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Broad-Band Dielectric Study on Poly(4-vinylphenol)/Poly(ethyl methacrylate) Blends

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ABSTRACT: The dielectric relaxation behavior of miscible poly(4-vinylphenol)/poly(ethyl methacrylate) (PVPh/PEMA) blends has been studied using broad-band dielectric spectroscopy in the frequency domain from 10^{-2} to 10^{7} Hz and at temperatures between 30 and 180 °C. The α and β processes are resolved from the dielectric spectra by modeling with Havriliak−Negami (HN) functions. PVPh enhances the splitting between the α and β processes and provides a better understanding of the splitting and merging mechanism. Arrhenius plots support the proposal that the α and β processes have the same molecular origin above the merging temperature. The local β process in the blends originates from side-chain rotation of PEMA and is only slightly influenced by PVPh. On the other hand, the α process includes contributions from both components, and its relaxation time increases rapidly with PVPh concentration. However, a fragility plot reveals that the presence of PVPh does not change the cooperativity beyond shifting T_g for the blends, which is inconsistent with the energy landscape model. The relaxation time for the merged $\alpha\beta$ process also increases significantly as a result of the participation of PVPh. Because of the strong hydrogen bonding between PEMA and PVPh, the blends exhibit only slight dielectric broadening or concentration fluctuations.

Introduction

It is well-known that amorphous polymers generally exhibit at least two kinds of relaxations: the α process (at high temperatures or low frequencies) corresponds to the cooperative relaxation correlated to the glass transition, and the β process (at lower temperatures or higher frequencies) is a local relaxation.[1,2] These relaxations are important for their ability to dissipate energy and thus influence the mechanical properties of the material. The poly(*n*-alkyl methacrylate) (PnAMA) family of polymers [poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPMA), poly(*n*-butyl methacrylate) (PnBMA), etc.] are excellent model polymers for investigating relaxation behavior, since they are active both dielectrically and mechanically. The α process in these materials arises from main-chain cooperative micro-Brownian motion and follows Vogel−Fulcher−Tammann (VFT) or Williams−Landel−Ferry (WLF) behavior.[3] The activation energy of the α relaxation is relatively high, e.g., >400 kJ/mol for PEMA. The β relaxation in this polymer family results from hindered rotation of the asymmetric side group $-COOC_nH_{2n+1}$ about the C−C bond connecting it to the polymer backbone and, possibly, also involves coordinated main-chain rearrangement.[2,4−6] The activation energy of the β process is relatively low (e.g., <100 kJ/mol for PEMA) due to its local character. The frequency maximum of the α relaxation increases rapidly with increasing temperature, and therefore, at a particular temperature above the glass transition temperature (T_g), it often merges with the β process. It is generally difficult to resolve a reliable, well-defined α relaxation for poly(*n*-alkyl methacrylate)s in an accessible temperature and frequency range with typical dielectric (DRS) or dynamic mechanical (DMA) instrumentation. However, several studies of the onset of the α process of PnBMA and PEMA by DRS[6−9] or by heat capacity spectroscopy (HCS)[10−12] have appeared in recent years. For PEMA, whose T_g is in the range 63−70 °C, it has been reported that its α and β relaxations are only separated in the temperature region from 79 to 88.5 °C,[2] although a very weak α process can be resolved at ~110 °C by curve fitting.[7]

The underlying mechanism of the $\alpha-\beta$ splitting behavior in the PnAMA family remains an active research topic. Garwe and co-workers[6,7] have suggested that the high-temperature merged process ($\alpha\beta$) is locally cooperative, such that the relaxation of the side group involves neighboring main-chain cooperation. The cooperation length scale increases with decreasing temperature, and they propose that at a particular temperature (the so-called onset temperature, T_{onset}), at which the relaxation strength ($\Delta\epsilon(\alpha)$) = 0, the cooperation length scale is large enough to be observed dielectrically and thus the α process emerges. This proposed mechanism is mainly based on the observed change in the Arrhenius behavior through T_{onset}, as will be discussed later. However, the temperature range in which the α process is well separated from the β process is too narrow to support this splitting mechanism. A wider splitting temperature window is desirable for studying $\alpha-\beta$ merging and splitting behaviors.

One way to enhance separation of the α and β processes is to form a miscible blend of the PnAMA with a polymer having a higher T_g. This shifts the α process of the blend to a lower frequency (or higher temperature), while the relaxation time of the β process (τ_β) of the PnAMA may not change much due to its local character. Therefore, the α and β processes will be more clearly resolved.

PEMA is known to be miscible with poly(4-vinylphenol) [PVPh] throughout the entire composition range, due to the strong hydrogen bonding between the PEMA carbonyl groups and the hydroxyl groups of PVPh.[13,14] Compared with PEMA, PVPh has a relatively high T_g,

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i.e., 160−170 °C depending upon its molecular weight. This blend system is expected to have a wider $\alpha\beta$ splitting temperature range than PEMA, and thus more information on the splitting behavior can be obtained.

Additionally, the formation of hydrogen bonds is interesting for other reasons, including their possible effects on the fragility and concentration fluctuations in the blends. Fragility is a measure of the rapidity with which a material changes its relaxation behavior in the vicinity of the glass transition temperature.[15,16] It has been found that the classical energy landscape model, although successful in many small molecules, cannot explain the fragility behavior in hydrogen-bonding systems, e.g., alcohols.[16,17] Concentration fluctuations in miscible polymer blends have been a popular research topic in recent years.[18,19] It is generally agreed that these fluctuations are favored by large ΔT_g, dissimilarity in chemical structure, and absence of intercomponent interactions. Consequently, it is expected that concentration fluctuations will be damped in PVPh/PEMA blends as a result of the strong intermolecular hydrogen bonding. In fact, there have been relatively few studies of the relaxation behavior of blends in which the component polymers interact strongly.[20,21]

This paper is organized in the following manner. First we present our DRS data on neat PVPh and PEMA and propose a tentative molecular mechanism for the $\alpha\beta$ splitting in PEMA. Then we will individually discuss the influence of blending on the relaxation behavior in three different regions: the low-temperature β process, intermediate temperatures where the α and β relaxations are separated, and α−β merging at higher temperature. The effect of PVPh on the fragility and concentration fluctuations is also discussed.

Experimental Section

A. Materials and Sample Preparation. PVPh (Polysciences, Inc.) was purified by dissolving in methyl ethyl ketone (MEK), filtering with a 0.45 μm PVDF Acrodisc, and finally precipitating in hexane. The purified PVPh has $M_w = 34\,000$ and $M_w/M_n = 2.5$. PEMA (Scientific Polymer Products, Inc.) has $M_w = 460\,000$ and $M_w/M_n = 3.6$. Molecular weights of both polymers were determined by gel permeation chromatography using dimethylformamide as the mobile phase and narrow molecular weight poly(ethylene oxide) standards.

Blends with PVPh concentrations of 10−40 wt % in 10% increments (designated as VE10−VE40) were prepared by solution casting. Then 5 wt % solutions of neat PEMA and PVPh in methyl ethyl ketone were prepared, and 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 in Teflon dishes. They were kept at room temperature for 24 h to allow for evaporation of most of the solvent. Following this, they were placed in a vacuum oven at room temperature for 24 h, at 60 °C for 24 h, and at 90 °C for 48 h. This procedure leads to solvent removal and elimination of bubbles in the films. The neat PEMA film was prepared using the same method. A neat PVPh film was prepared by compressing powdery PVPh at 180 °C, which was then aged in the vacuum oven following the same temperature scheme as the blend films. All films were 0.2−0.3 mm thick and were sputtered with a thin layer of gold on both sides in an argon atmosphere for DRS studies. The films were kept in a vacuum desiccator before measurement. Because of the strong dc conductivity in PVPh, the α process in blends with more than 40% PVPh cannot be reliably resolved.

B. DRS Experiments. The dielectric relaxation spectra (DRS) $\epsilon^*(f,T)$ were collected isothermally using a NOVOCONTROL GmbH Concept 40 broad-band dielectric spectrometer in the frequency domain (0.01 Hz−10 MHz) at temperatures between 30 and 180 °C in 5 °C increments. To define the α−β splitting more reliably, a smaller temperature interval was selected in this region, i.e., every 2 °C. Sample films were tightly sandwiched between two electrodes having a diameter of 20 mm. A thin piece of aluminum foil was placed between the sample and system electrode to prevent contamination by the polymer at high temperature. No significant difference in the dielectric spectra was observed in a control study conducted without the aluminum foil. Temperature was controlled by a NOVOCONTROL Quatro Cryosystem, having a stability of ±0.1 °C. The samples were cooled and heated in the presence of N_2 during the dielectric measurements.

C. DRS Curve Fitting. The isothermal dielectric loss $\epsilon''(f)$ was modeled with the phenomenological Havriliak−Negami (HN) equation.[22] One or a sum of two HN functions, plus one dc contribution if necessary, was used to fit the experimental loss curves using the WinFit program (developed by NOVOCONTROL). The HN[22] function is defined as

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

where $\omega = 2\pi f$, ϵ_∞ and ϵ_R are the unrelaxed and relaxed dielectric constant (ϵ') at very high and low frequency, respectively, and $\Delta\epsilon$ is the dielectric strength, $\epsilon_\infty - \epsilon_R$. σ_0, s, τ_{HN}, $\Delta\epsilon$, m, and n are fitting parameters. ϵ_0 is the dielectric permittivity of a vacuum. The exponents m and n ($0 < m$, $mn \leq 1$) are shape constants: $m = n = 1$ for a Debye process, and m is an indicator of the broadness of the relaxation while n represents the asymmetry. σ_0 is the dc conductivity constant with units of S/cm; the exponent s ($0 < s \leq 1$) characterizes the conduction process. τ_{HN} is related to τ_{max}, the relaxation time at which ϵ'' reaches its maximum, by[8]

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

In this paper, $f_{max} = 1/(2\pi\tau_{max})$, instead of τ_{HN}, is used to compare and calculate activation energies because the latter is a function of the shape parameters m and n, which are affected by the fitting process.

The peak in $\epsilon''(f)$ below T_g mainly arises from the β relaxation. We therefore fit curves in this region with only one HN function. In addition, the β relaxation in PEMA (and PnBMA) has generally been found to be symmetric[7,8,10,23] and can therefore be fit by fixing the HN parameter $n = 1$, i.e., assuming a Cole−Cole function.

In the splitting region, $\epsilon''(f)$ is fit with two HN functions and one dc contribution. To reduce the number of fitting parameters and thus to improve the fitting stability, we also assumed $n = 1$ for both α and β relaxations, following Schröter and co-workers[8] in their dielectric study of PEMA. This assumption appears to be reasonable on the basis of a dielectric study of PEMA and PnBMA, in which n was not fixed, and it was found that $m \approx mn$, implying $n \approx 1$.[7] Moreover, in the middle of the splitting region, where both α and β are well-defined, we found $n = 1$ even though it was a free fitting variable.

In the merged $\alpha\beta$ temperature region, the dielectric loss was fit with one dc contribution and one HN function, in which both m and n were free.

D. DSC. Samples for differential scanning calorimetery (DSC) experiments were cut from the DRS films. T_g was measured using a Perkin-Elmer DSC-7, calibrated using pure indium. The samples were first heated to 20 °C above the expected T_g, held for 3 min, and then quenched to 0 °C. T_g was taken as the midpoint of the heat capacity change (ΔC_p) in the second heating run at a rate of 20 °C/min. ΔC_p at T_g was determined from the difference between the extrapolated values of the glassy and liquid states.

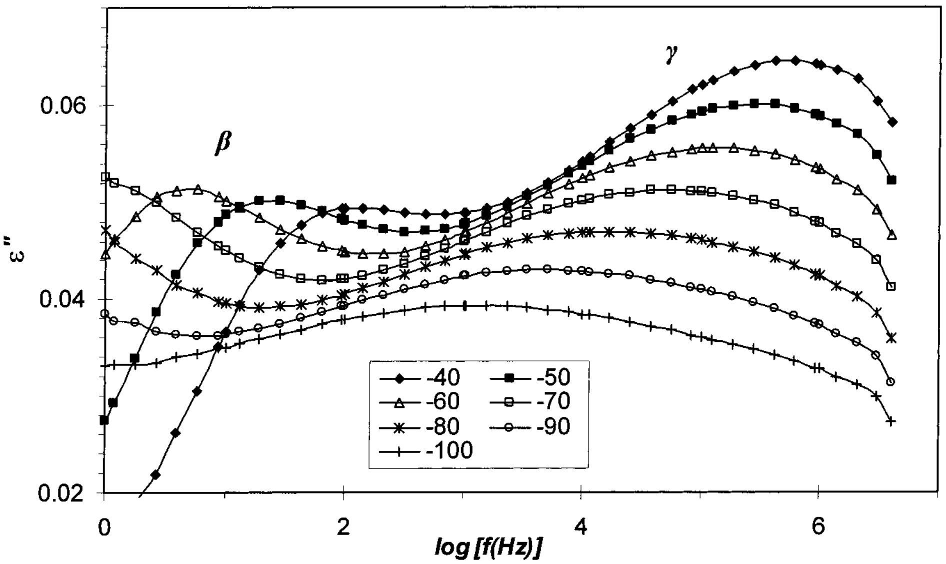

Figure 1. Dielectric loss (ϵ'') spectra of neat PVPh. Temperatures in °C.

Table 1. Characteristic Temperatures, Heat Capacity Change, and Fragility of PVPh/PEMA Blends

	PEMA	VE10	VE20	VE30	VE40	PVPh
T_g (DSC, °C)	74	85	90	101	107	171
ΔC_p (J/(g °C))	0.15	0.27	0.32	0.37	0.38	0.54
T_{ref} (°C)[a]	76	93	97	102	109	
T_{onset} (°C)	94	115	131	137	150	
$T_{onset} - T_{ref}$ (°C)	18	22	34	35	41	
F	84	107	89	82	89	

[a] At which $\tau_{max}(\alpha) = 1$ s.

Results and Discussion

All blends exhibit a single T_g in the DSC experiments, and these are listed in Table 1. In the temperature range where α and β are well separated, we found a single α process for all blends, located between that of neat PEMA and PVPh. This confirms that PVPh/PEMA is a miscible system in the composition range studied.

A. Dielectric Behavior of PVPh. PVPh has a relatively strong dipole associated with its phenol group and exhibits α, β, and γ relaxations in the dielectric spectra (Figure 1). The dc conduction in neat PVPh is so strong above T_g that it completely masks the α process. To our knowledge, the α relaxation of PVPh has not yet been reported in the literature. Compared to PEMA, the β relaxation of PVPh is weak and is located at a much higher frequency, so we do not consider this process further in this paper.

In our experiments, PVPh was tightly sandwiched between two electrodes and was in an N_2 environment during the entire measuring period. However, the PVPh phenol group is readily oxidized, and understanding the thermal stability of PVPh is a prerequisite for obtaining reliable information for both the neat polymer and blends. The maximum temperature at which data was acquired was 180 °C. This upper limit was arrived at on the basis of an FTIR temperature study, in which no observable changes in the spectra were detected after holding at 180 °C for 30 min.

B. α–β Merging of PEMA. The dielectric behavior of PEMA has been well documented. As discussed in the first section, PEMA exhibits a β peak below ~70 °C in the accessible DRS frequency window. An α process appears above T_g and with increasing temperature shifts to higher frequency at a faster rate than the β process. Moreover, the dielectric strength of the β process increases with increasing temperature while $\Delta\epsilon(\alpha)$ decreases. As a result of these two effects, only one peak is observed above ~90 °C. Figure 2a shows the splitting and merging process.

As typically found for other polymers, the low-temperature β process exhibits Arrhenius behavior, while the α transition, correlated with the glass transition, is VFT-like.[2] For the merged αβ process, although it includes some contribution from the α relaxation, it still displays Arrhenius behavior, as shown in Figure 3.

The Arrhenius plot of the β process in the splitting region is rather interesting. A plot of log $f_{max}(\beta)$ vs $1/T$ is generally linear, but close inspection of Figure 4a reveals a deviation from Arrhenius behavior when approaching the merging temperature. The slope of the log f_{max} vs $1/T$ plot at a temperature slightly above T_g is close to that observed in the low-temperature region, which arises from the local β relaxation only. However, as the temperature is increased, the data become curved, appearing more like the αβ process at T_{onset}. It is worth pointing out that the activation energy of the αβ process is higher than the low-temperature β process. The increase in E_a indicates that the mechanism of the β relaxation changes from a local process below T_g to a process with some cooperative character with increasing temperature, as confirmed by a multidimensional NMR study of PMMA and PEMA.[4,5] In this work it was observed that the β relaxation is accompanied by main-chain rocking, whose amplitude increases with temperature. The β process in PMMA arises from the 180° (±20°) flip of the $-O-(C{=}O)-$ plane of the side group between two potential energy minima.[4] This should also be true for PEMA. Because of its asymmetric shape, the $-OCOC_2H_5$ side group cannot match its initial environment after one flip; thus, the main chain must undergo some kind of simultaneous rearrangement. This process can be called a locally cooperative relaxation.[4,7] In PEMA the main-chain rearrangement is a rocking motion around the local chain axis with ±20° amplitude in the glassy state.[5] The main-chain cooperative rocking is achieved by free volume fluctuations; i.e., there is enough free volume in "microdomains" even well below T_g. According to Kulik et al.,[5] at 82 °C (~18 °C above T_g), the amplitude of the main-chain rocking increases

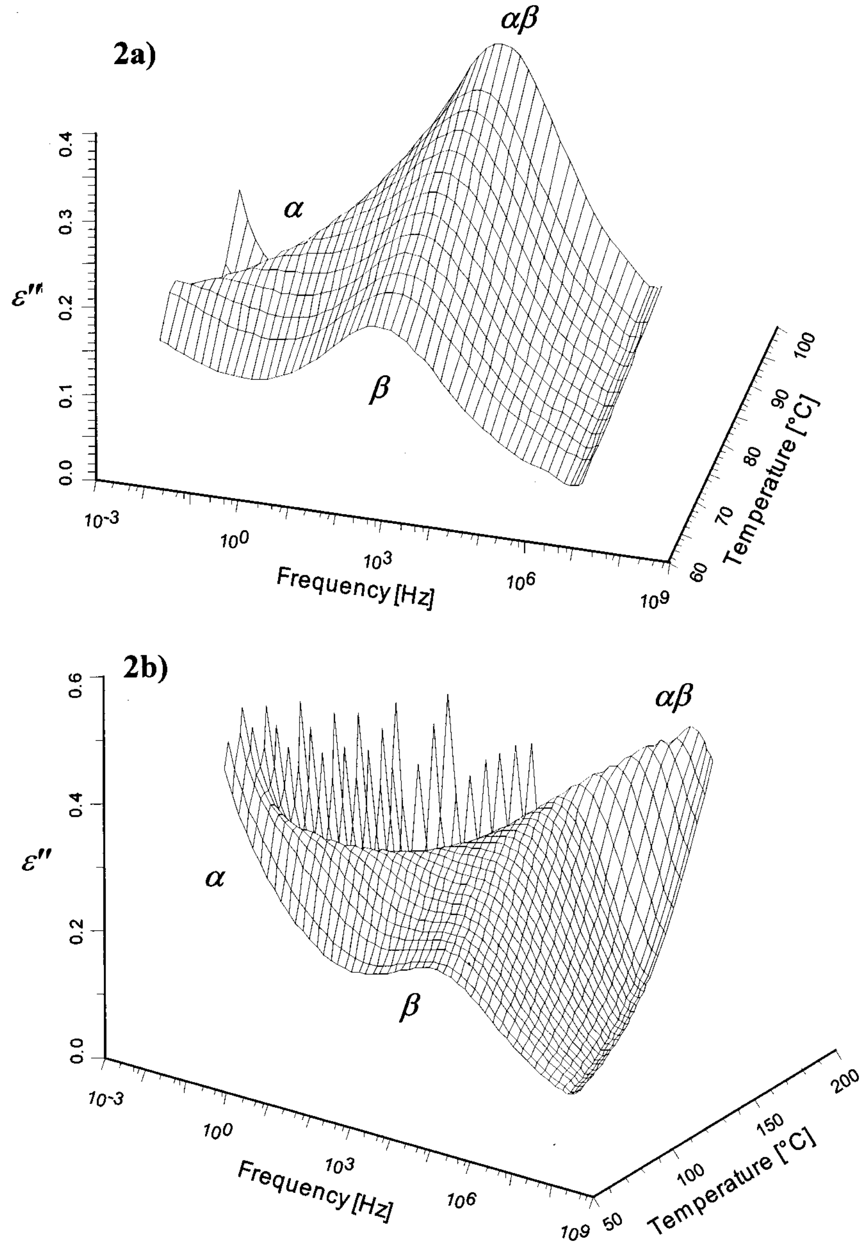

Figure 2. 3D DRS loss spectra of neat PEMA (a) and VE30 (b): $\alpha\beta$ splitting and merging process.

to about ±40°, and it increases to an amplitude of ±50° at 92 °C (28 °C above T_g).

The above NMR study strongly supports a change in the molecular mechanism of the β process with increasing temperature. The nonlinearity of the log f_{max} vs $1/T$ behavior of the β process in the splitting temperature region can be explained by the continued enhancement of accompanying main-chain participation with increasing temperature, i.e., an increase in the relaxation unit size. Combining our DRS data and the ideas proposed by Garwe et al.,[7] it seems that the ±20° main-chain rocking does not change the local nature of the β relaxation below T_g, while the ±50° main-chain rocking well above T_g endows some cooperative character.

On the other hand, while the amplitude of the accompanying main-chain participation in the β process increases with increasing temperature, the cooperativity, or the relaxation unit size, of the α process itself decreases with increasing temperature. These opposing trends suggest a reduction of the domain size associated with the α process to a value equivalent to that required to accompany the locally cooperative β process at T_{onset}. If this is true, there will be only one relaxation process, because the α and β relaxations have the same molecular origin above this temperature, the merged $\alpha\beta$ process. Donth's group[6–8,10–12] considers this explanation to be incorrect, because the log $f_{max}(\alpha)$ vs $1/T$ plot parallels that of log $f_{max}(\beta)$ vs $1/T$ when approaching the merging region, indicating that an extrapolation of log $f_{max}(\alpha)$ vs $1/T$ to log $f_{max}(\beta)$ vs $1/T$ is impossible. However, in our DRS study, which corresponds with results obtained by Bergman and co-workers (Figure 4 in ref 9), the log $f_{max}(\alpha)$ vs $1/T$ plot is not parallel to the corresponding plot for the β process in the vicinity of the merging temperature, and thus it is possible to obtain $f_{max}(\alpha) = f_{max}(\beta)$ by extrapolation. Nevertheless, our explanation of the $\alpha-\beta$ merging behavior needs further experimental verification by other techniques, e.g., two-dimensional FTIR.[24]

C. PVPh/PEMA Blends. Because the blends have a higher T_g than PEMA (Table 1), the α peak is shifted to lower frequencies or higher temperatures compared

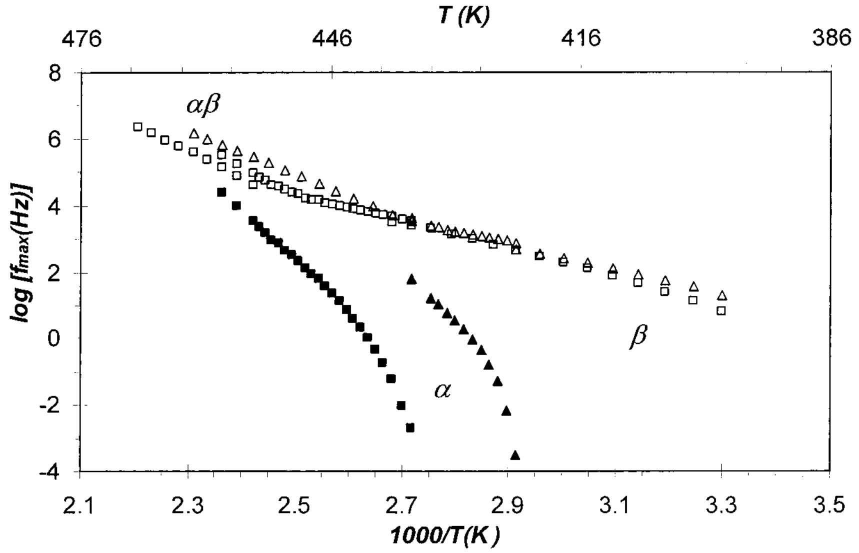

Figure 3. Arrhenius plots for PEMA (triangles) and VE30 (squares). Plots of other blends are not shown for clarity.

with the case of PEMA. However, the overall dielectric behavior of the blends is similar to that of neat PEMA: there are clear α−β splitting and merging regions, as shown in Figure 2b in a 3D manner or in the Arrhenius plot in Figure 3.

1. Low-Temperature β Process. This process in the blends also originates from side group flipping of PEMA and follows the Arrhenius law. The hydrogen bonds formed between PVPh and PEMA have a strength of about 15−40 kJ/mol,[25] while $E_a(\beta)$ of neat PEMA below T_g is 68 kJ/mol. These two values are roughly comparable, so one would expect that hydrogen bonding between PVPh and PEMA would significantly decrease the $f_{max}(\beta)$ of PEMA. However, only a slight decrease $f_{max}(\beta)$ at a given temperature was observed (see Figure 4b). Hydrogen bonding is a dynamic process, of course, and if the lifetime of hydrogen bonds (τ_{HB}) between PEMA and PVPh is shorter than $\tau_{max}(\beta)$, the β relaxation can readily occur during the dissociation interval. On the other hand, if $\tau_{HB} > \tau_{max}(\beta)$, additional energy will be needed to break the hydrogen bond before the −C═O groups can relax. It has been found that the formation and breaking of the hydrogen bond between *N*-methylacetamide (NMA) and methanol occurs on a time scale of 10−15 ps at room temperature.[26,27] The hydrogen bond between PEMA and PVPh is weaker than that between NMA and methanol; thus, its τ_{HB} should be even shorter. Therefore, τ_{HB} is smaller than $\tau_{max}(\beta)$ for PVPh/PEMA blends at the same temperature.

At 60 °C, the β processes of the blends and PEMA occur at almost the same frequency (Figure 5), while the β process of PVPh is located more than 5 decades higher in frequency and its relaxation strength is relatively low. Accordingly, it might contribute to the high-frequency shoulder of the blends. Although there appears to be some broadening of the β process in the blends, this is reduced considerably if we remove the contribution of PVPh on the high-frequency side and that of the α process on the low-frequency side.

Blending also increases the activation energy of the β relaxation. $E_a(\beta)$ of neat PEMA is about 68 kJ/mol (Table 2), which is consistent with the value obtained by Garwe et al.[8] (65 kJ/mol) but somewhat lower than that reported by McCrum et al.[2] However, blending with a high-T_g polymer does not necessarily increase $E_a(\beta)$ of the low-T_g component. In a dielectric study of bisphenol A polycarbonate (BPA−PC)/tetramethylbisphenol A polycarbonate (TMBPA−PC) blends, Katana and co-workers[28] found $E_a(\beta)$ of BPA−PC decreased with increasing concentration of the high-T_g component, TMBPA−PC.

Table 2. Activation Energies for Different Relaxation Processes and dc Conductivity in PEMA and PVPh/PEMA Blends[a]

	PEMA	VE10	VE20	VE30	VE40
β relaxation (low temp)	68	75	78	85	81
merged $\alpha\beta$ (high temp)	125	127	138	153	182
β (splitting region)	62	79	84	78	67
dc conduction (high temp)	161	157	149	145	140

[a] Units: kJ/mol.

2. Splitting Temperature Region. In this region, the dielectric spectra were fit with one dc contribution and two HN functions. An example of the final fit curves is shown in Figure 6, in which the α and β processes are rebuilt with the fitting parameters according to eq 3:[16]

$$\epsilon''(\omega) = \Delta\epsilon \frac{\sin(n\theta)}{\left[1 + 2(\omega\tau_{HN})^m \cos\left(\frac{\pi m}{2}\right) + (\omega\tau_{HN})^{2m}\right]^{n/2}} \tag{3}$$

in which

$$\theta = \arctan \frac{(\omega\tau_{HN})^m \sin\left(\frac{\pi m}{2}\right)}{1 + (\omega\tau_{HN})^m \cos\left(\frac{\pi m}{2}\right)} \tag{4}$$

At temperatures approaching the merging point, i.e., 90 °C, although there is only a small shoulder on the low-frequency side of the β peak, one HN function cannot provide a reasonable fit to the data, and the spectra must be fit with functions representing both α and β processes.

In contrast to the small change in $f_{max}(\beta)$ in the low-temperature region, the relaxation time of the α process in the blends increases significantly with PVPh content (Figure 7a). This can be easily understood if we consider that the α relaxation is correlated with the glass transition and T_g of PVPh is about 100 °C higher than PEMA. The issue is whether hydrogen bonding has

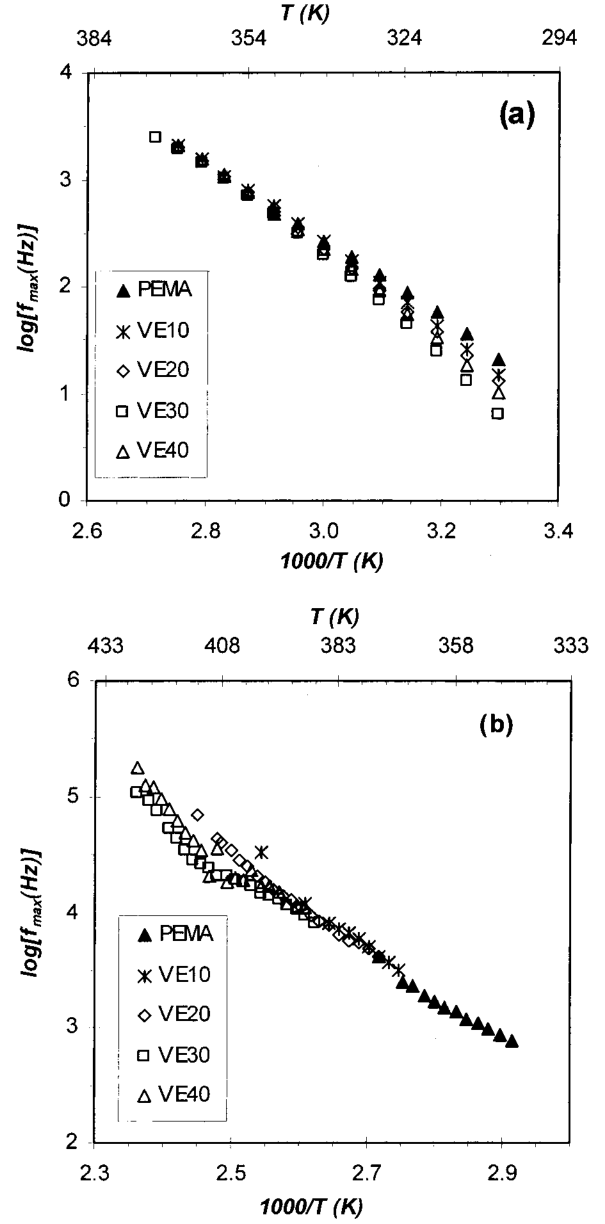

Figure 4. Comparison of Arrhenius behavior of the local β relaxation for PEMA and PVPh/PEMA blends at low temperatures (a) and in the splitting region (b).

some special influence on the α process, beyond a simple T_g effect. To determine this, we normalized the temperature as T_{ref}/T, in which T_{ref} is the temperature at which $\tau_{max}(\alpha) = 1$ s, to facilitate comparisons through a fragility plot. The fragility F^{16} of a material is defined as

$$F = \left.\frac{d \log \tau_{max}}{dT_{ref}/T}\right|_{T=T_{ref}} \tag{5}$$

Fragility reflects the temperature dependence of $\tau_{max}(\alpha)$. "Fragile" polymers have a higher slope and dramatically change their relaxation time through the reference temperature, while "strong" polymers maintain their properties in the transition region.[15,16] It is possible that intermolecular hydrogen bonds would restrict the polymers and render them more fragile, as found for PMA/PVPh blends.[20]

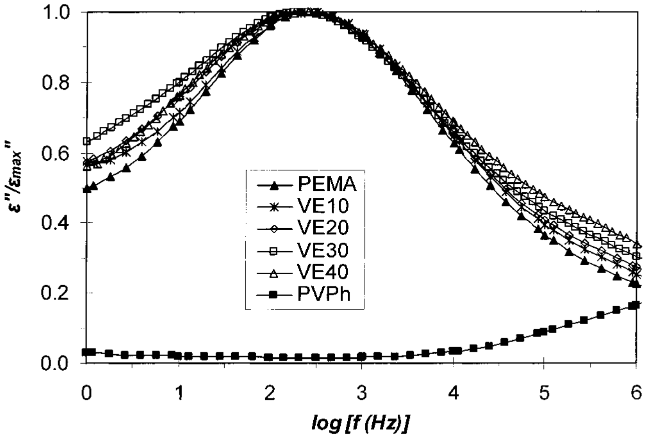

Figure 5. Dielectric β process of PEMA and PVPh/PEMA blends at 60 °C. ϵ'' of PEMA and the blends have been normalized to ϵ_{max}'', while that of PVPh is normalized to PEMA.

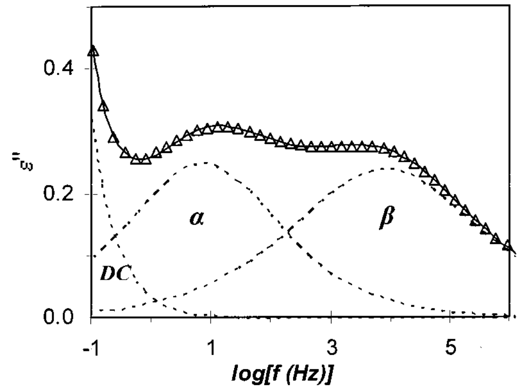

Figure 6. Dielectric loss spectrum of 30 wt % PVPh/PEMA blend at 112 °C. The triangles are experimental results; the dotted lines are HN curve fitting results for the α and β relaxations and dc conductivity. The solid line is the sum of the three components.

Despite this, Figure 7b does not show any significant difference in fragility between neat PEMA and PVPh/PEMA blends. Since fragility is related to cooperativity, this excludes the possible influence of the hydrogen bonding on the cooperative relaxation mechanism in PVPh/PEMA blends.

Fragile materials usually have a higher degree of intermolecular coupling (i.e., high cooperativity) which is quickly lost with rising temperature, so that the relaxation process changes rapidly.[16] For a hydrogen-bonded system, however, the intermolecular interaction is significantly larger than kT, which is roughly 3 kJ/mol at the T_g of PVPh/PEMA blends. Thus, the high fragility expected from high cooperativity is not observed.

On the other hand, based on the energy landscape model developed by Angell and co-workers,[15,16] fragility is correlated with the topology of the potential energy hypersurface. If the density of energy minima in this hypersurface is high, the material will have a greater probability of finding a new conformation and will thus exhibits higher fragility. The rapid change of conformation suggest a large entropy change, or large ΔC_p:[16]

$$S_c = \int \Delta C_p / T \, dT \tag{6}$$

PVPh/PEMA blends do have a larger ΔC_p than neat PEMA (Table 1), but this does not necessarily imply high fragility, because ΔC_p of the blends might include enthalpy contribution from the breaking of hydrogen

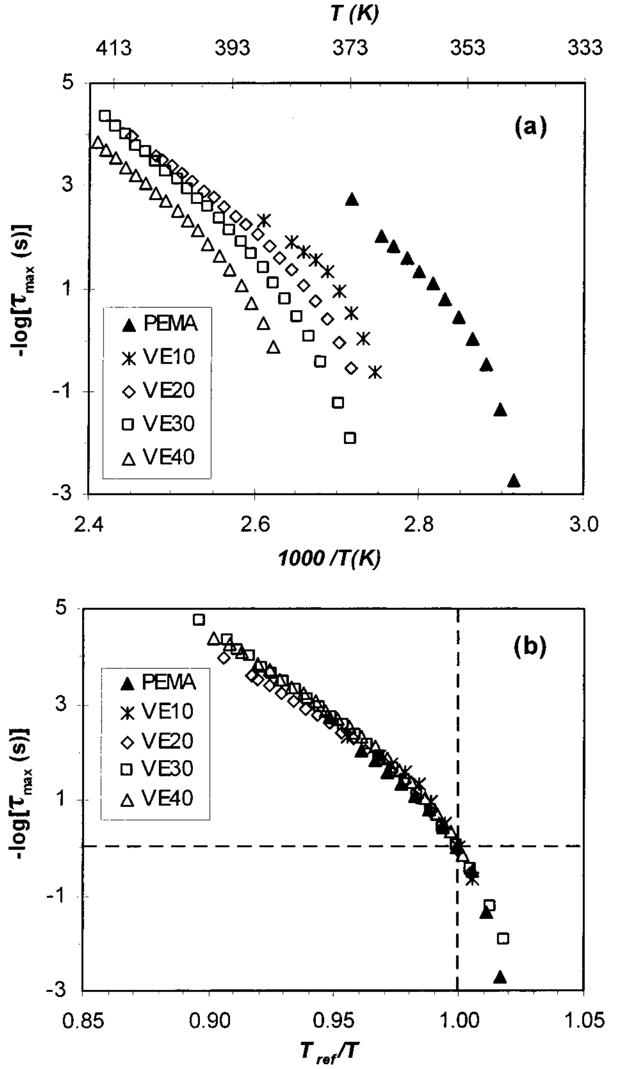

Figure 7. Arrhenius (a) and fragility (b) plots of the α relaxation for PEMA and PVPh/PEMA blends. $T_{\rm ref}$ and fragility F are shown in Table 1.

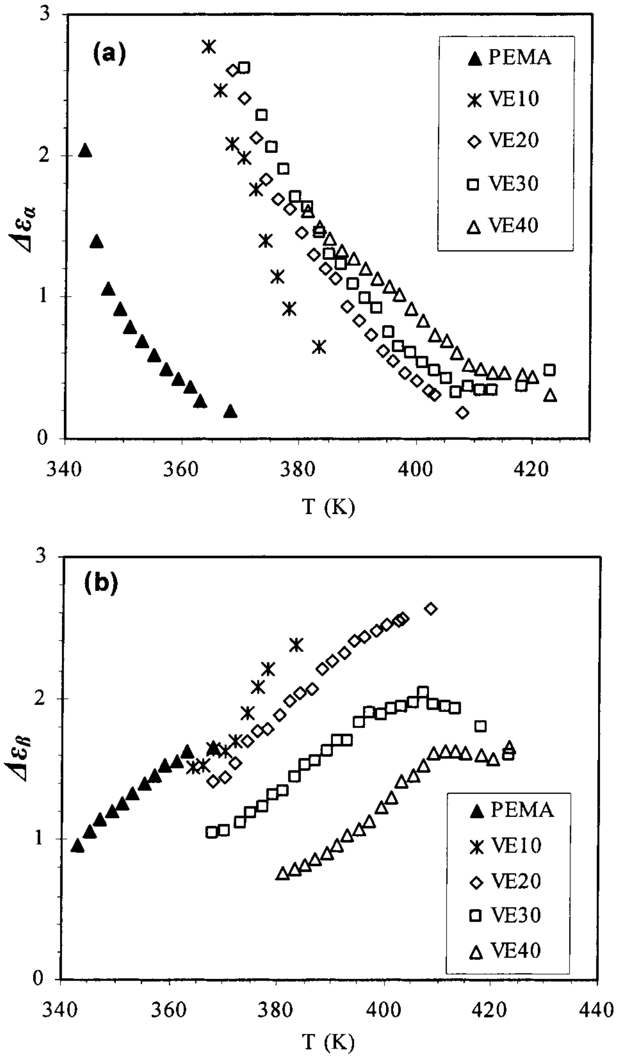

Figure 8. Dielectric strength of the α (a) and β (b) processes of PEMA and PVPh/PEMA blends.

bonds during heating. Moreover, although the density minimum is high, if the energy barrier between the minima is large, it will be difficult for the polymer to change from one conformation to another. This mechanism has been proposed to explain the same high-ΔC_p but medium-fragility behavior in hydrogen-bonded small molecules, e.g., alcohols. It is believed that hydrogen bonding increases this energy barrier.[15−17,29]

The insensivity of fragility to hydrogen bonding is also observed in styrene-*co*-4-vinylphenol (STVPh) copolymers.[30] Copolymers with different 4-vinylphenol contents have the same fragility as polystyrene, although ΔC_p increases with increasing 4-vinylphenol content. In the similar PMA/PVPh blends, the increase of fragility upon adding PVPh might be, as the authors mentioned, a result of concentration fluctuations.[20] T_g of PMA is only 18 °C, and the large ΔT_g is a favorable factor for observing concentration fluctuations.

It is worth pointing out that fragility of PEMA is roughly 84 (Table 1), while it has been reported to be 92 for STVPh with 18% 4-vinylphenol.[30] The small difference is also an important reason for the almost same fragility observed in PVPh/PEMA blends.

In contrast to the cooperative α process, the local β relaxation in this temperature range does not change much with the addition of PVPh. As observed for neat PEMA, the local β relaxation in this region exhibits a gradual curvature with increasing temperature (Figure 4b). It becomes more and more like the merged $\alpha\beta$ process as the onset point is approached. This has been explained in terms of an increase in main-chain participation earlier in this paper.

As a general rule, $\Delta\epsilon(\alpha)$ decreases with increasing temperature as a result of reduced cooperative domain size and $\Delta\epsilon(\beta)$ increases, because more dipoles gain mobility at higher temperatures (Figure 8a,b). Moreover, $\Delta\epsilon(\alpha)$ is very similar for the different blends while $\Delta\epsilon(\beta)$ becomes smaller with increasing PVPh concentration; i.e., the ratio $\Delta\epsilon(\alpha)/\Delta\epsilon(\beta)$ increases with blending. Since the β transition arises from PEMA, this observation confirms that PVPh participates in the dielectric α relaxation; otherwise, $\Delta\epsilon(\alpha)$ would have decreased proportionally with $\Delta\epsilon(\beta)$.

The HN parameter m is a function of temperature and composition (Figure 9) and takes on larger values for narrower peaks. In polymers, there is a distribution of molecular weight, structure, and chain environment, and dispersed relaxation time spectra usually are observed. For the cooperative α relaxation, the system becomes more homogeneous at higher temperatures, and a higher value of m_α is found for both PEMA and the blends with increasing temperature. Additionally,

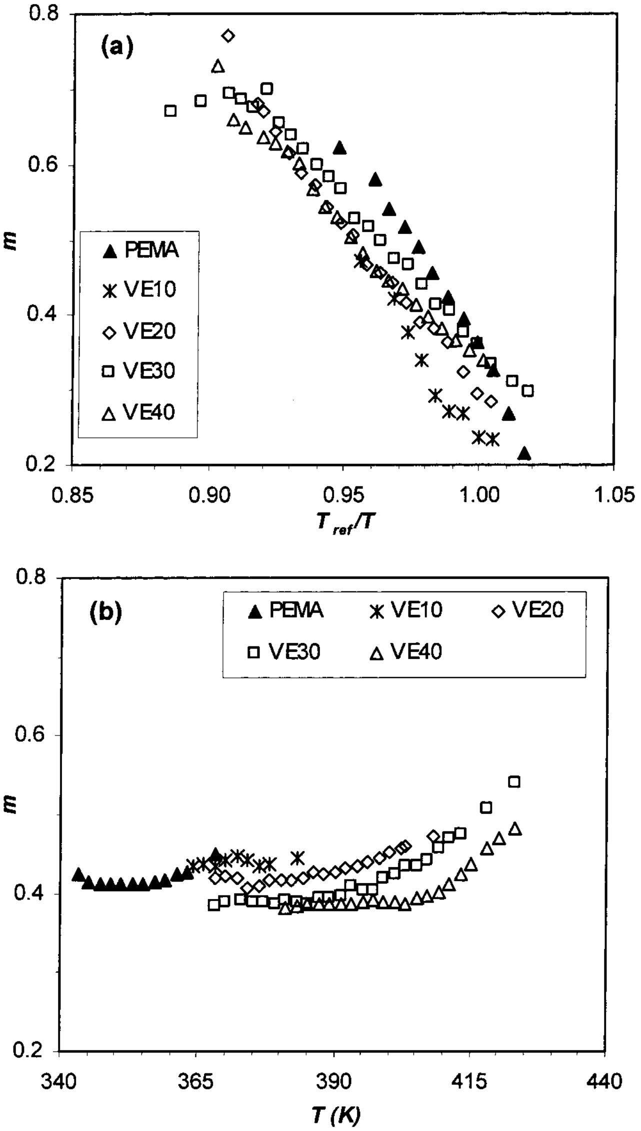

Figure 9. Curve-fitted HN parameter m of the α (a) and β (b) processes in the splitting temperature region.

the value of m_α for neat PEMA and blends with different compositions are similar after normalization by T_{ref} (Figure 9a), which indicates that the well-known concentration fluctuation effect in blends is insignificant our case. For the local β relaxation, we again did not find any significant effect of blending. That is, m_β is very similar for all systems, although it displays a small increase with rising temperature (Figure 9b).

As discussed earlier, the α relaxation in the blends is shifted to higher temperature or lower frequency compared to the case of PEMA, whereas the position of the β process changes little. Therefore, as expected, α and β are separated more clearly at the same temperature (Figure 10a). Moreover, the increase of $\Delta\epsilon(\alpha)/\Delta\epsilon(\beta)$ further enhances $\alpha-\beta$ separation in the blends, even after normalization with T_{ref} (Figure 10b). In Figure 10b, the α process of PEMA is only a small shoulder on the β peak, while in the blends it is more clearly resolved and exhibits a significantly higher strength than the α process for PEMA. Therefore, the increase in $\Delta\epsilon(\alpha)/\Delta\epsilon(\beta)$ of the blends facilitates the curve fitting, making it more reliable for the blends than in PEMA, particularly at temperatures approaching T_{onset}. Since the onset of the α process is defined as the temperature where $\Delta\epsilon(\alpha) =$ 0, blending also delays the merging process. This is verified by the observation of a larger splitting window, $T_{onset} - T_{ref}$, for the blends (Table 1) than for neat PEMA.

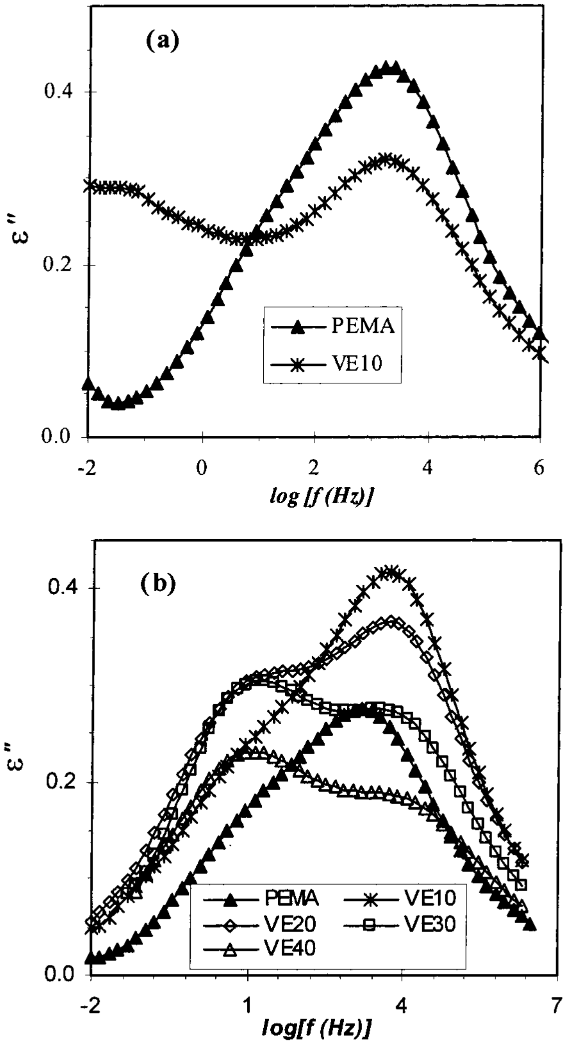

Figure 10. Comparison of the $\alpha-\beta$ splitting behavior of PEMA and PVPh/PEMA blends at 90 °C (a) and at T_{ref} + 10 °C (b). The dc contribution has been subtracted from the latter using fitting parameters σ_0 and s.

The $\alpha-\beta$ merging mechanism for PEMA is more apparent in the relaxation behavior of blends in the splitting temperature region as a result of the availability of a wider splitting window and thus the greater reliability of curve fitting in the blends. The nonlinear behavior of $f_{max}(\beta)$ and the nonparallel behavior of $f_{max}(\alpha)$ and $f_{max}(\beta)$ become more evident (Figure 3). To reiterate, the observed behavior clearly supports the enhancement of main-chain participation in the β process and the possibility of extrapolation of the log $f_{max}(\alpha)$ vs $1/T$ to intercept with log $f_{max}(\beta)$ vs $1/T$ data at T_{onset}.

In summary, PVPh does not change the general character of the splitting and fragility of PEMA, but the splitting does become better defined in the blends.

3. High-Temperature Merging Region. The merged $\alpha\beta$ process is a locally cooperative process. $f_{max}(\alpha\beta)$ decreases significantly with PVPh concentration (Figure 11), in contrast to the almost constant f_{max} for the isolated β process at lower temperature. The higher value of E_a, compared with that of the local β process,

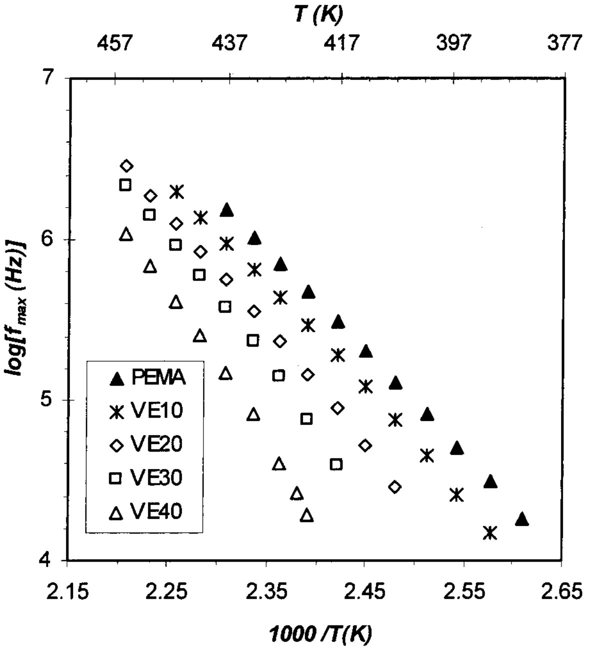

Figure 11. Comparison of Arrhenius behavior of the locally cooperative $\alpha\beta$ process for PEMA and PVPh/PEMA blends.

indicates that more chain segments are involved in the relaxation. All of this supports a locally cooperative relaxation mechanism. Close inspection of the Arrhenius plot in Figure 11 reveals weak VFT behavior, indicating some cooperative character. Again, E_a increases with PVPh content as a result of its participation in this process and the restrictive force from intermolecular hydrogen bonding. The measured E_a of neat PEMA, 125 kJ/mol, is close to that reported by McCrum et al. (130 kJ/mol)[2] but somewhat higher than the value of 109 kJ/mol reported by Garwe et al.[8] With increasing temperature, the local β process takes on increasing cooperative character and ultimately evolves into the $\alpha\beta$ process.

The dielectric strength of this cooperatively local process does not exhibit a noticeable change with temperature (Figure 12a), due to the opposing temperature dependences of $\Delta\epsilon(\alpha)$ and $\Delta\epsilon(\beta)$. The HN parameter m displays a trend similar to that in the splitting region (Figure 12b), while the slope at high frequencies, mn, is independent of both composition and temperature (Figure 12c).

Concentration fluctuations are an inherent characteristic of polymer blends.[18] Comparing the DRS spectra at $T = T_{ref} + 45$ °C (Figure 13, after subtracting the dc contribution), there is a slight broadening upon blending with PVPh. However, this effect is not as significant compared to the broadening observed in blends of ethylene-*co*-vinyl acetate (with 70 wt % vinyl acetate, EVA70) and poly(vinyl chloride) (PVC),[31] which exhibit a peak width at half-height much larger than both component polymers.

It was expected that hydrogen bonding in this blend would promote a closer intermolecular contacts. The length of a hydrogen bond is roughly 0.25 nm,[32] while the domain size detectable by DRS is about 2−3 nm, which is also the characteristic length scale of the glass transition.[33] Accordingly, the insignificant concentration fluctuations in PVPh/PEMA blends are a result of this strong intermolecular interaction. The lack of an equivalent strong specific interaction leads to an appreciable broadening in EVA70/PVC,[31] although it has a somewhat smaller ΔT_g, ~90 °C, compared with ~100 °C for PVPh/PEMA.

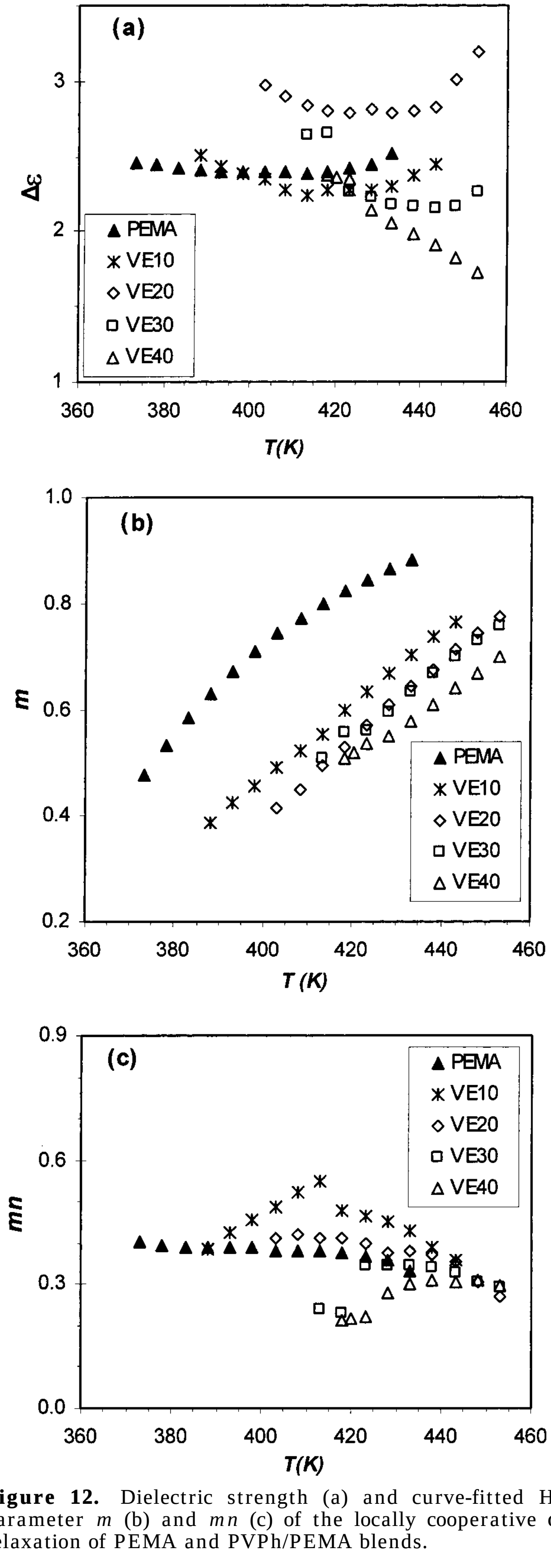

Figure 12. Dielectric strength (a) and curve-fitted HN parameter m (b) and mn (c) of the locally cooperative $\alpha\beta$ relaxation of PEMA and PVPh/PEMA blends.

Ionic conduction in polymers is a result of the transport of impurity ions. The conductivity σ_0 follows an Arrhenius law or VFT law with temperature, depending on the system and temperature region, and it is related to polymer chain relaxation.[34] PVPh is mainly respon-

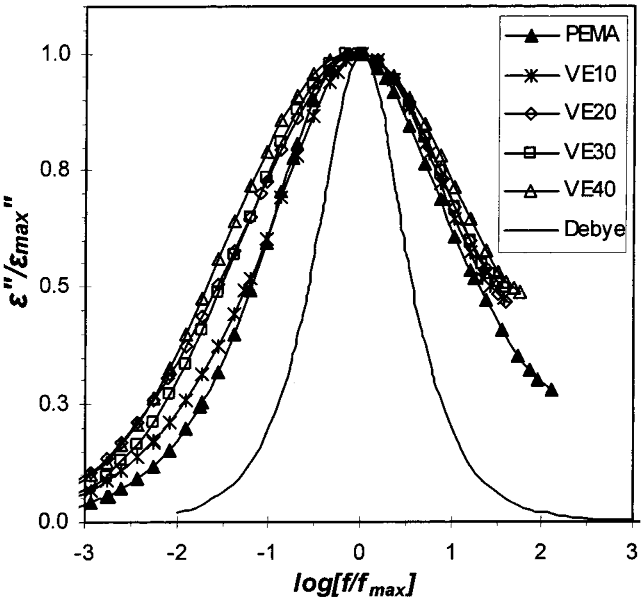

Figure 13. Dielectric broadening of PEMA and PVPh/PEMA blends at T_{ref} + 45 °C. The loss spectra have been normalized by f_{max} and ϵ''_{max}, and the dc contribution has been subtracted by using curve-fitted HN parameters.

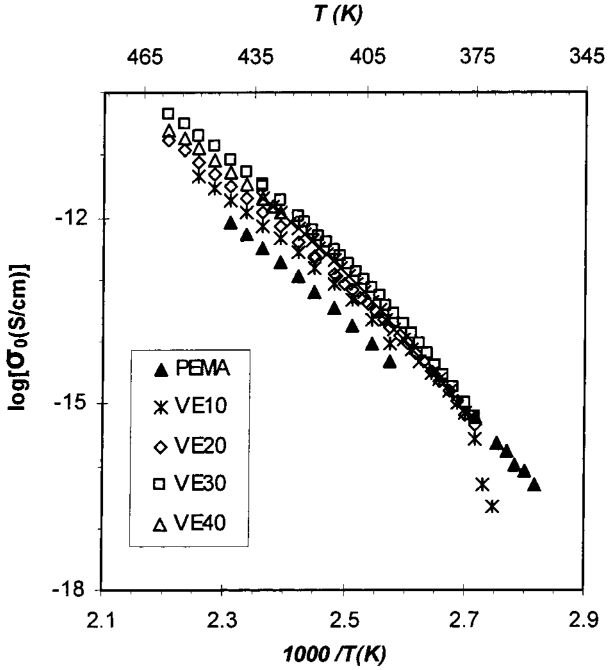

Figure 14. Arrhenius plots of the dc conductivity in PEMA and PVPh/PEMA blends.

sible for the dc conductivity in PVPh/PEMA blends. We found Arrhenius behavior for σ_0 in the high-temperature region and VFT behavior in the splitting temperature region (Figure 14). The activation energy for conduction is a decreasing function of PVPh content (Table 2), which indicates that the OH groups in PVPh might also facilitate dc conduction.

Summary

PEMA has complicated α−β splitting and merging behaviors. The increasing main-chain rocking amplitude converts the β process from a local relaxation to one that is locally cooperative with increasing temperature. We tentatively attribute the disappearance of the α process to a reduction in its cooperative domain size to a value that is comparable to that required for the locally cooperative β relaxation at the so-called onset temperature.

The presence of PVPh in blends influences different processes to different degrees. The local β process in the blends arises from PEMA and varies only slightly on blending. In contrast, PVPh participates in the α process and its addition leads to a pronounced increase in relaxation time $\tau_{max}(\alpha)$. PVPh also delays the high-temperature merged αβ relaxation and leads to a longer $\tau_{max}(\alpha\beta)$. The α relaxation of the blends is enhanced by the existence of PVPh. The activation energies of both the local and locally cooperative processes are larger for the blends as compared with neat PEMA. The αβ splitting and merging are observed more clearly and reliably in the blends, but their molecular mechanism is similar to that of PEMA.

The hydrogen bonding between PVPh and PEMA has no special influence on the relaxation behavior. The fragility of the blends does not change, although hydrogen bonding increases the ΔC_p and intermolecular coupling. This indicates that a correlation between fragility and thermodynamic properties is invalid in hydrogen-bonded PVPh/PEMA blends. The strong interaction between PVPh and PEMA manifests itself by promoting the miscibility and reducing concentration fluctuations in the blends.

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