Dynamics of Poly(vinylmethyl ether) Blends with a Strongly Interassociating Copolymer

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Summary: We apply broadband dielectric relaxation spectroscopy to probe the dynamics of hydrogen bonded polymer blends. A copolymer consisting of 2,3-dimethylbutadiene (DMB) [86%] and *p*-(hexafluoro-2-hydroxyl-2-propyl)styrene (HFS) [14%] was synthesized and blended with poly(vinylmethyl ether) (PVME). The copolymer is capable of forming strong intermolecular hydrogen bonds, while minimizing the degree of intramolecular associations, and its blends with PVME are predicted to be miscible over the entire composition range. Two segmental processes, α and α_1, are present in blends containing 26, 50, and 76 weight percent copolymer. The slower process (α_1) is assigned to the segmental motion of the intermolecularly associated copolymer, and the faster process (α) to segmental motions of PVME modified by the HFS:DMB copolymer. A relaxation associated with residual water is present in the glassy state. A local process due to motions of the PVME ether groups (β) is also present in the glassy state, and does not change with blend composition.

Keywords: broadband dielectric relaxation spectroscopy; dynamics; hydrogen bonding; polymer blends

Introduction

Intermolecular hydrogen bonding in polymer blends, and the effects of hydrogen bonding on blend dynamics, has been a topic of great interest.[1] Although clearly not as strong as chemical crosslinks (which exhibit a bond strength on the order of 50 kcal mol^{-1} versus a hydrogen bond strength of 1–10 kcal mol^{-1}), hydrogen bonds have a profound effect on the physical and chemical properties of polymers. A number of studies[2–8] have explored the influence of intermolecular hydrogen bonding on miscible blend dynamics. At intermediate compositions, it has been established that such mixtures exhibit a single (albeit broadened) segmental relaxation, even when the intrinsic component mobilities are very different.[2,4,5,9] However, when the composition is relatively asymmetric, these blends exhibit two segmental processes, arising from a simple hydrogen bonding stoichiometric effect. For example, in miscible poly(vinyl methyl ether) [PVME] - poly(p-vinylphenol) [PVPh] blends with a preponderance of PVME, two segmental processes are observed and assigned to intermolecularly hydrogen bonded PVME and PVPh relaxing segments, and to 'free' PVME segments.[2]

Functional group accessibility has been demonstrated to have a significant influence on polymer miscibility.[10–13] Specifically, it has been established that controlled steric shielding can increase the propensity for intermolecular hydrogen bond formation (to functional groups on a miscible second polymer) over intramolecular hydrogen bonding.[14,15] For example, poly(p-(hexafluoro-2-hydroxy-2-propyl)-styrene) (poly(HFS)) exhibits a much greater degree of intermolecular versus intramolecular hydrogen bonding, having self-association equilibrium constants K_2 and K_B of 2.5 and 3.4, respectively,[14] a result of the two CF_3 groups adjacent to the

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phenolic –OH. A polymer with a similar structure, lacking such steric shielding (PVPh), exhibits a much greater degree of intramolecular hydrogen bonding: its self-association equilibrium constants K_2 and K_B are 21 and 66.8, respectively,[11] an order of magnitude larger than those of poly(HFS). An extensive analysis of the hydrogen bonding characteristics of the HFS homopolymer and copolymers of HFS with styrene is provided in ref 14.

The overall goal of this and ongoing studies is to establish the role of reduced intramolecular hydrogen bonding on blend dynamics. We also control the number of interacting sites by copolymerizing HFS with a non-hydrogen bonding unit, 2,3-dimethylbuta-1,3-diene (DMB). PVME is selected as the second component in the blend to facilitate comparison with the dynamics of similar blends reported in the literature.[2,16] The ether groups in PVME form relatively strong intermolecular hydrogen bonds with the phenolic -OH of polymers such as PVPh and poly(HFS).[2] The addition of a relatively small number of HFS hydrogen bonding sites ($\sim$14 mole % of the repeat units) renders the otherwise immiscible poly(DMB) and PVME miscible over the entire composition range, as predicted by the Painter and Coleman association model.[1]

Experimental Part

A copolymer of *p*-(hexafluoro-2-hydroxyl-2-propyl)styrene and a low T_g comonomer, 2,3 - dimethylbutadiene was synthesized via bulk free-radical polymerization at 60 °C under an argon atmosphere. Several freeze-drying cycles were used prior to polymerization to ensure all oxygen was completely removed. Conversion was kept below 10% to minimize copolymer composition drift, and the copolymer composition is believed to be random, based on the reactivity ratios of DMB and poly(styrene). The polymerization was terminated by the addition of chilled methanol, and the copolymer was reprecipitated into methanol from tetrahydrofuran (THF) several times to remove all unreacted monomer. After purification, the copolymer was dried in a vacuum oven at 60 °C for several days to remove any traces of moisture, solvent, or unreacted monomers. Proton NMR was used to confirm the copolymer composition, determined to be 14 mole% HFS, 86 mole% DMB.

The molecular weight of the copolymer and poly(vinyl methyl ether) (PVME) was measured via GPC using poly(styrene) calibration standards. The copolymer's weight average molecular weight was determined to be 95 $\frac{Kg}{mol}$, having a polydispersity index of 2.0. PVME was purchased from Polymer Laboratories, having a weight average molecular weight of 102 $\frac{Kg}{mol}$, and a polydispersity index of 3.0. Blends consisting of 26, 50, 76, and 90 weight percent of the copolymer were created by mixing appropriate amounts of each component in THF, then removing the solvent. Each blend was dried under vacuum (2–3 μbar) at approximately 60 °C for 2–3 days prior to any measurement to remove all water.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments Q1000. Each sample was heated at 10 °C/min to 70 °C, held for two minutes, cooled at 10 °C/min to −70 °C, held for an additional two minutes, then reheated at 10 °C/min to 70 °C. T_g was determined from the midpoint of the heat capacity step on the second heating run.

Broadband dielectric relaxation spectroscopy (DRS) was carried out on a Novocontrol Concept 40, using an attached liquid nitrogen dewar which uses evaporated nitrogen to control the temperature of the sample within ±0.02 °C of the set point. A parallel plate capacitor sample configuration was used, with the sample thickness maintained with two, 50 μm silica spacers. The samples were measured isothermally from −150 °C to 60 °C in five degree intervals, using a frequency range of 10 MHz to 10 mHz, with seven data points per frequency decade.

The DRS results were analyzed with the traditional HN function with an added conductivity term:

$$\varepsilon'' = \frac{\sigma_o}{\varepsilon_o \omega^s} - \sum \mathrm{Im} \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{\mathrm{HN}})^{\mathrm{n}}]^{\mathrm{m}}} \qquad (1)$$

In equation 1, σ_o is the DC conductivity, ε_o is the vacuum permittivity, s is a fitting parameter relating to the type of conduction present, $\Delta\varepsilon$ is the dielectric strength, τ_{HN} is the relaxation time, 'n' is the symmetric broadening parameter, and 'm' is the asymmetric broadening parameter. Although used to fit the data, the conductivity contribution in equation 1 was generally ignored, since the derivative of the dielectric constant was used as an estimate of the conductivity-free loss:[17,18]

$$\varepsilon''_D = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \approx \varepsilon'' \qquad (2)$$

For details on the application of this method, the appropriate derivative HN equation to use in the analysis, and the considerations which need to be made when employing this method, the interested reader is referred to reference 18. The principle benefit of the derivative formalism is the elimination of the ionic (impurity) conductivity, inherent in any polymeric sample above its T_g. This conductivity contribution does not manifest itself in the dielectric constant, and is effectively removed with the application of equation 2.

In addition to the traditional method of fitting the isothermal data with an HN equation (equation 1), isochronal data were also examined. The method for determining the relaxation temperature yielded the same relaxation behavior as did traditional fitting, with far more datapoints. Note that the local relaxations were not analyzed in this fashion, due to their greater breadth and lower strength.

A Vogel-Fulcher-Tamman (VFT) equation was used to model the segmental relaxation times as a function of temperature:

$$f_{Max} = f_o \exp\left(\frac{-B}{(T - T_o)}\right) \qquad (3)$$

Where f_{Max} is the frequency of the relaxation, f_o is the infinite temperature frequency of the relaxation, B is related to the fragility,[19,20] and T_o is the Vogel temperature. An Arrhenius equation was used to model the local processes:

$$f_{Max} = f_\circ \exp\left(\frac{E_a}{RT}\right) \qquad (4)$$

The parameters f_{Max} and f_o have the same meaning as in equation 3, R is the universal gas constant, and E_a is the activation energy of the process, having units of $\frac{KJ}{mol}$.

Results

DSC

DSC results indicate the blends are miscible, with T_g between those of the components and dependent on blend composition (see Table 1). With the exception of the neat copolymer, the VFT-determined T_g (at $\tau = 100$s) (see Table 2) is in excellent agreement with the calorimetric T_g.

PVME

Our experimental dielectric spectra are in excellent agreement with those reported in the literature.[21,22] A comparison of our VFT and Arrhenius fitting parameters and those from the literature can be seen in Table 2, along with those of the relaxations for the HFS:DMB copolymer and the blends.

HFS:DMB Copolymer

The neat copolymer exhibited two relaxations, a segmental process and a smaller, broad local process in the glassy state, which by analogy to the dielectric relaxation

Table 1.
Glass transition temperatures of the PVME - HFS:DMB blends, determined by DSC.

Weight % HFS:DMB	T_g (°C) ± 5 °C
0	−26
26	−19
50	−6
76	12
90	23
100	23

Table 2.
VFT and Arrhenius fit parameters for each relaxation for neat polymers and blends under investigation.

Weight Percent Copolymer	Relaxation	f_o(Hz)	B (K)	T_o(K)	$E_a\left(\frac{KJ}{mol}\right)$	VFT T_g(°C)
0.0	α	10^{11}	1230	208		−28
	β	10^{13}			24	
0.0 - Literature	$\alpha^{Gomez\ 2001}$	10^{12}	1590	198		−29
	$\beta^{Casalini\ 2003}$	10^{12}			21	
	α_1	10^{11}	2340	182		−19
26	α	10^{11}	1250	213		−21
	β	10^{13}			25	
	α_1	10^{11}	2030	202		−7
50	α	10^{11}	1240	224		−10
	β	10^{12}			23	
76	α	10^{11}	1570	237		11
	β	10^{13}			26	
90	α	10^{12}	1850	242		23
	β	10^{12}			23	
100	α	10^{11}	1457	243		18
	$\beta_{Copolymer}$	10^{13}			40	

behavior of PVPh, is assigned to motions of the HFS side group. The dielectric loss for the HFS:DMB copolymer as a function of temperature and frequency is displayed in Figure 2. The VFT (equation 3) and the Arrhenius (equation 4) fit parameters characterizing the segmental process and local process of this polymer are located in Table 2. Note in Table 2 that the $\beta_{Copolymer}$ and the β process of PVME arise from different molecular motions.

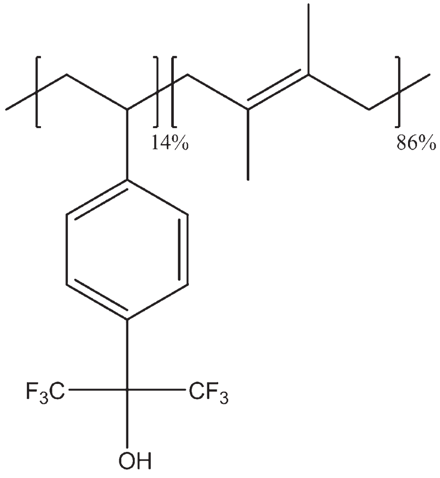

Figure 1.
Structure of the HFS:DMB copolymer.

The α and α_1 Processes

The dielectric loss as a function of temperature and frequency is shown in Figure 3 for the 26 wt% copolymer blend. This behavior is typical for the blends studied here. The locations of the relaxations are indicated on the plot with arrows.

Two segmental relaxations occur in the 26, 50 and 76 wt% copolymer blends. Due to the proximity of the two relaxations, the relaxation times of the α and α_1 processes could only be determined reliably for the 26 and 50 wt% copolymer blends.

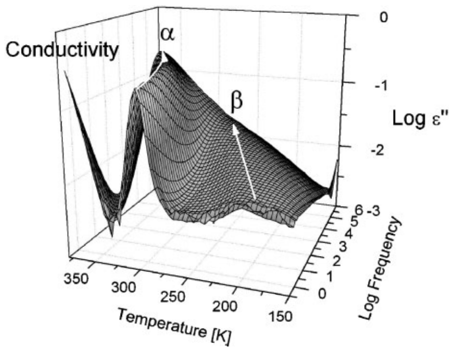

Figure 2.
Dielectric loss as a function of temperature and frequency for the 14 mole percent HFS, HFS:DMB copolymer.

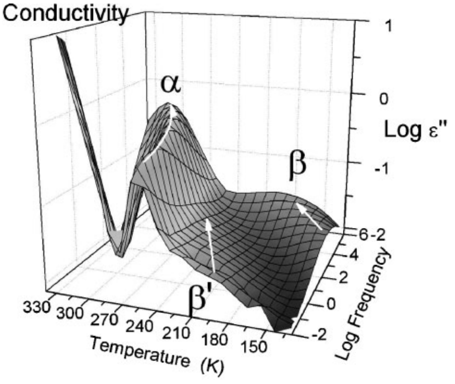

Figure 3.
Dielectric loss as a function of frequency and temperature for the 26 wt% copolymer blend.

Both relaxations appear to be present in the 76 wt% copolymer blend, but only a single relaxation time is reported here, which is likely a combination of those of the two processes. Data typical of the two segmental relaxations in the blends under investigation is shown in Figure 4.

The existence of two segmental relaxations in miscible binary blends exhibiting weak intermolecular interactions is not an uncommon feature, and arises from chain connectivity and the effective concentration of each component. In hydrogen bonded blends, specific interactions were initially predicted to couple the segmental dynamics of the two components,[23] resulting in a single segmental relaxation. However, as noted earlier, it has been demonstrated that even in the case of strong intermolecular hydrogen bonding, simple stoichiometric effects at asymmetric compositions can lead to two segmental processes.[2]

It is important to note that the intrinsic mobilities of PVME and the 14 mol% HFS:DMB copolymer are significantly different ($\Delta T_g \sim 50\,^{\circ}C$). The existence of two segmental relaxations at the 50/50 blend composition is clearly not consistent with a purely hydrogen bonding stoichiometric argument. Inherent in this simple model is that there are sufficient hydrogen bonding stickers to completely couple the segmental relaxations of the components at appropriate compositions. However, the parent copolymer contains only 14 mole% HFS segments and the findings suggest that this is insufficient to completely couple the component segmental processes.

We propose, therefore, that the faster segmental processes (α in Figure 5) in the 26 and 50 wt% blends arise from motions of the PVME component of the blend modified by the HFS:DMB, at least some of which are hydrogen bonded to HFS units. The slower component (α_1 in Figure 5) has a dielectric relaxation strength which is roughly proportional to the concentration of HFS segments in the blend. We therefore propose that this is the segmental process of the copolymer, whose dynamics have been

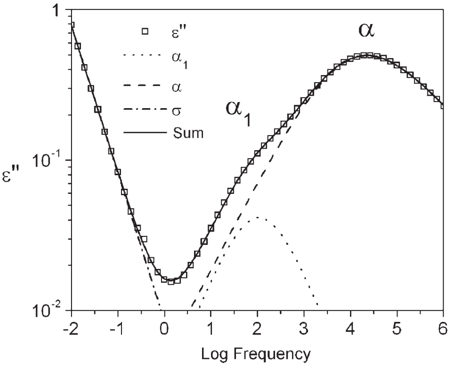

Figure 4.
Dielectric loss for the 26 wt% copolymer blend at 20 °C.

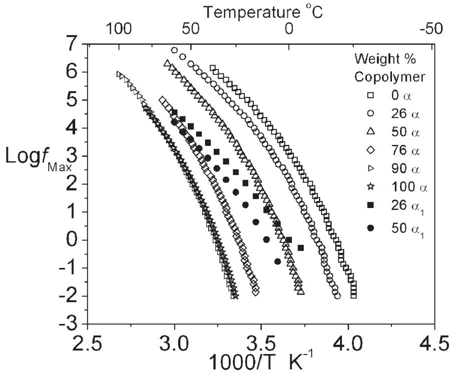

Figure 5.
Relaxation times of the α and α_1 processes as a function of inverse temperature.

modified by the faster PVME segments. The α_1 process exhibits a longer relaxation time in the 50 wt% copolymer blend (and a dielectric strength of ~2X that of the 26 wt% copolymer blend) due to the greater concentration of copolymer in the blend. This can be considered in terms of the Lodge-McLeish model in that the effective concentration of the copolymer is higher in the 50 wt% blend, and experiences an environment richer in itself than it does in the 26 wt% blend. This higher effective concentration should yield a longer relaxation time for the slower segmental process.[24]

The β' Process

The process designated as β' in the dielectric spectrum of PVME in Figure 3 is typically described as a high frequency shoulder on the segmental relaxation.[21,25] It is likely, however, that this is a separate process, associated with the relaxation of residual water in the polymer.[26] It was noted that the strength of this process decreased as the sample was dried and exhibited a small change (increase) in relaxation time. Capaccioli et al. reported a relaxation in the glassy state with an activation energy of ~50 $\frac{KJ}{mol}$ for a series of materials.[26] Cerveny et al. investigated the dynamics of water in several systems, including PVME, also observing a similar activation energy for this glassy state process in each system.[27,28] The fact that the strength of the observed process decreases with decreasing water content, and exhibits an activation energy and relaxation time in the glassy state similar to that seen in the literature,[26–28] strongly points to water, either on its own or coupled to PVME motions, as the origin of the β' process observed here.

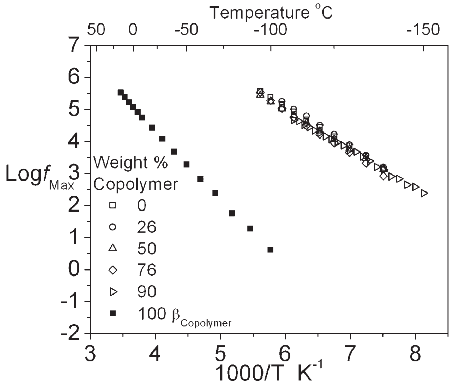

Figure 6.

Relaxation times of the PVME β process in neat PVME and the blends as a function of inverse temperature. The relaxation times of the β process of the HFS:DMB copolymer are also displayed for comparison purposes.

The β Process

An Arrhenius plot of the temperature dependence of the relaxation time of the β process is shown in Figure 6, with the corresponding Arrhenius fit parameters (equation 4) listed in Table 2. The PVME β process, assigned to rotation of the methyl ether groups in the side chain of PVME about the O-C bonds,[25] maintains the same relaxation time in the blends, independent of composition. Such behavior was also observed in non-interacting blends of PVME and PS.[29] In previous work on analogous PVPh-PVME blends, the findings strongly suggested that the relaxation of some side groups of both polymers were suppressed by blending, and these groups are likely those constrained by intermolecular hydrogen bonding.[2] However, the strength of the PVME β process in the blends simply decreases in proportion with decreasing PVME content and its relaxation time nor peak shape change with blend composition. This likely due to the modest concentration of HFS segments present and hydrogen bonded to the PVME ether pendant groups.

A low frequency shoulder appears on the PVME β process in the 90 wt% copolymer blend. This is the β process of the copolymer, and it is present due to the large amount of HFS segments present in the blend.

Conclusions

Two segmental relaxations were observed for most of the 14 mol% HFS:DMB copolymer - PVME blends. The α process is attributed to motions of the PVME component of the blend modified by the HFS:DMB copolymer, at least some segments of which are hydrogen bonded to HFS units. We propose that the slower α_1 process is associated with segmental motions of the copolymer, whose dynamics have been modified by the faster PVME segments.

The β' process of PVME was found to arise from the presence of trace amounts of water within the blends. A similar relaxation is commonly observed not only in polymeric systems, but in many others containing hydrogen bonds, and may provide a quantitative method of determining water content of materials from DRS spectra.

Due at least partly to the low concentration of hydrogen bonding species, the dynamics of the PVME β process are not affected by blending. The strength of the process is found to simply decrease with decreasing PVME content and the relaxation time and shape do not change with blend composition.

Acknowledgements: The authors would like to express their appreciation to the NSF Polymers Program, through DMR-0605627, for support of this research.

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