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Polymer 44 (2003) 1921–1926

polymer

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Free volume in two differently plasticized poly(vinyl chloride)s: a positron lifetime and PVT study

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Received 6 January 2003; received in revised form 6 January 2003; accepted 23 January 2003

Abstract

The temperature dependence of the specific volume, V, and of the mean size of local free volumes (holes), v_h, of poly(vinyl chloride) containing 10 wt% (PVC-h) and 30 wt% (PVC-s) of the plasticizer di-*n*-butyl phthalate (DBP) were studied by pressure–volume–temperature (PVT) and positron annihilation lifetime spectroscopy (PALS) experiments. Using the Simha–Somcynsky equation-of-state, the hole fraction h was calculated from the PVT data. It was found that the thermal expansivity of the specific volume V, the specific free volume $V_f = hV$, and v_h increase with the content of plasticizer. From the comparison of V and V_f with v_h the hole number per gram N'_h is estimated. Other than v_h, N'_h does not depend on the temperature nor on the content of plasticizer.

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Keywords: Specific volume; Free volume; Positron annihilation

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1. Introduction

Positron annihilation lifetime spectroscopy (PALS) provides unique information about the properties of subnanometer size local free volumes (holes) appearing due to the structural (static or dynamic) disorder in amorphous polymers [1]. The holes form the (excess) free volume which effects thermal, mechanical, and relaxation properties of polymers. While PALS itself is only able to measure the mean volume, v_h, and the size distribution of these holes, the combination of PALS with the macroscopic volume, for example from pressure–volume–temperature (PVT) experiments, allows the number of holes and their entire volume fraction to be estimated [2–4]. In this way, all parameters of free volume, at least from volumetric point of view, can be determined.

In the current work we studied, using PALS, the mean size of local free volumes in two types of poly(vinyl chloride) (PVC) containing different amounts of plasticizer. PVT experiments were performed and analysed by using the Simha–Somcynsky (S–S) equation of state (eos) (see Refs. [5,6] and references given therein). From our experiments we estimated characteristic parameters of the free volume, such as the S–S eos hole fraction, the specific free volume, the mean hole size, and the number density of holes. The main aim of our work is to study the temperature dependence of these parameters in PVC and the effect of plasticizer on them.

2. Experimental

2.1. Materials

The materials under investigation were two different types of PVC both supplied by Chemische Werke Buna-Schkopau/Germany (now European Vinyl Corporation). The samples denoted by PVC-hard (PVC-h) and PVC-soft (PVC-s) have molecular weights of $M_w/M_n = 150,000/65,000$ (g/mol) and $M_w/M_n = 193,000/89,500$ (g/mol) determined by GPC using PS standards for

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doi:10.1016/S0032-3861(03)00056-9

calibration and contain 10 or 30 wt% of the plasticizer di-*n*-butyl phthalate (DBP), respectively. The content of plasticizer was determined using a coupled system of a thermo-balance (Q-50, TA-Instruments) and a gas detection cell equipped with a FTIR spectrometer (FTS 7000, Digilab). The hardness and the elasticity modulus E (three-point bending corresponding to ISO 178) of PVC-h have been determined to be 77 Shore D and $E = 2430 \pm 280\ \mathrm{N/mm^2}$, respectively, the corresponding values of PVC-s are 34 Shore D and $E = 23.6 \pm 4\ \mathrm{N/mm^2}$. Glass transition temperatures of $T_g = 345$ K (PVC-h) and $T_g = 281$ K (PVC-s, Table 1) were determined using the differential scanning calorimetry (DSC 7, Perkin Elmer, Pyris-software Version 3.51, heating rate of 40 K/min, half-step method for the second heat). The densities at 300 K were determined to be $\rho = 1.393\ \mathrm{g/cm^3}$ (PVC-h) and $\rho = 1.291\ \mathrm{g/cm^3}$ (PVC-s) by means of an Ultrapycnometer 1000 (Quantachrome) with an accuracy of 0.001 cm^3/g. For our investigations, the PVC materials supplied as granulate were compressed into 1 mm plates at 180 °C (PVC-h) and 160 °C (PVC-s), respectively, at a pressure of 10 MPa, followed by a cooling down to room temperature at a rate of approximately 10 K/min.

2.2. PVT experiments

The PVT experiments were carried out by means of a fully automated GNOMIX high pressure dilatometer [7]. The data was collected in the range from room temperature to 180 °C in steps of 10 K. At every constant temperature the material was pressurized from 10 to 200 MPa. The specific volumes for atmospheric pressure were obtained by extrapolation of the values for 10–30 MPa in steps of 1 MPa according to the Tait equation using the standard GNOMIX PVT software. The accuracy is within 0.002 cm^3/g.

Table 1
Glass transition temperature T_g and volume parameters (see text) of PVC containing 10 wt% (PVC-h) and 30 wt% (PVC-s) of DBP plasticizer

Quantity	Uncertainty	PVC-h	PVC-s
T_g (DSC)	±4	345	281
T_g (PALS)	±5	320	250
T_g (spec. volume)	±5	325	n.d.
ρ (300 K)	±0.001	1.393	1.291
V_g (T_g from PALS) (cm^3/g)	±0.003	0.727	~0.76
E_r (10^{-4} cm^3/g K)	±0.04	4.42	4.67
E_g (10^{-4} cm^3/g K)	±0.07	1.65	n.d.
α_r (10^{-4} K^{-1})	±0.05	6.08	~6.2
α_g (10^{-4} K^{-1})	±0.08	2.27	n.d.
h (300 K)	±0.003	0.05	0.067
h_g (T_g from PALS)	±0.005	0.066	~0.038
V_{fg} (cm^3/g)	±0.005	0.048	~0.029
E_{fr} (10^{-4} cm^3/g K)	±0.06	4.12	4.80
E_{fg} (10^{-4} cm^3/g K)	±0.1	1.55	n.d.
α_{fr} (10^{-4} K^{-1})	±0.05	5.68	~6.3
α_{fg} (10^{-4} K^{-1})	±0.1	3.13	n.d.
ν_{hg} (Å^3)	±3	110	106
e_{hr} (Å^3/K)	±0.07	0.91	0.98
e_{hg} (Å^3/K)	±0.03	0.20	0.19
α_{hr} (10^{-4} K^{-1})	±0.8	83	92
α_{hg} (10^{-4} K^{-1})	±0.2	18	18
N'_h (10^{21} g^{-1}) from V	±0.07	0.47	0.48
N'_h (10^{21} g^{-1}) from V_f	±0.07	0.46	0.47
N_h (300 K) (nm^{-3}) from V	±0.1	0.82	0.77

2.3. PALS experiments

The PALS experiments were carried out using a fast-fast coincidence system [1] with a time resolution of 238 ps (FWHM) and a channel width of 50.12 ps. The sample–source–sample sandwich (4×10^6 Bq of ^{22}NaCl on an Al foil of 2 mg/cm^2) was placed in a vacuum chamber allowing a vacuum of 5×10^{-4} Pa. For heating the samples, a small resistivity heater was used. The temperature was controlled using a Eurotherm controller with an accuracy of ±1 °C. The measurements were performed in the temperature range between 100 K and at the maximum 420 K typically in steps of 10 or 20 K. For each spectrum a total number 3×10^6 of annihilation events were collected.

After subtraction of source components and background, the parameters of the lifetime spectra $s(t)$ are obtained from a non-linear least-squares fitting of a weighted sum of three exponentials [1], $s(t) = \sum (I_i/\tau_i)\exp(-t/\tau_i)$, $\sum I_i = 1$, $(i = 1, 2, 3)$, convoluted with the Gaussian resolution function to the experimental spectra using the routine LT (version 7.0, May 2001) [8,9]. τ_i denotes the mean (characteristic) lifetime of the positron/Ps state i, while I_i is the relative intensity of the corresponding lifetime component.

In molecular materials positrons annihilate either as free positrons or from a bound state called positronium (Ps) [1]. The Ps appears either as a *para*-positronium (*p*-Ps, singlet spin state) or as an *ortho*-positronium (*o*-Ps, triplet spin state) with a relative formation probability of 1:3. The three lifetime components decomposed from the lifetime spectra are consequently attributed to annihilation of *p*-Ps ($\tau_1 \sim 180$ ps), free (not Ps) positrons ($\tau_2 \sim 400$ ps), and *o*-Ps ($\tau_3 = 1.8$–2.7 ns). In the final spectrum analysis, the *o*-Ps lifetime τ_3 was allowed to be distributed. LT7.0/distribution mode [8,9] assumes a log–normal distribution of annihilation rates, here $\lambda_3 = 1/\tau_3$. By analyzing simulated spectra, we found that this procedure replays most accurately the lifetime parameters used as input for the spectra simulation. The standard deviation σ_3 of the τ_3 distribution varies slightly with the temperature from $\sigma_3 \approx 300$ ps at 100 K to $\sigma_3 \approx 400$ ps at 420 K for PVC-h. It exhibits slightly larger values for PVC-s.

The relative intensity of the *o*-Ps annihilation, I_3, mirrors the Ps yield. Due to the high polarity of PVC, the Ps formation is strongly inhibited when being compared with hydrocarbons, for example [1–4]. With increasing temperature, I_3 increased smoothly from 4.8 to 6.0% (PVC-h) and from 6.1 to 9.0% (PVC-s), respectively. In amorphous polymers, *o*-Ps is trapped by local free volumes (holes) of the disordered structure and their size controls the *o*-Ps lifetime τ_3 in the ns-range. From τ_3 the mean size of the local free volumes, v_h, may be calculated using a semi-empirical formula [10–12]. The τ_3 distribution comes from the size and shape distribution of these holes [1].

3. Results and discussion

3.1. The specific volume

Fig. 1 (upper part) shows the specific volume V as a function of temperature in the temperature range between 290 and 450 K. A difference between heating and cooling cycles was not observed, therefore only the results from the heating cycle are shown. For PVC-h a glass transition temperature of $T_g = 325(\pm 5)$ K was estimated as the temperature where the slope of the $V(T)$ curve changes abruptly (Fig. 1). The slopes of the $V-T$ curve in the rubbery and glassy state of the polymer near T_g (the expansivities) were estimated to be $E_r = dV/dT = 4.42(\pm 0.04) \times 10^{-4}$ cm^3/g K ($T > T_g$) and $E_g = dV/dT = 1.65(\pm 0.07) \times 10^{-4}$ cm^3/g K ($T < T_g$), respectively (Table 1). These values correspond to coefficients of thermal expansion of $\alpha_r = E_r/V_g = 6.08(\pm 0.05) \times 10^{-4}$ K^{-1} and of $\alpha_g = E_g/V_g = 2.27(\pm 0.08) \times 10^{-4}$ K^{-1}. The specific volume at T_g is $V_g = 0.727(\pm 0.003)$ cm^3/g which corresponds to a ratio of $V_g/V_W = 1.55$ where $V_W = 0.468$ cm^3/g is the van der Waals volume [13]. For PVC-s only the value of E_r, $E_r = dV/dT = 4.67(\pm 0.1) \times 10^{-4}$ cm^3/g K ($T > T_g$) corresponding to $\alpha_g = E_g/V_g =\sim 6.2 \times 10^{-4}$ K^{-1} ($V_g \sim 0.76$ cm^3/g) could be estimated.

3.2. The specific free volume

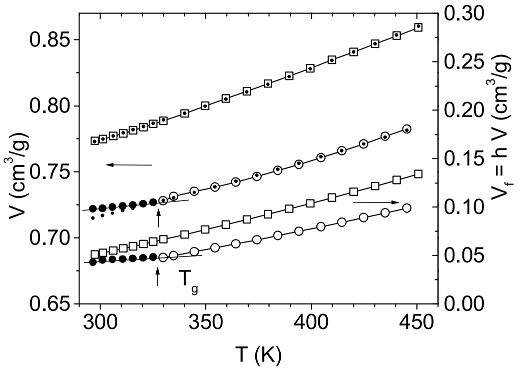

Fig. 1. Temperature dependence of the specific volume, V, and of the specific free volume, $V_f = hV$, of PVC-s (squares) and PVC-h (circles), calculated from the S–S eos hole fraction h. The solid points are fits of the equation $\ln(V/V^*) = a_0 + a_1(T/T^*)^{3/2}$ (see text) to the V data above T_g (open symbols). The lines were drawn to guide the eyes.

The specific volume data above T_g were fitted to a universal scaling relationship for the $V-T$ behavior of polymers at ambient pressure, $\ln(V/V^*) = a_0 + a_1(T/T^*)^{3/2}$ where $a_0 = -0.10346$ and $a_1 = 23.854$ are universal constants [5,6]. These fits are shown as solid points in Fig. 1. The values of the scaling parameters thus obtained are $V^* = 0.7573$ cm^3/g ($V^*/V_W = 1.62$) and $T^* = 9926$ K for PVC-s and $V^* = 0.7137$ cm^3/g ($V^*/V_W = 1.51$) and $T^* = 11{,}011$ K for PVC-h, respectively. From these parameters, the hole fraction, $h = h(V/V^*, T/T^*)$, of the Simha–Somcynsky (S–S) eos may be calculated. For calculation of the values of h at ambient pressure we used the analytical expression from the recent work of Utracki and Simha [6] which depends only on T/T^* :

$$h(T/T^*) = -0.09211(\pm 0.014) + 4.892(\pm 0.065)(T/T^*) + 12.56(\pm 0.70)(T/T^*)^2. \quad (1)$$

The values calculated in this way agree with those from Eq. (1) in Ref. [5], which was also used to calculate the hole fraction h below T_g in PVC-h using the same scaling parameters as above T_g. The values of h at 300 K and at T_g, h_g, are shown in Table 1.

The knowledge of the S–S eos hole fraction h allows to calculated the specific free volume V_f via $V_f = hV$. From the V_f vs. T curves (lower part of Fig. 1), one may derive the specific free (hole) volume at T_g, V_{fg}, the expansivities of the specific free volume, $E_{fg} = dV_f/dT(T < T_g)$ and $E_{fr} = dV_f/dT(T > T_g)$, and the corresponding coefficients of thermal expansion of the fractional free volume, $\alpha_{fg} = E_{fg}/V_g$ and $\alpha_{fr} = E_{fr}/V_g$. The results of these estimations are shown in Table 1. Since $\alpha_{fr} = \alpha_r - \alpha_{occ,r}$, it follows from $\alpha_r \approx \alpha_{fr}$ (Table 1) that $\alpha_{occ} \approx 0$ where $\alpha_{occ,r} = E_{occ,r}/V_g$ is the coefficient of thermal expansion of the fractional occupied volume, and $E_{occ,r} = dV_{occ}/dT(T > T_g)$. This conclusion differs remarkably from the conventional assumption [13], $\alpha_{fr} = \alpha_r - \alpha_g$, which is derived by assuming that $\alpha_{occ,r}$ can be approximated by α_g.

In agreement with this, the occupied volume $V_{occ,r} = V - V_f$, calculated from the S–S eos, for $T > T_g$ was found to be almost independent of the temperature. It was estimated to be $V_{occ,r} = 0.720$ cm^3/g (PVC-s) and $V_{occ,r} = 0.680$ cm^3/g (PVC-h) corresponding to $V_{occ,r}/V_W = 1.54$ and $V_{occ,r}/V_W = 1.45$, respectively. These values are larger than the traditionally accepted ratio of $V_{occ}/V_W = 1.3$ which is estimated for $T = 0$ K [13], but may be compared with the universal relationship $V_c/V_W = 1.45$ ($T = 300$ K) where V_c is specific crystalline volume [13]. These values show that the occupied volume of an amorphous polymer defined by the S–S eos contains an empty space of similar size to the interstitial free volume in polymer crystals ($V_W/V_c = 0.74$ and $V_c/V_W = 1.35$, respectively, for close packed fcc and hcp structures). The hole volume $V_f = hV$ is an excess free volume as a result of the structural (static or dynamic) disorder of the amorphous polymer.

3.3. The local free volume

The *o*-Ps lifetime τ_3 for PVC-h behaves in a similar manner to that reported previously in the literature for unplasticized PVC [14]. Fig. 2 shows the mean hole volume v_h calculated from τ_3 as a function of the temperature T for both PVC-h and PVC-s. At 100 K, v_h has values between 65 Å^3 (PVC-h) and 75 Å^3 (PVC-s). *Ortho*-Ps is trapped in local free volumes within the glassy matrix and v_h corresponds to the mean size of (pre-existing) static holes. The averaging occurs over the hole sizes and shapes. The hole volume v_h shows a slight increase with temperature which mirrors the thermal expansion of free volume in the glass due to the anharmonicity of molecular vibrations and local motions in the vicinity of the holes. In the rubbery phase, $T > T_g$, the molecular and segmental motions increase rapidly and the free volume holes obtain a dynamic character. This is observed as a steep rise in the hole size with temperature. Now v_h represents an average value of the local free volumes whose sizes and shapes fluctuate in space and time. For all temperatures the hole volume v_h in PVC-s is larger than in PVC-h. The addition of plasticizer to PVC weakens the bonds between neighbour chains which leads to an increase in the free volume. This increase in the static free volume can be observed below T_g. The larger free volume allows the segmental mobility to increase which can be observed as a lowering in the T_g and a strong increase in the hole volume above T_g. An almost linear increase in v_h with the content of different plasticizer in PVC has been observed recently [15].

At a higher, critical temperature T_k ('knee' temperature), a tendency of leveling-off of the hole volume expansion can be observed. The *o*-Ps lifetime and the hole size calculated from this does not mirror the true mean hole size anymore. Possible reasons for this behavior could be (i) The existence of Ps in self-trapped 'cage' states in the soft matrix of the polymer. (ii) Thermally exited detrapping of Ps from free volume holes. (iii) The disappearance of the dynamic and structural heterogeneity of the glass-forming system and transition to a homogeneous liquid. (iv) The structural relaxation time reaches the order of the *o*-Ps lifetime of ~2 ns leading to a smearing of holes during the life of *o*-Ps [16]. Future research may clear up this question.

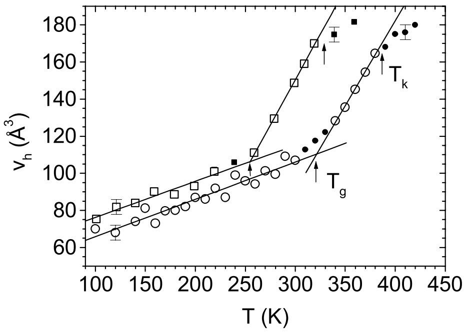

Fig. 2. The temperature dependence of the mean hole v_h of PVC-s (squares) and PVC-h (circles). The data shown by the open symbols were used for the linear fits.

The glass transition temperature, as seen via the *o*-Ps annihilation, may be determined from the intersection of two straight lines asymptotically fitted to the free-volume expansion curves in the temperature range below and above the expected T_g (Fig. 2). The values of $T_g = 250(\pm 5)$ K (PVC-s) and $T_g = 320(\pm 5)$ K (PVC-h) seem to agree with those obtained from the specific volume ($T_g = 325(\pm 5)$ K for PVC-h). The T_g values from PALS are, however, lower than the DSC midpoint temperatures of 281 K (PVC-s) and 345 K (PVC-h) by 31 and 25 K, respectively (Table 1). This discrepancy may be attributed to the different physical quantities probed by these techniques, and to the small effective heating rate in PALS of 0.3 K/min, although the differences seem to be rather large. Consolaty et al. [17] observed that the separation between the T_gs estimated from PALS and DSC increased from 6 to 40 K with decreasing molar weight of crosslinked polyurethanes. These authors speculated that PALS show a higher sensitivity for initial movements of short chain segments than DSC does.

From linear fits to the $v_h - T$ curves in the temperature range below and above T_g (see Fig. 2) the thermal expansivities, $e_{hg}(T < T_g)$ and $e_{hr}(T > T_g)$) and the coefficients of the thermal expansion of the holes, $\alpha_{hg} = e_{hg}/v_{hg}$ and $\alpha_{hr} = e_{hr}/v_{hg}$ were estimated. The results are shown in Table 1 together with the mean hole volume at T_g, v_{hg}. The α_{hr} values are larger by a factor of ~15 than those of the macroscopic coefficient of thermal expansion, α_r. From this a fractional free (hole) volume of $f_h \approx \alpha_r/\alpha_{hr} \approx 0.07$ follows from which also the number density of holes may be estimated.

3.4. The number density of local free volumes

A more accurate estimate of the number of holes per mass unit, N'_h, we may obtain by comparing PALS and PVT experiments in the following way. N'_h may be estimated from one of the relations [2–4]:

$$V = V_{occ} + V_{f0} + N'_h v_h, \tag{2}$$

$$V_f = (hV) = V_{f0} + N'_h v_h. \tag{3}$$

Here, the free volume is expressed by $N'_h v_h$, the term V_{f0} may count for a possible deviation of the mean hole volume v_h estimated from the *o*-Ps lifetime τ_3 from the true mean hole volume, v_h^{true} :

$$v_h = v_h^{PALS} = v_h^{true} + v_{h0}. \tag{4}$$

$v_h = V_h^{PALS}$ may be smaller than v_h^{true} ($v_{h0} < 0$) since the volume of stretched holes is underestimated [1] when being calculated from τ_3. It might be, however, also larger than the true average of the hole size distribution ($v_{h0} > 0$) as the result of a lower detection threshold and a possible preference of larger holes. Both effects act in opposite directions but it is not clear which sign and size the resulting effect may have. For simplicity we assume that v_{h0} is constant and not affected by the value of v_h, then also N'_h is not affected ($V_{f0} = -N'_h v_{h0}$). In principle, all values in Eqs. (2) and (3) including N'_h and V_{occ}, except V_{f0} as assumed, may vary with the temperature [2].

Fig. 3 shows the specific volume, V, and Fig. 4 shows the specific free volume $V_f = hV$, each plotted for the temperature range $T > T_g$ as a function of v_h. One observes that both V and V_f follow linear functions for the data from the temperature range $T_g < T < T_k$ (open symbols). This shows that N'_h is not a function of the temperature. Such a behavior has been observed already previously for other polymers [3,4]. From the weighted linear fits (total uncertainty of 0.003 cm^3/g from the uncertainty in V of 0.002 cm^3/g and in v_h of 3 $Å^3$; $r^2 = 0.9956$, and reduced chi-square of $\chi^2_v = 0.96$) we got $N'_h = 0.47(\pm 0.07) \times 10^{21}\ g^{-1}$ (PVC-h) and $N'_h = 0.48(\pm 0.07) \times 10^{21}\ g^{-1}$ (PVC-s). In this estimation we assumed, as it is usual, that $dV_{occ}/dv_h = 0$. The N'_hs estimated from the specific free volume V_f show the same values as those estimated from V. Allowing in Eq. (2) V_{occ} to vary linearly with v_h, we may conclude from this agreement, i.e. $dV/dv_h = dV_f/dv_h$, that $dV_{occ}/dv_h = E_{occ,r}/e_{hr} = 0$ and since e_{hr} has a finite value, $E_{occ,r} = 0$. Assuming linear variations of V, $V_{occ} V_f$, and v_h with the temperature ($T > T_g$) we may calculated the hole number density also from:

$$N'_h = (E_r - E_{occ,r})/e_{hr} \tag{5}$$

and

$$N'_h = E_{fr}/e_{hr}. \tag{6}$$

The results estimated from these relations agree within the uncertainties of the experiments with those estimated from Eqs. (2) and (3) and show that $N'_h = E_{fr}/e_{hr} = E_r/e_{hr}$ from which $E_{occ,r} \approx 0$ follows. We have concluded this already previously from the S–S eos analysis. For atactic polypropylene [18], for example, we estimated $E_{occ,r} = 0.2 \times 10^{-4}\ cm^3/g\ K$, which is distinctly smaller than the typical values of the expansivity in the glassy state, which are $E_g \approx 2 \times 10^{-4}\ cm^3/g\ K$.

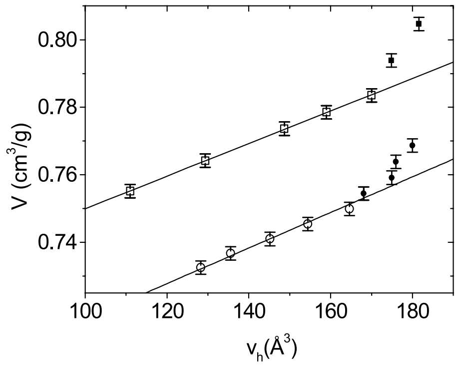

Fig. 3. Plot of the specific volume, V, for PVC-s (squares) and PVC-h (circles) vs. the hole volume, v_h. The straight lines are due least-squares fits to the data shown by open symbols.

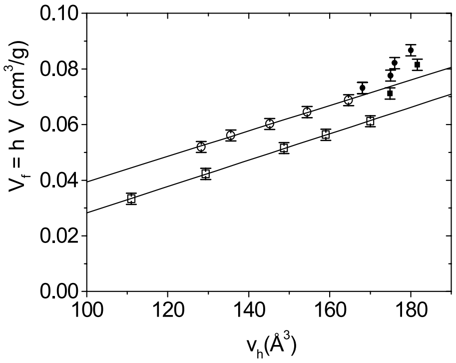

Fig. 4. As in Fig. 3, but the specific free volume, $V_f = hV$.

From the estimates $N'_h = 0.47 \times 10^{21}\ g^{-1}$ (PVC-h) and $N'_h = 0.48 \times 10^{21}\ g^{-1}$ (PVC-s) number densities of holes, $N_h = N'_h/V$, calculated for 300 K, of $N_h = 0.82\ nm^{-3}$ and $N_h = 0.77\ nm^{-3}$ follow. All of our estimates of v_{hg}, N'_h, and V_f, are in good agreement with data from the literature [3] for polymers whose T_gs are similar to those of our samples.

From the linear fits of Eq. (3) to the experimental data we obtained the constants $V_{f0} = -0.019(\pm 0.008)\ cm^3/g$ (PVC-s) and $V_{f0} = -0.006(\pm 0.008)\ cm^3/g$ (PVC-h) in agreement with the constants obtained from fits of Eq. (2), $(V_{occ} + V_{f0}) = 0.702\ cm^3/g$ (PVC-s) and $(V_{occ} + V_{f0}) = 0.672\ cm^3/g$ (PVC-h) if considering the values from the S-S eos, $V_{occ} = 0.720\ cm^3/g$ (PVC-s) and $V_{occ} = 0.680\ cm^3/g$ (PVC-h), respectively. Whilst the data for PVC-h, within the experimental uncertainty, agrees with $V_{f0} = 0$, the data for PVC-s may be interpreted as an overestimation of the true hole size by the PALS method. We must point out, however, that the estimation of V_{f0} depends very sensitively on the slopes of both, $V_f(T)$ and $v_h(T)$. Due to the small value of the o-Ps intensity I_3 in PVC, the $v_h(T)$ curve is not so accurate as for polymers with high Ps yield. Schmidt and Maurer [4] estimated recently for poly(methyl methacrylate) $V_{f0} \approx h_{f0} = 0.018$ from which an underestimation of the hole size would be concluded. Further research is necessary to clear up this question.

4. Conclusions

It was found that the glass transition temperature T_g of PVC decreases with increasing DBP plasticizer content, while the coefficients of thermal expansion of specific volume, V, of the specific free volume V_f, and of the mean local free (hole) volume, v_h, increase. The hole volume at 100 K was estimated to be 0.07 nm^3. It increases above T_g from 0.10 to ~0.18 nm^3. From the comparison of PVT and PALS data, the number density of holes was estimated to be $N_h = 0.8\ nm^{-3}$. The number of holes per gram, N'_h, does not change with the temperature nor with the content of plasticizer. This shows that the variation of the specific free volume and, in the current case also in the total specific volume, is completely controlled by the variation in the mean size of subnanometer-size local free volumes.

Acknowledgements

We like to thank H.-J. Radusch/Merseburg for supplying the samples and helpful discussions. D. Kilburn/Bristol is acknowledged for critical reading of the manuscript.

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