Spectroscopic Investigations of Specific Interactions in Amorphous Polymer–Polymer Blends: Poly(vinylphenol) and Poly(vinyl methyl ketone)

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ABSTRACT: Poly(4-vinylphenol) (PVPh), a proton donor, and poly(vinyl methyl ketone) (PVMK), a proton acceptor, represent an illustrative example of hydrogen-bonding-induced miscibility in amorphous polymer–polymer blends. The infrared vibrational absorptions of the OH group in PVPh and the ketone carbonyl moiety in PVMK reveal that site-specific interactions are operative between dissimilar chain segments in the blended states. High-resolution carbon-13 solid-state NMR spectroscopy provides further evidence for strong interaction and molecule-for-molecule mixing between the two components. Poly(vinylphenol)'s phenolic carbon NMR chemical shift can distinguish two types of segment interactions via resonances that differ in their peak positions by $\approx$2–3 ppm. Both spectroscopic probes, FTIR and ^{13}C solid-state NMR, reveal that overlapping signals persist when the hydrogen bond between dissimilar functional groups in the amorphous state competes with the self-association of PVPh's hydroxyl group. The line width of the phenolic carbon NMR signal is a strong function of blend composition, particularly when the lower T_g component, PVMK, is present in excess. From a macroscopic viewpoint, the single glass transition process for each blend investigated is consistent with the spectroscopic results.

Introduction

Many miscible or partially miscibile polymer–polymer blends have been investigated recently because of their importance in theoretical studies and industrial applications.[1-3] A substantial fraction of these blends exhibits strong intermolecular association which provides a favorable energetic contribution to the mixing process.[2,4] Attractive energetic interactions are extremely helpful to blend high-molecular-weight polymers because conformational entropy provides a negligible contribution to chemical stability. The introduction of functional groups which induce strong association between dissimilar chains is one of the most important and effective ways to enhance macromolecular miscibility. In this respect, hydrogen bonding between a proton donor and a proton acceptor is particularly attractive as a potential route to achieve miscibility in many case studies.

Previous work in this laboratory focused on hydrogen bonding and molecular complexation between poly(ethylene oxide) and resorcinol.[7,25-27] Site-specific interactions between the hydroxyl protons in the small molecule and the ether oxygen in the chain backbone are responsible for the rich phase behavior exhibited by these mixtures which includes two eutectic transformations separated by a cocrystallized solid solution. Subsequently, the identification of specific interactions in "model" polymer/small-molecule blends was extended to polymer–polymer blends that retain some elements of the association that is present in the model systems, with simplified phase behavior. In this respect, poly(4-vinylphenol) was chosen to represent the polymeric analogue of resorcinol, and our initial efforts revealed that this polymer is an attractive proton donor to blend with proton acceptors, such as poly(ethylene oxide).[5,6] It was found that partial miscibility is achieved via hydrogen bonding between the hydroxyl proton in poly(4-vinylphenol) and the ether oxygen of poly(ethylene oxide),[5] even though the immiscibility of polystyrene and poly(ethylene oxide) was verified experimentally in our laboratory.[7] The choice of PVPh and poly(ethylene oxide) as blend candidates eliminates any ambiguity in identifying specific interaction sites, particularly when association between dissimilar components is favored. Conclusive results for partially miscible blends of PVPh and poly(ethylene oxide) have been obtained from DSC, FTIR, and high-resolution ^{13}C solid-state NMR.[5,6]

Coleman and co-workers[8-11] have applied infrared spectroscopy to study a variety of hydrogen-bonded polymer–polymer blends containing poly(4-vinylphenol). In these pioneering case studies, the Penn State group focused on a quantitative description of the carbonyl infrared absorption and identified segment interactions via the FTIR-detectable hydrogen bond between dissimilar components. Recently, Coleman, Painter, et al.[11-15] developed a thermodynamic association model that incorporates competing hydrogen-bond equilibria to describe the high-temperature phase behavior of strongly interacting polymer–polymer blends. Kwei et al.[16] studied the amorphous-phase behavior of poly(4-vinylphenol)/poly(ethyloxazoline) blends by glass transition temperature measurements and infrared spectroscopy.

In the present work, poly(vinyl methyl ketone), a proton acceptor that contains a pendent ketone carbonyl group, was blended with poly(4-vinylphenol) to investigate (i) the strength of hydroxyl–carbonyl hydrogen bonds via infrared spectroscopy in comparison with our previous results focusing on hydroxyl/ether oxygen association,[5,6] (ii) carbon-13 solid-state NMR detection of near-neighbor segment interactions, and (iii) a potential correlation between the site-specific spectroscopic results for these polymer–polymer blends. PVMK was chosen as the dissimilar proton acceptor for at least three reasons: (i) in comparison with polyesters, there is only one oxygen site in this proton acceptor that can compete with the hydroxyl oxygen of PVPh for the available proton, (ii) all interacting functional groups in both blend components reside in the side chains and are not shielded sterically by the hydrocarbon backbones, and (iii) both components

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are amorphous in the undiluted and blended states, which should enhance the potential for interaction, since cocrystallization is not an issue here.

Experimental Section

Materials and Sample Preparation. Poly(vinyl methyl ketone) was purchased from Scientific Polymer Products, Inc., with a reported molecular weight of 500 000 (determined by GPC). Poly(vinylphenol) was obtained from Polysciences Inc. with a reported molecular weight range of 1500-7000. The reported densities for poly(vinyl methyl ketone) and poly(vinylphenol) are 1.12 and 1.2 g/cm^3, respectively, as provided by the commercial distributors. Individual 1% (w/v) solutions of the homopolymers in tetrahydrofuran (THF) at 60 °C were mixed at a concentration of 1 g of polymer/100 mL of solvent to obtain clear solution-state blends. The resulting solutions were subsequently cast at room temperature onto Petri dishes via solvent evaporation in a fume hood. The solution-cast films were then placed under vacuum to remove residual THF. To obtain homogeneous samples for solid-state NMR experiments, the solution-cast residues were compression molded three times in a Carver Laboratory press at 150 °C. Films from this multistep procedure did not reveal any superficial thermal degradation and were stored under vacuum for at least 2 weeks before physical characterization was attempted.

Fourier Transform Infrared Spectroscopy (FTIR). Thin films of poly(vinylphenol) and poly(vinyl methyl ketone) for FTIR measurements were cast from 1% (w/v) THF solution at 60 °C onto potassium bromide (KBr) and zinc sulfide (ZnS) windows at ambient temperature. After the majority of the solvent had evaporated, the films were transferred to a vacuum oven at 60-70 °C for more than 40 h to remove residual solvent, with subsequent storage under vacuum. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. A minimum of 64 scans was signal averaged at a resolution of 4 cm^{-1}. The experiments were carried out at room temperature ($\approx$20 °C). All of the films used for infrared studies were sufficiently thin to be within the range where the Beer-Lambert law is obeyed.[17] Film thicknesses in the range 10^{-4}-10^{-3} cm were calculated based on the solution concentration, polymer densities, and the dimensions of the infrared windows. The infrared spectra did not reveal any traces of residual solvent (THF) in the 1083-cm^{-1} region, characteristic of the cyclic ether stretching vibration.

Carbon-13 Solid-State NMR Spectroscopy. Proton-enhanced dipolar-decoupled carbon-13 solid-state NMR spectra were obtained on a modified Nicolet NT-150 spectrometer at the NSF-supported Regional NMR Center, Colorado State University, Fort Collins, CO. The carbon frequency was 37.735 MHz, and magic-angle spinning was performed at 3600 Hz. The spectrometer incorporates a home-built cross-polarization/magic-angle-spinning (CP/MAS) unit, including the probe. The spinner system is a modified version of Wind's[18] with a sample volume of 0.3 cm^3. A proton 90° pulse width of 5 μs was employed, corresponding to an rf field strength of 50 kHz. The rf field was maintained at 50 kHz during cross-polarization and subsequent high-power ^{1}H decoupling. The ^{13}C free induction decay (FID) was accumulated in a 2K time-domain window using quadrature detection. Prior to Fourier transformation, the signal-averaged FID was zero-filled to 4K. The spectral width encompassed a $\pm$10-kHz frequency range, and 5 Hz of line broadening was employed. Following Stejskal and Schaefer,[19] spin-temperature alternation in the rotating frame was used to suppress the buildup of artifacts that may occur in proton-enhanced spectra. The sample temperature was maintained at 15 $\pm$ 2 °C by passing the spinner air through a copper cooling coil immersed in an ice bath. Carbon-13 chemical shifts were referenced externally to the methyl resonance of hexamethylbenzene, 17.355 ppm deshielded from tetramethylsilane (TMS).[20]

Results and Discussion

Fourier Transform Infrared Spectroscopic Investigations of the Site-Specific Interactions. Coleman and Painter[10,17] pioneered applications of Fourier transform infrared spectroscopy to characterize specific interactions in polymer-polymer blends. Hydrogen bonding invariably weakens the vibrational force constant in the covalent bond between an electronegative atom and the proton of interest by extracting electron density from the bond and shifting its infrared absorption to lower wavenumber. Hence, the formation of stronger hydrogen bonds produces red shifts in the infrared spectrum that can be on the order of hundreds of wavenumbers. In previous studies of site-specific interactions in *semicrystalline* blends containing poly(ethylene oxide) (PEO) and PVPh[5,6] which originated in this laboratory, hydrogen bonding between the hydroxyl group in PVPh and the ether oxygen of PEO was identified by high-resolution solid-state ^{13}C NMR and FTIR spectroscopies. These interactions affect macroscopic properties, such as the kinetics of crystallization and melting,[3] mechanical strength,[21] and glass transition temperatures,[22] and they play an important role in the semicrystalline phase behavior of PEO and PVPh.

With the use of infrared spectroscopy in this contribution, hydrogen bonding between the hydroxyl proton in PVPh and the pendent carbonyl group in PVMK was detected at the molecular level. Specific interactions of this nature can be predicted based on the molecular structure of the two homopolymers and the superacid dissociation constants (i.e., pK_a values) of small-molecule conjugate acids containing analogous functional groups. Poly(vinylphenol) is an excellent proton donor via its hydroxyl proton. The hydroxyl oxygen of PVPh can also play the role of a proton acceptor as evidenced by FTIR support for the self-association of hydroxyl groups. Poly(vinyl methyl ketone) is considered to be a proton acceptor by virtue of its pendent carbonyl group. As mentioned above, PVMK was chosen as the proton acceptor because the ketone carbonyl functionality is the only polar site in its repeat unit. Hence, there is no ambiguity in identifying "site-specific" interactions when they involve two dissimilar chain segments.

The broad OH stretching vibration of PVPh spans the wavenumber range from 3600 to 3100 cm^{-1} as illustrated in Figure 1. There are three distinct hydroxyl absorptions in this region of the spectrum[10] which overlap extensively and contribute to the $\approx$300-cm^{-1} bandwidth. The "free" hydroxyl stretching vibration in PVPh appears[5,10,11] in the vicinity of 3521-3525 cm^{-1} as identified by the tick marks on the lower two FTIR spectra in Figure 1. The thermodynamics of hydrogen-bond equilibria[11-15] dictate that the intensity of the "free" OH absorption gradually decreases as the PVMK content in the blends increases. The self-association of hydroxyl groups in undiluted PVPh is identified[10] by the strong vibrational absorption at 3354 cm^{-1} in the lowermost FTIR spectrum of Figure 1 and the hydrogen-bonded OH absorption peaks at 3400 cm^{-1} when the interaction involves the ketone carbonyl group at high concentrations of PVMK as illustrated in the uppermost spectrum of Figure 1. The infrared data reveal that the strength of the hydrogen bond between PVPh's hydroxyl group and PVMK's carbonyl moiety is weaker than the self-association of hydroxyl groups in undiluted PVPh. This claim is based on the infrared peak position of the OH vibrational absorption for both types of segment interactions as discussed above and illustrated in Figure 1. Nevertheless, a simple thermodynamic analysis[24,30] of the infrared results suggests that the interaction free energy of mixing favors diffusional stability of both components in a homogeneous amorphous phase. This claim is supported by thermal analysis. For miscible polymer-polymer blends driven by specific interactions, one predicts that a single glass transition temperature should be

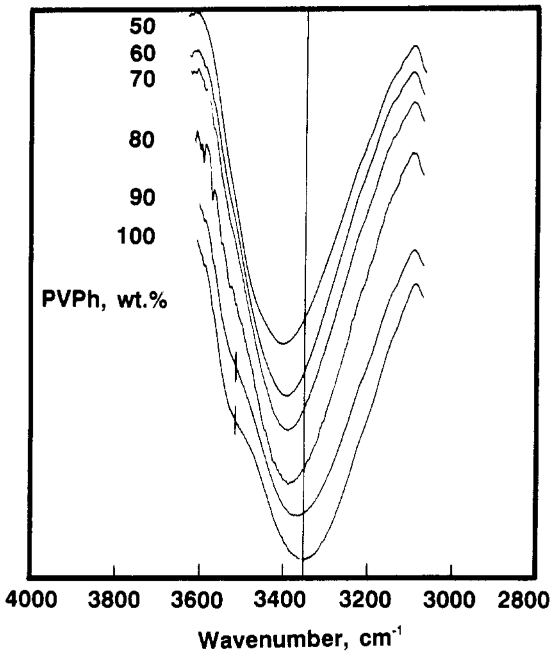

Figure 1. Fourier transform infrared spectra of PVPh's hydroxyl stretching vibration in solid-state blends with PVMK. Blend concentration is indicated at the left of each spectrum. The strong absorption highlighted by the solid vertical line represents the infrared peak for the self-association of OH groups in PVPh. The tick marks at higher wavenumber in the lower two spectra identify the non-hydrogen-bonded OH absorption. All measurements were obtained with ZnS as the substrate.

observed. Single-T_g behavior represents macroscopic evidence for compatibility in the amorphous phase—a concept that is supported by the spectroscopic study for the blends of interest, but it is not proved unambiguously by the infrared and ^{13}C NMR analyses alone. The spectroscopic results in this study are consistent with the fact that a conjugate acid of a low-molecular-weight aliphatic ketone (pK_a = −7), analogous to PVMK, is only slightly more acidic than a conjugate acid of an aromatic hydroxyl group (pK_a = −6.4), analogous to PVPh.[23] This suggests that the electronegativity of the hydroxyl-oxygen substituent on the aromatic ring in PVPh is slightly stronger than that of the carbonyl oxygen in PVMK. Hence, this rather simple qualitative interpretation of hydrogen-bond strength via association/dissociation equilibrium constants in small-molecule conjugate acids is consistent with the FTIR data.

Infrared spectra of the ketone carbonyl absorption, unique to PVMK, are presented in Figure 2. In this case, there are two distinct bands that overlap extensively in the 1700-cm^{-1} region of the spectrum.[10] The "free" carbonyl absorption in undiluted PVMK is asymmetric and exhibits an infrared peak at 1710 cm^{-1} as illustrated in the uppermost FTIR spectrum of Figure 2. The poorly resolved low-wavenumber shoulder at ≈1700 cm^{-1}, which becomes more pronounced when the concentration of PVPh increases, is representative of the carbonyl absorption that is perturbed by hydrogen bonding. These results provide direct support for the fact that site-specific interactions between the OH and C=O functional groups are operative in mixtures of PVPh and PVMK. The data in Figure 2 also reveal that there are considerable fractions of both free and bonded ketone carbonyl groups even when PVPh is the dominant component at a concentration of 80 wt % (70 mol %) as illustrated in the lowermost FTIR spectrum 2E.

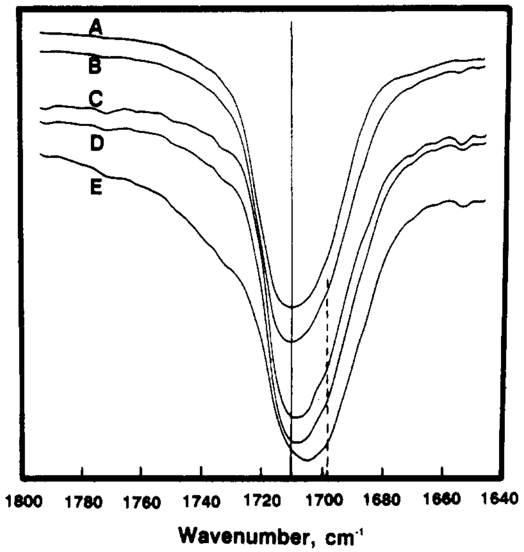

Figure 2. Fourier transform infrared spectra of PVMK's carbonyl stretching vibration in solid-state mixtures with PVPh. The solid line identifies the free absorption at 1710 cm^{-1}, and the dashed line highlights the infrared peak of the hydrogen-bonded band at lower wavenumber. A total of 256 interferograms was signal averaged before Fourier transformation, and the experiments were performed on both KBr and ZnS windows. Blend concentration is as follows for each FTIR spectrum: (A) undiluted PVMK; (B) 80 wt % PVMK; (C) 60 wt % PVMK; (D) 50 wt % PVMK; (E) 20 wt % PVMK.

Molecular-Level Mixing Phenomena via High-Resolution Carbon-13 Solid-State NMR Spectroscopy. The effect of hydrogen bonding on isotropic NMR chemical shifts in solid polymeric materials is not as predictable as the corresponding results from infrared spectroscopy. Nevertheless, this laboratory has generated a limited data base that illustrates phenomenologically how selected ^{13}C NMR signals are perturbed indirectly by strong interaction. In several cases, the observation of multiple resonances for chemically equivalent carbon sites in the phase-sensitive component is rationalized macroscopically by using the temperature–composition projection of the binary phase diagram, particularly when the mixtures chemically separate into more than one phase.[21,25–27] For the system of interest in this contribution, the critical component is PVPh, and the phenolic carbon resonance is chosen for observation due to its proximity to the hydroxyl group. NMR investigations of model polymer/small-molecule blends containing various isomers and derivatives of dihydroxybenzene[26] have illustrated that the phenolic carbon chemical shift is sensitive to the phase or phases that contain the "critical component". Consequently, in previous studies of strong intermolecular association in polymer–polymer blends that have originated in this laboratory, the phenolic carbon NMR signal of PVPh was chosen to probe the mixing process at the molecular level.[5,6] Both poly(ethylene oxide)[6] and poly(*N*,*N*-dimethylacrylamide)[28] perturb the overall line shape of the rather broad phenolic resonance of amorphous PVPh. This perturbation results from the fact that the chemical shift of PVPh's phenolic carbon is sensitive to near-neighbor segment interactions that distort its electronic environment. Consequently, the phenolic carbon signal of PVPh in all of the blends mentioned above is comprised of at least two poorly resolved absorptions separated by ≈2–3 ppm. In addition to the fact that the resonance is broadened by conformational and packing heterogeneities common to noncrystalline materials, the phenolic carbon signal characteristic of the PVPh hydroxyl self-association resonates at a lower chemical shift relative to the signal that is sensitive to the interaction between dissimilar components. In semicrystalline PEO/small-molecule blends that exhibit multiple eutectic phase transitions,[21,25–27] the phenolic carbon resonances of resorcinol and 2-methylresorcinol are sensitive to the presence of the polymer as a nearest neighbor. Fortuitously, the phenolic carbon resonances of the crystallizable small molecules exhibit a full width at half-height of $\approx$1–2 ppm. Hence, multiple NMR signals that are highly resolved suggest that different hydrogen-bond strengths and distances are characteristic of the coexisting semicrystalline phases below the eutectic solidification temperatures. This claim is supported by results from infrared spectroscopy. In all of these strongly interacting blends which contain a phenolic carbon component[5,6,21,25–29] for indirect detection of site-specific polar attractive forces via the adjacent OH group, it was not possible to correlate unambiguously the FTIR-determined hydrogen-bond strength between functional groups in dissimilar molecules (relative to the self-association of hydroxyl groups) with the upfield/downfield shift of the new blending-induced phenolic carbon NMR signal. As a consequence of mixing and the introduction of potentially new hydrogen-bonding sites that compete with self-association for the hydroxyl proton of PVPh, the phenolic carbon NMR signal that is representative of the hydrogen bond between dissimilar functional groups is invariably downfield (i.e., larger chemical shift) relative to the self-associated signal in the undiluted polymer (PVPh) or small molecule—at least for the systems that have been investigated to date in this laboratory. In reference to the FTIR data discussed above, however, we have measured segment interactions that are both stronger (hydroxyl/ether oxygen in the main chain [PEO][5,6] and side chain [PVME]) and weaker (hydroxyl/ketone carbonyl[29] and hydroxyl/ester carbonyl[29]) than the self-association of hydroxyl groups.

Carbon-13 solid-state NMR spectra of eight blends and one undiluted component are illustrated in Figure 3. The phenolic carbon chemical shift region between 150 and 160 ppm is unique to PVPh, with minor overlapping spinning-sideband contributions from the carbonyl signal of PVMK. One observes that there are two major contributors to this broad amorphous signal. This is analogous to the phenolic carbon resonance envelope of resorcinol and 2-methylresorcinol in model blends with poly(ethylene oxide)[7,25,26] except that the materials of interest in this study are amorphous, which limits the resolution of the experiment to $\approx$3–5 ppm. The resonance in undiluted PVPh at 154 ppm (spectrum A), representative of the predominant self-association, exhibits a full width at half-height of 5 ppm. When PVMK is the dominant component in the mixtures, the phenolic carbon resonance narrows considerably and peaks at 156 ppm as illustrated in spectra 3F–I. At intermediate blend concentrations, both signals are marginally detectable and represent indirect detection of the fact that the hydroxyl oxygen and ketone carbonyl oxygen compete for the hydroxyl proton of PVPh. The data in Figure 3 reveal that the NMR signal of the phenolic carbon is indirectly sensitive to these competitive hydrogen-bond equilibria that are also manifested directly in the FTIR spectra. If one compares the infrared and ^{13}C NMR results in Figures 1 and 3, respectively, for amorphous blends of PVPh and PVMK with those obtained previously in this laboratory for *semicrystalline* blends of PVPh and poly(ethylene oxide),[5,6] the following similarities and differences are observed. In both cases, the broad phenolic carbon resonance of PVPh is sensitive to the presence of the other polymeric component in the *amorphous* phase. Consequently, two poorly resolved phenolic carbon signals, separated by $\approx$2 ppm, can be detected in the overall resonance envelope when competing equilibria produce hydrogen bonds of different strength that are NMR sensitive, with the signal at lower chemical shift representative of hydroxyl self-association. When PVPh is increasingly diluted with either PVMK or PEO, the *single glass transition* process characteristic of compatibility in the amorphous phase decreases to temperatures (i) slightly above ambient for mixtures of PVPh and PVMK or (ii) considerably below ambient for mixtures of PVPh and PEO. In both cases, the increase in chain mobility that accompanies the observed decrease in T_g produces a substantial narrowing in the line width of the phenolic carbon resonance as illustrated in the lower spectra of Figure 3 for the PVPh/PVMK system. Infrared spectroscopy reveals that the hydrogen bond between PVPh and PVMK is *weaker* than the self-association of hydroxyl groups, whereas the hydrogen bond between PVPh and PEO is *stronger*. Hence, the chemical shift of PVPh's phenolic carbon is sensitive to the presence of the other blend component, but hydrogen-bond strength is not the only factor that affects the resonance position.

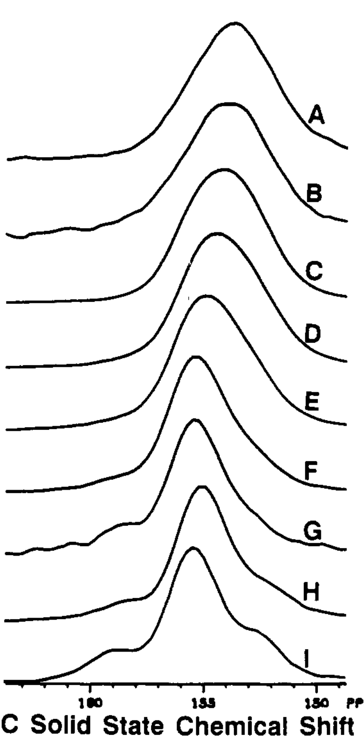

Figure 3. High-resolution solid-state NMR spectra of PVPh's phenolic carbon in amorphous blends with PVMK. Previous studies in this laboratory have revealed that the phenolic ^{13}C resonances in PVPh and in dihydroxybenzene are sensitive to the presence of dissimilar nearest neighbors, particularly when hydrogen-bonding interactions are operative in the solid state. Proton-acceptor sites that produce a second chemically shifted phenolic carbon signal include ether oxygens, ketone carbonyls, ester carbonyls, and acrylamide carbonyls. Blend concentration is as follows for each ^{13}C spectrum: (A) undiluted PVPh; (B) 90 wt % PVPh; (C) 80 wt % PVPh; (D) 70 wt % PVPh; (E) 60 wt % PVPh; (F) 40 wt % PVPh; (G) 30 wt % PVPh; (H) 20 wt % PVPh; (I) 10 wt % PVPh.

Conclusions

Solid-state mixtures of poly(vinylphenol) and poly(vinyl methyl ketone) form a homogeneous amorphous phase over the complete range of blend concentrations. This claim is supported by thermal analysis, which probes macroscopic aspects of the mixing process. One concentration-dependent glass transition temperature is observed for all mixtures. Kwei's quadratic modification of the Gordon–Taylor equation with two adjustable parameters,[31] as well as a two-parameter Gordon–Taylor model based on a concentration-dependent ratio of thermal expansion coefficients, produces the most accurate predictions of the experimental T_g results. Rather accurate step increments in thermal expansion coefficient (i.e., $\Delta\alpha$) for both components can be extracted from Kovacs' modified free-volume analysis[32] of the T_g–composition data. At the site-specific molecular level, spectroscopic techniques such as high-resolution carbon-13 solid-state NMR and FTIR reveal that hydrogen bonding induces micromixing to the extent that dissimilar chain segments reside as nearest neighbors. As expected, infrared spectroscopy directly identifies the hydroxyl proton in PVPh and carbonyl oxygen in PVMK as hydrogen-bonding partners. This claim is supported by the choice of blend components and the fact that the infrared absorptions of the OH and C=O stretching vibrations contain multiple overlapping, but poorly resolved, signals in the blended states that superficially shift the composite infrared peak as a function of blend concentration. It should be emphasized that there is no ambiguity in identifying the interaction sites for the association between dissimilar segments. The infrared results also prove that the hydroxyl–carbonyl interaction is weaker than the self-accociation of hydroxyl groups in undiluted PVPh. This difference in hydrogen-bond strength is quite small ($\approx$0.14 kcal/mol), and it is explained qualitatively via association–dissociation equilibrium constants. A simple thermodynamic analysis of the infrared data suggests that the dimensionless interaction free energy of mixing, denoted by the χ parameter, is negative, favoring chemical stability of two high-molecular-weight amorphous polymers in the blended states. Solid-state NMR illustrates that the phenolic carbon chemical shift in PVPh is sensitive to the presence of PVMK. For some blends, two phenolic carbon NMR absorptions, separated by $\approx$2 ppm, can be detected but not resolved due to the rather large line widths that are characteristic of amorphous environments. At high blend concentrations of PVMK when the glass transition occurs slightly above ambient, the line width of PVPh's phenolic carbon resonance is at least a factor of 2 narrower than its line width in the undiluted state. Finally, the similarities and differences between (i) amorphous blends of PVPh with PVMK and (ii) semicrystalline blends of PVPh with poly(ethylene oxide) discourage the use of a universal correlation to interpret phenolic ^{13}C NMR chemical shift information in terms of hydrogen-bond strength.

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