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Abstract. The positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC) techniques were utilized to study high-vinyl polybutadiene (HVBD)/*cis*-polyisoprene (CPI) blends. A single DSC glass transition temperature T_g is observed, whose composition dependence strongly deviates from additivity, showing an apparent cusp when the weight fraction of HVBD $\sim$0.75. The orthopositronium (o-Ps) intensities, I_3, and lifetimes, τ_3, obtained from PALS were used to determine the free-volume hole size, V_h, and the scaled fractional free volume, $h_{ps}/C = I_3 V_h$. In the glass, V_h and h_{ps}/C are smaller for CPI than for HVBD, but the thermal expansion coefficient for the hole volume, α_f, is larger for CPI than for HVBD in the melt; thus, an iso-hole-volume temperature occurs in these blends at $T_{iso} \sim -34\ ^\circ$C. Using free-volume quantities obtained from PALS, a quantitative interpretation of the cusp in the composition dependence of T_g can be obtained, via a modified version of the analysis of Kovacs, from which we assume that the free volume of the high-T_g component becomes constant. Specific volume analysis was also performed on the pure materials, from which the fractional free volume at room temperature, and hence the values of the scaling constants C_{CPI} and C_{HVBD}, are obtained. This enables us to determine that the free volume of the high-T_g component 'freezes in' at a particular value intermediate between those of the pure components at their respective T_gs

1. Experimental procedure

1.1. Materials

Following the procedure of Stearns and Forman [4], a high *cis*-1, 4-polyisoprene (99%), with $M_w = 933\,000$, was prepared. High-vinyl polybutadiene (79% vinyl, 10% *cis*- and 11% *trans*-structure), with $M_w = 465\,500$, was prepared following the procedure of Halasa *et al* [5]. The chemical structures of CPI and HVBD are shown in figure 1.

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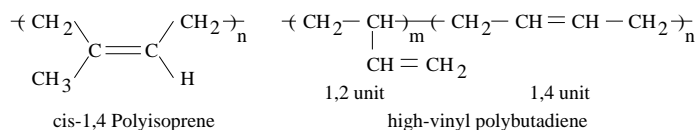
Figure 1. The chemical structures of the homopolymers used in this study.

1.2. Differential scanning calorimetry

The glass transition temperatures of the homopolymers and blends were determined using a differential scanning calorimeter at a heating rate of 10 °C min^{-1}. Each DSC testing cycle consisted of heating, cooling, and repeating scans. The first heating scan provides a rough estimate of T_g. The samples were next annealed at 150 °C for 30 minutes. The final heating scan was performed immediately after rapid cooling (10 °C min^{-1}) from the annealed state. T_g for the sample was determined from the final scan as the mid-point of the transition zone. Selected experiments at slower cooling rates (1 °C min^{-1}) showed no significant change in T_g. To estimate the change in heat capacity associated with the glass transition, modulated DSC analysis was performed, in which a small modulation is superposed on the heating rate (mean heating rate: 5 °C min^{-1}; modulation: ± 1 °C per 80 s).

1.3. Positron annihilation lifetime spectroscopy

A fast–fast coincidence system having a time resolution of 230 ps was utilized for the positron annihilation experiments. This system has been described in detail elsewhere [6–9]. For each polymer studied, two identical samples were sandwiched around a 30 μCi ^{22}Na source which was then placed in the measurement chamber with a vacuum of about 10^{-3} mbar^{-1}.

The program PATFIT [10] was employed to determine the positron lifetimes and intensities. The positron annihilation spectra were fitted to three exponentially decaying lifetime components and the variances of the fits were smaller than 0.12. The short-lived component with a lifetime $\tau_1 = 125$ ps and the intermediate-lifetime component with a lifetime $\tau_2 = 350$–400 ps are attributed to p-Ps and free-positron annihilation, respectively. The longest-lifetime component, which is very sensitive to the structural changes in the polymer, arises from pick-off annihilation of o-Ps in the free-volume holes of the polymer matrix. We point out that, as is common in many studies in the literature, the measured intensities of the p-Ps (I_1) and o-Ps (I_3) components do not agree with the predicted ratio $I_1 = I_3/3$ for all of our experimental spectra. This is attributed to the inadequacy to resolve the short p-Ps lifetime component from free-positron and positron–molecule complexes.

The influence of prolonged exposure to positron irradiation has been previously reported for HVBD, CPI, and the 50/50 blends [1], along with a procedure for minimizing its effect on the o-Ps parameters. Following this procedure, all of the PALS measurements below -10 °C were performed after first annealing the sample at room temperature for 30 minutes, and then cooling to the measurement temperature.

2. Results and discussion

2.1. T_g-values of HVBD/CPI blends

The glass transition was determined by thermal analysis (DSC), which indicates a single transition as shown in figure 2. This is expected due to the well known miscibility of
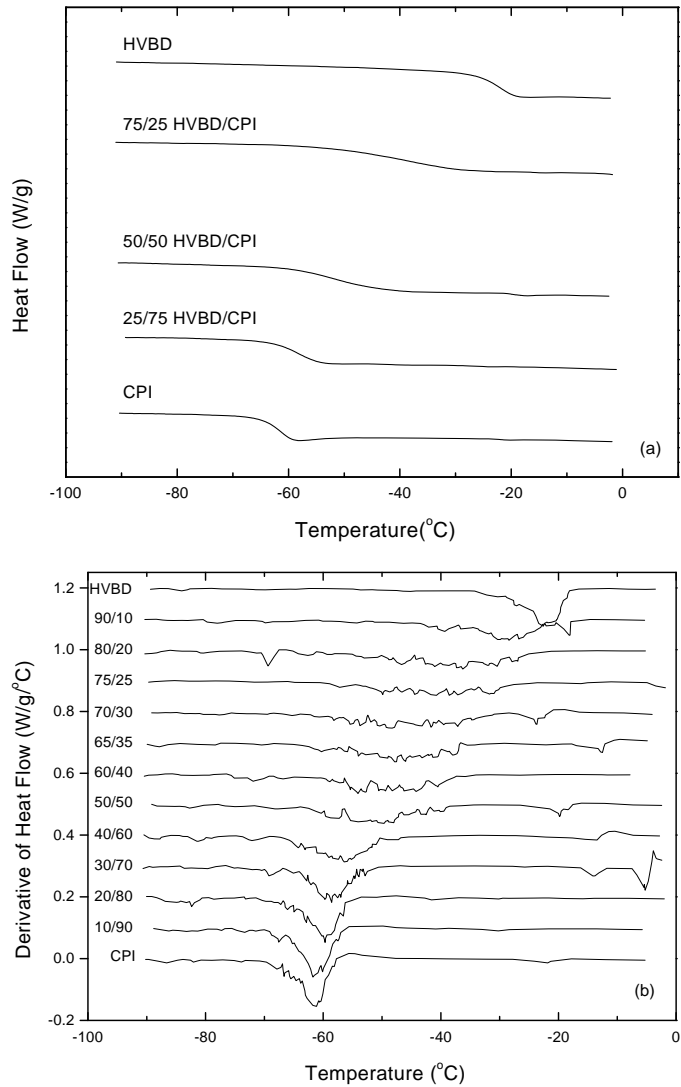
Figure 2. DSC measurements of the pure polymers, HVBD and CPI, and several blends showing the (a) heat flow and (b) derivative of the heat flow.

HVBD/CPI blends. The blends have a transition range which is noticeably broadened, as compared to that for the pure polymers; this is most probably a consequence of heterogeneities in the local concentration [11–13]. In figure 2(b) the derivative of the heat flow is shown for most of the blend compositions studied; the results indicate an asymmetry in the composition dependence of the broadening of the transition region consistent with previous observations [24, 23]. The glass transition temperatures determined from the inflection point of the heat flow curve, as a function of blend composition, are shown in figure 3.

The glass transition temperatures of the blends are seen to be between those of the homopolymers; they also exhibit an asymmetry in the form of a 'cusp' at about 75% HVBD. Such cusps have been reported previously for various blend systems [14], and
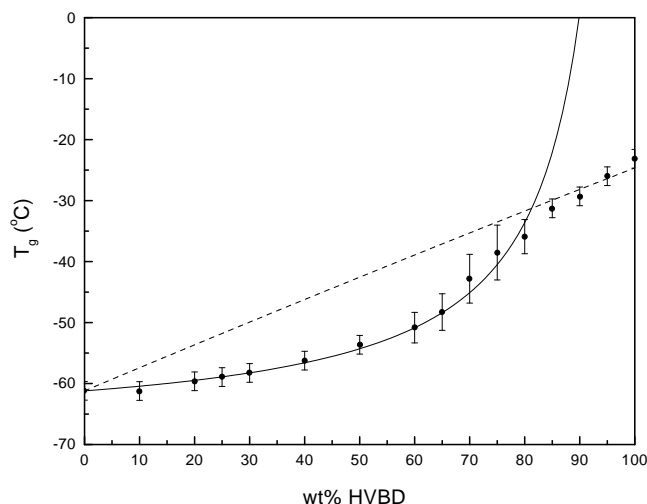
Figure 3. DSC T_g-values (●) as a function of composition obtained with modified Kovacs (——) and Kelley–Bueche, $k = 1.04$ (- - - -) procedures as derived from specific volume and PALS measurements.

have been interpreted using free-volume arguments [15]. The broadening of the transition region at about 75% has been interpreted in terms of different molecular mobilities of the blend components, which can be viewed in terms of distinct effective T_g-values for each species [23].

The glass transition temperature behaviour of miscible blends is commonly analysed using the Gordon–Taylor equation [16]

$$T_g = \frac{w_1 T_{g,1} + k w_2 T_{g,2}}{w_1 + k w_2} \tag{1}$$

where w_1 and w_2 are the weight fractions of the blend components, $T_{g,1}$ and $T_{g,2}$ the corresponding glass transition temperatures, and k is an adjustable parameter. From figure 3, it is clear that the DSC T_g-values of the blends exhibit strong negative deviation from additivity, i.e., equation (1) with $k = 1$.

The best fit to the Gordon–Taylor equation, with $k = 0.36$, gives calculated T_g-values which are too large for compositions less than 75% HVBD, and underestimates T_g for richer HVBD compositions. This is a direct consequence of the asymmetry in the dependence of T_g on the composition. A theoretical analysis by Couchman [17], assuming that $T_{g,1}/T_{g,2} \simeq 1.0$, predicts a composition dependence of T_g which is similar in form to that of Gordon and Taylor, in which k is expressed as the ratio of the heat capacities of the high- and low-T_g components: $k = \Delta C_{p2}/\Delta C_{p1}$. Modulated DSC analysis determines $\Delta C_p(\text{CPI}) = 0.52$ J g^{-1} K^{-1}, and $\Delta C_p(\text{HVBD}) = 0.42$ J g^{-1} K^{-1} which gives a value, $k = 0.81$, also inconsistent with the data in figure 3. Due to the large discrepancy between the calculated experimental T_g-values, a theoretical analysis, which explains the existence of a 'cusp', is required.
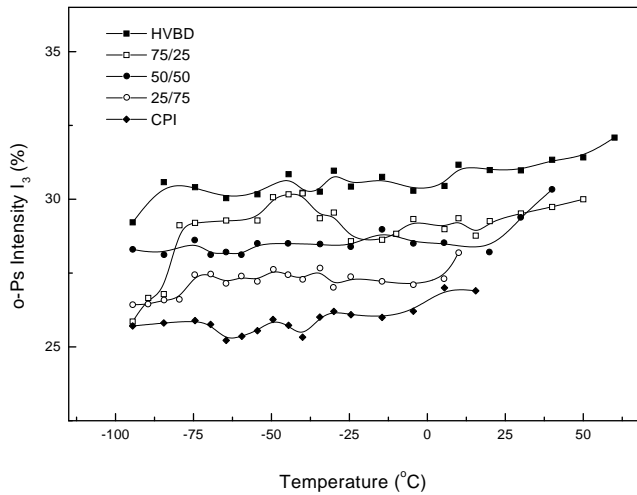
Kelley and Bueche [18] have derived an expression of the Gordon–Taylor form employing assumed additivity of free volumes at all temperatures:

$$h_{\text{blend}} = w_1 h_1 + w_2 h_2 \tag{2}$$

where w_1 and w_2 are the weight fractions of each component in the blend. Assuming a
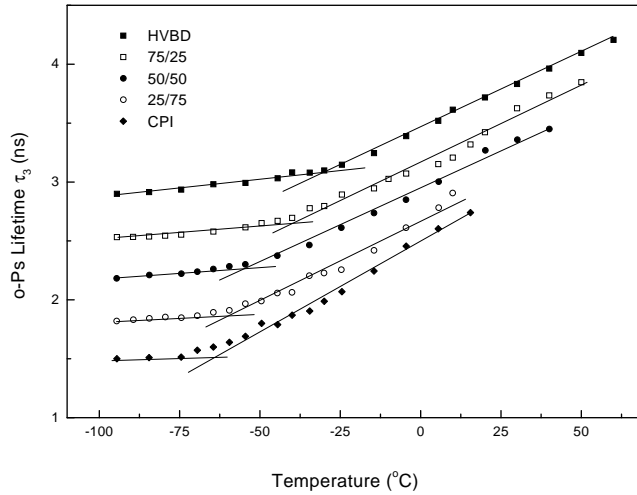
(a)

(b)

Figure 4. The temperature dependence of the o-Ps parameters (a) τ_3 and (b) I_3 encompassing both the glassy and melt states of several HVBD/CPI blends. The τ_3-values are successively shifted up by 0.3 ns from those of CPI.

linear dependence of the constituent free volumes on temperature in the melt,

$$h_i = h_{i,g} + \alpha_{h,i}(T - T_{i,g}) \tag{3}$$

and, at the blend T_g,

$$h_{\text{blend},g} = w_1 h_{1,g} + w_2 h_{2,g}. \tag{4}$$

An expression of the form of (1) is derived such that k is given by the ratio of the thermal expansion coefficients for the free volume of each constituent in the melt, $k = \alpha_{h,2}/\alpha_{h,1}$. Furthermore, the appearance of a cusp in the composition dependence of T_g has been explained by Kovacs [15] on the basis that, following a temperature dependence of the form of (3), the free volume of the high-T_g component becomes zero on cooling the blend

Table 1. The composition dependence of the free-volume parameters and T_g for HVBD/CPI blends.

HVBD:CPI	T_g (°C)	α_f (Å^3 °C^{-1})	α_h/C (Å^3 °C^{-1})	$h_{ps,g}/C$ (Å^3)
0:100	−61.2	1.54	43.01	1449.89
10:90	−61.2			
20:80	−59.6			
25:75	−58.9	1.34	37.21	1864.85
30:70	−58.3			
40:60	−56.2			
50:50	−53.9	1.25	36.37	1965.52
60:40	−50.8			
65:35	−48.3			
70:30	−44.3			
75:25	−38.0	1.32	40.18	2378.62
80:20	−35.9			
85:15	−31.3			
90:10	−29.3			
95:5	−26.0			
100:0	−23.1	1.23	40.24	2648.07

at the cusp composition, prior to the onset of T_g, at which point the applicability of an expression of the Gordon–Taylor type fails.

Specifically, Kovacs assumed additivity of free volumes in the melt and at T_g, i.e. (2) and (4), and also that the free volumes of individual blend components follow (3). Kovacs [15] further postulated that the free volume of the high-T_g component becomes zero at a temperature, T_∞, at which the blend is still in the melt. Equations (2)–(4) can then be combined to give

$$T_g = T_{g,1} + \frac{w_2}{w_1 \alpha_{h,1}} h_{2,g} \tag{5}$$

which is valid for compositions below that of the cusp, i.e. CPI-rich blends. This theoretical model has been subjected to experimental test using the PALS technique, as described below.

2.2. o-Ps measurements of the free volume

The temperature dependence of the o-Ps parameters for several blends and the homopolymers is shown in figure 4. Typical temperature variation of the o-Ps lifetime is observed, with a sharp change in the slope at a temperature indicating the transition between glassy and melt states, while the intensity is only weakly dependent on temperature. This is consistent with theoretical predictions where τ_3 is considered to be a measure of the free-volume size and I_3 a concentration of the free volume. A semi-empirical equation relating τ_3 to the free-volume hole size is given by [3]

$$\tau^{-1} = 2\left(1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right)\right) \tag{6}$$

where the hole boundary layer thickness is $\Delta R = R_0 - R = 0.1656$ nm. Assuming a spherical cavity of free volume, $\langle V_f \rangle = (4/3)\pi R^3$, the fractional free volume can be determined from [7, 2]

$$h_{ps} = C I_3 \langle V_f \rangle \tag{7}$$

where C is a scaling constant that reflects contributions to the probability of o-Ps formation that do not depend on the free volume. The DSC T_g and PALS-derived thermal coefficients, $\alpha_f = \mathrm{d}V_f/\mathrm{d}T$, $\alpha_h/C = C^{-1}\,\mathrm{d}h/\mathrm{d}T$, and the scaled fractional free volumes at T_g, $h_{ps,g}/C$, are shown in table 1. Figure 5 shows the hole size and fractional free volume at several temperatures, as a function of temperature. The dashed lines represent the values expected on the basis of an additivity relation. For all temperatures, the free volume shows a negative deviation from additivity, except at $T \sim -34.5$ °C where an iso-free-volume condition exists. This is consistent with previous observations of Liu *et al* [25], where a negative deviation from additivity of the PALS free volume in the miscible blends of polystyrene and tetramethyl-bisphenol A polycarbonate was found. The DSC T_gs for compositions at the cusp value and above are all in the vicinity of the iso-free-volume temperatures, implying that an additivity relation holds approximately for these compositions.

We attempted to fit the T_g-data to (1) with $k = \alpha_{h,2}/\alpha_{h,1}$ at compositions above that of the cusp and simultaneously to (5) at compositions below the cusp with a single value of the ratio of the scaling constants, C_2/C_1. However, a self-consistent fit of the PALS and T_g-data, above and below the cusp composition, could not be achieved in this way.

Therefore, we are led instead to make the proposal, consistent with spectroscopic evidence that each blend component has its own effective T_g, that the free volume of the high-T_g component 'freezes in' at a finite value h_2' which lies between the values $h_{2,g}$ and $h_{1,g}$. Equations (2)–(4) can then be expressed, following analysis identical to that of Kovacs, in the form

$$T_g = T_{g,1} + \frac{w_2}{w_1 \alpha_{h_1}}(h_{2,g} - h_2'). \tag{8}$$

In earlier work [1], we assumed that $h_2' = h_{1,g}$, i.e. that the free volume of component 2 in the blend cannot fall below the value at which component 1 has its glass transition, so that (8) leads to

$$T_g = T_{g,1} + \frac{w_2}{w_1 \alpha_{h,1}}(h_{2,g} - h_{1,g}) \tag{9}$$

which is applied to compositions below the cusp. A satisfactory interpretation was obtained by carrying out simultaneous fits of the compositions below the cusp to (9) and those above it to (1) of the Kelley–Bueche form with a fitted value of $C_2/C_1 = 0.67$ (see figure 1(b) in reference [1]).

More recently, however, we performed specific volume measurements on HVBD and CPI. The measured specific volumes at $T = 24.5$ °C are $V_{\mathrm{CPI}} = 1.1147$ and $V_{\mathrm{HVBD}} = 1.1219$ cm^3 g^{-1}. The fractional free volume can be defined as

$$h = \frac{V - V_{occ}}{V} \tag{10}$$

where the occupied volume is expressed in terms of the van der Waals volume [21, 22], $V_{occ} = 1.3V_w$. Equating this to the fractional free volume found from PALS at $T = 24.5$ °C, values for C_1 and C_2 can be determined:

$$C_i I_3 \langle V_f \rangle = \frac{V_i - V_{occ,i}}{V_i}. \tag{11}$$

The calculated values of the scaling constants are $C_1 = 3.7 \times 10^{-3}$, and $C_2 = 4.1 \times 10^{-3}$ which gives an experimental value $C_2/C_1 = 1.11$. This is quite different from the fitted ratio of 0.67 determined above. Using the experimental value of C_2/C_1, the composition dependence of the DSC T_gs can be fitted to equations (8) and (1) leading to an estimate of $h_2' = 0.096$, which lies between the fractional free volume of the two homopolymers

(a)

(b)
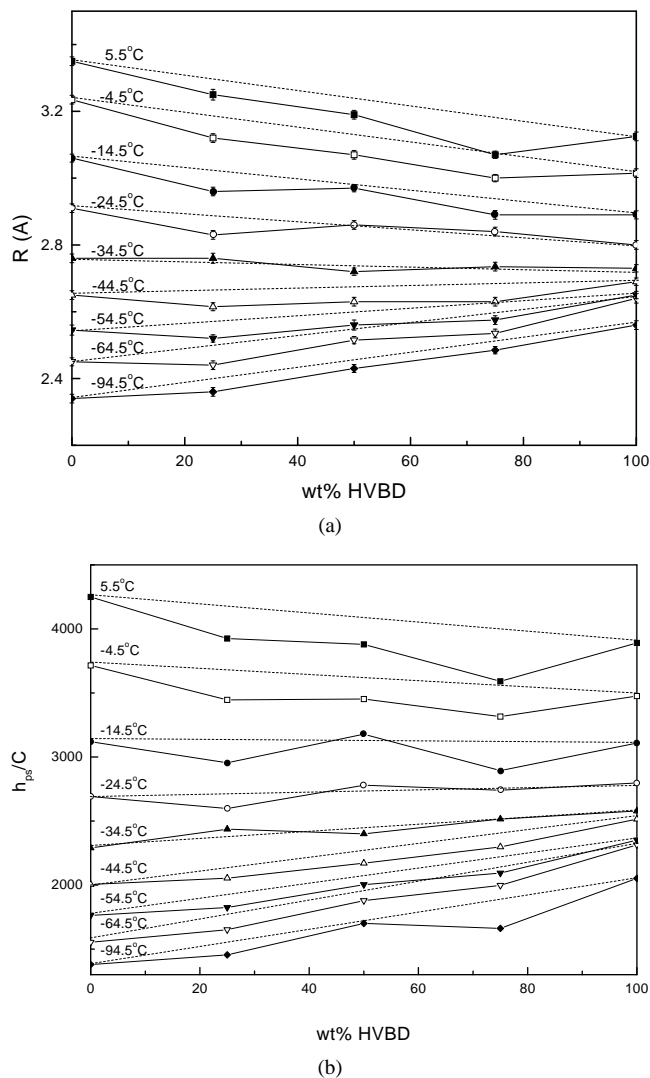
Figure 5. The composition dependence of the free-volume parameters (a) hole radius and (b) scaled fractional free volume, $h_{ps}/C = I_3 \langle V_f \rangle$.

at their respective T_gs, $h_{g,1} = 0.062$ and $h_{g,2} = 0.115$. The corresponding fit is shown in figure 3.

3. Conclusions

PALS, DSC, and specific volume measurement analyses have been used to study the miscibility of HVBD/CPI blends. DSC analysis shows a composition dependence of T_g which exhibits negative deviation from an additivity relation, with the presence of an apparent cusp between 75% and 80% HVBD content. Using free-volume parameters determined from PALS, we tested a theoretical prediction of the cusp effect proposed by Kovacs. A self-consistent fit of experiment and theory could not be achieved. A modified

version of the Kovacs model was therefore developed which seems more consistent with physical intuition. Using the modified Kovacs analysis, with free-volume parameters derived from PALS and specific volume analyses, a satisfactory description of the DSC T_g-values can be obtained, with no adjustable parameters.

Acknowledgment

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