

Viscoelastic Behavior and Submolecular Level Dynamic Heterogeneity of Hydrogen-Bonded Polymer Blends Probed by Dynamic FTIR Spectroscopy

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ABSTRACT: Viscoelastic behavior and submolecular (functional group) level dynamic heterogeneity of hydrogen-bonded poly(vinyl phenol)/poly(methyl acrylate) (PVPh/PMA) blends were investigated by using dynamic FTIR spectroscopy. It has been found that the viscoelastic behaviors of the blends, measured by the dynamic (in-phase and quadrature) spectra of both “free” and hydrogen-bonded carbonyl groups are dependent on the compositions, i.e., the T_g of the blends, and the degree of hydrogen bonding between the two components. In all the blends studied, elastic response of the hydrogen-bonded carbonyl groups to the applied strain has been found. The free carbonyl groups respond differently to the applied strain in these blends. Essentially, elastic response of the free carbonyl groups to the applied strain is observed in blends with both a high T_g and a higher fraction ($\sim 40\%$) of intermolecular hydrogen bonding between PVPh and

PMA, and the submolecular level dynamic heterogeneity is suppressed. The free carbonyl group has a viscous component to its response, in blends having a lower fraction ($\sim 20\%$) of hydrogen bonds, even at temperatures well below the thermal T_g of the blends, suggesting that there is a degree of submolecular level dynamic heterogeneity in these blends. Almost entirely viscous response of the free carbonyl group is found in blends whose T_g is close to room temperature and fraction of PVPh/PMA hydrogen bonds is very low. The results reported here suggest that dynamic FTIR has considerable potential for studying specific interactions and viscoelastic behaviors in hydrogen-bonded polymer blends on submolecular level. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 662–666, 2009

Key words: dynamic FTIR; viscoelastic behavior; dynamic heterogeneity; blends

INTRODUCTION

Dynamic FTIR spectroscopy is a combination of the dynamic mechanical analysis (DMA) and FTIR spectroscopy. It is well known that DMA is a useful tool to characterize the mechanical properties of materials. DMA, however, does not reveal information on the molecular level. On the other hand, FTIR spectroscopy gives (sub) molecular information, but no information on the mechanical properties of materials. Therefore, dynamic FTIR spectroscopy is a powerful technique to study the mechanical properties of materials, especially polymers on the (sub) molecular level. Various materials such as wood polymers,¹ polyethylene fibers,² lignin,³ bacterial cellulose composites,⁴ *Bombyx mori* fibroin film,⁵ syndiotactic polypropylene (PP),⁶ polyurethane elastomer,⁷ poly(ethylene terephthalate),⁸ polyisoimide

prepolymer,⁹ high-/low-density polyethylene blends, and liquid crystals¹⁰ have been studied using dynamic FTIR spectroscopy. However, no dynamic FTIR studies on hydrogen-bonded polymer blends have been found.

Hydrogen-bonded polymer blends bear some special interests because hydrogen bonding interaction provides a unique route to develop new miscible polymer blend materials to meet the challenging requirements for industrial applications. In addition, the compositions of the hydrogen-bonded polymer blends and therefore the degree of hydrogen bonding can be adjusted, so that the dynamical and viscoelastic properties of the polymer blends may be tuned. This is of significant importance because understanding the influence of blending on mechanisms of segmental relaxation is the crucial step to tailor the aforementioned properties of polymer blends.

One of the remarkable characteristics of miscible polymer blends is the distinct segmental dynamics of the component polymers. A miscible blend is generally believed to have a morphology that is homogeneous on the segmental level; each component

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experiences the same average environment apart from chain connectivity. However, the interaction of the components with their local environment, as well as intrinsic mobility differences, can cause them to exhibit different relaxation times (i.e., distinct component T_g s). This phenomenon has referred to as dynamic heterogeneity, which has gained keen interest in the past decade,^{1–21} and various techniques such as differential scanning calorimetry (DSC), DMA, dielectric relaxation spectroscopy (DRS), nuclear magnetic resonance (NMR), quasi-elastic neutron scattering (QENS), thermally stimulated depolarization current measurements, electron spin resonance (EPR) have been used to characterize the dynamic heterogeneity in miscible polymer blends with or without hydrogen bonding interactions. No dynamic FTIR studies on the dynamic heterogeneity in miscible polymer blends have appeared so far.

Because of the two reasons mentioned earlier, we report the viscoelastic behavior and dynamic heterogeneity of hydrogen-bonded poly(vinyl phenol)/poly(methyl acrylate) (PVPh/PMA) blends probed by dynamic FTIR spectroscopy. It will be demonstrated later that dynamic FTIR method is a powerful tool to study the viscoelastic behavior and dynamic heterogeneity in hydrogen-bonded miscible polymer blends on the submolecular (functional group) level instead of molecular (segmental) level.

EXPERIMENTAL

Blends of PVPh ($M_w = 20,000$; Aldrich Chemical, St. Louis, MO) with PMA ($M_w = 40,000$; Scientific Polymer Products, Ontario, NY) were used in this study. Films were cast onto a PP substrate from 2-butanone solutions, and then the samples were left in air for 24 h and subsequently dried in a vacuum oven at 110°C to remove the trace amount of solvent 2-butanone. The sides of the PP film were abraded with #600 carborundum paper to prevent the appearance of interference fringes.

A Bio-Rad FTS-60A FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector, was used for both the normal and dynamic FTIR measurements. All dynamic FTIR experiments were performed at room temperature with a dynamic mechanical stretcher/polymer modulator, PM-100 (Manning Applied Technologies Inc., Troy, ID), with a frequency of 20 Hz. The maximum strain amplitude is about 0.6% to ensure a linear response. The step-scanning mode was used to measure the dynamic (in-phase and quadrature) spectra under a small sinusoidal mechanical perturbation. Two dynamic measurements were conducted: one with the wire grid linear polarizer in a parallel orientation (relative to the strain direction) and one with the polarizer in a perpendicular orientation. Subtraction of

the data measured from the two polarizations provides the dynamic infrared linear dichroism (DIRLD) spectra, as obtained by the photoelastic modulator method.²² From the DIRLD spectra, information regarding the reorientation of functional groups may be obtained, which is beyond the scope of this publication. In this article, however, only the dynamic (in-phase and quadrature) spectra obtained with the polarizer in parallel or perpendicular orientation will be presented.

To obtain a reasonably high signal-to-noise ratio (S/N), the spectra were obtained at a resolution of 8 cm^{-1} , using eight scans and a DTGS detector, whose greatest sensitivity is in the 2000–500 cm^{-1} region. Because we were concerned about film stability, we did not want to obtain spectra using a large number of scans (which would take hours). Accordingly, at least four separate measurements were carried out, and the results were averaged to obtain reproducible results.

Differential scanning calorimetry (DSC) measurement was performed on a TA DSC Q100 apparatus over a temperature range from –30 to 220°C. The heating and cooling rates were 10°C/min.

RESULTS AND DISCUSSION

PVPh/PMA blends are typical miscible blends with hydrogen bonding interactions.^{23–26} A simple DSC measurement also confirms this conclusion, as shown in Figure 1, where a single T_g has been found for blends with various compositions. In the DSC results (Fig. 1), no significant broadening of the single glass transition is noted. This observation indicates that the dynamic heterogeneity in PVPh/PMA blends is not significant on the molecular (segmental) level. It would be interesting to see what one can get from the dynamic FTIR measurements, where submolecular (functional group) level information may be gained.

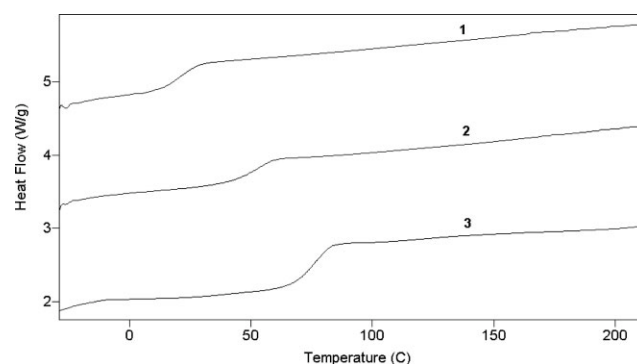


Figure 1 Glass transition behaviors of PVPh/PMA blends (wt %): (1) PVPh/PMA = 10/90; (2) PVPh/PMA = 30/70; (3) PVPh/PMA = 50/50.

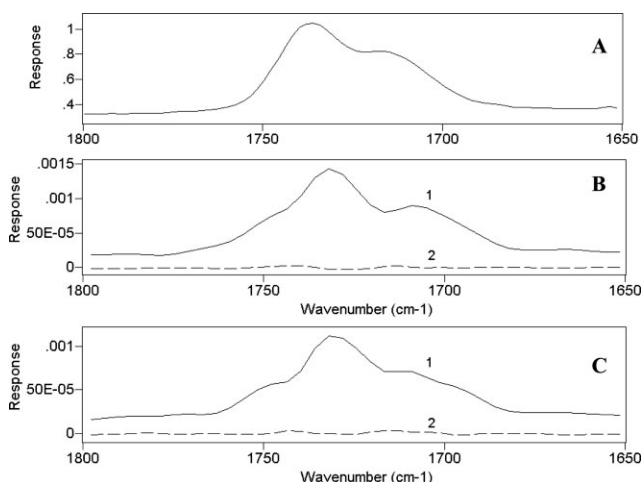


Figure 2 Normal absorbance spectrum of the 50/50 PVPh/PMA blend (A), together with the in-phase (1) and quadrature (2) spectra obtained with the polarizer parallel (B) and perpendicular (C) to the stretching direction.

Figure 2 shows the normal infrared spectrum of the PVPh/PMA = 50/50 blend and the dynamic (in-phase and quadrature) spectra obtained with the polarizer placed parallel and perpendicular to the stretching direction. From the normal infrared spectrum shown in Figure 2(A), two bands are well resolved; the band at higher wavenumber is assigned to the free C=O group, and the band at lower wavenumber to the hydrogen-bonded C=O group. This is a well-known result.^{23–25} Two bands, corresponding to the free and hydrogen-bonded C=O groups, are also well resolved in the dynamic in-phase spectra; although the band shapes are somewhat distorted and the peak positions are shifted quite a bit.²⁵

The intensity of the quadrature spectra obtained from this blend (PVPh/PMA = 50/50) is very weak, barely detectable. This indicates that both free and hydrogen-bonded C=O groups are essentially responding in-phase or elastically with the applied strain. However, if a 30/70 PVPh/PMA blend composition is used, the results shown in Figure 3 are obtained. It can be seen that the quadrature spectra are no longer negligible when compared with the in-phase spectra, and the response of the free and hydrogen-bonded bands now differs. The intensity of the hydrogen-bonded C=O band in the quadrature spectra is close to zero, indicating that hydrogen-bonded C=O groups are still responding in-phase with the strain. However, the intensities of free C=O bands in the quadrature spectra are appreciable, indicating that free C=O groups have an out-of-phase or viscous component to their response.

The out-of-phase change of free C=O groups with stretching becomes more pronounced in the PVPh/

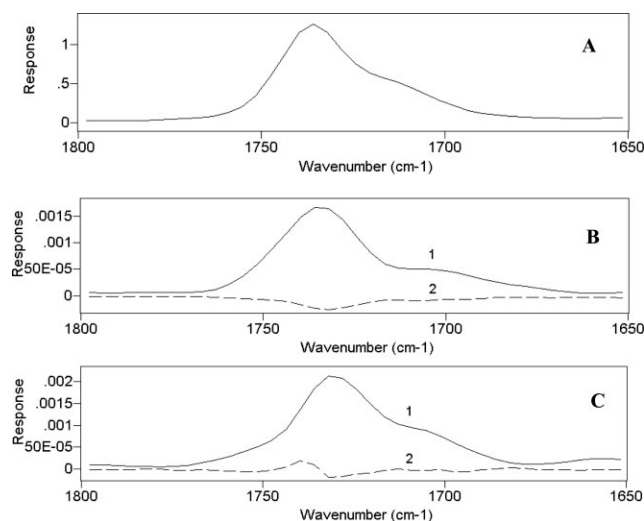


Figure 3 Normal absorbance spectrum of the 30/70 PVPh/PMA blend (A), together with the in-phase (1) and quadrature (2) spectra obtained with the polarizer parallel (B) and perpendicular (C) to the stretching direction.

PMA = 10/90 blend, as shown in Figure 4, where the intensity of the in-phase spectra is lower or close to that of the out-of-phase spectra. In other words, the response of the free C=O groups appears to be essentially out-of-phase with the applied strain in this blend, indicating a largely viscous response. (It is straightforward to predict that the out-of-phase change of the C=O groups in the neat PMA system would be even more pronounced than in the PVPh/PMA = 10/90 blend, because there is no hydrogen bonding in neat PMA. In fact, PMA ($T_g \sim -5^\circ\text{C}$) is a liquid at room temperature and it is not practical to form an even film on PP substrate, when the substrate is vertically placed under the experimental condition.) Unfortunately, because the intensity of

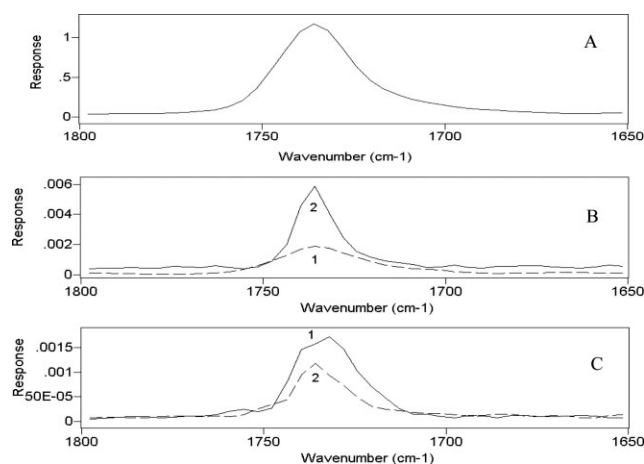


Figure 4 Normal absorbance spectrum of the 10/90 PVPh/PMA blend (A), together with the in-phase (1) and quadrature (2) spectra obtained with the polarizer parallel (B) and perpendicular (C) to the stretching direction.

TABLE I
 T_g and Degree of Hydrogen Bonding of PVPh/PMA Blends

PVPh/PMA	Viscoelastic Response		T_g (°C)	Degree of hydrogen bonding ^a (Ref. 24)
	"Free" C=O	H-bonded C=O		
50/50	Elastical	Elastical	72	~ 40%
30/70	Viscous component	Elastical	52	~ 20%
10/90	Largely viscous	Elastical	21	/

^a In terms of hydrogen-bonded C=O groups.

the hydrogen-bonded band in this latter spectrum is so weak, it is not possible to draw any reasonable conclusions concerning the response of hydrogen-bonded C=O groups. However, it is safe to speculate that the response of the hydrogen-bonded C=O groups will still be elastic as in the aforementioned two blends, because they are hydrogen bonded to PVPh which has a high T_g (173°C).²³

The change in viscoelastic behavior, measured by the in-phase and quadrature spectra of both free and hydrogen-bonded carbonyl groups in the PVPh/PMA blends, is related to their glass transition temperatures and degree of hydrogen bonding between the two components (Table I).

It is easy to understand that the response of the hydrogen-bonded C=O groups in all the PVPh/PMA blends is elastic, because they are hydrogen bonded to PVPh which has a high T_g (173°C), as mentioned earlier. The hydrogen bonding should constrain the motion of the C=O groups that are bonded to the O—H groups. The response of the free C=O groups, however, is different in the blends.

The 10/90 PVPh/PMA blend has a T_g near 21°C as determined by DSC measurements, shown in Figure 1, which is close to room temperature. Besides, the degree of hydrogen bonding between the PVPh and PMA components is very small, so that a viscous response of the free carbonyl band of PMA is not surprising.

The T_g of the 30/70 PVPh/PMA blend is around 52°C, about 30°C higher than the room temperature, suggesting that we should observe a largely elastic response of the blend material at room temperature, because the blend is in the glassy state at this temperature. However, partly viscous response of the free C=O groups was observed. This is counterintuitive at the first sight but actually understandable. PMA has a much lower T_g (~ -5°C) than PVPh (~ 173°C) and it is well known that dynamic heterogeneity dominates the relaxation behavior of miscible polymer blends having a large T_g difference and weak intermolecular interactions (see refs. 13–16 and citations therein). Two separated segmental relaxation processes, corresponding to the individual components, are sometimes observed, representing extreme heterogeneity. If the dynamic heterogeneity is signifi-

cant and the component chains exhibit well-separated segmental relaxation processes, the DSC curve should become significantly broadened. In the DSC results (Fig. 1), however, no significant broadening of the single glass transition is noted. This observation indicates that the dynamic heterogeneity in PVPh/PMA blends is not significant at the molecular level, as mentioned earlier. Nevertheless, on the submolecular (functional group) level, the partly viscous response of the free C=O groups in the PVPh/PMA = 30/70 blend suggests that there is a degree of dynamic heterogeneity in this mixture, and the degree of hydrogen bonding between PVPh and PMA (~ 20% in terms of hydrogen bonded C=O groups)²⁴ is not high enough to eliminate this dynamic heterogeneity, though the dynamic heterogeneity is not significant at the molecular (segmental) level.

These speculations may be easily verified by the dynamic FTIR result of a PVPh/PMA = 50/50 blend as shown in Figure 2. This blend has a T_g near 72°C, indicating that the blend is in the glassy state at room temperature. More importantly, this blend has a higher degree of hydrogen bonding between PVPh and PMA (~ 40%) than the PVPh/PMA = 30/70 blend (~ 20%).²⁴ It is this higher degree of hydrogen bonding that suppressed the dynamic heterogeneity in PVPh/PMA = 50/50 blend on the submolecular (functional group) level. Accordingly, at room temperature, elastic response of both free and hydrogen-bonded C=O groups is observed.

CONCLUSIONS

Viscoelastic behavior and dynamic heterogeneity of hydrogen-bonded PVPh/PMA blends whose components exhibit a large difference in their respective T_g s (173°C for PVPh and -5°C for PMA) have been studied using dynamic infrared spectroscopy on the submolecular (functional group) level. In blends with both a high T_g and a higher fraction of PVPh/PMA hydrogen bonds, the response of both the free and hydrogen-bonded carbonyl groups to the applied strain is essentially elastic, and the dynamic heterogeneity on the submolecular (functional group) level is suppressed. As the concentration of PMA in the blend is increased and the degree of

intermolecular hydrogen bonding between PVPh and PMA is decreased, the free carbonyl group exhibits a viscous component to its response, even at temperatures well below the thermal $T_{g'}$, suggesting that there is a degree of dynamic heterogeneity at the submolecular (functional group) level in these blends. At temperatures close to the T_g of the blend, the response of the free carbonyl group becomes almost entirely viscous.

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