by Müller and co-workers.[64] While the segmental α relaxation of PBD was shifted to lower frequency after chemical modification, a consequence of the restrictions imposed by hydrogen bonding, these authors also observed an additional relaxation process which is related to the association and dissociation of hydrogen bonds and is even slower than the α process. More recently, the ability of hydrogen bonding to couple relaxations was also demonstrated in studies of the orientation of PS/PVME and PVPh/PVME blends using polarization modulation infrared linear dichroism.[65,66] In PS/PVME blends, it is relatively difficult to orient PVME, whereas in PVPh/PVME both components can be oriented. At the same time, the orientation of PVPh relaxes at the same rate as PVME, even though the PVPh chain is much stiffer than PVME.[65]

Finally, the ability of hydrogen bonds to couple the segmental dynamics in polymer blends will depend on their strength. Complete coupling is not possible unless chemical bonds are formed between the two segments. Intermolecularly hydrogen-bonded PVPh/PVEE is only a transient network with relatively weak bonds compared to covalently cross-linked systems. ^{13}C CP/MAS NMR studies on PVPh/PEO and PVPh/PMA[67] blends indicate that the two components still have different relaxation times, although they have been significantly coupled. The different results from DRS and NMR can be rationalized by considering the broad distribution of relaxation times observed in DRS and by their different measuring mechanisms. NMR measures the ^{1}H spin−lattice relaxation time, whereas DRS examines the orientation and relaxation of dipoles. That is, NMR reveals heterogeneity at a smaller length scale than DRS.

Summary

In this paper, we have demonstrated the ability of hydrogen bonding to couple the component segmental relaxations in a polymer blend with very large ΔT_g and thus with a very large intrinsic mobility difference. PVPh/PVEE blends with sufficiently high hydrogen-bonding fractions [i.e., with PVPh concentration ≥ 30 wt %] exhibit a single α relaxation process. In similar blends without specific interactions, two segmental relaxation processes have been observed, even in 50/50 mixtures, as a consequence of the differences in component mobilities. Two distinct α relaxations are postulated through HN fitting of the dielectric loss spectra of blends with ≤20% PVPh, although a single T_g is observed by DSC for these compositions. The fast segmental process is attributed to the relaxation of "free" PVEE segments, whereas the slow one is attributed to the coupled relaxation of hydrogen-bonded segments of PVEE and PVPh. The difference in the relaxation behavior of high and low PVPh content blends is rationalized by a simple stoichiometric model for hydrogen bonding. The coupling effect is also confirmed by the success of applying the TTS principle, which is only valid if the components have matched WLF parameters or exhibit strong intermolecular interactions, and by the increase in blend fragility and the value of the coupling parameter compared to neat PVEE, indicating an increase in intermolecular coupling.

Hydrogen bonding is also capable of suppressing concentration fluctuations in polymer blends. PE30, PE40, and PE50 have similar segmental relaxation peak widths, and this broadening does not change much with temperature. However, these relaxations are broader than the α relaxation of neat PVEE. We attribute this to the distribution of intermolecular hydrogen bonds; some segments may have formed one, two, or multiple hydrogen bonds, whereas others may be in an environment where intermolecular coupling is minimal. Segments with different degrees of coupling will exhibit different relaxation times, thus broadening the DRS spectra of the blends.

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