Glass transition and free volume in the mobile (MAF) and rigid (RAF) amorphous fractions of semicrystalline PTFE: a positron lifetime and PVT study

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Abstract

The structure of the free volume and its temperature dependence in poly(tetrafluoroethylene) (PTFE) and of its copolymer with perfluoro(propyl vinyl ether) (PFA) was studied by pressure–volume–temperature (PVT) experiments ($T=27$–$380\,^\circ\text{C}$, $P=0.1$–200 MPa) and positron annihilation lifetime spectroscopy (PALS, $T=-173$–$250\,^\circ\text{C}$, $P=10^{-5}$ Pa). From the analysis of these experiments we conclude on the volumetric properties of the mobile (MAF) and rigid amorphous fractions (RAF) in these semicrystalline polymers. The specific volumes of the MAF and RAF, V_{MAF} and V_{RAF}, were estimated assuming that V_{MAF} agrees with the specific volume of the melt extrapolated down to lower temperatures using the Simha–Somcynsky equation of state (S–S eos). V_{RAF} was then estimated from the specific volume of the entire amorphous phase, V_{a}, and the known V_{MAF}. The specific free volume $V_{\text{f}}=V_{\text{a}}-V_{\text{occ}}$ was also estimated from V_{a} using the S–S eos hole fraction h, $V_{\text{occ}}=(1-h)V_{\text{a}}$. From the analysis of PALS data with the routine LT9.0 the mean volume, $\langle v_{\text{h}}\rangle$, and the width, σ_{h}, of the local free volume size distribution (holes of subnanometre size) were obtained. A comparison of $\langle v_{\text{h}}\rangle$ with V_{f} delivered the hole density N_{h}'. The volume parameters show that the RAF which is formed during crystallisation from the melt has a distinctly smaller specific free and total volume than the MAF. During cooling the contraction of the RAF slows down and finally, below room temperature, the RAF possesses a larger free volume than the MAF shows. Obviously, the restriction of the segmental mobility in the RAF by the crystals limits at high temperatures the free volume expansion and at low temperatures dense packing of the polymer chains. These conclusions from the analysis of the specific volume are confirmed by PALS experiments.
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1. Introduction

The structure of semicrystalline polymers is still under discussion [1–7]. In the last years it has become clear that a simple two phase model—crystallites embedded in amorphous surroundings—is not sufficient to understand the properties of theses materials. Consensus seems now to be reached that at least three different regions must be considered. The non-crystalline phase must be subdivided into the non-crystalline amorphous and the crystalline-amorphous interfacial portions. The cause for the intermediate interfacial region is the continuation across the phase boundaries of the molecules which are much longer than the phase dimensions. This region is amorphous but has a constrained molecular mobility and is usually described as rigid-amorphous fraction (RAF) [1]. The non-crystalline amorphous region is expected to exhibit properties like the completely amorphous bulk polymers and may be termed as mobile amorphous fraction (MAF). Mechanical and

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dielectric spectroscopy, nuclear magnetic resonance, Raman spectroscopy, and temperature-modulated calorimetry are employed to investigate semicrystalline polymers [1–7]. However, many questions with respect to the structure and dynamic properties of the RAF remain. One question is, for example, whether the RAF undergoes its own glass transition or vitrifies during crystallisation [5–7].

The purpose of our paper is to contribute to the understanding of these problems. To this aim, we have investigated the volumetric properties on a molecular scale and combined these experiments with macroscopic volume measurements. The free volume of a polymer, particularly the size of local free volumes, is an important parameter, being closely related to the molecular mobility. We will attempt to distinguish the volumetric properties of both amorphous portions, the MAF and the RAF, and to conclude on their temperature dependency and glass transition.

We employed positron annihilation lifetime spectroscopy (PALS) in this study, a method which has developed during the past decade to be an important tool for studying the local free volume of polymers [8–13]. In molecular solids and liquids, a fraction of the positrons injected from a radioactive source forms positroniums [12,13] and these can annihilate from the *para* (*p*-Ps, singlet spin state), or the *ortho* state (*o*-Ps, triplet spin state) with a relative formation probability of 1:3. Three decay components appear in the positron lifetime spectrum of amorphous polymers and these are attributed to the annihilation of *p*-Ps, free (not Ps) positrons, e^+, and *o*-Ps.

In amorphous polymers Ps is formed in subnanometre size holes of the excess free volume (Anderson localisation [14]) When localised at a hole the Ps moves in internal regions of the hole and collides frequently with the molecules of the hole walls. During a collision *o*-Ps may annihilated with an electron other than its bound partner and with opposite spin with the consequence that the (mean) *o*-Ps lifetime decreases from its value in a vacuum, 142 ns (self annihilation), to the low ns-range (1–6 ns, pick-off annihilation [12,13]). The smaller the hole is, the higher is the frequency of collisions, and the shorter the *o*-Ps life. Assuming the shape of the holes (usually spheres) the hole size can be calculated from the *o*-Ps lifetime employing a semi-empirical model [6–10].

In some semicrystalline polymers an extra, intermediate (∼1 ns), *o*-Ps lifetime appears. This lifetime is attributed to *o*-Ps formed in crystals [15–19] and is expected to mirror the lattice plane spacing (interstitial free volume). The lifetime of *o*-Ps annihilation from holes in the amorphous phase can be separated from this lifetime in those cases where both lifetimes are not too similar. In this way the microstructure of the amorphous phase in semicrystalline polymers which contains both the MAF and RAF can be studied. First experiments to investigate these fraction employing PALS can be found in the literature [20–22].

For studying the temperature dependence of the macroscopic volume we performed PVT experiments [23].

We used the Simha–Somcynsky equation of state (S–S eos [24,25]) for an extrapolation of the specific volume from the melt down to lower temperatures, identified this volume with the MAF and used this for an estimation of the RAF volume from the specific volume of the entire amorphous phase. The S–S eos theory also allows the specific occupied and free volume of the equilibrium amorphous phase to be calculated. We will use this information in combination with the results from PALS to conclude on the density of free volume holes. Until now this method has been applied only to completely amorphous polymers [26–32].

As materials of our studies we selected poly(tetrafluoroethylene)s (PTFE) of different crystallinity and a semicrystalline copolymer (PFA) and compared the results with those for a completely amorphous copolymer (PFE) studied previously [32] (for a review of properties of PTFE, PFA, and PFE copolymers see Ref. [33]). One advantage of PTFE is that the intermediate lifetime attributed to *o*-Ps annihilation from crystals can be well separated from that of the amorphous phase which exhibits, due to the stiffness of the tetrafluoroethylene chains, rather large holes. PALS studies of PTFE have been performed already in past [15–18,34,35], very instructive results can be found in the papers of Kindl et al. [15]. The progress in our work is that we used for the analysis of the positron lifetime spectra the new routine LT in its latest version 9.0 [36,37] and correlate the PALS results with those from PVT experiments. The routine LT9.0 allows log normal distributed annihilation rates which lead to a more accurate fitting of the lifetime spectra than when using the conventional discrete term analysis and avoids possible artefacts [38]. Moreover, from the distribution of the *o*-Ps annihilation rate the size distribution of free volume holes and a reasonable value for the mean hole volume can be calculated.

2. Experimental

2.1. Polymers

The samples under investigation were two pure poly(tetrafluoroethylene)s (-[C_2F_4]-) in virgin, as-polymerised (TFv) and sintered, melt crystallised state (TFs), two poly(tetrafluoroethylene)s modified with a small amount, 0.1–2.0 wt%, of perfluoro(propyl vinyl ether) (–[F_2C–$CFOC_3F_7$]–) in virgin (TFMv) and sintered state (TFMs), and a copolymer of tetrafluoroethylene and 2–5 mol% perfluoro(alkoxy vinyl ether) (–[CF_2–$CFOC_xF_{2x+1}$]–, $x=3$–4) in sintered, melt crystallised state (PFAs). Highly crystalline PTFE powder of ∼25 μm mean diameter was pressed at room temperature with a pressure of 35 MPa into 2 mm thick plates for making the virgin samples. A second set of samples were sintered at 375 °C under a pressure of 35 MPa for 4 h. Subsequently these samples, plates of 2 mm thickness, were cooled down with a rate of approximately 10 K/min. Table 1 shows the characteristic properties of