Miscibility of Poly(methacrylate)/Poly(vinyl chloride) Blends

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ABSTRACT: Methyl, cyclohexyl, and benzyl methacrylate homopolymers (PMMA, PCHMA, and PBZMA) of similar molecular weight and tacticity were each blended with poly(vinyl chloride) (PVC) via solution precipitation. The blends were then investigated by using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and solid-state cross-polarization magic angle spinning (CP-MAS) NMR. These methods provided a determination of the effect of the benzyl and cyclohexyl groups on blend compatibility and molecular interactions in comparison to the miscible PMMA/PVC system. The PMMA/PVC and PCHMA/PVC blends exhibited single T_g's at intermediate compositions. Solid-state CP-MAS NMR measurement of $T_{1\rho}$(H) relaxation times confirmed an upper limit to immiscibility on a ~4.0-nm distance scale for both blends. The DSC results for the PBZMA/PVC blends were consistent with a phase-separated system, and the blend $T_{1\rho}$(H) relaxation behavior indicated phase heterogeneity at a 4.0-nm level. FTIR spectra of the methacrylate polymers showed carbonyl band shifts consistent with Lewis acid–base interactions upon dissolution in low molecular weight PVC analogue solvents. Weaker band shifts were observed for cast films of the miscible blends, but not for blends incorporating poly(benzyl methacrylate). Lower critical solution temperature (LCST) behavior was observed for PMMA/PVC blends, but not for PCHMA/PVC blends. Taken together, the results indicate the bulkier cyclohexyl group does not inhibit miscibility with PVC, nor does it affect interactions with the carbonyl group. However, the PBZMA benzyl group does significantly inhibit miscibility with PVC.

Introduction

Previous work on PVC/poly(methacrylate) blends has concentrated primarily on studies involving poly(methyl methacrylate). The most frequently cited reference is an early report by Schurer and co-workers which reported PMMA/PVC to be miscible only in blends having PVC contents greater than 60% w/w.[1] A second group reported PMMA/PVC blends to be immiscible.[2] This discrepancy is understandable in view of the likelihood of different sample preparation methods and/or molecular weights, which can significantly affect miscibility. The influence of other factors such as tacticity can be equally as important for this system, as demonstrated recently.[3,4] This work showed that increasing the PMMA syndiotactic triad content led to increasingly miscible blends with PVC. Another important question is the definition of the distance scale over which a blend is deemed to be miscible or immiscible. Teyssie, McBrierty, and co-workers used nonradiative energy transfer and NMR techniques to study PMMA/PVC miscibility on a 50-Å scale.[5]

Other poly(methacrylate)/PVC blends have been studied to a lesser extent. A report by Walsh and McKeown indicates that polymers of ethyl, propyl, butyl, and *n*-hexyl methacrylate are miscible with PVC.[6] Work by Tremblay and Prud'homme concurs, although in both studies blends of only one composition were examined.[7] There was disagreement regarding the miscibility of poly(*n*-hexyl methacrylate) with PVC.[6,7] In general, the literature indicates that bulkier ester group structures tend to inhibit the miscibility of methacrylate polymers with PVC or other chlorinated polymers, yet there are contradictions. For example, recently it has been demonstrated that poly(isopropyl methacrylate) is immiscible with PVC.[8]

It is apparent that poly(methacrylate)/PVC blends provide an excellent opportunity for examining the role of various factors on polymer–polymer miscibility. We are aware of no previous studies regarding the miscibility of cyclohexyl or benzyl methacrylate polymers with PVC. These polymers were chosen for study to evaluate the effect of the bulkier ester side groups on miscibility with PVC. There also has been recent commercial interest in blends incorporating alkyl methacrylate copolymers and PVC.[9,10]

Although there have been other studies on the PMMA/PVC system, it is important to minimize discrepancies which might arise from differences in sample history. Hence, the studies on the PMMA/PVC blends were done in order to provide a direct comparison with the PCHMA/PVC and PBZMA/PVC blends under identical experimental conditions. Blends were prepared using methacrylate polymers of similar tacticity and molecular weight to try to minimize possible differences due to these parameters. We feel that the combined use of several characterization techniques (DSC, NMR, FTIR) is very important, providing a broad data base with which to evaluate these systems. Much of the disagreement in the literature regarding miscibility in polymer–polymer blends can no doubt be attributed to differences in sample preparation methods, thermal history, and characterization techniques.

Table I
Polymer Molecular Weights As Determined by GPC

polymer	M_w	M_n	PD
PMMA	102 000	95 000	1.1
PCHMA	246 000	112 000	2.2
PBZMA	290 000	115 000	2.5
PVC	62 000	57 100	1.1

Experimental Section

The atactic poly(vinyl chloride) used throughout this study was additive free material supplied courtesy of B.F. Goodrich Company. The PMMA was prepared by using anionic polymerization methods. Other methacrylate polymers were purchased from commercial sources or synthesized via free-radical polymerization as required. ^{1}H NMR showed all the methacrylate polymers to be atactic. Molecular weights were determined by using gel permeation chromatography and are provided in Table I. All blends were prepared by dissolving the appropriate amounts of each polymer in tetrahydrofuran and stirring for a minimum of 24 h, followed by precipitation into a large excess of methanol. The resulting powders were then repeatedly washed and subsequently dried in a vacuum oven at 50 °C for 48 h, followed by

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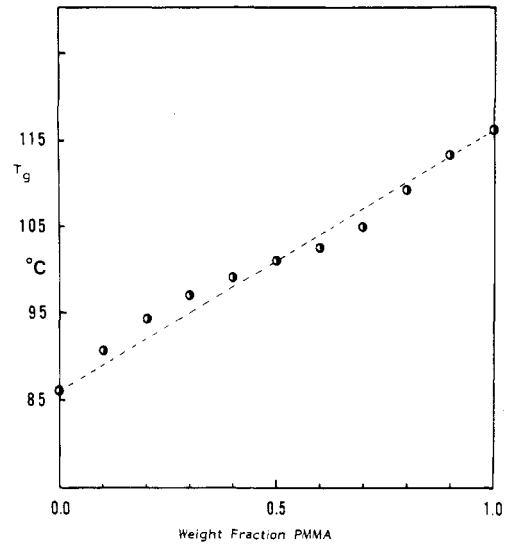

Figure 1. Glass transition temperature as a function of PMMA content in PMMA/PVC blends. The dashed line represents the behavior based on simple weight function, $T_g = (W_1/W_T)T_{g^1} + (W_2/W_T)T_{g^2}$.

a 3-h vacuum oven treatment at 125 °C to remove any last traces of solvent. No evidence of solvent was seen in IR or NMR spectra following this procedure. Some additional blend film samples for FTIR analysis were prepared by slow solvent casting from THF. All blend films were clear in appearance.

Differential scanning calorimetry measurements were made with a Perkin-Elmer DSC-4. Glass transition temperatures were obtained on second heating at a scan rate of 10 °C/min. The glass transition widths were obtained from the DSC scan first-derivative curves, using the initial and final slope changes as the limits of the transition.

Cloud-point determinations were performed by using a Mettler programmable hot stage in conjunction with a He–Ne laser light scattering device. Heating rates were 2 deg/min. A small amount (0.5 wt %) of a dioctyltin thermal stabilizer was used to inhibit oxidative degradation.

All solid-state NMR experiments were performed by using an IBM AF-200 spectrometer equipped with a magic angle spinning probe manufactured by Doty Scientific Inc. A preamp blanking circuit was added to prevent preamp overloading. Samples were packed in sapphire rotors equipped with Vespel or Kel-F endcaps. Spinning rates were generally 3.5–4.5 kHz; spinning rate adjustments were made as necessary for the removal of spinning side bands. A 90° pulse width of 5 μs was employed, in conjunction with 256 FID signal accumulations. Digital resolution was 9.7 Hz. The Hartman-Hahn match was adjusted prior to every run using a di-*tert*-butylbenzene standard. Adamantane was used to adjust field homogeneity. Proton spin–lattice relaxation times (in the rotating frame) were measured via carbon signal intensities using a 90_x–τ–spin lock pulse sequence prior to cross-polarization. Acquisition was performed with ^{1}H decoupling, and delay times (τ) ranged from 1 to 40 ms. All spectra were obtained at ambient temperature, except where noted otherwise.

FTIR spectra of the blend films were obtained by using an IBM IR-98 spectrometer operating at 2-cm^{-1} resolution. FTIR spectra of the poly(methacrylate) solutions were obtained with an IBM IR-30S using 2-cm^{-1} resolution. Polymers were dissolved in spectral grade solvents, and solution concentrations were approximately 3% polymer by weight.

Results

Thermal Analysis. Glass transition temperatures were measured as a function of blend composition for each of the methacrylate/PVC blends. Figure 1 shows a plot of T_g versus weight fraction PMMA for a series of PMMA/PVC blends. The dashed line represents the behavior expected for a simple weight proportionality function. It is apparent that there is a slightly sigmoidal deviation from the dashed line. Although the difference

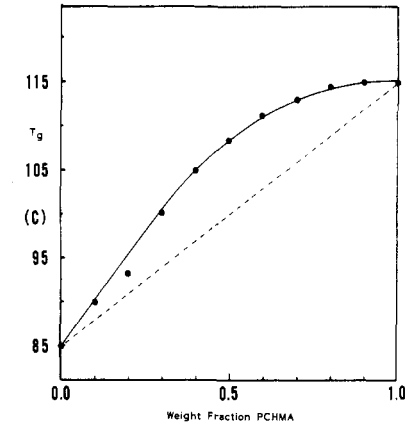

Figure 2. Plot of glass transition temperature as a function of PCHMA content for a series of PCHMA/PVC blends. The dashed line represents behavior predicted by a simple weight additivity function.

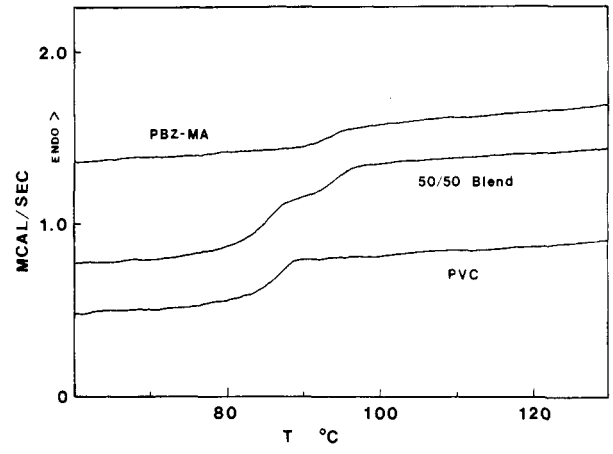

Figure 3. Second heating DSC traces for pure PVC, pure PBZMA, and a 50/50 wt/wt blend of PVC and PBZMA.

in the glass transition temperatures for the two polymers is not great, this behavior was observed consistently for several samples. Figure 2 presents the T_g behavior for the blends incorporating poly(cyclohexyl methacrylate). Blend T_g is plotted as a function of PCHMA content, with the dashed line again representing the behavior predicted by a simple weight-average expression. In this case, there is a strong positive deviation observed. None of the PCHMA/PVC blend samples showed any evidence for two glass transitions. First heating scans occasionally indicated enthalpy relaxation phenomena, but second heatings gave reproducible T_g values in all cases. For the blends of PVC with PBZMA, the DSC scans were indicative of a phase-separated system, yet the temperatures of the pure component glass transitions were similar. This precluded presentation of the data in a manner similar to that of the first two blend systems. Figure 3 depicts second heating DSC scans for pure PVC, pure PBZMA, and a 50/50 w/w blend. The T_g for the blend appears to have a two-component character, consistent with an immiscible system.

The effect of blend composition on the width of the glass transition was also determined for each system. In the case of the PMMA/PVC blend (Figure 4), there is a sharp increase in the T_g width starting at about 50 wt % PMMA, with a maximum occurring at about 70 wt % PMMA. The width of the T_g remains constant for PMMA contents below 50 wt %. The PCHMA/PVC blends (Figure 5) show a different trend, as the T_g width increases gradually with increasing PVC content. At 50 wt % PVC, there is a sudden decrease in transition width to a level consistent

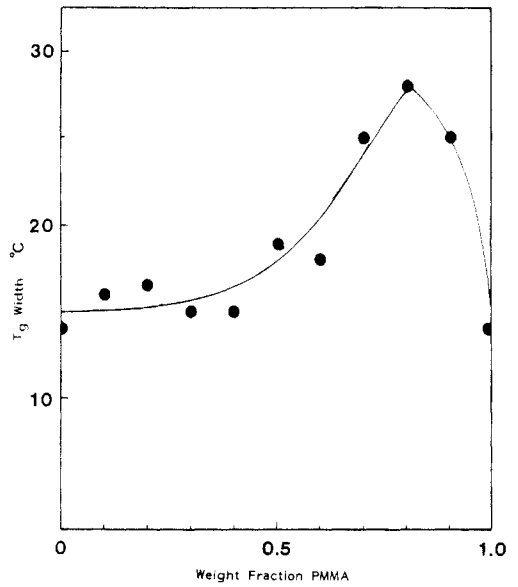

Figure 4. Glass transition width for PMMA/PVC blends plotted as a function of PMMA content.

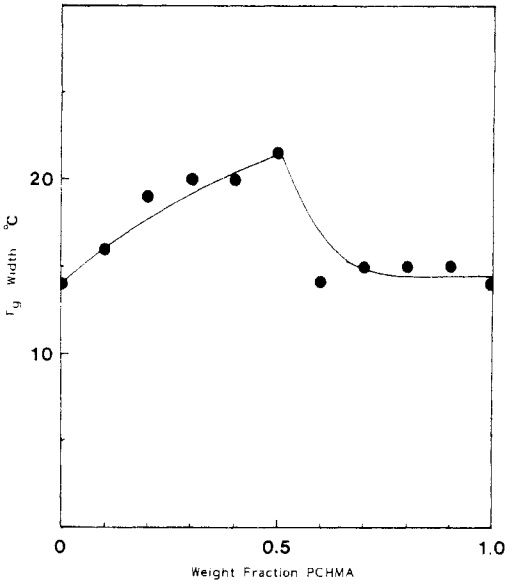

Figure 5. Glass transition width for PCHMA/PVC blends plotted as a function of PCHMA content.

with that of the pure components. Note that the maximum transition width of the PMMA/PVC blends is 10 deg greater than that of the PCHMA/PVC blends. As can be seen in Figure 3, the transition width for the 50/50 PBZMA/PVC blend is equal to the 15 deg difference in the T_g's of the pure components.

Using a simple laser light scattering device to monitor scattered intensity as a function of temperature, it was observed that the PMMA/PVC blends showed distinct lower critical solution temperature (LCST) behavior with a minimum at 190 °C at a blend composition of 60 wt % PMMA. Phase separation occurred only in blends having less than 50 wt % PVC. No LCST behavior was observed for PCHMA/PVC blends prior to the onset of degradation at about 230 °C.

FTIR Spectroscopy. FTIR spectroscopic studies were performed on several blends and on solutions of the various methacrylate polymers dissolved in PVC analogue solvents. The carbonyl band for each of the methacrylate polymers was examined for changes in line shape and/or frequency shifts which might be indicative of specific interactions with the PVC or the analogue solvents. The results for

Table II
Carbonyl Band Absorption Maxima for PMMA, PCHMA, and PBZMA Blended with PVC and Dissolved in PVC Analogue Solvents. The Last Column Represents the Band Shift for Polymers Dissolved in $CHCl_3$, Relative to CCl_4

	carbonyl band position, cm^{-1}				
polymer	CCl_4[b]	PVC[a]	1,3-dichlorobutane	$CHCl_3$	$\Delta\nu$
PMMA	1735	1732	1734	1729	6
PCHMA	1725	1723	1723	1718	7
PBenMA	1730	1730	1730	1725	5

[a] Blends were 70 wt % PVC, cast from THF. [b] Reference solvent band maxima.

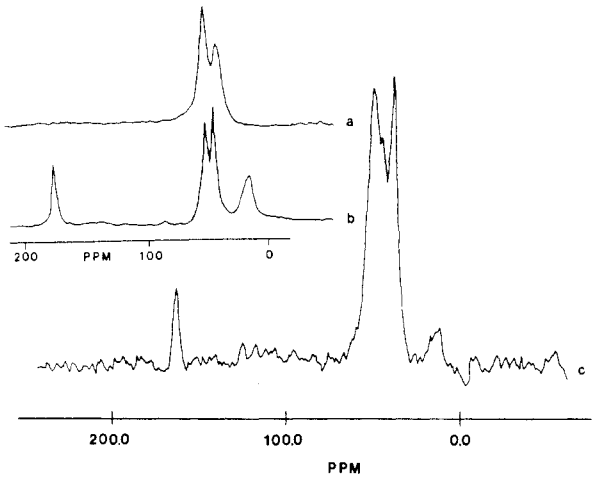

Figure 6. Solid-state ^{13}C spectrum for PVC (a) showing the chlorinated carbon peak downfield from the methylene resonance and PMMA spectrum (b) showing the signals for the α-methyl, quaternary, methoxy, and carbonyl carbons, moving downfield. The spectrum for a blend containing 80% PVC is shown in spectrum (c).

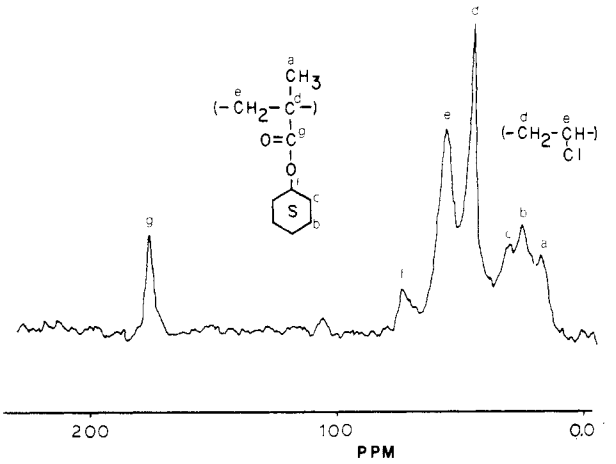

Figure 7. Spectrum obtained for a 50/50 blend of PCHMA and PVC; peak assignments as indicated.

the methacrylate solutions and blends are provided in Table II. Shifts to lower frequencies and line broadening can be indicative of Lewis acid–base or hydrogen-bonding interactions. When the methacrylate polymers are dissolved in chloroform, there is a shift to lower frequency by ~6 cm^{-1}, as well as a slight broadening (2 cm^{-1}) of the band. When the PMMA is dissolved in 1,3-dichlorobutane, a small molecule PVC analogue, a 1–2-cm^{-1} shift was observed. This was also the magnitude of band shifts observed for PMMA and PCHMA blends prepared by solvent casting, with PVC present in excess. The observed

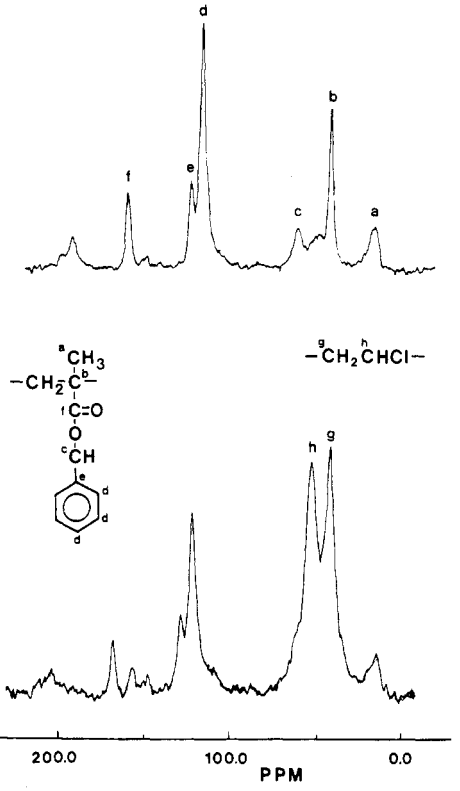

Figure 8. Top spectrum is for a pure sample of PBZMA; bottom spectrum is for a 30/70 PBZMA/PVC blend; peak assignments as indicated.

band shifts were consistent for several samples of each blend and solution.

Solid-State NMR: Proton Spin–Lattice Relaxation. Solid-state carbon spectra for each of the three blend systems are shown in Figures 6–8. In general, resolution of the various polymer carbon signals was quite good, and interference from spinning side bands was not a problem under our spectral accumulation conditions. Measurements of rotating frame spin–lattice relaxation times were made by using a 90_x–τ–SL pulse sequence. The carbon signal intensity decay curves were fitted to a standard first-order kinetic expression.[18] Use of this procedure allowed the determination of the proton spin–lattice relaxation times for the blends and component polymers by monitoring the change in carbon signal intensities as a function of delay time (τ). Depending on the polymer ^{13}C peak chosen, the nature of the proton spin–lattice relaxational process in the immediate vicinity of either blend component can be studied and compared to the relaxation behavior in the pure polymers. If the proton spin system is tightly coupled, the relaxation times should be independent of the carbon peak used to monitor signal decay. This was observed to be the case for each of the pure component polymers; relaxation times were independent of the peak chosen for the calculation. We also measured proton relaxation behavior using different carbon resonances for each of the three blend systems. Although the PVC CH_2 resonance overlaps with the quaternary methacrylate carbons, there was never any indication of two-component relaxation processes (with the exception of the pure PVC).

For the PMMA/PVC system, initial $T_{1_\rho}(H)$ experiments were run on the pure component polymers at room temperature. It was found that the relaxation times were too similar to permit effective analysis of blend relaxation times. A second series of experiments at 50 °C provided a sufficiently larger difference in relaxation times. (A detailed study of temperature effects was not attempted.) Figure 9 shows a semilog plot of carbon signal intensity as a function of delay time (τ) for PMMA, PVC, a 60/40 blend, and a 30/70 blend. For the pure PMMA, a single-component relaxation process was observed, with a time constant of 9.7 ms. For the pure PVC, there is a slight two-component decay process occurring, as indicated by the change in slope in the signal intensity plot. The slope of the curve at longer delay times yields a $T_{1_\rho}(H)$ of 6.9 ms. Although there is not a large difference between the PMMA and PVC relaxation times, it is readily apparent that the relaxation processes for the blends are intermediate in value as compared to the pure components. The relaxation times were identical for all peaks in the blend spectrum, thus indicating efficient proton spin coupling in the blends. Both the 60/40 and 30/70 blends exhibit single-component decay processes, and as the PVC content of the blends was increased, the relaxation times decreased.

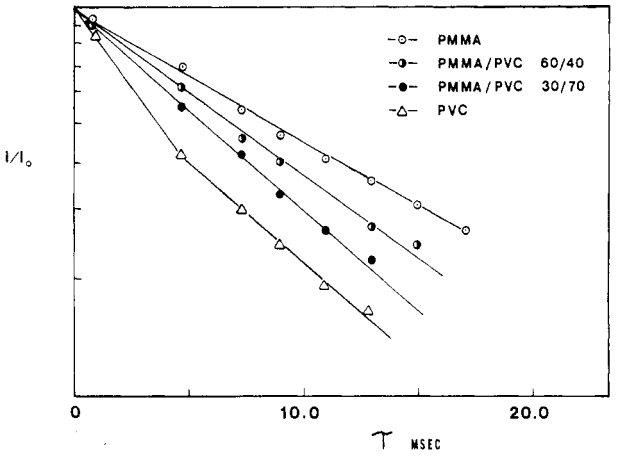

Figure 9. Semilog plot of carbon signal intensity as a function of delay time for PMMA, PVC, and two PMMA/PVC blends at 50 °C. The slope yields the proton spin–lattice relaxation time in the rotating reference frame.

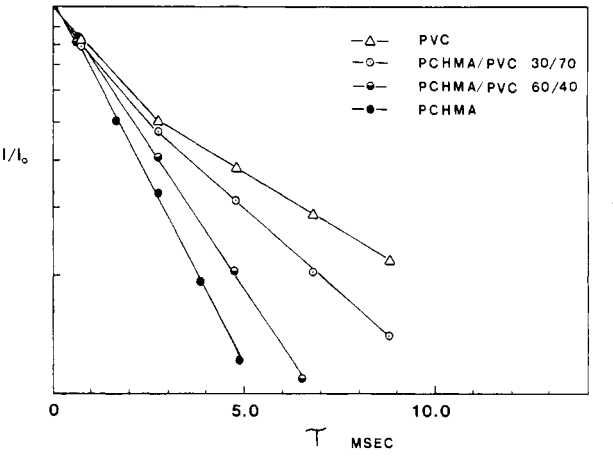

Figure 10. Semilog plot of carbon signal intensity as a function of delay time for PCHMA, PVC, and two PCHMA/PVC blends at ambient temperature. The slope yields the proton spin–lattice relaxation time in the rotating reference frame.

Figure 10 shows the results obtained at ambient temperature for the PCHMA/PVC blend system. In this case, the pure PCHMA shows a shorter (2.4 ms) relaxation time than the pure PVC. For each of the blends, single-component relaxation times intermediate in value as compared to the pure components were observed. As with the PMMA/PVC blends, the proton relaxation times were identical when measured by each of the carbon peaks in the spectrum. Increasing the PVC content resulted in

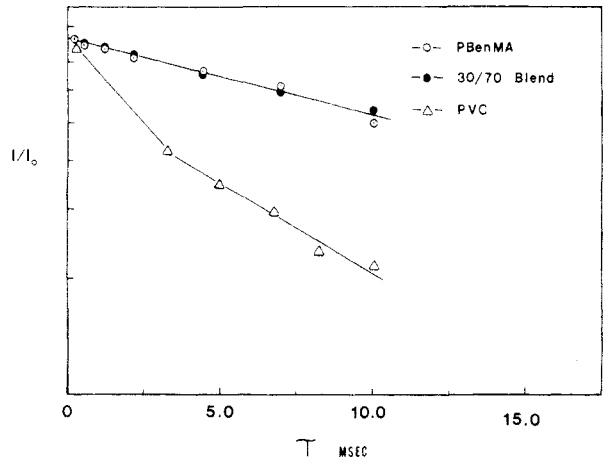

Figure 11. Proton T_{1_ρ} relaxation time plot for pure PVC, pure PBZMA, and a 30/70 PBZMA/PVC blend at ambient temperature. Blend relaxation time was measured via PBZMA carbonyl signal.

longer relaxation times, indicative of efficient spin coupling on the time scale of the relaxation process.

The T_{1_ρ}(H) behavior for the PBZMA/PVC system is shown in Figure 11. Even at high PVC contents of greater than 70% by weight, there was no observable change in the T_{1_ρ}(H) relaxation times.

Discussion

The DSC studies of the methacrylate/PVC blends provided some interesting and perhaps surprising results. It was expected that the PCHMA would be immiscible with PVC, due to the influence of the bulkier ester group as compared to PMMA. This was based on earlier reports which indicate that poly(*n*-hexyl methacrylate), poly(*n*-octyl methacrylate), and poly(decyl methacrylate) form immiscible blends with PVC.[6,7] The bulkier ester groups would act to inhibit miscibility due to increasingly positive polymer/polymer interaction parameters, possibly due to dispersive forces. However, the thermal analyses show quite clearly that the PCHMA/PVC blends have a single intermediate T_g for all compositions, and in fact, a strong positive deviation in the T_g versus blend composition plot is observed.

Explanations for positive deviations have been proposed which are based on molecular interactions between the component polymers.[11] For example, if the two polymers have strong exothermic or favorable specific interactions, a negative volume of mixing or densification may result at intermediate compositions. The negative ΔV_{mix} could result in a higher T_g than expected, due to a reduction in free volume. However, it should be remembered that DSC does not provide a molecular level measurement of molecular interactions, only a determination of the bulk thermal properties of the system.

There are other possible explanations for the T_g behavior exhibited by the PCHMA/PVC blends. For example, the Kelly–Bueche expression is given as[12-14]

$$T_g = [T_{g^1} + (KT_{g^2} - T_{g^2})\Phi_2]/[1 + (K - 1)\Phi_2] \quad (1)$$

where T_{g^1}, T_{g^2}, Φ_1, and Φ_2 are the component glass transition temperatures and volume fractions. The fitting parameter K is equal to $\Delta\alpha_1/\Delta\alpha_2$, the ratio of the thermal expansion coefficients above and below the glass transition temperature for each component. The Kelly–Bueche expression gives a reasonable fit to the PCHMA/PVC data using a K value of $\sim$2; however, the $\Delta\alpha$ values have not been measured. A more recent approach relates the T_g/blend composition behavior to differences in the relative heat capacities above and below the T_g for the component polymers.[15] Both of these treatments (Kelly–Bueche and Couchman) rely on the assumption that their respective key parameters, $\Delta\alpha$ or ΔC_p, are unaffected by the act of blending the two polymers. While this may be the fortuitous truth in many cases, it does not always hold. For example, the somewhat sigmoidal shape to the T_g/composition plot for the PMMA/PVC system cannot be explained using the above assumption. Other examples of sigmoidal T_g/blend composition curves have been found as well.[11]

The T_g width as a function of blend composition is dissimilar for the PCHMA/PVC and PMMA/PVC blends. The PMMA blends show a wider transition of 30° for PVC contents of <40 wt %, whereas the PCHMA blends show a transition width of 15–20° across the board. The width of the transition may be related to the magnitude of local compositional fluctuations in polymer blends, thus giving a qualitative indication as to the relative homogeneity or miscibility of the system. The fact that PMMA/PVC blends show LCST behavior whereas PCHMA/PVC blends do not phase separate at elevated temperatures is also noteworthy. These observation would appear to indicate that the PCHMA/PVC blend is thermodynamically more miscible with PVC than is PMMA.[16]

Another issue which must be addressed when discussing blend miscibility is the question of scale. The criteria for determination of miscibility rests on the inherent limitations of the technique one uses to characterize the system. In the use of DSC to monitor changes in blend T_g's, the operative distance scale is generally taken to be in the range 20–30 nm. Any heterogeneities which may be present on a smaller scale will not be detected by using thermal analysis. Visual determination of optical clarity establishes the absence of domains exceeding 100 nm, assuming there is a difference in the refractive indices of the components. Other techniques such as CP-MAS NMR offer the potential to probe blend miscibility on a much smaller dimensional scale. Various experiments can be used which operate on a distance scale ranging from a few angstroms to tens of nanometers.[17] For this reason, solid-state NMR was used to further evaluate the poly(methacrylate)/PVC blends.

Several examples of the use of T_1(H), T_{1_ρ}(H), and spin diffusion measurements to characterize polymer/polymer miscibility have been reported.[5,18-20] By determining the T_{1_ρ}(H) values for a blend in comparison to the T_{1_ρ}(H) values for the pure component polymers, it may be possible under certain circumstances to estimate an upper limit to the scale of heterogeneity present in the blend. If the scale of the phase separation in the blend is sufficiently small to permit rapid diffusion of proton spin energy such that a single-component relaxation process is observed, which is proportional to the weight fractions of the blend components, eq 2 may be used to estimate the upper limit to

$$\langle L^2 \rangle \simeq (t/T_2)\langle l_0^2 \rangle \quad (2)$$

the domain size,[17,21] where l_0 is the distance between protons, T_2 is the proton spin/spin relaxation time, t is the spin diffusion time constant set equal to the observed T_{1_ρ}(H) value, and $\langle L^2 \rangle$ is the mean square distance over which magnetization is transported. Our data do not provide direct measurement of spin diffusion coefficients but do provide for application of eq 2 to estimate the upper limit to heterogeneity in the blends. For the PMMA/PVC blends, substituting in t = 8 ms, T_2 = 10 μs, and l_0 = 0.1 nm yields an upper limit for mean diffusion distance (L) of approximately 2.8 nm. For the PCHMA/PVC blends, the shorter relaxation times of 5.0 ms lead to a value of

2.2 nm for the upper limit to mean diffusion distance (L). Uncertainty as to the exact value of the spin diffusion coefficient requires that these numbers be subject to error limits of ±50% of the reported value. The criterion regarding the proportionality of the blend $T_{1\rho}$(H) to the weight fractions (adjusted to account for proton density) appears to be satisfied for these blends.

The NMR results permit the conclusion that the PMMA and PCHMA blend systems are miscible on a comparable scale. The various protons in the blends are efficiently communicating spin energy on the time scale of the relaxation process. This is proven by the intermediate single-component relaxation times observed for the blends. Additional evidence for intimate mixing and efficient spin energy transfer in PMMA/PVC systems has been provided by using intermolecular cross-polarization experiments.[23]

Any changes in molecular motions which may be occurring as a result of the blending are irrelevent insofar as the above conclusion is concerned. It does not matter which specific motional process provides the chief pathway for relaxation to the lattice, only that all the protons relax via the pathway on the appropriate time scale. Measuring the effects of temperature on proton relaxation processes can provide additional information regarding molecular motions, yet such experiments are not always feasible nor are they necessary for the simple yet effective analysis presented here. It should also be noted that measurements of carbon spin–lattice (T_1) relaxation times at ambient temperature for the PMMA/PVC and PCHMA/PVC systems showed no significant changes as a consequence of blending.[24]

Returning to the question about the influence of molecular interactions on the miscibility of polymer/polymer blends and the behavior of the glass transition behavior as a function of blend composition, the FTIR experiments provide some additional insight. It has previously been theorized that the miscibility of polymers containing carbonyl groups such as polyesters or methacrylates and PVC can be attributed to interactions between the weakly basic methacrylate carbonyl groups and the weakly acidic α-protons of PVC.[7] Shifts of the carbonyl band to lower frequencies have been established to be indicative of such interactions, with the magnitude of the band shift being proportional to the strength of the interaction.[22] The results provided in Table II show that each of the methacrylate polymers exhibit band shifts to lower frequencies when the polymers are dissolved in PVC analogue solvents. Weaker shifts are observed for the carbonyl bands in PVC-excess blends, with the exception of the PBZMA/PVC blends. This is consistent with an interaction between PVC protons and the methacrylate carbonyl groups. However, the magnitude of the band shifts is identical within experimental error. This was also seen for other methacrylate polymers such as poly(ethyl methacrylate) and poly(butyl methacrylate). Hence, an explanation of the positive deviation in T_g as a function of blend composition behavior for the PCHMA/PVC system based on stronger molecular interactions is not supported by the FTIR results. Positive deviations in the glass transition temperature alone are not adequate proof of strong polymer–polymer interactions. There is no obvious reason based on chemical structure as to why PCHMA should interact more favorably with PVC than PMMA.

Conclusions

In summary, it has been shown that PCHMA and PMMA of similar molecular weight and tacticity form miscible single-phase blends with atactic PVC on similar distance scales. The bulkier cyclohexyl ester group does not appear to inhibit miscibility with PVC nor is there any apparent effect on the interaction between the ester carbonyl group and PVC. The positive deviation in T_g as a function of PCHMA content is not due to significantly stronger interactions with the carbonyl group as compared to PMMA/PVC systems. PBZMA, on the other hand, does not form a miscible blend with PVC. The immiscibility of PBZMA and other methacrylate polymers (*n*-octyl, for example) with PVC may well be due to increasingly unfavorable dispersive interactions or entropic considerations resulting from the larger ester group structure. For ester groups of six carbons or less, it appears that other variables such as tacticity, molecular weight, polydispersity, and thermal history play a more significant role in determining the extent of miscibility with PVC. The various methacrylate/PVC blends studied here and elsewhere provide an excellent example of the complex interplay among the factors which affect polymer–polymer miscibility.

Registry No. PMMA, 9011-14-7; PVC, 9002-86-2; PCHMA, 25768-50-7; PBZMA, 25085-83-0.

References and Notes

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