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Free volume and mechanical properties of Palacos® R bone cement

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The free volume and the mechanical properties of Palacos® R bone cement were determined from positron annihilation lifetime spectroscopy (PALS) and from dynamic mechanical thermal analysis (DMA) in the temperature ranges 24–220 °C and 30–120 °C, respectively.

The heating of bone cement caused an appreciable reduction of the free volume, measured as a decrease in the ortho-positronium lifetime τ_3 from 2.04 to 1.91 ns, as well as a clear increase in the storage modulus from 2.3 to 3.0 GPa. The changes in free volume and storage modulus after the heat treatment were interpreted as an effect of elimination of residual monomer from the bone cement. The free volume of the bulk-polymerized phase of bone cement was estimated from a simple difference method, suggesting that the residual monomer was eliminated from the bone cement between 60 and 90 °C, thus implying a glass transition temperature of only 60 °C for the bulk-polymerized phase.

The spherical free volume cavity size estimated from the ortho-positronium lifetime $V(\tau_3)$, and the storage modulus E'_{storage} from DMA measurements were found to correlate by a linear relationship throughout the studied temperature range, and the correlation appeared to be independent of the presence of residual monomer.

1. Introduction

Acrylic bone cement is used in hip and knee joint replacements where it serves as an intermediary material between the metal prosthesis and the bone of the patient. It is inserted into the patient as a viscous paste before the implantation of the prosthesis. Thus, bone cement facilitates the surgical task of fitting the prosthesis to the patient by filling in the gaps between the prosthesis and the bone of the patient. It also provides a rapid fixation of the prosthesis, often enabling the patient to use the artificial joint only hours after insertion. Palacos® R is a commercial acrylic bone cement consisting of a phase of poly(methylmethacrylate) (PMMA) and a dispersed phase of spherical particles of poly-(methylmethacrylate-co-metylacrylate) (PMA/PMMA). Fig. 1 displays a scanning electron micrograph, in which the spherical particles are visible at the surface of a pore inside the bone cement.

The bone cement is prepared by mixing liquid methylmethacrylate (monomer) with the particles and initiator (powder) into a viscous paste (Table I).

The paste is then injected into the site of application in the patient. The monomer polymerizes in an exothermic radical addition reaction, and before the paste has vitrified, the metal prosthesis is inserted. Within minutes, the conversion of monomer into polymer has raised the glass transition temperature (T_g) of the paste to that of the temperature of reaction, and the diffusion rate of monomer becomes too low to sustain the reaction [1]. Consequently, the temperature drops, and the material eventually reaches ambient temperature (37 °C). At this temperature, the material is in a glassy state, and the prosthesis is locked into place.

Complete curing of bone cements is rarely achieved, since full conversion of monomer in the bulk polymerization process requires a reaction temperature close to the glass transition temperature (T_g). In the case of PMMA, with a $T_g \approx 100\,^\circ\text{C}$, this would cause severe damage to the surrounding tissue and can not be tolerated. Thus, monomer will invariably be present to some extent in bone cement. The presence of monomer influences the mechanical and thermal properties of the bone cement, e.g. by reducing the mechanical stiffness, T_g and the thermal stability, but on the other hand, increasing the impact strength [2–5]. Analysis of the residual monomer in bone cement by gas chromato-

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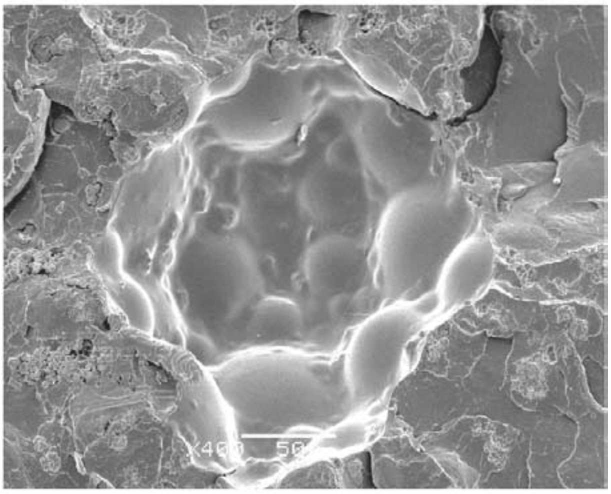

Figure 1 Spherical particles of prepolymerized PMA/PMMA in a bulk polymerized PMMA matrix (the internal scale bar is 50 μm).

TABLE I Contents of Palacos® R bone cement

40 g powder	Weight (g)
Methyl-methacrylate-methylacrylate copolymer	33.8
Benzoyl peroxide	0.2
Zirconium dioxide	6.0
Chlorophyll	0.020
20 ml liquid	
Methyl-methacrylate	18.4
N,*N*-dimethyl-*p*-toluidin	0.4
Hydrochinon	0.0012
Chlorophyll	0.0080

graphy has revealed values in the range of ca 0.25–2%, depending on the storage media and temperature [4, 6]. Also, the possibility of measuring the conversion of monomer in bone cement *in situ* has been demonstrated, by use of Fourier Transform Raman spectroscopy [7].

The aim of this study was to use dynamic mechanical thermal analysis (DMA) and positron annihilation lifetime spectroscopy (PALS) to investigate the influence of residual monomer on the mechanical and free volume properties of Palacos® R bone cement, with samples prepared in agreement with clinical practice. Another aim was to study the relationship between the free volume and mechanical properties of the bone cement, and to compare the results with literature data on a universal relationship between free volume and mechanical properties of amorphous polymers.

2. Materials

The bone cement samples were prepared according to the instructions supplied by the manufacturer (Schering-Plough Vnr 388157). The two components of Palacos® R bone cement (Table I) were cooled to ca 4 °C and mixed using an Optivac® vacuum mixing system. The mixture was extruded into a plastic mold producing coin-shaped samples with a thickness of 2.1 mm and diameter of 25 mm. The DMA was performed 1 week after sample preparation, and the PALS measurements were performed 4 weeks after sample preparation. The difference in concentration of residual monomer between the samples for PALS and DMA, due to different age, was expected to be little [4, 6].

Samples of the powder with the same dimensions as the bone cement samples were prepared by a simple sintering process (120 kN, 130 °C, 10 min). Samples for DMA measurements were ca $16 \times 12 \times 3\,\mathrm{mm}^3$. All samples were stored after preparation in air at room temperature.

3. Methods

3.1. The PALS

PALS is a technique based on the implantation of positrons into solids and the recording and analysis of the positron lifetime spectrum. The positron is the anti-particle to the electron and may be obtained from the decay of the radioactive isotope ^{22}Na. Positrons that penetrate into a polymer material will annihilate together with an electron of the polymer. Some positrons annihilate with the electrons of a polymer through an intermediary species (the ortho-positronium, o-Ps) which prolongs the lifetime of the positron to a value that is characteristic of the dimensions of the free volume cavities in the polymer material. Thus, by measuring the lifetime of the o-Ps, information about the microscopic free volume is obtained. The lifetime of the o-Ps is often denoted as τ_3, and an equation correlating τ_3 to actual cavity size, has been proposed for a spherical model cavity [8, 9]:

$$\begin{aligned}
\tau_3 &= \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \\
\Delta R &= R_0 - R \\
\Delta R &= 1.656\,\text{Å} \\
V(\tau_3) &= 4\pi R^3/3 \qquad (1)
\end{aligned}$$

with R = the radius of an equivalent spherical cavity. It has been found that the estimated free volume cavity size $V(\tau_3)$ obtained from Equation (1) correlates with a number of other physical properties of polymers, such as the fractional free volume obtained from pressure–volume–temperature measurements [10] and diffusion of gas through polymer [11, 12]. The PLS of a two-phase material, such as Palacos® R bone cement, represents the sum of all the positrons that have annihilated in each phase or in the interphase. In the correct interpretation of such spectra one must naturally consider the spatial distribution of the positrons. The probability of a positron annihilating in one of two phases is equal to its mass fraction, provided that trapping of positrons at the interphase can be neglected.

In the case of Palacos® R bone cement, the measured PLS is assumed to consist of a linear combination of the PLS characteristic for the continuous bulk polymerized phase and the dispersed phase consisting of pre-polymerized particles, respectively. The PLS of the continuous phase was obtained using Equation 2 (below) in which S_{BC}, S_{P} and S_{C} denote the PLS of the bone cement, particle material and the continuous phase, respectively. x is the probability of a positron annihilating in the particle material, which in the case of bone cement is assumed to be equal to the mass fraction of the pre-polymerized particles ($x = 0.67$).

$$S_{BC} = xS_P + (1 - x)S_C \qquad (2)$$

S_C was thus obtained indirectly from Equation 2, by measurements of the bone cement spectra (S_{BC}) and samples of sintered particles (S_P). PALS measurements as a function of temperature (Figs. 2 and 3) were performed with a resolution function of ca 250 ps, channel width 26.8 ps and a pressure of 5×10^{-3} Torr. Each spectrum contained at least 1.8×10^6 counts recorded during 8 h. All spectra were evaluated with PATFIT [13]. A source correction term was used in the evaluation, by fixing one lifetime at 384 ps with a relative intensity of 7%, corresponding to the fraction of positrons annihilating in a thin protective polymer foil surrounding the radioactive source.

3.2. DMA

In DMA, the correlation between a sinusoidal stress and strain is studied as a function of frequency and temperature. The two basic quantities obtained from DMA in tensile mode are the dynamic modulus $E_d(\omega, T)$ and the phase shift $\delta(\omega, T)$, and they are both frequency and temperature-dependent. E_d is defined as the ratio between the amplitudes of the sinusoidal stress and strain, and δ is the phase angle between the sinusoidal stress and strain. The storage modulus $E'_{storage}$ and loss modus E''_{loss} are calculated directly from E_d and δ by the following equations:

$$E'_{storage} = E_d \cos(\delta)$$
$$E''_{loss} = E_d \sin(\delta)$$

$E'_{storage}$ is proportional to the per cycle stored and released elastic energy. E''_{loss} is proportional to the amount of energy dissipated as heat during one cycle and reaches a maximum in the glass transition region. The measurements were performed at 1 Hz in single-cantilever bending mode, with a 50 μm amplitude, between 30 °C and 120 °C (DMA 2980, TA Instruments). The rate of heating was 0.1 °C/min.

4. Results and discussion

4.1. Free volume versus temperature

Fig. 2 displays the ortho-positronium lifetime τ_3 of the bone cement as a function of temperature in the range 24–222 °C, as measured during heating and subsequent cooling. The difference in τ_3 between the heating line and cooling in the temperature range 24–90 °C was interpreted as the presence of residual monomer in the material under heating. Any residual monomer was expected to be completely eliminated from the bone cement after heating to 222 °C, and the cooling line should thus provide a reference of bone cement free of monomer. All data points on the cooling line are in good agreement with PALS measurements of pure PMMA reported in Schmidt and Maurer [10], Mohamed *et al.* [14] and Wang *et al.* [15]. The presence of ca 10% weight of ZrO_2 appears to have no influence on τ_3, which is most likely due to the typical absence of o-Ps formation in dense inorganic materials.

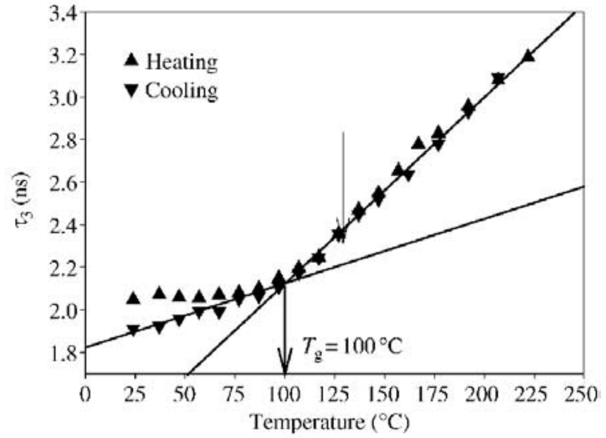

Figure 2 τ_3 of bone cement as a function of temperature.

The influence of low-molecular substances on the free volume properties of polymers have been studied for other systems, and in general the effect is an increase of the free volume. In some cases, there appears to be an almost linear relationship between the concentration of the low-molecular substance and τ_3, e.g. for dioctylphtalate in polyvinylchloride [16] and for dioctylphtalate in polyethylene oxide, although more complicated (and reversed) relationships have been observed, for instance, in the case of small amounts of water in nylons [17].

The good agreement in Fig. 2 between the heating and the cooling line at $T > 100$ °C indicates that the residual monomer has been eliminated from the bone cement at this stage of the heating. This is in good agreement with the T_g of bone cement, which can be evaluated from Fig. 2 at ca 100 °C. Above this temperature, any remaining monomer is expected to evaporate quickly, due to the drastically increased molecular mobility associated with the melt state of amorphous polymers.

Since bone cement is prepared by the mixing of two separate components (pre-polymerized particles and monomer), the resulting material is not expected to be completely homogeneous. As is clearly visible from fracture surfaces, bone cement is far from homogeneous, and a substantial fraction of the pre-polymerized particles retain to some degree their spherical shape inside the bone cement. The bone cement could be described as consisting of a ‘‘dispersed’’ phase, made of pre-polymerized particles, and a ‘‘continuous’’ phase of PMMA, which is formed by bulk-polymerized only after the mixing of the two components. Since the residual monomer originates from incomplete conversion of monomer in the continuous phase, the distribution of the remaining monomer can be expected to have a higher concentration in this phase than in the dispersed phase. Assuming that the particles retain their free volume characteristics after mixing with monomer, a PLS will be a linear combination of the spectra of each phase, weighted by their respective weight fraction (Equation 2). The positron lifetime spectrum of the continuous phase could thus be obtained through Equation 2 with the possibility of estimating a τ_3 characteristic for the continuous phase of bulk polymerized PMMA.

Spectra of the powder were recorded, and Fig. 3 displays τ_3 of the particle samples as a function of temperature. There is good agreement between the

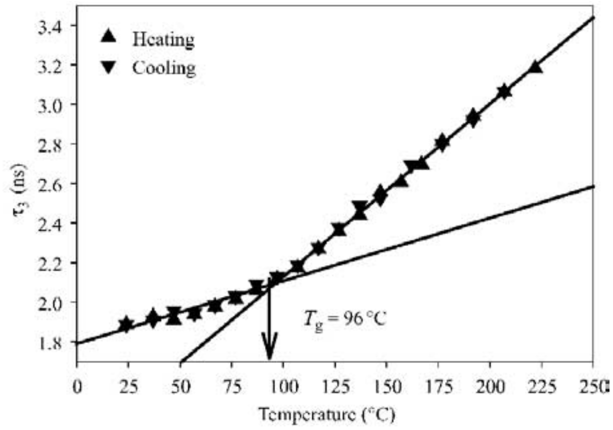

Figure 3 τ_3 of the particle material as a function of temperature.

heating curve and the cooling curve, and the glass transition temperature can be resolved from the increase of the slope at ca 100 °C.

Linear regression of the data points below and above the glass transition temperature revealed slopes of $\tau_3(T)$ in good agreement with PALS measurements of pure PMMA reported in the literature [10, 14, 15] (Equations 3a and b).

$$\tau_3(T) = 0.00335 \cdot T + 0.867 \text{ at } T < 90\,^\circ\mathrm{C} \tag{3a}$$

$$\tau_3(T) = 0.00874 \cdot T - 1.134 \text{ at } T > 105\,^\circ\mathrm{C} \tag{3b}$$

The results of the difference method (Equation 2) are shown in Fig. 4 and are interpreted as the τ_3 resolved for the continuous phase of the bone cement. The nearly constant value of τ_3 in the temperature region 24–50 °C indicates that the continuous phase is below its glass transition temperature. In the region 60–90 °C, τ_3 decreases with temperature from 2.28 to 2.17 ns. The decrease in τ_3, caused by the elimination of residual monomer, indicates that the initial glass transition temperature has been reached with an estimated value of ca 60 °C. At ca 100 °C, the T_g of the monomer-free bone cement is revealed as the increase of the slope of τ_3 versus T at ca 100 °C, which is in good agreement with the T_g of pure PMMA.

The sensitivity of PALS for the presence of residual monomer can be appreciated by considering the increase in τ_3 as a function of monomer concentration. The difference between τ_3 measured for the bone cement with and without residual monomer (i.e. before and after heat cycle) is 7% for the conventional analysis of the PLS spectra (Fig. 2) and 21% for the analysis using the difference method. This change in τ_3 may be compared to the relatively small amounts of residual monomer quantified for samples of bone cement stored under similar conditions (air and room temperature): 1.5% after three months [4] and 2.4% after seven months [6]. Thus, PALS appears to be a sensitive tool for assessing residual monomer in bone cement.

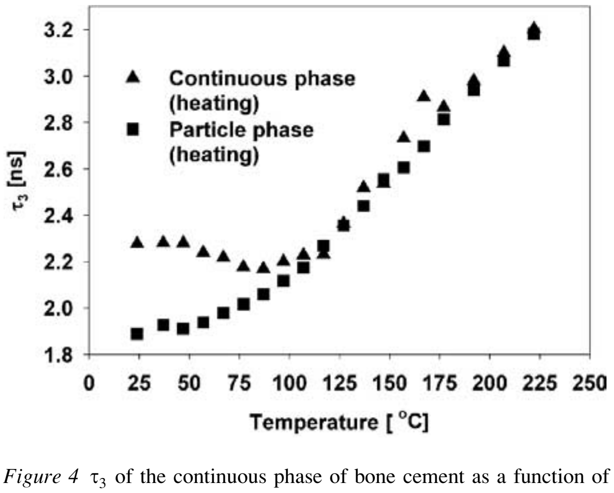

Figure 4 τ_3 of the continuous phase of bone cement as a function of temperature.

4.2. Mechanical properties versus temperature

The results from the DMA of bone cement are displayed in Fig. 5. The storage and loss modulus were studied during heating in two consecutive runs, between 30 and 120 °C, with a heating rate of 0.1 °C/min, followed by a constant temperature of 120 °C during ca 30 min. It was assumed that all residual monomer was eliminated from the sample after the first heating. The plasticizing effect of residual monomer is clearly appreciable as the difference in the storage modulus between the first and the second heating. After the first heating, the storage modulus at room temperature is increased from 2.3 to 3.0 GPa, due to the absence of plasticizing monomer. These values found for the storage modulus are relatively close to the secant modulus of 3.21 GPa of Palacos® R bone cement, measured at 10 MPa at a strain rate of 5 mm/min [18].

The T_g of the bone cement was estimated from DMA as the location of the maximum of the loss modulus on the temperature axis. The effect of the residual monomer can thus be appreciated as a reduction in the T_g from ca 95 °C to ca 80° from Fig. 5.

4.3. Free volume versus mechanical properties

The storage modulus obtained from DMA and the free volume spherical cavity size $V(\tau_3)$ estimated from PALS are displayed in Fig. 6 in the temperature range 30–120 °C. Each data point in Fig. 6 represents separate measurements of E'_{storage} and $V(\tau_3)$, measured at the same temperature. The data labeled ''with monomer'' are based on the heating curve of the PALS measurements and the first run of the DMA; the data labeled ''free of

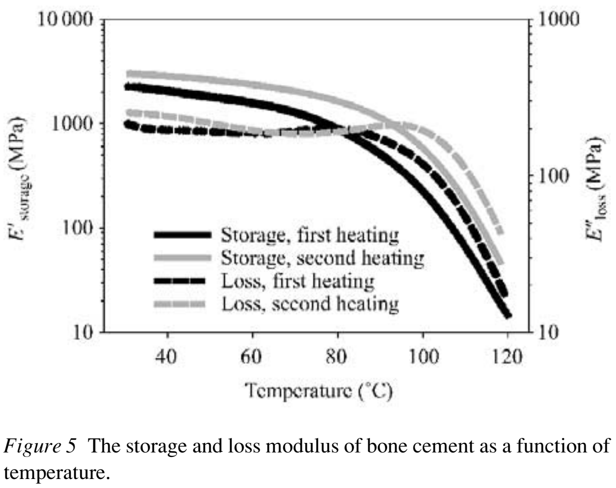

Figure 5 The storage and loss modulus of bone cement as a function of temperature.

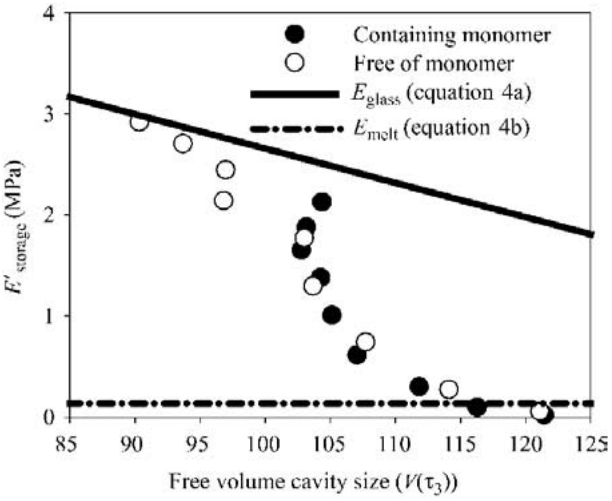

Figure 6 Free volume cavity size versus storage modulus of bone cement.

monomer'' are based on the cooling curve of the PALS measurements and the second run of the DMA. Both plots display a linear correlation between $V(\tau_3)$ and $E'_{storage}$ in the transition between the glassy state and the melt state.

A similar relationship between the microscopic free volume as measured by PALS and a macroscopic mechanical property of amorphous polymers has been investigated [19, 20]. A large range of different polymers were studied with PALS and pressure–volume–temperature measurements (PVT). A universal relationship between the bulk modulus K as determined from PVT-measurements, and $V(\tau_3)$ determined from PALS, was concluded. The relationship between $V(\tau_3)$ and K was reported to be linear and was described with two equations, valid in the glassy state, and in the equilibrium melt state, respectively (Equations 4a and b)

$$K_{glass} = 8.407 - 0.04714\ V(\tau_3) \tag{4a}$$

$$K_{melt} = 3.115 - 0.008473\ V(\tau_3) \tag{4b}$$

with K in GPa and $V(\tau_3)$ in $\mathring{A}^3$.

In order to compare Equations 4a and b with the present data, they were converted to give the corresponding relationship between the tensile modulus E and $V(\tau_3)$, by combination with Equation 5. A value of $\nu = 0.38$ for the glassy state and $\nu = 0.49$ for the melt state was used for the Poisson constant.

$$E = 3K(1 - 2\nu) \tag{5}$$

The combinations of Equations 3 and 4 with Equation 5, resulted in the following equations:

$$E_{glass} = 6.053 - 0.03394\ V(\tau_3) \tag{6}$$

$$E_{melt} = 0.1869 - 0.0005084\ V(\tau_3) \tag{7}$$

with E in GPa and $V(\tau_3)$ in $\mathring{A}^3$.

It should be noted that the reliability of Equation 7 crucially depends on the correct assignment of the value of ν, for instance, if ν is changed, e.g. from only 0.490–0.492, the calculated value of E increases by 20%. Due to lack of accurate literature data of the Poisson ratio for melts of PMMA, the values of Equation 7 should be interpreted with caution.

Equations 6 and 7 are plotted in Fig. 6 together with the measured values of $E'_{storage}$ and $V(\tau_3)$ of the present study. Clearly, at low values of $V(\tau_3)$ (corresponding to measurements at low temperatures), there is good agreement between the predictions of Equation 6 and the measured values of $E'_{storage}$ and $V(\tau_3)$. This is a further support for the universal relationship between the macroscopically determined bulk modulus and the microscopic free volume quantities proposed in Schmidt *et al.* [19] and Schmidt [20] and that this relationship can also be applied to predict other macroscopic properties, such as, the storage modulus from measurements of the microscopic free volume by PALS.

As $E'_{storage}$ decreases as a function of $V(\tau_3)$, a strong deviation between Equation 6 and the measured data is evident. The increasing deviation between the measured data points and Equation 6, as a function of $V(\tau_3)$, is most likely resulting from Equation 6 only being valid for the truly glassy state, which is not true for the data points at approximately $V(\tau_3) > 105\,\mathring{A}^3$. Moreover, the temperature dependence of ν for PMMA is not taken into account, probably leading to an over-estimation of E by Equation 5 as a function of temperature.

5. Conclusions

PALS and DMA measurements were performed on bone cement as a function of temperature. The elimination of residual monomer was found to decrease the value of the o-Ps from 2.04–1.91 ns and to increase the storage modulus from 2.3 to 3.0 GPa. Further analysis of the PALS measurements revealed that the elimination of monomer started at ca 60 °C.

The correlation between the microscopic free volume $V(\tau_3)$ and storage modulus $E'_{storage}$ was investigated. To a first approximation, a linear relationship between $V(\tau_3)$ and $E'_{storage}$ was found in the temperature range 24–120 °C. At low temperatures and absence of residual monomer, the relationship was found to be in good agreement with a previous investigation of the bulk modulus versus $V(\tau_3)$ for glassy materials.

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References

1. A. MAFFEZZOLI, D. RONCA, G. GUIDA, I. POCHINI and L. NICOLAIS, *J. Mater. Sci. Mater. Med.* **8** (1997) 75.
2. C. I. VALLO, *Polym. Int.* **49** (2000) 831.
3. C. I. VALLO, P. E. MONTEMARTINI and T. R. CUADRADO, *J. Appl. Pol. Sci.* **69** (1998) 1367.
4. J. L. HAILEY, I. G. TURNER, A. W. MILES and G. PRICE, *J. Mater. Sci. Mater. Med.* **5** (1994) 617.
5. C. I. VALLO, T. R. CUADRADO and P. M. FRONTINI, *Polym. Int.* **43** (1997) 260.
6. G. M. BRAUER, D. J. TERMINI and G. DICKSON, *J. Biomed. Mater. Res.* **11** (1977) 577.

7. I. REHMAN, E. J. HARPER and W. BONFIELD, *Biomaterials* **17** (1996) 1615.
8. S. J. TAO, *J. Chem. Phys* **56** (1972) 5499.
9. M. ELDRUP, D. LIGHTBODY and J. N. SHERWOOD, *Chem. Phys.* **63** (1981) 51.
10. M. SCHMIDT and F. H. J. MAURER, *Polymer* **41** (2000) 8419.
11. Y. C. JEAN, J.-P. YUAN, J. LIU, Q. DENG and HSINJIN YANG, *J. Polym. Sci. B: Polym. Phys.* **33** (1995) 2365.
12. Y. KOBAYASHI, K. HARAYA, S. HATTORI and T. SASUGA, *Polymer* **35** (1994) 925.
13. PATFIT-1998 Computer Program, Risø National Laboratory, Denmark.
14. H. F. M. MOHAMED, A. M. A. EL-SAYED and G. G. ABD-ELSADEK, *Polym. Degrad. Stabil.* **71** (2000) 93.
15. C.L. WANG, T. HIRADE, F. H. J. MAURER, M. ELDRUP and N. J. PEDERSEN, *J. Chem. Phys.* **108** (1998) 4654.
16. J. BOREK and W. OSOBA, *J. Polym. Sci. B: Polym. Phys.* **34** (1996) 1903.
17. G. DLUBEK, F. REDMANN and R. KRAUSE-REHBERG, *J. Appl. Polym. Sci.* **84** (2002) 244.
18. E.J. HARPER and W. BONFIELD, *J. Biomed. Mater. Res.* **53** (2000) 605.
19. M. SCHMIDT, M. OLSSON and F. H. J. MAURER, *J. Chem. Phys.* **112** (2000) 11095.
20. M. SCHMIDT, PhD Thesis, Department of Polymer Technology, Chalmers University of Technology, Gothenburg, Sweden (2000).

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