

Synthesis Characterization and Miscibility of Polyvinyl Butyrals of Varying Vinyl Alcohol Contents

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Received 15.8.1997

Polyvinyl butyrals (PVB) of systematically varying vinyl alcohol content have been synthesized and characterized using wet chemistry, IR, DSC, and TGA. The miscibility of PVB-PVB blends was studied by DSC as a function of vinyl alcohol content and vinyl alcohol content differences between the respective blend components. These data were used to construct an isothermal miscibility map of PVB and to calculate the intramolecular interaction parameter $\chi_{VA,VB}$. The $\chi_{VA,VB}$ was a function of the absolute level of the vinyl alcohol (VA) and vinyl butyral (VB) contents of the polymers.

In addition, the thermal stability of polyvinyl butyral was found to be inversely related to the residual vinyl alcohol content of the polymer.

Introduction

Polyvinyl butyral (PVB) has been widely used in laminated safety glass, paint, adhesives, primers and binders. This industrially important random copolymer of vinyl alcohol and vinyl butyral units is synthesized by reacting polyvinyl alcohol (PVA) with butyraldehyde in an acid medium. Although the product of this reaction is generally termed "polyvinyl butyral", this name itself is ill-defined since normally substantial amounts of unreacted vinyl alcohol groups remain in the macromolecular chain. The cyclization reaction requires the presence of two adjacent hydroxyl groups on the PVA chain, assuming there is no intermolecular acetalization reaction. Flory¹ calculated the statistical maximum degree of acetalization, assuming the aldehyde groups that randomly react with the hydroxyl groups to be 86.5 mole %. Thus, under normal acetalization conditions, 1,3 glycol bonding of the PVA forms the acetal rings in the polymer and the lowest vinyl alcohol content in any polyvinyl acetal is 13.5 mol %

Attempts have been made to synthesize polyvinyl acetals with a degree of acetalization exceeding the predicted value² and some examples of such acetals are in the patent literature³. Flory assumed that acetalization was an irreversible reaction; however, while discussing the possibility of chains exceeding the statistical maximum degree of acetalization, he also considered the reversibility of the formation of acetal rings. In 1983 Reghavendachar and coworkers⁴ suggested the possibility of achieving a degree of acetalization

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over 86.5 % while still maintaining the assumption that acetalization is an irreversible reaction. However, in spite of various reports, the maximum acetalization degree predicted by Flory has not been significantly exceeded. Nevertheless it is clear that a wide range of random copolymer compositions is possible, ranging from near 100 mole % PVA to 13.5 mole % PVA. In this contribution we focus on the mutual miscibility of these copolymers from which the intramolecular interaction of the two component moieties can be calculated.

The random structure of PVB results in glassy polymers with no discernible crystallinity except at very high alcohol content. The chain contains both hydrophilic vinyl alcohol groups and hydrophobic (or less hydrophilic) vinyl butyral groups. The nonpolar, polar and hydrogen bonding components of PVB can interact favorably with other macromolecules and it may therefore be compatible (and possibly miscible) with both hydrophilic polymers and hydrophobic polymers. PVB has been studied with regard to its compatibility with polyvinyl chloride⁵, bisphenol A polycarbonate⁶, thermoplastic polyurethane⁷, and certain polyesters and polyamides⁸. To quantify such interactions it is necessary to understand the intramolecular interaction of VA and VB. This will facilitate the use of PVB as a copolymer with potential miscibilities with polymers having widely dissimilar groups. This basic understanding can thus lead to the design of additional blend with improved properties.

Polymer blends composed of two random copolymers containing the same monomers A and B (i.e., $A_x B_{(1-x)} / A_y B_{(1-y)}$) require one dimensionless interaction parameter $\chi_{A,B}$ to describe the interaction between component A and component A and component B. Scott⁹ showed that the copolymers are thermodynamically miscible if the difference in the compositions of the constituents of a given blend $|x - y|$ is smaller than a critical value which depends on pressure, temperature, the composition of the blend, the polymerization degree, and the interaction parameter. A first order assumption is that the critical composition difference $|x - y|_{cr}$ is independent of the absolute composition of the copolymers. A blend is thus immiscible when the copolymer composition difference is greater than this critical value; phase separation will take place. This critical copolymer composition difference can be experimentally determined by investigating the phase behavior of a series of blends as a function of the constituent copolymer composition ratios.

Theoretical

A result of copolymer/copolymer mean field theory¹⁰ is that blends of random copolymers containing identical segments but different overall compositions are immiscible when the corresponding polymers are of infinite molecular mass for any positive (unfavorable) χ_{ij} . For finite polymerization degrees (DP) of two polymers, N_1 and N_2 , the free energy of mixing of two random copolymers comprising the same monomers A and B with an interaction parameter $\chi_{A,B}$ is given by:

$$\Delta G/RT = (\theta_1/N_1)\ln\theta_1 + (\theta_2/N_2)\ln\theta_2 + \theta_1\theta_2(x - y)^2\chi_{A,B} \quad (1)$$

where x and y denote the copolymer compositions expressed in volume fractions of the two copolymers, and θ_1 and θ_2 are the volume fractions of the copolymers in the blend. The critical condition is given by the Flory-Huggins theory and a critical point occurs at a temperature and blend composition for which χ_{cr} equals χ_{blend} where:

$$\chi_{blend} = \chi_{cr} = 1/2 \left(1/N_1^{1/2} + 1/N_2^{1/2} \right)^2 \quad (2)$$

For a mixture of two copolymers that differ only in composition, mean field theory has shown¹⁰

$$\chi_{blend} = (x - y)^2\chi_{A,B} \quad (3)$$

for the critical blend composition which approximates equal volume fractions of the constituents. Thus the interaction parameter $\chi_{A,B}$ is given by:

$$\chi_{A,B} = 1/2(x - y)_{cr}^{-2} \left(1/N_1^{1/2} + 1/N_2^{1/2} \right)^2 \quad (4)$$

and from the critical composition differences of two copolymers. the interaction parameter $\chi_{A,B}$ can be calculated.

Experimental

Synthesis of Polyvinyl Butyral

Polyvinyl alcohol (DP=2000, Aldrich) containing a residual vinyl acetate content of 1% was dissolved in distilled water at 85°C by stirring for about 2 hours to prepare an 8 to 10 wt% solution. The temperature of the solution was reduced to 8 to 12°C and a quantity of a 70% solution of nitric acid was added. To this, a pre-determined amount of butyraldehyde was added, according to the desired acetalization degree, and the reaction was initially carried out at 10°C for 3 hours with continuous stirring, followed by one hour at 60 to 70°C to complete the acetalization reaction. The reactor contents were washed with distilled water once, neutralized with 50% sodium hydroxide to a pH of 11 to 12, held at this pH at 70°C for 1 hour and then washed again with distilled water to a final pH of 7.5 to 8. The product was filtered and dried at 50°C in a vacuum oven until a constant weight of sample was achieved. GPC measurement of the PVBs indicated that no degradation occurred during the synthesis of the modified polymers. The overall reaction and reaction mechanism are shown in Figure 1.

Analysis of Vinyl Alcohol Content

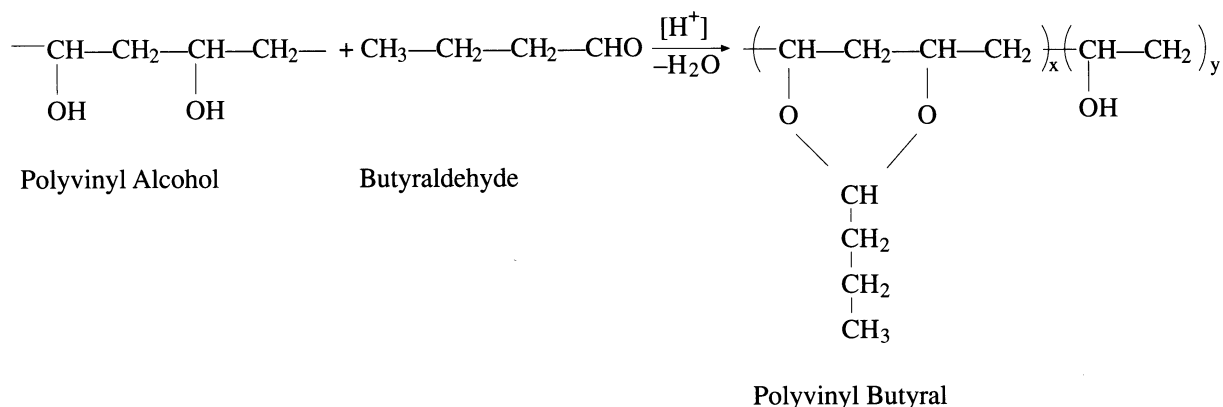
The vinyl alcohol content was determined both by near-infrared analysis and by a chemical method in which the residual hydroxyl was acetylated with acetic anhydride in pyridine, followed by titration of the liberated acid¹¹.

Thermal Analysis

A DSC-7 (Perkin-Elmer) AND A TGA-7 (Perkin-Elmer) were used to determine the glass transition temperature of the PVBs as a function of vinyl alcohol contents and their thermal stability, respectively. The miscibility of PVB/PVB blends were also determined by DSC, using a scanning rate of 20°C/min. In each case, the DSC samples were annealed at 180°C for 10 min. and then quenched at 500°C/min to 30°C before T_g measurement was carried out.

Preparation of the PVB/PVB Blends

Blends of 50/50 weight % polymers were prepared by freeze milling the powder mixture in a liquid nitrogen-cooled mill, followed by molding into thin film at 220°C. The film was released, folded, and remolded three times to enhance the initial level of mixing. To study the influence of the blend preparation conditions, certain blends were also prepared by precipitating from MEK or THF into hexane, or by casting film from the same solution, which was then dried in vacuum at 50°C for two days. No difference in the miscibility behavior for the blends prepared by these different methods was found.



The Reaction Mechanism

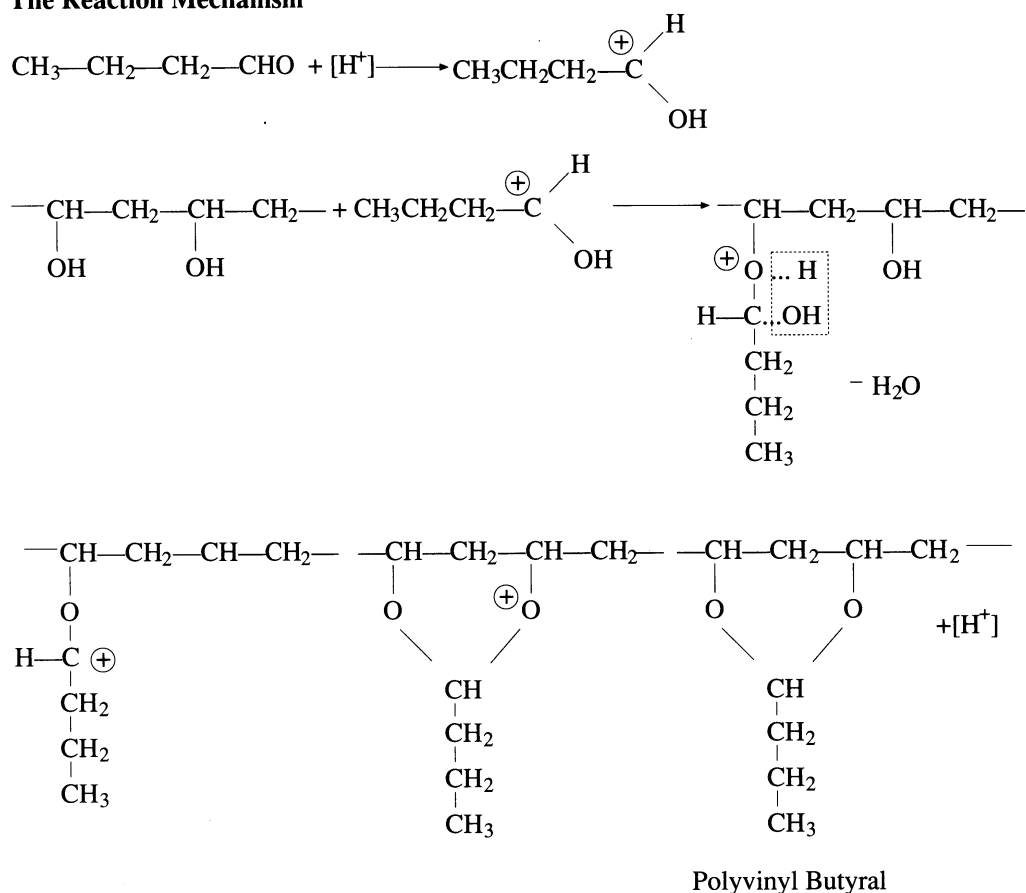


Figure 1. Synthesis of poly(vinyl butyral)

Results and Discussion

The analysis of the PVBs of different VA contents is shown in Table 1.

In this table we compare the vinyl alcohol contents of the samples expressed in weight fractions (analytical determination), molar concentrations, and the corresponding volume fractions used for the miscibility calculations. The volume fraction was obtained from the corresponding weight fraction by using the specific volumes of the respective monomer units. The specific volume of a polymerized vinyl alcohol unit was experimentally determined by measuring the density (1.31 g/cm³) of polyvinyl alcohol (100% hydrolyzed polyvinyl acetate). The specific volume of the cyclized repeat unit of polyvinyl butyral however, cannot be

determined directly. It can be determined from the densities of two PVBs (the density is 1.100 g/cm³ for PVB of 19 wt % VA and 1.083 g/cm³ for PVB of 11wt % of VA); the calculated value is 134 cm³/mol. The specific volumes of the repeat units were also calculated from group molar volume additivities to be 135 cm³/mol for the polymerized vinyl butyral units and 33.8 cm³/mol for polymerized vinyl alcohol units^{12,13}. These values of the specific volumes are thus in good agreement with the experimental results.

Table 1. Analytical Results for PVBs

PVB Sample No	VA wt%	VA mol %	VA Vol.Fraction	T _g (°C)
1	11.0	28.6	0.091	67
2	14.7	35.7	0.122	72
3	18.7	42.6	0.157	-
4	19.2	43.4	0.161	75
5	21.5	46.9	0.181	-
6	21.7	47.2	0.183	-
7	23.6	49.9	0.200	77
8	32.9	61.3	0.284	-
9	33.9	62.3	0.293	80
10	43.0	70.9	0.379	82
11	58.0	81.8	0.530	85

The glass transition temperatures of the PVBs were measured by DSC (Figure 2) and the results show that the T_g of PVB increases monotonically with increasing vinyl alcohol content (Figure 3).

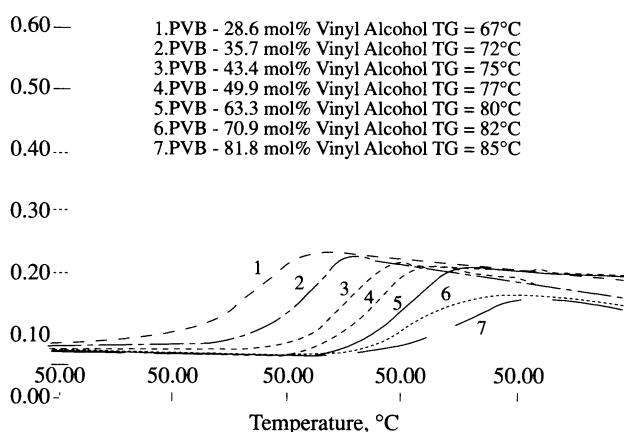


Figure 2. DSC curves showing the glass transitions of samples of poly(vinyl butyral) (PVB) with differing vinyl alcohol contents

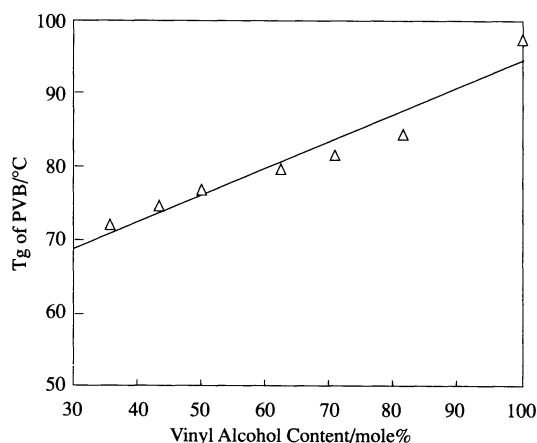


Figure 3. T_g of poly(vinyl butyral) as a function of the vinylalcohol content of the copolymers

This result can be attributed to the plasticising effect of butyral groups and/or to decreased hydrogen bonding between chains as the hydroxyl content is lowered.

The thermal stability of selected polyvinyl butyrals was investigated using TGA. The results (Figure 4) were determined in a nitrogen atmosphere at a scanning rate of 20°C/min.

It was noted that the thermal stability of PVBs with 50 mole % VA content or less (curves 4, 5, 6, and 7, Figure 4) was significantly increased compared to that of PVA (curve 1, Figure 4), while the PVBs with 82 mole% and 70.9% VA contents (curves 2 and 3) began to lose weight at slightly lower temperature

than PVA. However the rate of weight loss at fixed heating rates was still less than that of pure PVA. The thermal degradation of PVA itself in the absence of oxygen has been extensively studied¹⁴⁻²⁰) and normally occurs in two stages. The first stage mainly results from dehydration followed by the formation of a volatile product. With an increase in the acetalization degree, there is a reduction in hydroxyl group concentration which undergo dehydration and this suggests that the thermal stability of PVBs is significantly improved, in terms of dehydration, as the acetalization increases.

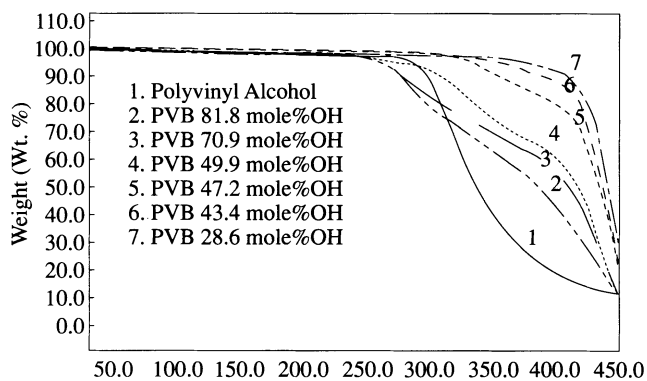


Figure 4. Weight loss of PVB as a function of temperature for samples containing varying vinyl alcohol contents

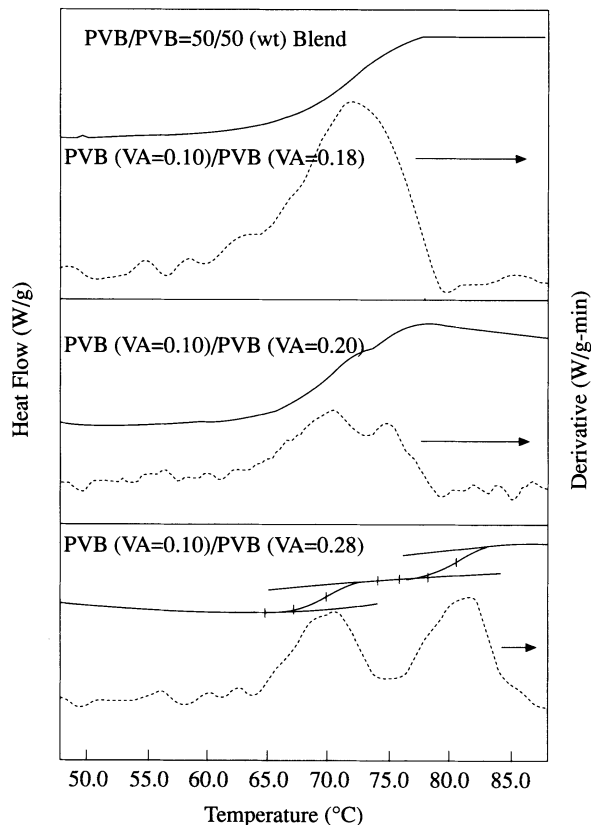


Figure 5. Examples of DSC curves used to determine the phase behavior of 50/50 PVB blends

Phase behavior of PVB/PVB blends

The DSC measurements (typical results are shown in Figures 5 and 6) illustrate the thermal behavior of PVB-PVB blends (50/50 wt %) in the glass transition regions. The respective derivative curves (dashed lines) which enhance resolution are also shown.

As an example, it can be seen from Figure 5 that the blend of a PVB containing 10 vol.% of VA ($T_g=67^\circ\text{C}$) with a PVB containing 18 vol % of VA ($T_g=75^\circ\text{C}$) has a single T_g while the blend of the former with a PVB containing 20 vol % of VA ($T_g=77^\circ\text{C}$) begins to show two glass transitions which are partially resolved. This is more clearly shown in the derivatives of these curves and demonstrates that phase separation occurs in the blend of PVB (VA=0.10)/PVB (VA=0.20) with the cited thermal histories. When the same PVB (VA=0.10) is blended with PVB containing 28 vol % ($T_g=80^\circ\text{C}$), two completely separate T_g s are readily detected (Figure 5) indicating phase separation.

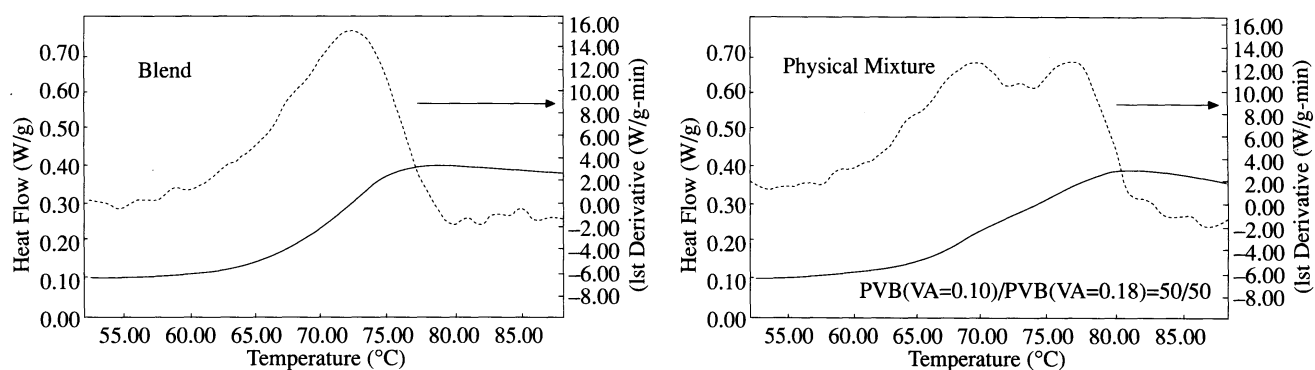


Figure 6. DSC results for PVB (VA=0.12 vol. frac.)/PVB (VA=0.18 vol. frac.) blend, and for the corresponding physically separated mixture

Although the derivative curve of the PVB (VA=0.10)/PVB(VA=0.18) mixture shows only one peak, it cannot be assumed that a single phase is achieved since the T_g s of the two individual components are relatively close. To measure the resolution of this T_g determination, a physically separated mixture of the two components in the form of a cut film mixture (50/50) was also scanned by DSC (Figure 6). For comparison, the results for the blend and for the physical mixture are both shown and it can be seen that the derivative curve for the physical mixture shows two clearly defined peaks while that for the blend has only one peak. This result indicates that the resolution of the DSC experiment, in this case, is sufficient and that the particular blend forms a single phase.

A series of blends were made in which, for convenience, a PVB of a given residual vinyl alcohol content was systematically blended with a series of PVBs of greater and lesser vinyl alcohol content to establish the phase boundaries. These phase boundaries constitute upper and lower miscibility limits for the composition of each PVB blend of arbitrary fixed level of vinyl alcohol content. The boundaries between the miscible (open triangles) and immiscible (filled triangles) define the miscibility window (Figure 7) at 180°C.

It can be seen that the width of the window is not independent of the absolute composition of the PVB. It is in fact known that in some cases the critical composition and the interaction parameter are composition dependent^{21,22}.

The miscibility window in blends, particularly in the case of mixing of random copolymers, is often considered to be a function of the surface area of the interacting segments¹⁶. A composition dependence of $\chi_{A,B}$ may therefore in principle arise from the differences in size and shape of the interacting segments A and B. It should be noted that the difference in the size of VA (specific volume 33.6 cm³/mol) and VB groups (specific volume 134cm³/mol) is comparatively large and the average segment size of the copolymer PVB is therefore dependent on the composition of PVB. We have shown¹⁰ that, as a general principle, for random copolymers blended with either a second random copolymer or a homopolymer, intramolecular repulsion will lead to miscibility if the repulsion between dissimilar segments in the copolymer is sufficient to overcome the repulsion between these segments and those in the second component of a mixture.

The Interaction Parameter $\chi_{VA,VB}$

From equation 4 the interaction parameter $\chi_{VA,VB}$ was calculated. The results (Table 2) and the miscibility boundary determined from a least-squares fit are shown in Figure 7. Estimations of the miscibility of PVB/PVB blends using a group additive model^{12,23,24} compare well with the experimental results.

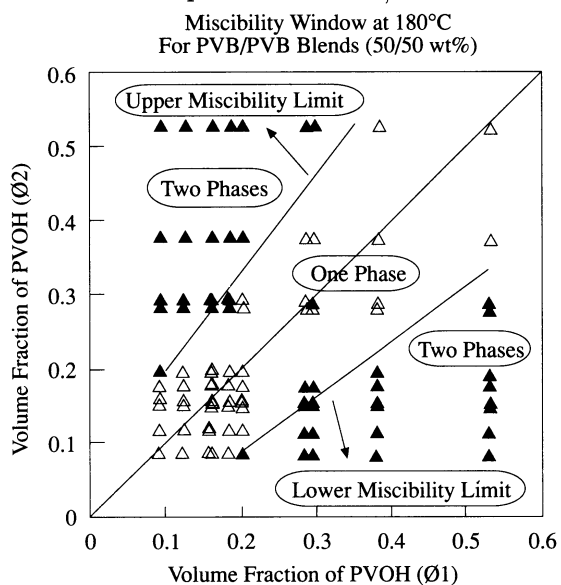
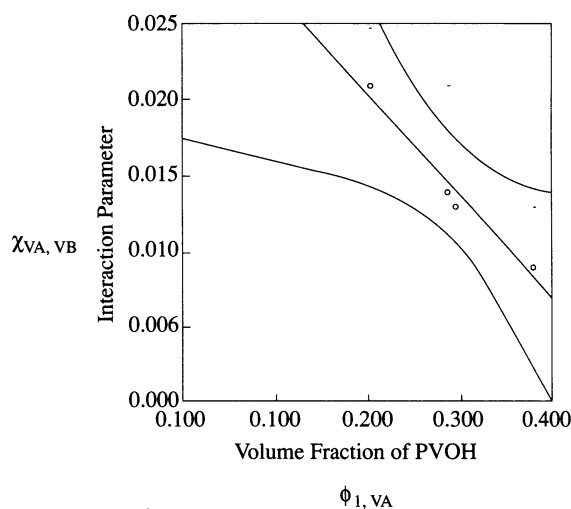
Table 2. Miscibility Data and Interaction Parameters, $\chi_{VA,VB}$, of PVB Blends at 180 °C

	$\theta_{1,VA}$	N	$\theta_{2,VA}^{UML}$	X_{cr}	$\theta_{2,VA}^{LML}$	$\chi_{VA,VB}$
1	0.091	1000	0.191	0.0015	—	—
2	0.122	2000	—	0.0010	—	—
3	0.157	2000	—	0.0010	—	—
4	0.161	2000	0.272	0.0010	—	—
5	0.181	2000	—	0.0010	—	—
6	0.183	2000	—	0.0010	—	—
7	0.200	2000	0.325	0.0010	0.106	0.021
8	0.284	2000	0.443	0.0010	0.172	0.014
9	0.293	2000	0.456	0.0010	0.179	0.013
10	0.379	2000	0.577	0.0010	0.239	0.009
11	0.530	2000	—	0.0010	0.344	—

Nomenclature

- $\theta_{1,VA}$ = volume fraction of vinyl alcohol for PVB 1
 $\theta_{2,VA}$ = volume fraction of vinyl alcohol for PVB 2
 N = DP of parent polyvinyl alcohol
 $\theta_{2,VA}^{UML}$ = upper miscibility limit
 $\theta_{2,VA}^{LML}$ = lower miscibility limit
 $X_{VA,VB}$ = interaction parameter

The $\chi_{VA,VB}$ values listed in Table 2 are plotted in Figure 8 together with the boundaries displaying 95 % confidence level limits. This curve ($R^2 = 0.966$) shows that the compositional heterogeneity affects the miscibility window at low vinyl alcohol contents differently from at higher vinyl alcohol contents. The value of the interaction parameter $X_{VA,VB}$ reflects this (Table 2).


Figure 7. Miscibility window (at 180 °C) of PVB/PVB blends (50/50 wt %)

Figure 8. Copolymer composition dependence of the interaction parameter $\chi_{VA,VB}$ as a function of volume fraction of vinyl alcohol in polyvinyl butyral

As is seen above, the formation of each vinyl butyral unit consumes two vinyl alcohol groups. It may be noted that we therefore need to define the degree of polymerization, N , of the modified polymer. Since the choice is arbitrary, we have defined N as the original DP of the parent PVA polymer since the contour length of the polymer chain was not changed as a result of acetalization. In fact, alternative estimation of χ_{cr} , taking into account that the formation of the vinyl butyral groups consumed two vinyl alcohol groups did not affect the absolute values of $\chi_{VA,VB}$ within the error of the measurement (∓ 0.01 units).

The composition dependence of $\chi_{VA,VB}$ shown in Figure 8 can be attributed to the following factors: 1) the size difference of the interacting segments of PVB; 2) volume changes upon mixing²⁵⁻²⁷, since stronger hydrogen bonding may reduce the free volume of mixing when vinyl alcohol content is increased; and 3) the different shapes and accessibilities of the interacting segments of PVB as the vinyl alcohol content is changed.

Conclusions

The results show that the glass transition temperature of PVB correlates with vinyl alcohol content, and that the thermal stability of PVB is significantly improved with decreasing VA content. For PVB/PVB copolymer blends, a widening in the miscibility window with increasing vinyl alcohol content of PVB was experimentally observed and the composition dependent interaction parameter of VA with VB units was calculated.

Acknowledgment

We gratefully acknowledge the Corporation of the Monsanto Co. who generously contributed analytical help and support, and particularly to Mr. Charles Ferrante. We would also like to acknowledge the support of the Center for University of Massachusetts Industry Research on Polymers and (FEK) for support from AFOSR Grant No. 97-01.

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