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Microstructure of free volume in SMA copolymers I. Free volume from Simha–Somcynsky analysis of PVT experiments

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Abstract

The structure of the free volume and its temperature dependence between 25 and 200 °C of copolymers of styrene with maleic anhydride, SMA (0–35 mol% MA), is studied by pressure–volume–temperature (PVT) experiments and positron annihilation lifetime spectroscopy (PALS). In this first part of the work, PVT data are reported which were analysed with the Simha–Somcynsky equation of state to estimate the volume fraction of holes, h, which constitute the excess free volume. The temperature and pressure dependence of the specific volume V, the specific occupied and free volume, $V_{\mathrm{occ}}=(1-h)V$ and $V_{\mathrm{f}}=hV$, and the corresponding isobaric expansivities and isothermal compressibilities for both the rubbery and glassy state are estimated. We obtained the unexpected results that (i) the occupied volume changes its coefficient of thermal expansion at T_{g} from $\alpha_{\mathrm{occ,g}}\approx 0.5\alpha_{\mathrm{g}}\approx 1\times 10^{-4}\ \mathrm{K}^{-1}$ below T_{g} to almost zero ($\approx 0.2\times 10^{-4}\ \mathrm{K}^{-1}$) above T_{g} and (ii) the isothermal compressibility of the occupied volume at zero pressure below T_{g} is rather high, $\kappa_{\mathrm{occ}}\approx 2.5\times 10^{-4}\ \mathrm{MPa}^{-1}$, and decreases only slightly at T_{g} to about $2\times 10^{-4}\ \mathrm{MPa}^{-1}$ above T_{g}. The variation of total, occupied, and free volume parameters with the composition of the SMA copolymers is discussed.

Keywords: Specific volume; Free volume; Glass transition

1. Introduction

Motion of molecules in amorphous structures is primarily governed by two physical characteristics: energy available to make a molecule move; and open space for said molecule to move into. This means that open, or free, volume is a critical parameter in determining the properties of an amorphous material that depend on molecular motion. This in fact encompasses all thermal properties, as well as any relaxations involving either localised or cooperative molecular movement [1–8]. Thus macroscopic as well as microscopic characterisation of free volume in an amorphous material is significant both for predictions of how materials will behave in a technological setting, and also a more fundamental understanding of such phenomena as the glass transition.

Experimental techniques involving the annihilation of positrons with electrons have been used for many years to investigate the microscopic nature of open volume defects (holes) in materials, with an increasing number of studies focusing on polymers [9–13]. The ‘holes’ in the case of amorphous polymers are the regions of free volume between molecules that are present due to the structural disorder. Positron annihilation lifetime spectroscopy (PALS) can be used to measure the dimensions of such holes, giving a microscopic view of the free volume. The macroscopic volume can be measured by PVT measurements [14] and, in combination with PALS data, the number of holes can be calculated [15–27].

We are currently engaged in a systematic study of the effects of reduction in mobility on the structure of the free volume. For this study we have chosen a series of copolymers of styrene (S, [–$CH_2CH(C_6H_5)-$]) and maleic

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Table 1
Characterisation of SMA copolymers

	±	PS	SMA12	SMA15	SMA25	SMA31	SMA35
mol%	0.2	0	11.8	14.5	25.3	30.9	34.7
vol%[calc]		0	7	8.7	16	20.1	23.1
wt%[calc]		0	11.1	13.8	24.2	29.6	33.4
M_w (kg/mol)	10%	394[LS]	89[ext]	73	52	54	58
M_n (kg/mol)	10%	175[LS]	46[ext]	38[ext]	27	28	30
T_g (DSC) (K)	2	377	391	403	426	439	449
δT_g (K)	1	5	6	7	7	7	7

[calc] Calculated from mol% values [32]; [LS] LS detector [26]; [ext] after processing with DACA Micro-Compounder to remove air inclusions.

anhydride (MA, [–CHCOOCHCO–]), SMA, with an MA content between 0 and 35 mol%. The SMA system is particularly suited for our study, since the MA units are expected to stiffen the molecular chain of the copolymers and therefore systematically reduce the mobility of the chains. Polysterene (PS) has been frequently studied in the literature by PALS [16,18–21,23,26,27], while for SMA only two papers presenting a series of room temperature measurements [21,28] are known to us.

In our work we have combined the study of the impact of mobility on the macroscopic nature of the free volume via PVT with the miroscopic characterisation via positron annihilation. In this paper, we present PVT experiments and determine from these, using the Simha–Somcynsky (S–S) equation of state [29–31], the hole fraction h. The temperature dependence of the specific total (V), occupied ($V_{occ}=(1-h)V$) and (excess) free volume ($V_f=hV$) are determined. We also calculate the isothermal compressibilities of the various volume components and comment on how these change with composition.

The microscopic measurements of the local free volume using PALS is presented in the second part of this work and involves hole size distribution in relation to theoretical models describing thermal volume fluctuation. From a comparison of specific total and free volumes, V and V_f, with the mean hole volume, the hole number density is estimated. Finally, we will show relations between the bulk modulus of amorphous polymers and the free volume.

2. Experimental procedure

2.1. Samples

The polystyrene (PS), free of any additives, was kindly provided by the BASF AG. The random poly(styrene-*co*-maleic anhydride)s (SMA) SMA12 and SMA15 are commercial grade products of Arco Chemicals, while the SMA25, SMA31 and SMA35 were kindly supplied by DSM Research. The characteristic data of the products are given in Table 1. The determination of the molar masses of the copolymers has been performed with a modular chromatographic equipment containing a refractive index detector at ambient temperature. 2 Zorbax PSM Trimodal-S columns have been used with DMA containing 2 vol% H_2O and 3 g/L LiCl as eluent (0.5 mL/min). The calibration was done using a random poly(propylene-*co*-maleic anhydride) standard of known molecular weight distribution. The content of the maleic anhydride units in the polymers was calculated from the sequence distribution of the triads, which was determined from the methylene ^{13}C-NMR sub-spectra. A detailed description of the method is given in Ref. [32].

2.2. DSC experiments

The DSC measurements were performed with a DSC 7 (Perkin Elmer), Pyris-software Version 3.51, in the temperature range from 10 to 200 °C. The temperature was calibrated with In and Pb standards using a heating rate of 10 K/min. The glass transition behavior was investigated in cycles of heating at a rate of 10 K/min and then cooling at a rate of 80 K/min. The heat flow of the second heating was used for analysis. The glass transition temperatures T_g were estimated by the half-step method. The broadness of the glass transition δT_g is defined as the temperature range between the intersections of the tangent of the deepest slope during the glass transition and the tangents of the slopes of the Δc_p–T-curve just above and below the glass transition. As shown in Table 1, the T_g increases with increasing MA content of the copolymers. The broadness of the glass transition δT_g is small. This indicates a rather homogeneous distribution of the MA units within the main chain.

2.3. PVT experiments

The PVT experiments [14] were carried out by means of a fully automated GNOMIX high-pressure dilatometer. The data were collected in the range from room temperature to 250 °C in steps of 10 K. At each temperature the material was pressurized from 10 to 200 MPa. The specific volumes for atmospheric pressure were obtained by extrapolating 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. The data obtained in a cooling run after the heating showed a disappearing small hysteresis to the heating data and are therefore not discussed. The densities of the samples at room temperature

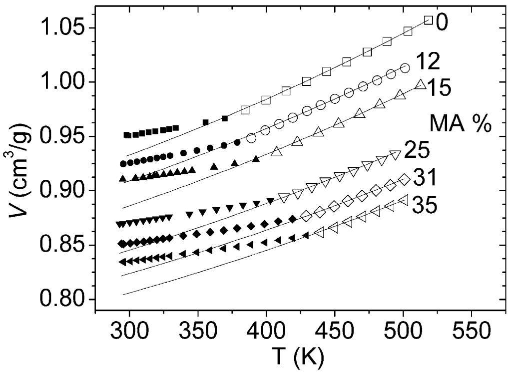

Fig. 1. The specific volume V of SMA copolymers as function of temperature T at ambient pressure. Symbols: experimental data; line: fits to the data above T_g (empty symbols) according to Utracki and Simha [31] (Eq. (4)).

were determined by means of an Ultrapycnometer 1000 (Quantachrome) with an accuracy of 0.03%.

3. Results and discussion

3.1. Specific volume

Fig. 1 shows the temperature dependence of the specific volume, V, of the SMA copolymer series at zero pressure—the pressure dependence will be discussed later. Preliminary results for PS have been discussed previously [33], results for a series of styrene-acrylonitrile copolymers can be found in Refs. [26,27]. As is usually observed for amorphous polymers, the T_g can be seen as the position where the almost-linear increase of V with temperature suddenly changes its gradient, with a higher thermal expansivity in the rubbery phase above T_g ($E_r = dV/dT$, $T > T_g$) than below in the rigid glassy phase ($E_g = dV/dT$, $T < T_g$). These expansivities for the series of materials are shown in Table 2. It can be seen that E_g and E_r decrease roughly linearly with the content of MA comonomer, $E_g = (2.2-1.8)\times10^{-4}$ cm³/g K and $E_r = (6.1-4.8)\times10^{-4}$ cm³/g K. The difference of the coefficients of thermal expansion in the rubbery and glassy state ($\alpha_r - \alpha_g$) ($\alpha_g = E_g/V_g$, $\alpha_r = E_r/V_g$), decreases slightly from 4.1 to 3.5×10^{-4} K^{-1} (Fig. 2). Table 2 also lists the volumetric T_gs determined in this way, along with the specific volume at T_g (V_g), and the van der Waals volume (V_w) of the polymers. The T_gs increase almost linearly with the content of MA comonomer and are systematically lower by about 10 K than those from DSC. This slight discrepancy may be attributed to the different physical quantities probed by these techniques, and to the specific way that the T_g is calculated as the 'midpoint' temperature of the glass transition. The increase of T_g with increasing MA content follows the relation

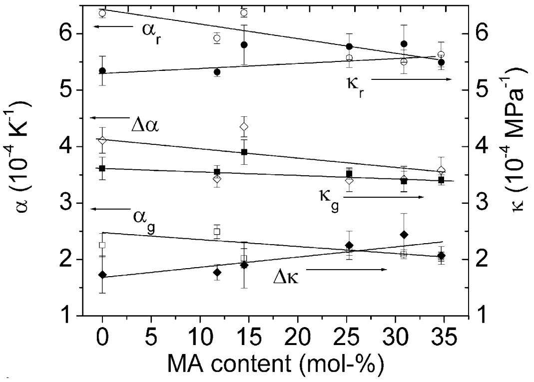

Fig. 2. Coefficient of thermal expansion α of the total volume for the glassy (subscript g) and rubbery state (subscript r) and their difference $\Delta\alpha = \alpha_r - \alpha_g$ (empty symbols), and the analogous compressibility coefficients κ_g, κ_r, and $\Delta\kappa = \kappa_r - \kappa_g$ (filled symbols) as a function of the content of MA comonomer in SMA.

$$T_g^{\mathrm{DSC}} = 100(\pm4) + 2.07(\pm0.19)X_{\mathrm{MA}} \tag{1}$$

where T_g is given in °C and is X_{MA} the content of MA comonomer in mol%.

As shown in Fig. 3, the values of V_g show a linear decrease from PS to SMA35 which is almost parallel to the van der Waals volume, the ratio of these $V_g/V_w = 1.60 \pm 0.01$. A linear extrapolation of the equilibrium specific volume from above T_g down to 0 K leads to $V_r(0)/V_W = 1.22$ (±0.01). When using the S–S equation of state analytic

Table 2
Specific volume parameters of SMA copolymers

	±	PS	SMA12	SMA15	SMA25	SMA31	SMA35
ρ (25 °C) (g/cm³)	0.002	1.052	1.081	1.098	1.149	1.175	1.198
V_w (cm³/g)		0.6033	0.5821	0.5771	0.5574	0.5471	0.5402
T_g[a] (K)	2	373	377	396	409	426	433
V_g (cm³/g)	0.017	0.967	0.944	0.928	0.892	0.874	0.858
V_g/V_w	0.03	1.602	1.621	1.608	1.56	1.598	1.574
E_g (10^{-4} cm³/g K)	0.04	2.17	2.35	1.88	1.94	1.82	1.76
E_r (10^{-4} cm³/g K)	0.04	6.14	5.58	5.91	4.97	4.81	4.83
α_g (10^{-4} K^{-1})	0.13	2.25	2.49	2.02	2.17	2.09	2.05
α_r (10^{-4} K^{-1})	0.14	6.36	5.92	6.37	5.57	5.5	5.63
κ_g (10^{-4} MPa^{-1})	0.03	3.61	3.55	3.9	3.52	3.38	3.41
κ_r (10^{-4} MPa^{-1})	0.05	5.34	5.32	5.8	5.77	5.82	5.49

[a] T_g from specific volume (see text), and $T \to T_g$.

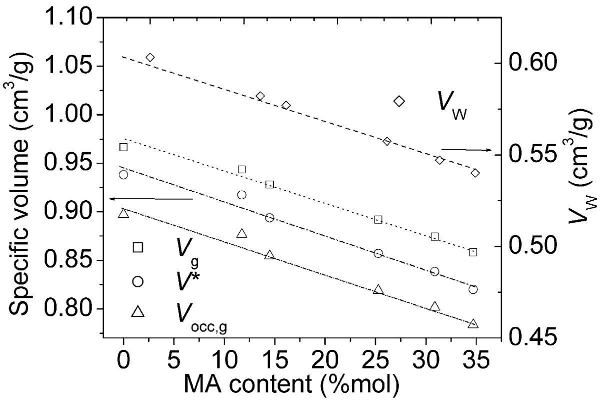

Fig. 3. Parameters of various specific volumes of SMA copolymers as a function of the content of MA comonomer. Shown are the total and the occupied volume at T_g, V_g and $V_{occ,g}$, the S–S equation of state scaling volume, V^*, and the van der Waals volume, V_W.

expression for extrapolation (see Eq. (4)) one obtains $V_r(0)V_W = 1.46$ (± 0.01). Both values can be compared with $V_r(0)/V_W = 1.3$ (Bondi [34,35]), frequently assumed as general value of the occupied volume of amorphous polymers at 0 K. We remark that the following values are constant within their uncertainties: $(\alpha_r - \alpha_g)T_g = (0.15 \pm 0.02)$ and $\alpha_r T_g = (0.24 \pm 0.01)$. All these values agree well with those found in the literature [16,36].

3.2. Free volume from Simha–Somcynsky equation of state

The S–S equation of state [29] describes a macromolecular liquid as a collection of cells of equal volume, each one of which is either occupied or unoccupied. Each cell in the occupied fraction contains the van der Waals volume of an s-mer as well as an inherent free volume. An s-mer is defined by envisioning each of the total of N molecules, each consisting of n chemical repeating units, n-mers, with molecular weight M_{rep}, as being divided into s (s is material dependent) equivalent segments (the s-mers), $sM_0 = nM_{rep}$, where M_0 is the molecular mass of an s-mer. The occupied fraction, y, consisting of sN cells, is given by $y = sN/(sN + N_h^{SS})$, where N_h^{SS} is the number of unoccupied cells. These unoccupied cells contain, as the name implies, only unoccupied space and they constitute the excess free volume in the liquid where the free, or hole fraction is defined as $h = 1 - y$.

The S–S equation of state is based on the principal of corresponding states [37], whereby a single equation of state in terms of reduced variables is valid for all macromolecular liquids. These reduced variables are $\tilde{P} = P/P^*$, $\tilde{V} = V/V^*$ and $\tilde{T} = T/T^*$. P^*, V^*, and T^* are characteristic, material-dependent scaling parameters and are related by the equation

$$(P^* V^* / T^*) M_0 = (c/s) R \tag{2}$$

R is the gas constant and $3c$ is the number of external degrees of freedom per macromolecular chain. c and s are further linked by the condition that $3c/s = 1$, meaning that each s-mer, or chain segment, has one external degree of freedom, and for general macromolecular systems it is assumed that $s \rightarrow \infty$.

The S–S equation of state then follows from the pressure equation $P = -(\partial F/\partial V)_T$, where $F = F(V, T, y)$ is the configurational (Helmholtz) free energy F of the liquid,

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = [1 - y(2^{1/2} y\tilde{V})^{-1/3}]^{-1} + y\tilde{T}[2.002(y\tilde{V})^{-4} - 2.409(y\tilde{V})^{-2}] \tag{3}$$

The occupied volume fraction y is coupled with $\tilde{T}$ and $\tilde{V}$ in a second equation derived from the minimization condition $(\partial F/\partial y)_{V,T} = 0$. It was shown that both equations may be replaced in the temperature and pressure ranges $\tilde{T} = 0.016$–0.071 and $\tilde{P} = 0$–0.35 by the universal interpolation expression (Utracki and Simha [31], also containing the values of the constants a_0 to a_5)

$$\ln \tilde{V} = a_0 + a_1 \tilde{T}^{3/2} + \tilde{P}[a_2 + (a_3 + a_4 \tilde{P} + a_5 \tilde{P}^2)\tilde{T}^2] \tag{4}$$

A similar expression is written for h in terms of $\tilde{T}$ and $\tilde{V}$ but there is presently no universal relationship for the h-function in the glassy state. Eq. (4) is useful as it gives an analytical expression, which can be fitted to experimental data in order to determine the scaling parameters for use in Eq. (3).

The S–S equation of state, Eq. (3), is derived under the general assumption of equilibrium, however the specific assumption that the free energy is a minimum, has not been made. Therefore, it is usual to calculate the h values from the specific volume below $T_g(P)$ (the pressure dependent glass transition) via Eq. (3) assuming constant scaling parameters P^*, V^*, and T^*. These values are considered to be sufficiently good approximations for conditions not too far from equilibrium [7,38–42].

Our aim from this analysis was to be able to calculate, for a given polymer, the occupied and unoccupied fractions as a function of temperature and pressure. To this aim, we carried out the following steps:

1. A nonlinear least squares fit of Eq. (4) to zero pressure volume data ($P = 0$) was carried out to determine T^* and V^*. Since Eq. (4) is valid for the rubbery phase only, we fitted in the temperature range from $T_g + 10$ °C to 250 °C. This step was performed first as the zero pressure isobar was most critical to our work, particularly for comparison with positron annihilation data (see part II of this paper), which were measured only at $P = 0$.
2. Using the values of T^* and V^* from step 1, a second fit was performed, this time using all of Eq. (4) for the measured PVT field in the ranges 125–215 °C and 0–200 MPa which allowed P^* to be calculated.
3. Solving Eq. (3) numerically using experimental PVT data and P^*, V^*, and T^* determined from the previous

Table 3
S–S equation of state parameters of SMA copolymers

	±	PS	SMA12	SMA15	SMA25	SMA31	SMA35
V^* (cm^3/g)	0.002	0.938	0.917	0.894	0.857	0.838	0.820
V^*/V_w	0.002	1.555	1.576	1.548	1.54	1.532	1.518
T^* (K)	60	11,682	11,979	11,925	12,372	12,733	12,716
P^* (MPa)	50	859	823	878	890	930	955
M_{rep} (g/mol)		104.1	103.4	103.2	102.6	102.2	102
M_0 (g/mol)	0.4	40.2	43.9	42.1	45	45.2	45
ω (Å^3)	6	60	64	60	61	60	59

two steps we were able to calculate y and therefore h at all measured temperatures and pressures. We could also calculate the specific occupied and free volume, V_{occ} and V_{f}, respectively, by simply multiplying the relevant fraction by the total specific volume.

Values for the scaling parameters are listed in Table 3. It can be seen in Fig. 1 that the scaling parameters, together with Eq. (4), give an excellent approximation to the experimental data above T_g. V^* is shown as a function of MA content in Fig. 3 and P^* and T^* are shown in Fig. 4 with varying material composition. It can be seen that V^* decreases and T^* increases linearly with MA content. As noted by Simha and Wilson [38] an increase in T^* implies a decrease in the number of effectively external degrees of freedom with increasing temperature. As the ratio c/s is assumed to be constant, this therefore requires a corresponding increase in the size of a segment, which agrees well with other indications that MA essentially stiffens the polymer chains. V^* has a constant ratio to the van der Waals volume, V_W, of $V^*/V_W = (1.54 \pm 0.03)$. This ratio is close to that found in Ref. [18] (1.57–1.60) for a different series of copolymers and can be compared with the universal relationship $V^*(\text{cm}^3/\text{mol}) = (1.45 \pm 0.01)V_W + (3.88 \pm 3.82)$ derived in Ref. [38] from a larger series of polymers.

The molecular mass of an s-mer occupying a lattice cell, M_0, and the cell volume ω at a given temperature can be estimated using Eq. (2). Our scaling parameters deliver values between $M_0 = 40.2$ g/mol (PS) and 45.0 g/mol (SMA35) which correspond to ratios of $M_0/M_{\text{rep}} = 0.39$–$0.44$. From these values a constant cell volume at T_g, $\omega_g = M_0 V_{\text{occ,g}}/N_A$ (N_A, Avogadro's number) $= 60.7$ (± 0.3) Å^3 follows.

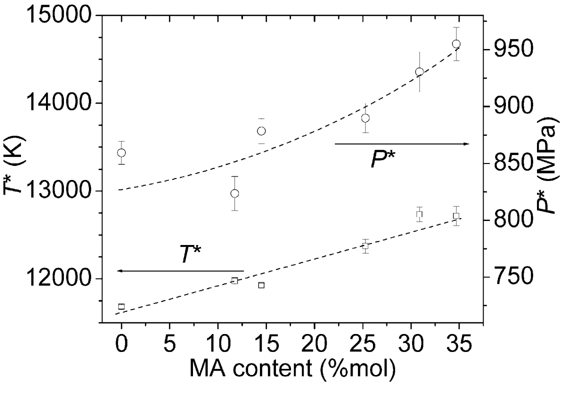

Fig. 4. The S–S equation of state scaling parameters T^* and P^* of SMA copolymers as a function of the content of MA comonomer. Lines to guide the eyes.

Figs. 5 and 6 show the results of our analysis displayed as the specific occupied ($V_{\text{occ}} = yV$) and free volume ($V_{\text{f}} = hV$). As in the S–S equation of state, we assume that the partial volumes V_{occ} and V_{f} behave additively and are exposed to the same temperature T and hydrostatic pressure P as applied externally to the sample, $V(T,P) = V_{\text{occ}}(T,P) + V_{\text{f}}(T,P)$. Under these assumptions, their expansivities and compressibilities also behave additively. The occupied and unoccupied volumes exhibit an abrupt change in expansivity at T_g, with that change being a decrease and an increase, respectively. Below and above T_g both follow a linear expansion.

Recently it was observed that the hole fraction increases from $h_g \approx 0.02$ for polymers with $T_g = 200$ K to $h_g \approx 0.08$ for polymers with $T_g = 400$ K [18,38]. Using our results, we obtain $h_g = 0.0716$ for PS and 0.0867 for SMA35 (T_gs and h_g values are given in Tables 2 and 4) which agree with this T_g dependence for h_g.

3.3. Thermal expansion and free volume

The total increase of the specific free volume V_{f} comes from the increase in N_h^{SS}, i.e. the creation of new empty cells, and to a small extent from the thermal expansion of the cells assumed to have the uniform size $\omega = V_{\text{occ}}/Ns$.

Treating the holes as (quasi-) point defects their

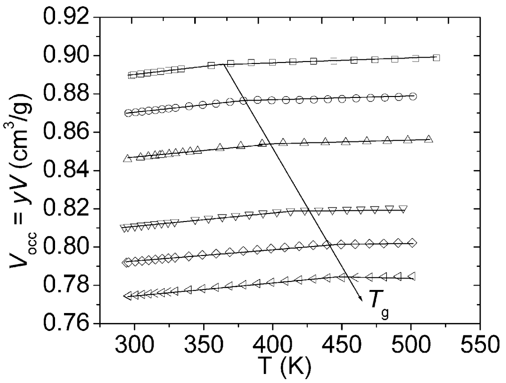

Fig. 5. The specific occupied volume, $V_{\text{occ}} = yV$, of SMA copolymers as function of temperature T at zero pressure. Symbols as in Fig. 1.

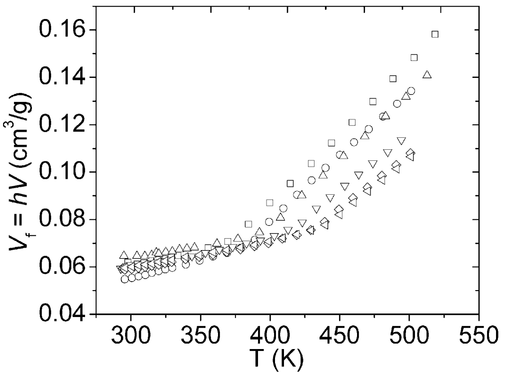

Fig. 6. The specific hole free volume, $V_f = hV$, of SMA copolymers as function of temperature T at zero pressure. Symbols as in Fig. 1.

concentration can be derived from minimizing the Gibbs free energy with respect to the hole number to be [43,44]

$$h = \exp(S_h/k_B)\exp(-H_h/k_B T) \quad (5)$$

where $h = N_h^{SS}/(Ns + N_h^{SS}) = V_f/V$ is the number of holes per lattice site, H_h is the hole formation enthalpy, S_h is the hole formation entropy, and T is the absolute temperature. An Arrhenius-plot of the h data from above T_g shows straight lines (Fig. 7) with a typical variance of 0.004 and r^2 value of 0.9997. From the slopes molar activation enthalpies can be estimated: we calculate these to be $H_h = 7.65$ kJ/mol for PS, increasing to 8.39 kJ/mol for SMA35. The fit parameters correspond to $H_h = (2.5-2.3)RT_g$, which is close to $H_h \approx 3RT_g$ estimated by Perez from calorimetric data [44], and $S_h/R = 0.867 \pm 0.003$.

We may imagine the hole creation like the formation of a Schottky defect whereby an s-mer migrates to the surface leaving an unoccupied lattice site in the internal region of the sample. For this migration to occur, the bonds between an s-mer and its neighbours must be broken and on average half of them are reconstructed at the surface. Following this reasoning the hole formation enthalpy, H_h, should correspond approximately to half of the cohesive energy. One may calculate the cohesive energy per mole lattice site from

$$E_c = \delta^2 V_{mol}(M_0/M_{rep}) = \delta^2 (M_{rep}/\rho)(M_0/M_{rep}) = \delta^2 (M_0/\rho)$$

where ρ is the density, $V_{mol} = M_{rep}/\rho$ is the molar volume of the polymer, M_{rep} is the mean molecular mass of a repeat unit, and δ is the solution parameter defined as the square root of the cohesive energy density, $\delta = (U_{mol}/V_{mol})^{1/2}$ with U_{mol} is the mean value of the intermolecular interaction energy per mol. In van Krevelen's collection [35] values of $\delta \approx 18$ and 21 J$^{1/2}$/cm$^{3/2}$ for PS and P(S-*co*-MA (34.7%)), respectively, can be found. The value for P(S-*co*-MA (34.7%)) was calculated using the group contribution method (for details see [35]). These values lead to $E_c = 12.4$ kJ/mol for PS and a mean value of $E_c = 16.0$ kJ/mol for SMA35. These energies are, as expected, close to double the values found for H_h.

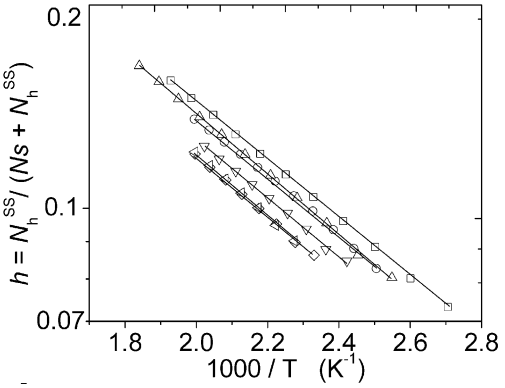

Fig. 7. Arrhenius plots of the number of empty lattice cells related to the total number of cells, $h = N_h^{SS}/(Ns + N_h^{SS}) = V_f/V$, of SMA copolymers for $T > T_g$. Symbols as in Fig. 1.

The fractional coefficient of thermal expansion of the free volume in the rubbery state of the polymer, $\alpha_{fr}* = E_{fr}/V_g$, decreases linearly with increasing content of MA comonomer from $(6.1$ to $5.2)\times 10^{-4}$ K^{-1} (not shown). This is mentioned as further evidence that the MA units have the effect of stiffening the polymer chains. As stiffened chains find it more difficult to move with respect to each other, it means that under heating conditions they cannot move apart in a relaxation of the overall structure, hence the lower $\alpha_{fr}*$.

Since the parameters of the occupied volume are not usually known, the thermal expansion coefficients are frequently approximated in the literature by $\alpha_{occ,r}* \approx \alpha_g$ and $\alpha_{fr}* \approx \alpha_r - \alpha_g$ [36]. We find, however, that α_g is greater than $\alpha_{occ,r}*$ ($\sim 2\times 10^{-5}$ K^{-1}) by approximately one order of magnitude and that $(\alpha_r - \alpha_g)$ is generally smaller than $\alpha_{fr}*$ by $\sim 2\times 10^{-4}$ K^{-1}.

From plots of $V_{occ} = yV$ vs. T expansivities and coefficients of thermal expansion of the occupied volume can be estimated, these are shown in Table 2. From our data, we obtain the ratio $V_{occ,g}/V* = 0.956 \pm 0.001$, this is denoted in the literature as $K(\tilde{T})$ [29–31] and, in reasonable agreement with us, was reported to be a constant value of 0.954.

We report a constant ratio of $V_{occ,g}/V_W = 1.47 \pm 0.02$ which is larger than the traditionally accepted ratio of $V_{occ,g}/V_W = 1.3$ (estimated for $T = 0$ K), but may be compared with the universal relationship $V_c/V_W = 1.45$ ($T = 300$ K) where V_c is the specific crystalline volume (van Krevelen [35]). Furthermore, we obtain $V_W/V_g = 0.625$ as the packing coefficient of the total volume and $V_W/V_{occ} = 0.68$ for the occupied volume. These values show that the occupied volume of an amorphous polymer defined by the S–S equation of state contains an empty space of similar size to the interstitial free volume in polymer crystals ($V_W/V_c = 0.74$ for close packed fcc and hcp structures). The hole volume $V_f = hV$ is an excess free volume as a result of the structural disorder. The result $V_{occ,g}/V_W \approx V_c/V_W$ justifies our previous judgment [45] to identify the occupied volume with the crystalline one when V_{occ} is not known for calculations of the hole density N_h' from positron annihilation.

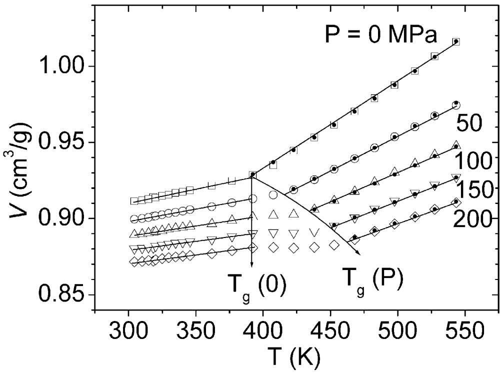

Fig. 8. Specific volume V of SMA15 as a function of temperature T and as selection of isobars (in MPa). $T_g(0)$ and $T_g(P)$ represent the zero-pressure glass transition and the glass transition temperature as a function of pressure. Open symbols: experimental data; dots: S–S equation of state fits using Eq. (4) in the range of 125–250 °C and 0–100 MPa. Lines: to guide the eyes.

3.4. Hydrostatic compression and free volume

In this section we shall discuss the results of the S–S equation of state analysis of the PVT measurements for nonzero pressure, P. As an example, Fig. 8 shows the temperature dependence of the specific volume of SMA15 at selected pressures. Fig. 9 displays the variation of the specific occupied volume, V_{occ}, with the temperature. The fractional expansivity in the glassy state, $E_{occ,g}^* \approx 1\times10^{-4}$ cm³/g K, does not change as function of pressure, but in the rubbery state it decreases from $E_{occ,r}^* = 0.2\times10^{-4}$ cm³/g K for $P=0$ to $E_{occ,r}=0$ for $P=200$ MPa.

Fig. 10 shows the variation of the specific free volume, $V_f = hV$, with temperature. V_f exhibits a linear expansion both below $T_g(0)$ and above $T_g(P)$. Between $T_g(0)$ and $T_g(P)$ it is compressed to lower values than those recorded when the glass was originally loaded for measurement. Furthermore, the expansivity of the specific total and free volume in the glassy and rubbery states decreases with increasing pressure. An Arrhenius plot of h vs. $1/T$ (Eq. (5)) gives straight lines in the temperature range above $T_g(P)$ with activation enthalpies for hole formation H_h decreasing only slightly with increasing pressure.

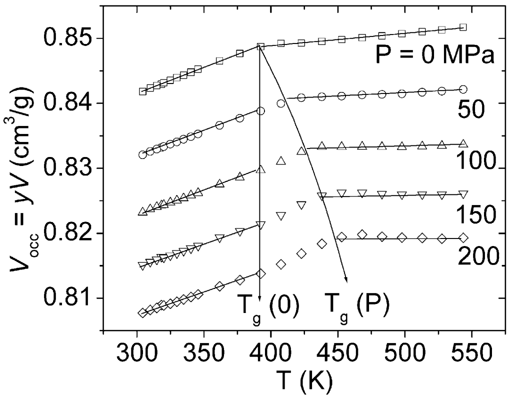

Fig. 9. As in Fig. 8, but specific occupied volume, $V_{occ} = yV$.

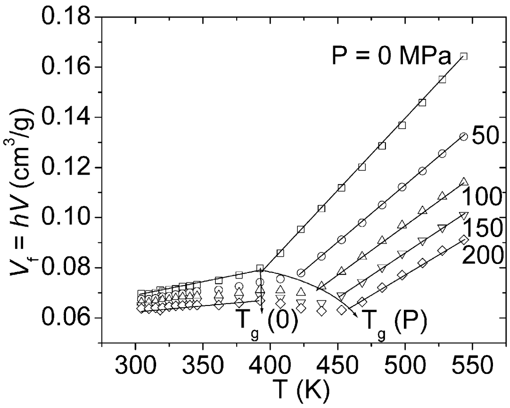

Fig. 10. As in Fig. 8, but the specific free volume, $V_f = hV$.

Figs. 11 and 12 show the isothermal compressibilities of the total, $\kappa = -(1/V)[dV/dP]_T$, occupied, $\kappa_{occ} = -(1/V_{occ})[dV_{occ}/dP]_T$, and free volume, $\kappa_f = -(1/V_f)[dV_f/dP]_T$. The compressibilities were calculated from the derivative of a third-degree polynomial fitted to the $V(P)_T$, $V_{occ}(P)_T$, and $V_f(P)_T$ data in the pressure range 0–100 MPa. The compressibility κ of PS and the SMA copolymers show a slight increase from ~ 0.25 GPa^{-1} at room temperature to ~ 0.35 GPa^{-1} at T_g, an abrupt jump to ~ 0.6 GPa^{-1} above T_g and a further continuous increase to ~ 1 GPa^{-1} at 525 K.

The compressibility κ_g ($T<T_g$, $T\to T_g$) shows a slight decrease but κ_r ($T>T_g$, $T\to T_g$) an increase with increasing content of MA comonomer (Table 2, Fig. 2), resulting in an increasing difference, $\Delta\kappa = (\kappa_r - \kappa_g)$.

The value of κ_{occ} is smaller that that of κ_g, and somewhat larger than the compressibility of crystals of PE which can be estimated to be between 0.15 GPa^{-1} (20 °C) and 0.16 GPa^{-1} (66 °C) from the data of Jain and Simha [46]. Bohlen and Kirchheim [23] assumed $\kappa_{occ} = 0$ when estimating the specific free volume hole number, N_h', from isothermal compression experiments by a comparison of the specific, V, and hole volume, v_h, derived from PALS. The estimated values are higher by a factor of 1.5–2.5 than those from thermal expansion experiments. An agreement between the results from both types of experiments is,

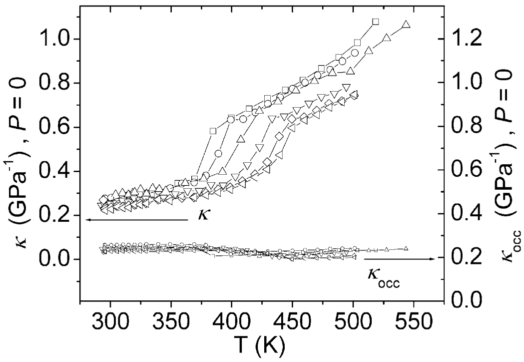

Fig. 11. Temperature dependence of the isothermal compressibilities for $P\to0$ of the total volume, κ, and the occupied volume, κ_{occ}, for SMA copolymers. Symbols as in Fig. 1.

Table 4
Free volume parameters of SMA copolymers ($T \rightarrow T_g$)

	±	PS	SMA12	SMA15	SMA25	SMA31	SMA35
V_{fg} (cm^3/g)	0.002	0.0692	0.0668	0.0735	0.0727	0.0726	0.0744
h_g	0.002	0.0716	0.0707	0.0792	0.0815	0.0831	0.0867
E_{fg} (10^{-4} cm^3/g K)	0.025	1.205	1.521	1.047	1.186	1.095	1.087
E_{fr} (10^{-4} cm^3/g K)	0.09	5.89	5.41	5.689	4.803	4.562	4.683
κ_{fg} (10^{-3} MPa^{-1})	0.5	1.73	1.62	2	1.49	1.34	1.46
κ_{fr} (10^{-3} MPa^{-1})	0.5	4.52	4.56	4.7	4.46	4.53	4.13
H_h ($T > T_g$) (kJ/mole)	0.06	7.65	7.37	7.83	7.54	8.16	8.39

however, obtained when taking into account the above estimated values for κ_{occ}.

The compressibility of the free volume, κ_f, is one order of magnitude larger than the total compressibility, and dominates the total compressibility despite its volume fraction being only between 6 and 16%. κ_f decreases with increasing content of MA comonomer while the decrease in the total compressibility at a given temperature, κ, is due to both the decreasing κ_f and the decreasing free volume content.

In order to prove the correlation between κ and free volume in more detail we have plotted, following Schmidt et al. [21], the bulk elasticity modulus, $B = 1/\kappa$, vs. different quantities. We found that plots of B vs. T, V, and h do not give uniform master curves, but if B is plotted vs. V_f then all the data does, as shown in Fig. 13. The data above and below T_g were each fitted by straight lines, giving the relations

$$B_{T>T_g} = (2.37 \pm 0.03) - (8.9 \pm 0.3) V_f \qquad (6)$$

$$B_{T<T_g} = (11.1 \pm 0.3) - (111 \pm 4) V_f$$

Here, B is given in GPa and V_f in cm^3/g. While for the rubbery state the fits are good, a larger scatter of experimental data around the master curve is observed for the glassy state. Some of us find exactly the same relation in the rubbery phase for a different series of copolymers (styrene-acrylonitrile) [26,27]. These interesting relations show that the compressibility of an amorphous polymer at a temperature T and ambient pressure can be determined from the values of the specific free volume.

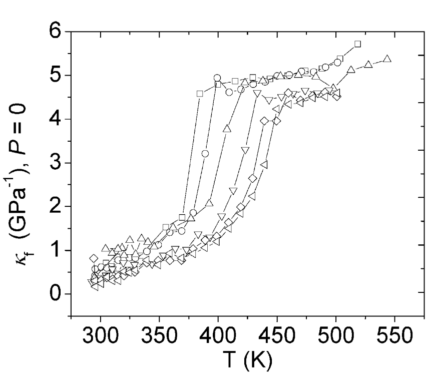

Fig. 12. Temperature dependence of the isothermal compressibilities for $P \rightarrow 0$ of the free volume, κ_f, for SMA copolymers. Symbols as in Fig. 1.

4. Conclusion

The specific and the free volume parameters, derived from PVT experiments using the S–S equation of state analysis, show a systematic variation with the composition of the SMA copolymers (0–35 mol% MA comonomer). All the parameters measured were consistent with a stiffening of the copolymer chains due to the incorporation of MA units. The stiffening results in a slowing down of the segmental movements, as shown by the increase of T_g and reduces the density of molecular packing below T_g. The specific free volume at T_g, V_{fg}, increases slightly from 0.069 to 0.074 cm^3/g, while the hole fraction h_g shows an increase from 0.072 to 0.087. We found constant values of $(\alpha_r - \alpha_g)T_g$ and $\alpha_r T_g$, consistent with those found in the literature.

The unexpected result was found that the coefficient of thermal expansion of V_{occ} changes at T_g from $\alpha_{occ,g} \approx 0.5\alpha_g \approx 1 \times 10^{-4}$ K^{-1} ($T < T_g$) to $\alpha_{occ,r} \approx 0.2 \times 10^{-4}$ K^{-1} ($T > T_g$) (Table 5). From this it follows that the traditional approximation, whereby the fractional coefficient of thermal expansion of the free volume in the rubbery state, α_{fr}^*, is set equal to the difference of the coefficients of total volume expansion above and below T_g, $\alpha_{fr}^* = (\alpha_r - \alpha_g) \approx 4 \times 10^{-4}$ K^{-1}, which comes from $\alpha_{occ,r} = \alpha_g$, is incorrect. Since

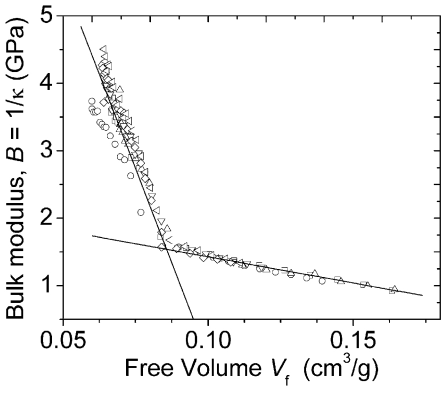

Fig. 13. Bulk modulus B of SMA copolymers as a function of specific free volume $V_f = hV$. Symbols as in Fig. 1.

Table 5
Occupied volume parameters of SMA copolymers ($T \rightarrow T_g$)

	±	PS	SMA12	SMA15	SMA25	SMA31	SMA35
$V_{occ,g}$ (cm^3/g)	0.002	0.896	0.876	0.854	0.819	0.801	0.784
$V_{occ,g}/V^*$	0.002	0.9552	0.9553	0.9554	0.9554	0.9555	0.9558
$V_{occ,g}/V_w$	0.003	1.4852	1.5053	1.4795	1.4688	1.4641	1.451
$\alpha_{occ,r}$ (10^{-5} K^{-1})	0.07	9.08	8.36	8.91	8.15	7.81	7.83
$\alpha_{occ,g}$ (10^{-5} K^{-1})	0.1	1.94	1.71	2	2.04	1.87	1.64
$\kappa_{occ,r}$ (10^{-4} MPa^{-1})	0.01	2.47	2.59	2.44	2.48	2.38	2.34
$\kappa_{occ,g}$ (10^{-4} MPa^{-1})	0.01	2.04	2.16	1.97	2.01	1.89	1.9

$\alpha_{occ,r} \approx 0$, $\alpha_{fr}^* \approx \alpha_r \approx 6\times10^{-4}\,\mathrm{K}^{-1}$ is a distinctly better approximation.

The compressibility of the occupied and free volume, κ_{occ} and κ_f, behave in the following way: κ_{occ} exhibits a small change at T_g from $\kappa_{occ,g} = 2.5\times10^{-4}\,\mathrm{MPa}^{-1}$ to $\kappa_{occ,r} = 2\times10^{-4}\,\mathrm{MPa}^{-1}$, a value which seems to be unexpected high but corresponds well to the compressibility of PE crystals. The compressibility of the free volume, κ_f, has values of $\kappa_f \approx 1\times10^{-3}\,\mathrm{MPa}^{-1}$ below T_g and $\kappa_f \approx 5\times10^{-3}\,\mathrm{MPa}^{-1}$ above. It was found that the hole number per *s*-mer follows an Arrhenius law with an activation enthalpy of approximately half of the cohesive energy. In the second part of the work the mean size, mean number density, and size distribution of subnanometer size free volume holes is determined from the PALS experiments and their comparison with PVT data. We show that our unexpected findings $\alpha_{occ,r}^* \approx 0$ and $\kappa_{occ,g} \approx \kappa_{occ,r} \approx 2\times10^{-4}\,\mathrm{MPa}^{-1}$ from this paper have a large effect on the estimation of the hole densities (Table 5).

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