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The Temperature and Pressure Dependence of the Free Volume in Fluoroelastomers from PALS and PVT Experiments

G. DLUBEK^a, A. SEN GUPTA^{b,c}, J. WAWRYSZCZUK^d, D. KILBURN^e,
J. PIONTECK^f, R. KRAUSE-REHBERG^b, T. GOWOREK^d,
M.A. ALAM^e, H. KASPAR^g AND K.H. LOCHHAAS^g

^aITA Inst. Innovative Technologies

Wiesenring 4, 06120 Lieskau (Halle/S.), Germany

^bDepartment of Physics, Martin-Luther-University, 06099 Halle/S., Germany

^cDep. of Physics, Visva-Bharati, Central University

Santiniketan, West Bengal-731235, India

^dInstitute of Physics, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

^eH.H. Wills Physics Laboratories, Univ. of Bristol

Tyndall Avenue, Bristol, BS8 1TL, UK

^fLeibniz-Institute of Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany

^gDyneon GmbH & Co. KG, Werk Gendorf, 84504 Burgkirchen, Germany

Positron lifetime and pressure–volume–temperature experiments were performed as function of T (100–485 K) and P (10^{-5} Pa–500 MPa) on a fluoroelastomer. From positron annihilation lifetime spectroscopy, analyzed with LT9.0 assuming a dispersion in the e^+ (τ_2) and o -Ps (τ_3) lifetime, the mean, $\langle v_h \rangle$, and the width (standard deviation), σ_h , of the hole size distribution were calculated. The pressure–volume–temperature data were analyzed using the Simha–Somcynsky hole–lattice theory to estimate the specific hole free volume V_f . From a comparison of V_f with $\langle v_h \rangle$ the specific hole number, N'_h , is estimated. The data from thermal expansion and pressure experiments show complete agreement when taking into account the compressibility of the occupied volume.

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1. Introduction

From positron annihilation lifetime spectroscopy (PALS) experiments the free volume hole size distribution, its mean and width, but not directly the num-

ber density and the hole free volume fraction, can be estimated. The latter value, however, can be obtained from the analysis of pressure–volume–temperature experiments using the Simha–Somcynsky theory ([1] and [2–4]). This theory models the disordered structure of a liquid by a cell or lattice model with lattice sites randomly occupied by a mer with a fraction y of less than one. From a fit of the equation of state (S–S eos) to the specific volume V the occupied, y , and the unoccupied, $h = 1 - y$, volume fractions and from this specific occupied, $V_{\text{occ}} = yV$, and hole free, $V_f = hV$, volumes can be calculated. In this work we demonstrate the potential of the comparison of PVT and PALS data in thermal expansion and hydrostatic compression experiments, and discuss briefly the question how to analyze correctly PALS data.

2. Results and discussion

The polymer under investigation is a commercial copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether) made by Dyneon GmbH & Co. KG, Germany (a 3M Company) and known as perfluoroelastomer PFE. The PVT experiments were performed in the T, P range of $T = 295.8\text{--}485.3$ K and $P = 10\text{--}200$ MPa. Positron lifetime spectra ($2\text{--}6 \times 10^6$ counts, resolution ≈ 230 ps) were measured in the range $T = 100\text{--}473$ K and $P = 10^{-5}$ Pa (thermal expansion [3]) and $T = 295.8$ K and $P = 0.1\text{--}448$ MPa (hydrostatic compression [4]). More conditions of the experiments can be found in Refs. [3, 4]. Figure 1 shows the results of the S–S eos analysis of PVT experiments extrapolated to $P = 0$ MPa. The following coefficients of thermal expansion of the total, occupied, and free volumes at 300 K were estimated: $\alpha = 8.67$, $\alpha_{\text{occ}} = 0.38$, and $\alpha_f = 72.4$ in units of 10^{-4} K $^{-1}$. The corresponding values for the compressibility are

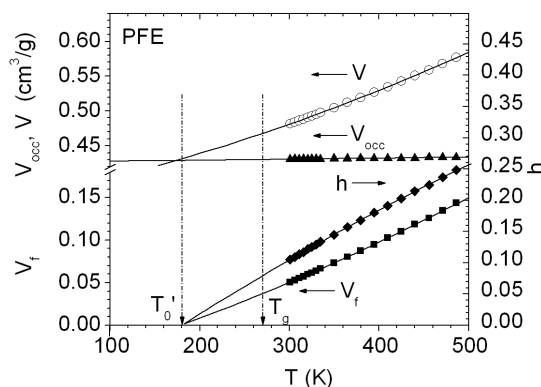


Fig. 1. The specific (total) volume V , the hole fraction h , and the specific occupied and free volumes $V_{\text{occ}} = (1 - h)V$ and $V_f = hV$ for PFE at $P = 0$ Pa (extrapolated). The solid lines are linear (V_{occ}) or quadratic fits (V , V_f , h) and extrapolations. T_g is from differential scanning calorimetry (DSC), and T'_0 indicates the temperature where the extrapolated (hypothetical) hole free volume disappears.

$\kappa = 7.87$, $\kappa_{\text{occ}} = 2.5$, and $\kappa_f = 53$ in units of 10^{-4} MPa^{-1} . The results show that V_{occ} exhibits almost no thermal expansion (for $T > T_g$) but is compressible. This result is in agreement with our previous study of polystyrene where we found the unexpected but important result: $\alpha_{\text{occ,r}}(T > T_g) \approx \alpha_g/10 \approx 0$, $\alpha_{\text{occ,g}}(T < T_g) \approx \alpha_g/2$ ($\alpha_g = 2.25 \times 10^{-4} \text{ K}^{-1}$) and $\kappa_{\text{occ,g}}(T < T_g) \approx \kappa_{\text{occ,r}}(T > T_g) \approx 2.2 \times 10^{-4} \text{ MPa}^{-1}$ [2].

The treatment of the positron lifetime spectra employing the routine LT9.0 [5] showed us that a correct analysis requires to allow both the e^+ (τ_2) and the o -Ps (τ_3) lifetime to be distributed (widths σ_2 and σ_3). In that case p -Ps parameters come out as theoretically expected: $\tau_1 \approx 125 \text{ ps}$ ($\eta \approx 1$) and $I_1/I_3 = 1/3$ [3, 4]. From τ_3 the mean hole radius can be calculated using a well known, semi-empirical equation, $r_h = r_h(\tau_3)$ and $v_h = 4\pi r_h^3/3$ [6]. Since the o -Ps lifetime has a broad distribution, it is more correct to calculate the mean hole volume as the mass centre of the hole size distribution. The radius probability distribution $n(r_h)$ can be obtained from $n(r_h) = -\alpha_3(\lambda)d\lambda_3/dr_h$ where $\alpha_3(\lambda)$ is the o -Ps annihilation rate distribution [6] ($\alpha_3(\lambda) \times \lambda$ is assumed to be a log normal function in LT9.0). The volume fraction hole size distribution follows from $g(v_h) = n(r_h)/4\pi r_h^2$ and the number fraction hole size distribution from $g_n(v_h) = g(v_h)/v_h$. Moreover, we calculated the modified distribution $g_n(v_h)^* = g_n(v_h)/v_h$. The mean and the variance of $g_n(v_h)$, $\langle v_h \rangle$ and σ_h^2 , and of $g_n(v_h)^*$, $\langle v_h \rangle^*$ and σ_h^{*2} , were calculated numerically as first and second moment of these distributions (for more details see Refs. [3, 4]). Figure 2 shows that the slopes of the v_h vs. T curve and the extrapolation to $v_h = 0$, T'_0 , depend on the definition of $v_h = v_h(\tau_3)$, $\langle v_h \rangle$, or $\langle v_h \rangle^*$. v_h shows a normal glass transition (T_g) behaviour and a levelling off at T_k .

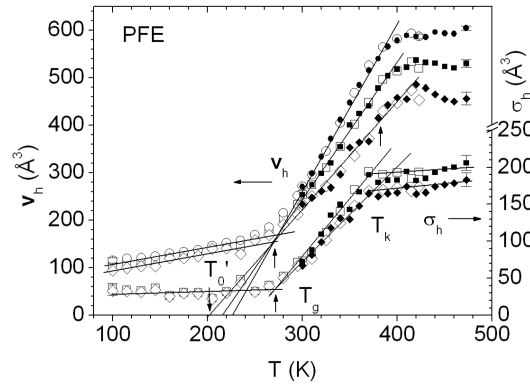


Fig. 2. Mean hole volume v_h for PFE calculated either as $v_h = v_h(\tau_3)$ (circles), the number average, $\langle v_h \rangle$ (squares), or the corrected average, $\langle v_h \rangle^*$ (diamonds), volume and the corresponding hole volume dispersions $\sigma_h = \sigma_h$ and σ_h^* at $P = 10^{-5} \text{ Pa}$. Empty and filled symbols: two PFE samples. T_k denotes the “knee” temperature, above T_k the o -Ps lifetime does not further mirror the true hole size. T_g and T'_0 are given as in Fig. 1. The straight lines are due to linear fits.

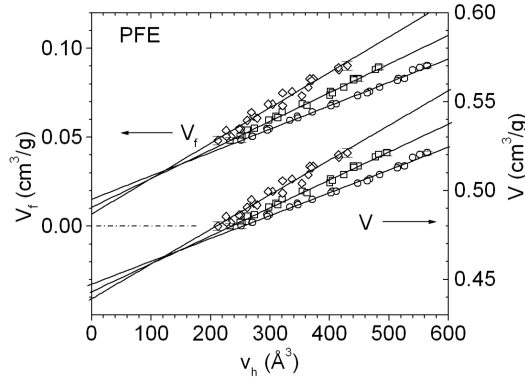


Fig. 3. Specific hole free volume V_f and specific total volume V plotted vs. the mean hole volume calculated as $v_h = v_h(\tau_3)$ (circles), $\langle v_h \rangle$ (squares), or $\langle v_h \rangle^*$ (diamonds) for PFE (all for $P \approx 0$ Pa). The lines show linear fits to the data from the temperature range between $T_g + 30$ K and T_k .

In Fig. 3 plots of the specific hole free, V_f , and total, V , volume vs. the o -Ps hole volume v_h are shown. The specific hole number N'_h can be estimated from the relations

$$V_f = V_{f0} + N'_h v_h \quad (1)$$

or

$$V = V_{occ} + V_{f0} + N'_h v_h. \quad (2)$$

The figure shows that $\langle v_h \rangle^*$ corresponds best to the expectation $V_{f0} = 0$. From this it follows that probably o -Ps detects holes with a preference which corresponds approximately to the hole volume v_h . This preference is corrected in calculating $\langle v_h \rangle^*$ as the mean of the modified distribution $g_n(v_h)^* = g_n(v_h)/v_h$. The specific hole number estimated from $N'_h = dV_f/d\langle v_h \rangle^*$, $N'_h =$

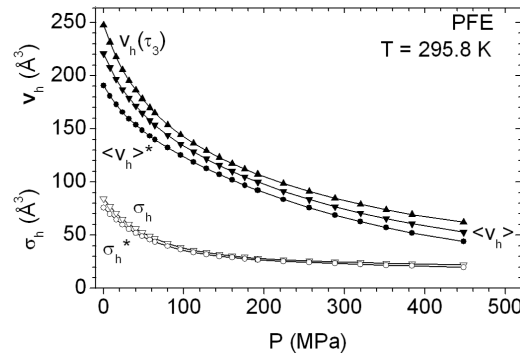


Fig. 4. As in Fig. 2, but as a function of the pressure P at $T = 295.8$ K.

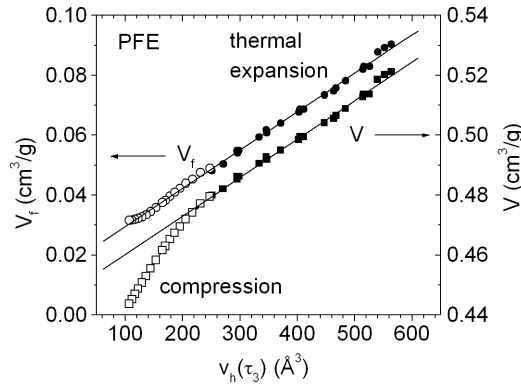


Fig. 5. Specific free volume V_f (circles) and specific total volume V (squares) plotted vs. the mean hole volume calculated as $v_h(\tau_3)$ for PFE. Empty symbols: compression experiments ($T = 295.8$ K, $P = 0.1$ – 192 MPa), filled symbols: thermal expansion experiments ($P = 10^{-5}$ Pa, $T = T_g + 20$ K $- T_k$). The lines show linear fits to all data (V_f , slope = $128(\pm 0.01) \times 10^{21}$ g $^{-1}$) or only to thermal expansion experiments (V , slope = $0.129(\pm 0.01) \times 10^{21}$ g $^{-1}$).

$199(\pm 0.01) \times 10^{21}$ g $^{-1}$, corresponds to a volume related hole density of $N_h = N'_h/V = 0.41(\pm 0.03)$ nm $^{-3}$.

Figure 4 shows the hole volume v_h as a function of the pressure P . The decrease in v_h flattens at the glass transition at $P \approx 100$ MPa ($T = 295.8$ K). In Fig. 5 plots of V_f and V vs. v_h , here calculated from simplicity directly from τ_3 , $v_h = v_h(\tau_3)$, for the thermal expansion and isothermal compression experiments, are shown. The V_f vs. v_h curve shows a linear behaviour indicating the agreements of the $N'_h = dV_f/dv_h$ values estimated from both types of experiments. The change in the slope of the V vs. v_h curve has his origin in the compressibility of the occupied volume and disappears when taking this into account, $N'_h = dV/dv_h - dV_{occ}/dv_h$ and $dV_{occ}/dv_h = (dV_{occ}/dP)/(dv_h/dP) = V_{occ}\kappa_{occ}/v_h\kappa_h$.

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