Miscibility and Phase Behavior in Blends of Poly(vinyl butyral) and Poly(methyl methacrylate)

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ABSTRACT: The miscibility and phase behavior in blends of poly(vinyl butyral) (PVB) and atactic poly-(methyl methacrylate) (PMMA) were studied by dynamical mechanical thermal analysis (DMTA) and optical microscopy (OM). PVB is regarded as a random copolymer containing vinyl butyral (VB) and vinyl alcohol (VA) units. In this study the copolymer composition was varied over a wide range, and PMMA was varied with respect to molecular weight. DMTA measurements show two distinct T_g's for the blends of all PVBs with PMMAs of high molecular weights ($M_w = 1.2 \times 10^5$ and 1.5×10^4), indicating completely immiscibility. However, OM observations show that the size of phase-separated domains of PVB blends with PMMA ($M_w = 1.2 \times 10^5$) depends on copolymer composition and displays a minimum in the range 22−33 wt % VA content. For low molecular weight PMMAs ($M_w = 2 \times 10^3$ to 5×10^3), miscibility with UCST-type phase behavior was observed in certain blends, the miscibility range depending on the copolymer composition and the molecular weight of the PMMA. The segmental interaction parameters of $\chi_{VA,MMA}$, $\chi_{VB,MMA}$, and $\chi_{VA,VB}$ and their temperature dependence were determined from the study. The copolymer composition dependence of the averaged interaction parameter between PVB and PMMA, χ_{12}, was then calculated and displayed a minimum around 30 wt % VA content. These finding can all be interpreted in terms of a copolymer effect in which the unfavorable interaction between PVB and PMMA is minimized at a certain copolymer compositions due to the repulsive interaction between VA and VB units within the PVB chains.

Introduction

Poly(vinyl butyral) (PVB) has been used in specific applications for many years. The polymer is synthesized by reacting poly(vinyl alcohol) (PVA) with butyralde-hyde in an acidic medium.[1] Although all products of this reaction are generally termed "poly(vinyl butyral)", the name lacks definition since normally substantial amounts of unreacted vinyl alcohol groups remain in the macro-molecular chain. Hence, it is more useful to consider PVB as a random copolymer of vinyl butyral and vinyl alcohol units (Figure 1). The vinyl alcohol unit is polar and hydrophilic while the vinyl butyral unit is hydro-phobic. It is known that random copolymers are in principle more likely to be miscible with other polymers than are homopolymers due to the intrachain repulsion of the two monomer units in the copolymer.[2,3] Therefore, PVB may be expected to form either compatible or even miscible blends with diverse polymers. Some of these have already been investigated, including blends with poly(vinyl chloride),[4] thermoplastic polyurethane,[5] and specific polyamides.[6,7]

For the past two decades, the copolymer effect in polymer blends has been investigated extensively.[2,3,8] One of the results is that a copolymer may form a miscible blend with a given homopolymer within a certain copolymer composition and temperature range, provided that there is a strong unfavorable interaction between the comonomer units in the copolymer, not-withstanding the fact that all three segmental interac-tions in such of system may be positive (unfavorable). This type of miscibility behavior gives rise to a so-called miscibility window,[2,3] when the phase state is plotted as a function of copolymer composition and temperature. Mixing the copolymer with a second homopolymer (or

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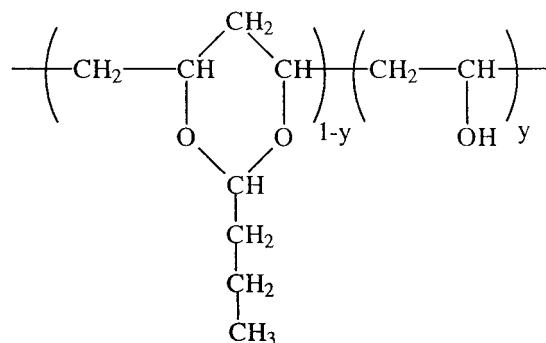
Figure 1. Chemical structure of PVB.

second copolymer) reduces the number of unfavorable nonbonded contacts between the two types of segments in the copolymer. This concept has been widely used to explore miscible polymer blends in which there are no attractive interactions. Miscibility windows have been reported for very many blends containing a random copolymer as one component, e.g., poly(styrene-*co*-acrylonitrile) (SAN) with poly(methyl methacrylate) (PMMA).[9−11] There is also the implication that in an immiscible, phase-separated blend unfavorable interac-tion between two polymers, one or both of which is a copolymer, can be minimized by tailoring the copolymer composition(s); an example is the case of the blend of bisphenol A polycarbonate (PC) and SAN.[12] In this blend, thermodynamic miscibility is not achieved; how-ever, the optimum performance of such a blend is attained at the random copolymer composition providing the least unfavorable interaction. This provides a gen-eral method of compatibilization by finding the ap-propriate copolymer composition. Here compatibility is defined as the state of aggregation at which the syner-gistic improvement of properties resulting from the blending of polymers is optimized. This concept of

Table 1. Characterization of Samples Used in This Study

| samples	VA content (wt %)	VA content (vol fraction)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	DP[b]
PVB15	14.7	0.122			2×10^3
PVB16	16.5	0.138			2×10^3
PVB18	18.2	0.152			2×10^3
PVB22	21.6	0.182			2×10^3
PVB25	24.8	0.211			2×10^3
PVB28	28.0	0.239			2×10^3
PVB31	30.9	0.266			2×10^3
PVB33	32.9	0.284			2×10^3
PVB36	36.4	0.316			2×10^3
PVB46	45.6	0.404			2×10^3
PVB55	55.0	0.497			2×10^3
PVB63	63.3	0.582			2×10^3
PMMA2			2.16	1.96	21.6
PMMA3[a]			2.98	2.5	29.8
PMMA4			3.99	3.64	39.9
PMMA5[a]			5.30	4.0	53.0
PMMA7			6.88	6.44	68.8
PMMA15			15	9	150
PMMA120			113	53	1130

[a] The samples were made by blending appropriate homopolymer fractions of PMMA2 and PMMA7. [b] Weight-average degree of polymerization (DP) for PVBs are obtained from its "mother" poly(vinyl alcohol).

compatibilization, without the aid of a third compatibilizing component, has been widely applied in polymer blends.[13]

In this contribution, atactic poly(methyl methacrylate) was used as the second component in a range of PVB blends; a-PMMA is amorphous and has excellent optical and relatively good mechanical properties. The copolymer effect on the miscibility of PVB blended with PMMA was systematically investigated over a range of VA contents in the PVB copolymers. The miscibilities of such blends with different molecular weight PMMA fractions were investigated by dynamical mechanical thermal analysis (DMTA) and optical microscopy (OM). The thermodynamic interaction parameters between the three segments relevant to this system and their respective temperature dependencies were evaluated from the investigation of miscibility behavior with low molecular weight PMMA fractions. This approach provides quantitative insights into the thermodynamic aspects and phase behavior of the PVB/PMMA system. Further, by assessing the magnitude of the unfavorable interaction as a function of copolymer composition, the region of copolymer compositions with minimum unfavorable interaction between two components was characterized.

Experimental Section

Samples. Poly(vinyl butyral)s (PVBs) with several vinyl alcohol (VA) contents were synthesized from the acetalization reaction of a "mother" poly(vinyl alcohol) with butyraldehyde as described previously.[14] Poly(vinyl alcohol) (Aldrich Chemical Co., Inc.) had weight-average degree of polymerization (DP) of 2×10^3 and contained 1 wt % of residual vinyl acetate. Poly-(methyl methacrylate) (PMMA) samples with weight-average molecular weights (M_w) of 1.2×10^5 and 1.5×10^4 (Aldrich) were used as received. In addition, narrow molecular weight distribution PMMAs with M_w's of 2.2×10^3, 4×10^3, and 6.9×10^3 were obtained from Polymer Laboratories, Ltd. The end groups of the low molecular weight PMMA samples are known to be 2,2-diphenylhexyl. Codes and the relevant characterization data for samples used in this study are presented in Table 1. The numbers immediately followed "PVB" denote the approximate weight percent of residual vinyl alcohol content in the sample, and the code numbers affixed to "PMMA" are related to the molecular weight of this polymer. We also
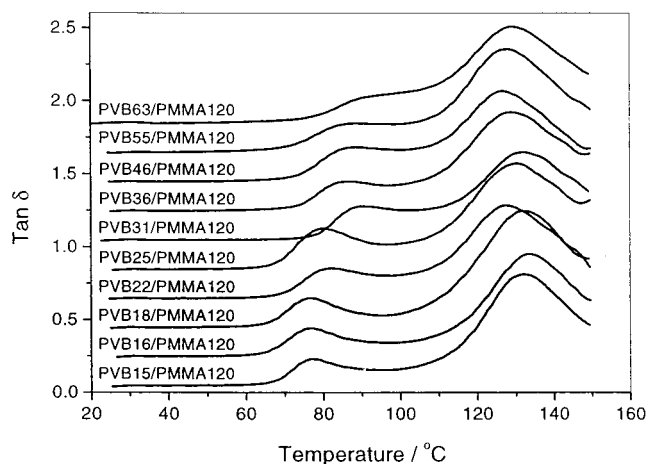
Figure 2. Loss tangent (tan δ) as a function of temperature from DMTA measurements at 1 Hz for 50/50 wt/wt PVB/PMMA120 blends for 10 PVBs. The curves are shifted vertically by intervals of 0.2 for clarity.

employed PMMAs with M_w's of 3×10^3 and 5×10^3 made by blending appropriate homopolymer fractions of PMMA2 and PMMA7.

Blend Preparation. The 50/50 (wt/wt) PVB/PMMA samples for DMTA studies were prepared by molding after melt-blending at 200–210 °C for 10 min with a Mini-Max Molder (Atlas Electric Devices Co., CS-183 MMX). The rotation speed was 80 rpm, and the samples were quenched to 78 K and dried under vacuum for 24 h at 50 °C.

The samples for optical microscopy observation were prepared by dissolving the selected PVB and PMMA samples in DMF at a total polymer concentration of 2 wt % at 50–55 °C and solution casting onto glass slides at 50–55 °C. The solvent was evaporated quickly at this temperature to form a defect-free specimen. The solution-cast films were then dried and annealed under vacuum at 120 °C for 3 days.

Measurements. Dynamic mechanical thermal analysis (DMTA) used a Rheometric Scientific IV DMTA instrument in the single cantilever bending mode and the dynamic temperature ramp scan method with a scanning rate of 5 °C/min and a frequency of 1 Hz. Sample size was 38 mm × 12 mm × 2 mm.

Optical microscopy was conducted using a phase-contrast microscope (Olympus BX60). To investigate the phase-separated structures in PVBs blended with high molecular weight PMMA, the solution-cast films were further annealed at 150 °C in a vacuum for 24 h after drying at 120 °C in a vacuum for 3 days to obtain equilibrium phase structures. To obtain miscibility diagrams for PVB blends containing low molecular weight PMMAs, the solution-cast blended films after initial drying at 120 °C in a vacuum for 3 days were annealed on a hot stage at selected temperatures for 15 min before observation. The experiment was conducted by changing the temperature in steps of 10 °C. The phase transition temperature in each case was confirmed by observing two phase/one phase reversibility. With this protocol, kinetic effects in determining the phase transition temperature in blends containing low molecular weight PMMA were eliminated.

Results and Discussion

DMTA Results. Figure 2 shows plots of loss tangent (tan δ) as a function of temperature for the 50/50 wt/wt PVB/PMMA120 blends for 10 PVBs with a systematic variation in VA contents. Two distinct peaks are observed in each case, indicating all the blends are phase-separated. The peak with the higher transition temperature is associated with the glass transition of a PMMA-rich phase, and the lower transition temperature is attributed to the T_g of a PVB-rich phase.
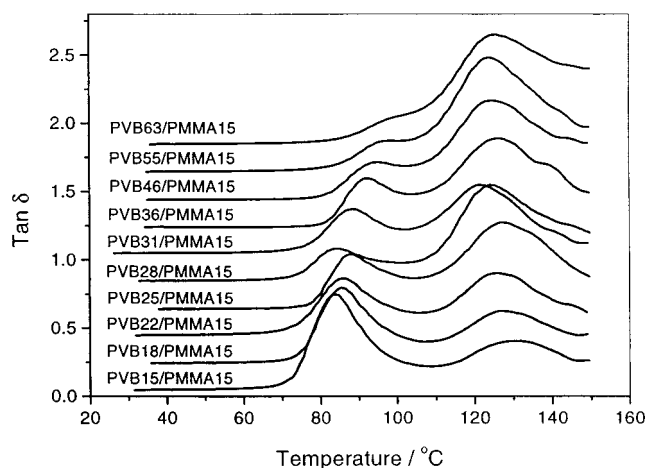
Figure 3. Loss tangent (tan δ) as a function of temperature from DMTA measurements at 1 Hz for 50/50 wt/wt PVB/PMMA15 blends for 10 PVBs. The curves are shifted vertically by intervals of 0.2 for clarity.
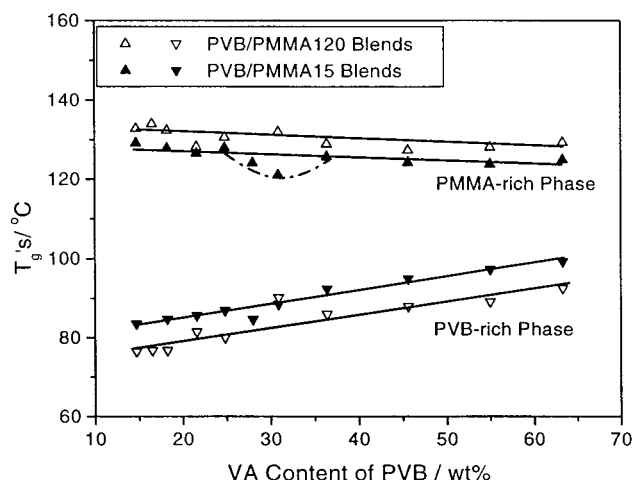
Figure 4. Glass transition temperatures (T_g's) of 50/50 wt/wt PVB/PMMA120 and PVB/PMMA15 blends as a function of VA content of PVB.

The miscibility of PVB with PMMA15 ($M_w = 1.5 \times 10^4$) was also investigated. Figure 3 shows the tan δ curves as a function of temperature for 50/50 wt/wt PVB/PMMA15 blends again as a function of VA content. Two distinct T_g's are observed, similar to those in the PVB/PMMA120 blends. This indicates that the PVB/PMMA15 blends are also essentially phase-separated, despite the lower molecular weight PMMA used.

The T_g's of the two phases in PVB/PMMA120 and PVB/PMMA15 blends are plotted together in Figure 4 as a function of copolymer VA content. In the case of the PVB/PMMA120 blends, the T_g of the PMMA-rich phase is virtually invariant with the change of VA content, while the T_g of the PVB-rich phase increases nearly linearly with VA content, as may be anticipated from the change of the copolymer composition. The T_g of the PVB copolymer itself has been found previously to increase linearly with VA content.[14] It is observed that the T_g's of the PMMA-rich phases and the T_g's of the PVB-rich phases for the PMMA15 systems lie respectively lower and higher than those of the PMMA120 systems. Moreover, it can see that in the PMMA15 containing systems T_g's of PMMA-rich phases representing systems containing PVB's with VA contents 28 and 31 wt % deviate from the linear curve. The T_g of the PVB-rich phase in the PVB31/PMMA120

system also deviates somewhat from the linear curve. These observations together suggest first that there is generally some partial mixing in the systems containing the lower molecular weight PMMA and second that this partial mixing is enhanced with PVB's containing the VA contents around 30 wt %. The data (Figure 4) show that deviation of T_g from a linear dependence on VA content in the region of 30 wt % VA content is asymmetric, in that such deviation is observed for the PMMA-rich but not the PVB-rich phase. This is presumably due to asymmetry of the phase diagram itself with respect to the solubility of one polymer in the other and is indeed a common manifestation in such systems.

Size of Phase-Separated Structures. The phase-separated structures in the PVB/PMMA120 blends were investigated by phase-contrast optical microscopy. Micrographs obtained from solution-cast films of 50/50 wt/wt PVB/PMMA120 blends with several PVBs are shown in Figure 5. The solution casting was performed with the objective of imposing identical solvent/thermal histories on the different blends. Solvent evaporation in casting at 50−55 °C is rapid; thus, the effect of gradients in solvent concentration across the film due to solvent evaporation is minimal.[15] Moreover, as has been described above, specimens were annealed thoroughly before investigation.

Two-phase structures can be clearly observed in all blends. The identity of the darker, PMMA-rich, phase in these micrographs was established by varying the overall blend composition. A two-phase structure with dispersed PMMA-rich phases of somewhat irregular shape and domain size can be seen in most of the blends (except in the case of the PVB46/PMMA120 system), demonstrating that these phase structures resulted most likely from a late coarsening stage of phase separation on annealing at 150 °C.

The micrographs also show that the finest dispersion is obtained for blends with PVBs containing 22−33 wt % VA. The average domain size estimated from the micrographs is shown as a function of VA content of PVB copolymers in Figure 6. There is a clear minimum in the domain size for blends containing PVBs with 22−33 wt % VA. The size of the phase-separated structure resulting from solution-casting blends is governed by the dynamics of phase separation induced by solvent evaporation and the coarsening process during annealing at temperatures above T_g. In the present case, the annealing process plays a more important role in determining the size of the phases, because it was conducted at 150 °C for an annealing time of 24 h.

During the annealing process, phase-separated structures resulting from solution casting coarsened with time. The driving force for the coarsening of phase structure arises from the reduction in the free energy of the system realized when the total interfacial area is reduced by domain growth. The smaller the interfacial tension between the phases, the smaller is the reduction in the free energy for a given reduction in the interfacial area. From the mechanisms accounting for the coarsening process, such as the Lifshitz and Slyozov evaporation−condensation model[16] or the Siggia model which takes into account both diffusive coalescence and hydrodynamic flow effects,[17] it is known that the growth rate of domains during coarsening is proportional to inverse viscosity and interfacial tension.[16,17] The interfacial tension in turn is related to $\chi_{12}^{1/2}$, as proposed by Helfand et al.[18] Thus, it can be concluded that the
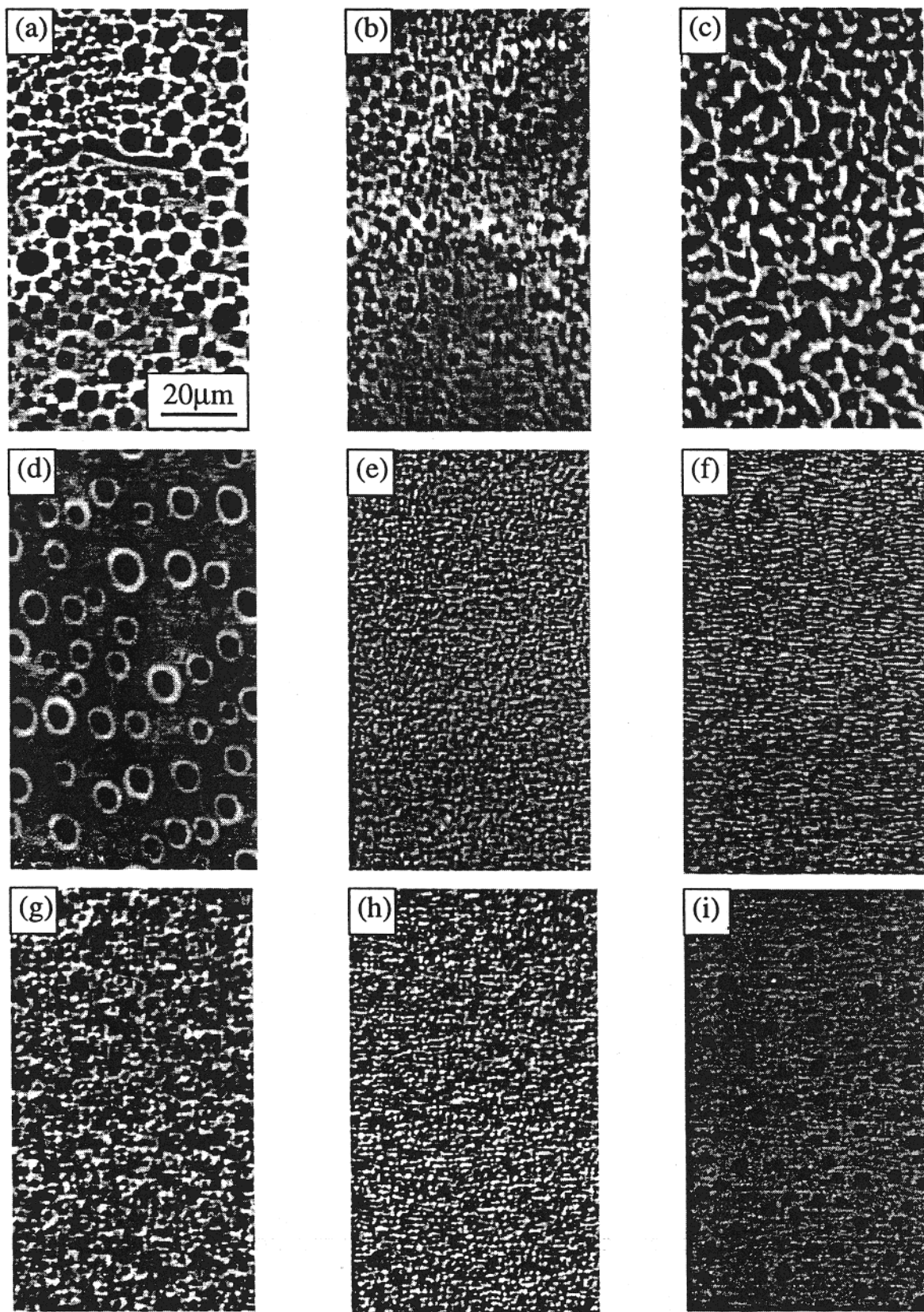
Figure 5. Optical micrographs of cast films of 50/50 wt/wt PVB/PMMA120 blends with varying VA content of PVBs: (a) PVB63, (b) PVB55, (c) PVB46, (d) PVB36, (e) PVB33, (f) PVB31, (g) PVB25, (h) PVB22, and (i) PVB15.

growth rate of domains is determined by the viscosity and the thermodynamic interaction parameter χ_{12} between two constituent polymers. Since the samples for phase-separated structure observation were prepared in the same time scale, the size of domains is a function of the viscosity and the thermodynamic interaction parameter χ_{12} between the two polymers. The viscosity in the present system changes monotonically with VA content of the copolymer; as a consequence, the size of domains should change monotonically with the VA content as well if it is dominated solely by the viscosity effect. Obviously, given the observed minimum, this is
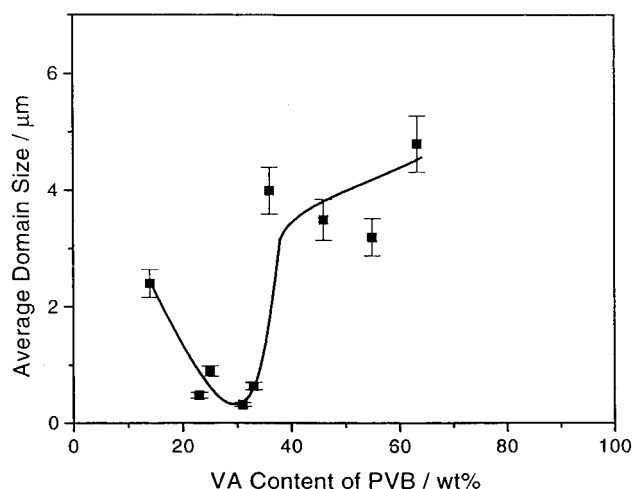
Figure 6. Average domain size estimated from optical micrographs of 50/50 wt/wt PVB/PMMA120 blends as a function of VA content of PVB.

not the case. Hence, the PVB/PMMA blends showing the finest dispersion of PMMA-rich phase can be understood to arise from the minimization of the unfavorable thermodynamic interaction parameter χ_{12} in PVB/PMMA blends for certain copolymer compositions, rather than arising from a change of viscosity with copolymer composition. The result from microscopic observation that the finest domain dispersion is achieved at 22−33 wt % VA content of PVB is thus totally consistent with the DMTA measurements and in turn supports the conclusion that a minimum in the value of the interaction parameter χ_{12} is attained in PVBs in this range of VA contents.

Miscibility Diagram and Interaction Parameters. To further explore this result, miscibility behavior in PVB blended with low molecular weight PMMA was investigated.

Miscibility diagrams, as a function of temperature and copolymer composition plotted in terms of volume fraction of VA in the copolymer, for 50/50 wt/wt PVB blends with four low molecular weight PMMAs ($M_w = 2 \times 10^3$, 3×10^3, 4×10^3, and 5×10^3) are shown in Figure 7. Figure 7a shows that there is a "miscibility valley" for PVB/PMMA2 blends in which miscibility is observed at lower temperatures with PVBs containing 21−27 vol % VA content. The miscibility region expands at higher temperature. Upper critical solution temperature (UCST) phase behavior is obtained on either side of the "valley"; i.e., blends in these regions change from immiscible to miscible with increasing temperature. With increasing PMMA molecular weight (Figure 7b−d), the size of the miscible region is reduced, and the UCSTs are shifted to higher temperatures. As a specific example of UCST phase behavior, Figure 8 shows the phase diagram for the PVB22/PMMA2 blend; a UCST-type phase boundary with a broad maximum can be observed. For the blend system containing the lowest molecular weight PMMA, the effect of the PMMA end groups on the miscibility may need to be considered. However, in the present case the nature of these groups is such that specific interactions are likely to be absent. The end group effects are thus not taken into account in the following discussion.

The miscibility diagrams obtained here differ qualitatively from the more frequently observed "miscibility window" behavior in systems such as poly(2,6-dimethyl-

1,4-phenylene oxide) (PPO) with random copolymers of *p*- and *o*-chlorostyrene,[2] polystyrene/poly(*o*-chlorostyrne-*co*-*p*-chlorostyrene),[19] PMMA/SAN,[10] etc., in which miscibility is observed at low temperature within a certain range of copolymer composition, but phase separation occurs with temperature rise; i.e., a lower critical solution temperature (LCST) behavior can be observed. UCST phase behavior in polymer blends is normally restricted to cases in which one or both of the blend components are of low molecular weight. A change from LCST phase behavior to UCST phase behavior with decrease in molecular weight has also been reported, for example, in PMMA/SAN blends.[20]

Given these measurements of miscibility as a function of copolymer composition with different molecular weights, it is possible to calculate the segmental interaction parameters and their temperature dependence. In standard copolymer treatment, the average interaction parameter χ_{12} for a binary mixture of homopolymer, PMMA ($(MMA)_n$), and copolymer poly(vinyl butyral-*co*-vinyl alcohol) ($((VB)_{1-y}(VA)_y)_{n'}$), can be expressed as a linear combination of the three segmental interaction parameters $\chi_{VA,MMA}$, $\chi_{VB,MMA}$, and $\chi_{VA,VB}$:

$$\chi_{12} = y\chi_{VA,MMA} + (1-y)\chi_{VB,MMA} - y(1-y)\chi_{VA,VB} \quad (1)$$

where y denotes the volume fraction of VA monomer in the copolymer.

The standard criterion for miscibility in blends is that χ_{12} must be less than a critical value χ_{cri}. In the usual Flory−Huggins theory,[21] χ_{cri} is given by

$$\chi_{cri} = \frac{1}{2}\left(\frac{1}{\sqrt{n}} + \frac{1}{\sqrt{n'}}\right)^2 \quad (2)$$

where n and n' are the weight-average degrees of polymerization (DP) of the two polymers. Therefore, miscibility in systems of PVB/PMMA is determined by the sign of the quadratic function $f(y)$ defined by[2]

$$f(y) = \chi_{12} - \chi_{cri} = y\chi_{VA,MMA} + (1-y)\chi_{VB,MMA} - y(1-y)\chi_{VA,VB} - \chi_{cri} \quad (3)$$

Miscibility occurs in the copolymer composition range for which $f(y)$ is negative, and immiscibility−miscibility boundaries ($y_{min}(T)$ and $y_{max}(T)$) at a given temperature T are given by solution of[2]

$$y\chi_{VA,MMA} + (1-y)\chi_{VB,MMA} - y(1-y)\chi_{VA,VB} - \chi_{cri} = 0 \quad (4)$$

The values of $y_{min}(T)$ and $y_{max}(T)$ for the four miscibility diagrams can be established from Figure 7. In principle, we can calculate the three segmental interaction parameters (eq 4) by solving sets of three independent linear equations in three unknowns. However, we found that the solutions are inordinately sensitive to $y_{min}(T)$ and $y_{max}(T)$. Since these are only measurable with an uncertainty of ±5%, in practice it is impractical to calculate the three segmental interaction parameters from these data.

However, $\chi_{VA,VB}$ can in fact be obtained from studies of the miscibility of 50/50 wt/wt PVB/PVB blends at 180 °C.[14] This miscibility data are shown in Figure 9 for the range of VA contents relevant to the present study. The analysis, in terms of mean-field theory for a mixture
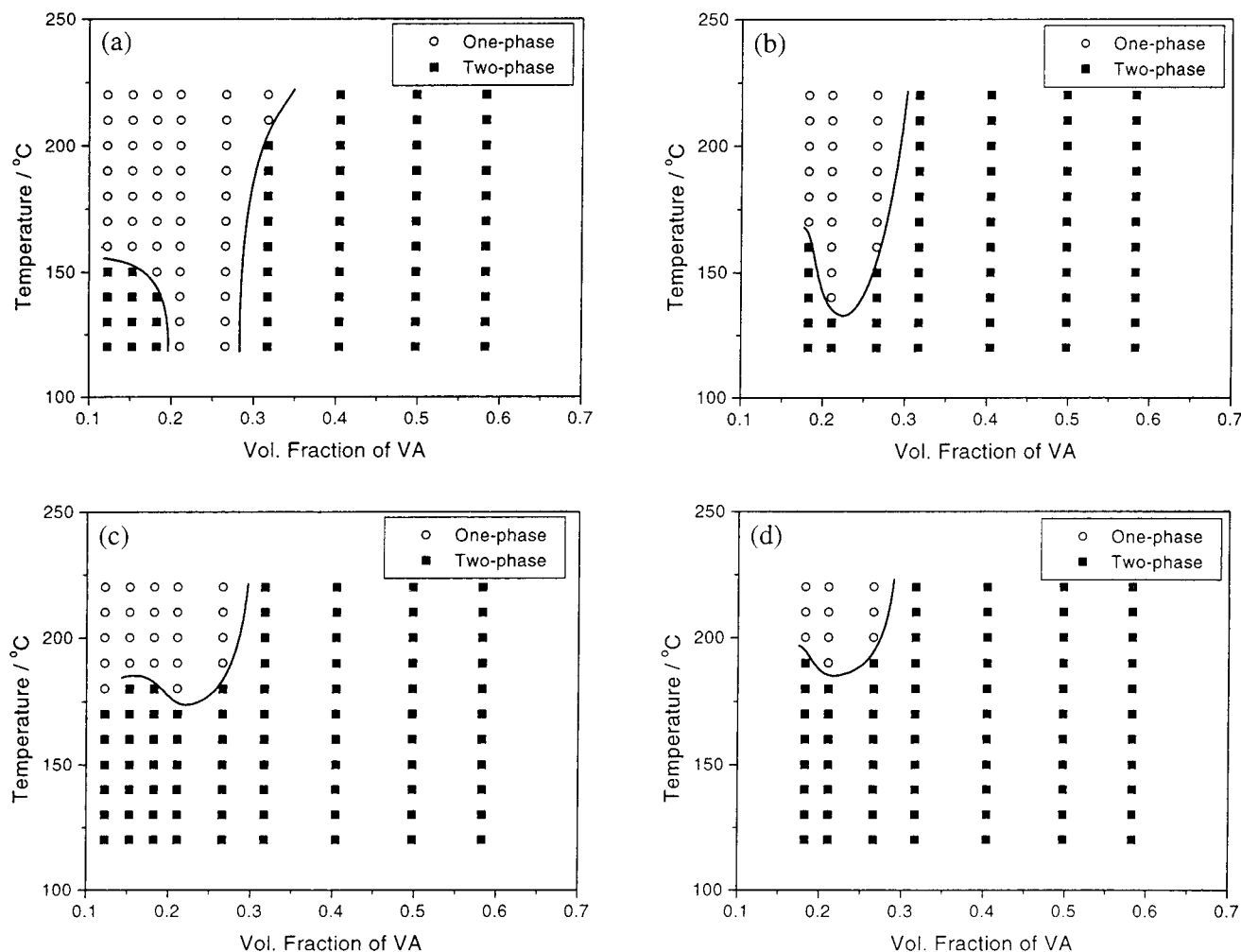
Figure 7. Miscibility diagrams showing the dependence of the miscible region on copolymer composition, temperature and molecular weight of PMMA for 50/50 wt/wt PVB/PMMA blends: (a) PVB/PMMA2, (b) PVB/PMMA3, (c) PVB/PMMA4, and (d) PVB/PMMA5.
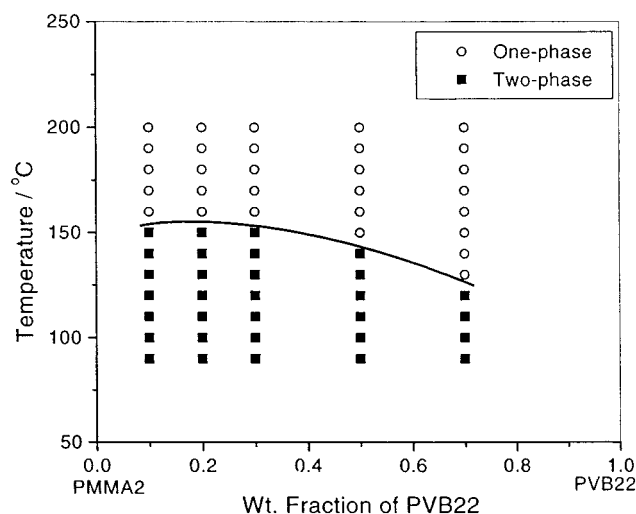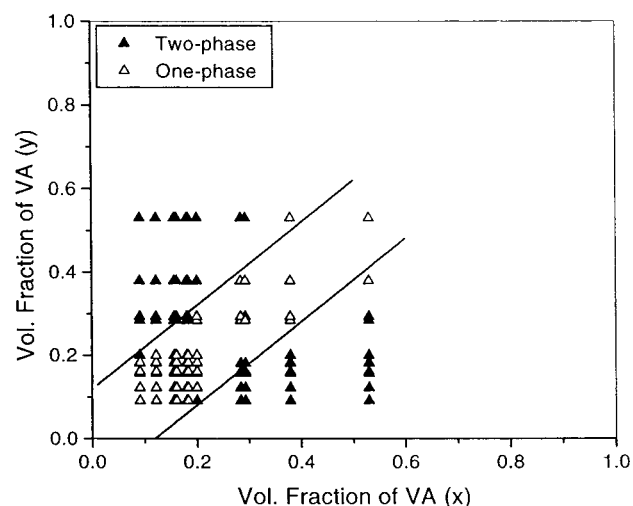

Figure 8. Phase diagram for PVB22/PMMA2 blend.

Figure 9. Miscibility map of PVB/PVB blends (50/50 wt/wt) at 180 °C; data from ref 14. Miscibility boundaries are indicated by solid lines.

of two copolymers that differ only in composition, yields[2]
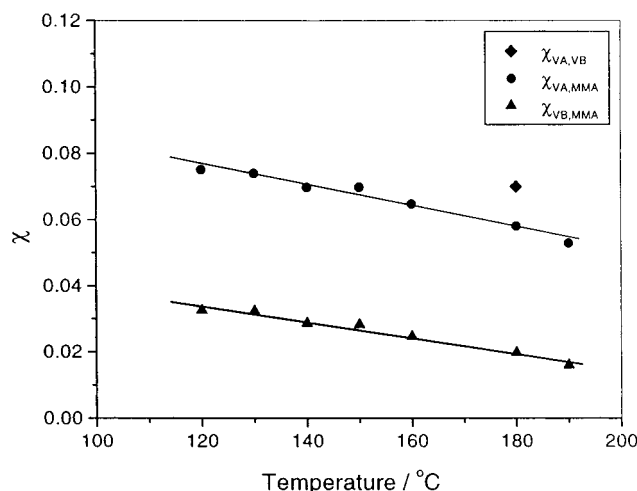
$$\chi_{12} = (x - y)^2 \chi_{VA,VB} \tag{5}$$

in which x and y are the volume fraction of VA units in the respective PVB copolymers. Miscibility occurs when the composition differences of the two copolymers $|x -$

$y|$ are smaller than a critical composition difference, $|x - y|_{cri}$. At this critical condition, χ_{12} is equal to χ_{cri} determined by eq 2. This yields

$$|x - y|_{cri} = (x_{cri}/\chi_{VA,VB})^{1/2} \tag{6}$$

Figure 10. Calculated segmental interaction parameters $\chi_{VA,VB}$, $\chi_{VA,MMA}$, and $\chi_{VB,MMA}$ as a function of temperature.

Figure 11. Averaged interaction parameter χ_{12} between PVB and PMMA at 140 and 160 °C as a function of VA content in PVB (eq 1) using $\chi_{VA,VB}$, $\chi_{VA,MMA}$, and $\chi_{VB,MMA}$'s presented in Figure 10. Dotted lines indicate the χ_{cri}'s for PVB/PMMA2, PVB/PMMA15, and PVB/PMMA120 blends, respectively.

The critical composition differences were determined from the miscibility–immiscibility boundaries shown in Figure 9 by solid lines and yield an interaction parameter $\chi_{VA,VB}$ (eq 6) equal to 0.07. The temperature range of the $\chi_{VA,VB}$ data obtained does not permit a meaningful extraction of the second-order constant B in the expression $\chi(T) = A/T + B$, which is a commonly used empirical expression for the temperature dependence of χ. Here A and B are constants, and T is the absolute temperature. Therefore, the second-order term B which is temperature-independent was arbitrarily set equal to zero. Given that this term is usually small, we believe that this approximation can only have a minor quantitative and certainly not a qualitative effect on the conclusions. The $\chi_{VA,VB}(T)$ values at several experimental temperatures were then estimated. From this quantity, the values of $\chi_{VA,MMA}(T)$ and $\chi_{VB,MMA}(T)$ were calculated and are shown in Figure 10. It is noted that $\chi_{VA,MMA}$, $\chi_{VB,MMA}$, and $\chi_{VA,VB}$ are positive throughout the experimental range. We also see that $\chi_{VA,MMA}(T)$ is larger than $\chi_{VB,MMA}(T)$ for a given T, which suggests that favorable interactions such as hydrogen bonding between the VA and MMA groups do not play an important role in the present system. This can well be attributed to the fact that self-association between VA groups in the PVB itself is much stronger than the interaction between VA and MMA groups.

The interaction parameter between the PVB and PMMA polymers, χ_{12}, as a function of VA content of PVB was calculated from eq 1 and is shown in Figure 11 for 140 and 160 °C. The critical interaction parameters χ_{cri} (eq 2) for the PVB/PMMA2, PVB/PMMA15, and PVB/PMMA120 systems are indicated in Figure 11 by dotted lines. The parameter χ_{12} displays a minimum at about 25 vol % (i.e., 30 wt %) VA content, consistent with the results described earlier. Figure 11 also shows that χ_{12} is positive for all compositions and substantially exceeds χ_{cri} for the PVB/PMMA15 and PVB/PMMA120 blends, confirming that miscibility cannot be attained for blends of any PVB with high molecular weight PMMA, whereas it can be seen that χ_{12} for a certain range of VA contents is less than χ_{cri} for the PVB/PMMA2 blends. This is consistent with the observed miscibility (Figure 7) and supports in turn the interaction parameter calculations reported above. Moreover, the temperature dependence of the miscible regions observed in Figure 11 based on
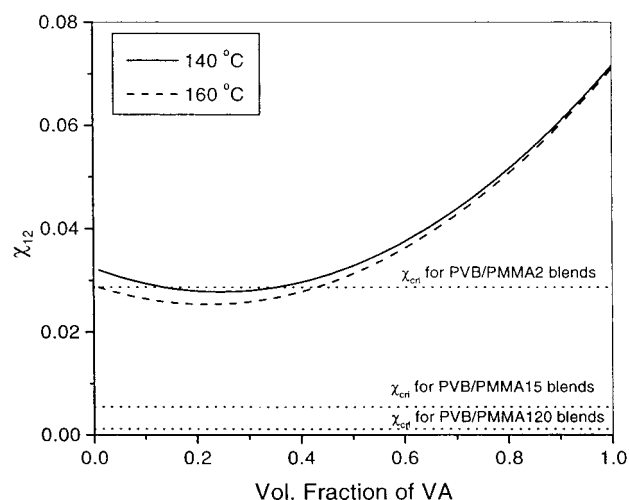
the calculated interaction parameters χ_{12} is also consistent with the UCST directly observed.

It is worth mentioning that χ_{12} as shown in Figure 11 does not go to zero even at the optimum VA content, implying that solubility parameter theory cannot be applied to explain the copolymer effect. If solubility parameter theory were applicable, χ_{12} has to go to zero at the optimum VA content. The important difference between copolymer theory used here involving intra-macromolecular interaction and the traditional solubility parameter approach has been frequently emphasized (e.g., refs 3 and 22). In the present case results of Figure 11 clearly demonstrate that the analysis based on solubility parameters would be inconsistent with the experimental results.

Both UCST and LCST phase behaviors in polymer blends can be predicted using the Prigogine–Flory equation-of-state theory by taking into account the volume of mixing.[23,24] The observation of a UCST is possible for polymer blends when the interaction parameter χ_{12} is positive and small enough to satisfy the critical condition ($<\chi_{cri}$) in an accessible temperature range. Such a very small positive value of χ_{12} may be realized when both the enthalpic interactions and the effect of free volume differences are small. In the present system, it is understood that the observation of UCST phase behavior is favored by the copolymer effect, which renders the interaction small enough to satisfy the critical condition in the observed temperature range. It is anticipated, according to this theory, that both UCST and LCST behaviors might exist.[25,26] However, none of the blends studied here displayed a LCST in the experimental temperature range.

Conclusion

We have systematically studied the miscibility and phase behavior for blends of PVB with varying VA content and several different average molecular weight PMMAs. PVB and PMMA blends are completely immiscible for high molecular weight PMMA ($M_w = 1.2 \times 10^5$ and 1.5×10^4) for all VA contents. Phase-separated structures from these blends display the finest dispersion in the range of 22–33 wt % VA content of PVB. A deviation of T_g's for blends containing PVBs with the

same range of VA contents is also seen, implying some partial miscibility in this range. Actual miscibility is observed for PVB blends with PMMAs having molecular weight in the range $2 \times 10^3 - 5 \times 10^3$. The systems show a UCST-type phase behavior. From the experimentally observed miscibility diagrams, binary segmental interaction parameters between all three units, i.e., $\chi_{VA,MMA}$, $\chi_{VB,MMA}$, and $\chi_{VA,VB}$, were determined. The copolymer composition dependence of the average segmental interaction parameter between the PVB and PMMA macromolecules, χ_{12}, was calculated and shows a concave curve with a minimum around 30 wt % VA content. It is thus understood that the all findings in the present system arise from the fact that the unfavorable interactions between PVB and PMMA are minimized in the range $22-33$ wt % VA content and that this involves primarily a large repulsive interaction between VA and VB units in the PVB copolymers.

References and Notes

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