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This is the accepted version of:

G. Consolati, F. Quasso, E. Yaynik, F. Briatico Vangosa, O. Šauša, K. Ehrmann, H. Švajdlenková *Thermal Expansion of Free Volume in "classic" and Regulated Dimethacrylates: Photocured Directly and via a Mask to Study Pillar Formation* Physical Chemistry Chemical Physics, Vol. 24, N. 23, 2022, p. 14299-14309 doi:10.1039/d2cp00882c

The final publication is available at https://doi.org/10.1039/d2cp00882c

Access to the published version may require subscription.

When citing this work, cite the original published paper.

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eceived 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000>

Thermal expansion of free volume in "classic" and regulated dimethacrylates: photocured directly and via mask to study pillar formation

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The temperature dependence of free volume in dimethacrylates (poly2M), cured by direct irradiation (poly2M-A) or via mask (poly2M-B), and in thiol-based 2M sample (poly2M-co-EDDT) was investigated by positron annihilation lifetime spectroscopy (PALS) and dilatometry (DIL) to study the influence of thiol regulation on the microstructure via free volume characteristics. It was found that the free volume fraction as determined from experimental data by using the standard spherical approach for the hole shapes showed systematic differences with the analogous quantity as evaluated from the lattice-hole theory. Much better results were obtained for cylindrical holes, which expand 'anisotropically' in poly2M samples and 'isotropically' in the poly2M-co-EDDT resin. In addition, the hydrogen bond changes and the conversion of monomers in cured samples studied by near infra-red spectroscopy (NIR) revealed spectrum-structure correlations for the final cured thermosets.

1. Introduction

Dimethacrylate resins (poly2M) are widely used in many applications such as protective and decorative coatings,1 dental medicine² and 3D lithography³ due to fast photopolymerization. Photocuring is used to fabricate 3D objects, 2D open periodic structures and a micro-pillar array. An interesting phenomenon in photopolymerization is that the optical beam passing through the photopolymerizable medium can propagate without divergence in a

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self-induced polymer light guide and can thus form microscopic channels, 'so called' micropillars.4

These widely used micropillar-structured surfaces improve surface properties such as anti-icing, anti-fouling or better adhesion. Fu Hao Chen studied the growth of periodic pillar arrays in thin films, where the intensity of irradiation and the film thickness are the main parameters of pillar formation and the tuning of the surface.⁵ Photopolymerization of 2M forms inhomogeneous highly crosslinked and brittle network structures. For the network formation via radical chain growth mechanism, $^{\rm 6}$ the gelation appears at low conversion of monomers (less than 20%) and builds up high shrinkage stress. The overall shrinkage stress is one of the most important factors, which contributes to increased brittleness of materials. A very promising direction for improvement is regulated photopolymerization using chain transfer agents such as thiols7 or addition-fragmentation chain transfer agents (AFCT)8 leading to homogeneous network architecture with reduced shrinkage stress and high toughness.9,10 Recently, the positron annihilation lifetime spectroscopy (PALS) study of a cured mixture of dimethacrylates (poly2M) and a regulated poly2M using a dithiol and a difunctional beta allyl sulfone revealed that both modified poly2M samples have homogeneous network structure creating smaller free volume voids, more uniform void sizes¹¹ and reduced void fraction¹² than poly2M. Reduced void volume and void fraction determined from positron lifetime measurements by the standard

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reference sample B (2M-B) was irradiated via mask (see geometry in SI) by the LED diodes of the average flux density \sim 174 μW cm^-2 for 12 hours. The flux density was measured by Ophir Photonics StarLite meter with the probe PD300-UV.



Fig. 1 Chemical structures of the two dimethacrylates: UDMA and D3MA forming 2M, the photoinitiator (TPO-L) and the dithiol (EDDT).

2.3. Characterization Methods

2.3.1. Bulk density measurements

The bulk density of two dimethacrylate-based samples, i.e. poly2M-A and poly2M-B, was determined by the gravimetric method. The discs from PALS and dilatometry measurements were weighed dry (m_0) and immersed in ethanol (m_1) . Their bulk density was calculated based on the equation:

$$\rho = \rho_{EtOH} \left[\frac{m_0}{m_0 - m_1 + m_{wire}} \right] \tag{1}$$

where ρ_{EtOH} is the density of ethanol at the laboratory temperature of 298 K, and m_{wire} is the weight of the wire in EtOH.

In the case of thiol-based sample poly2M-co-EDDT, the bulk density was estimated with the helium pycnometer (Gas pycnometer – Gas Helium 5.0 - Pycnomatic – ATC Thermo Scientific). The sample volume (V_o) is calculated based on the equation:

$$V_p = V_c \left[\frac{V_a}{1 - \left(\frac{p_1}{p_2}\right)} \right]$$
⁽²⁾

where V_c is the volume of the sample cell, V_a is the volume of the reference cell, and p₁, p₂ correspond to the pressure after helium pressurization of the sample cell and to the pressure equalization after the connection between the sample and the reference cells.

approach, i.e. Tao-Eldrup quantum mechanical model,^{13,14} can be the key structural factors responsible for improved material properties. Important progress in PALS brought the new methodology combining two experimental methods, i.e. the microscopic and macroscopic examinations from PALS and dilatometry, respectively, and the theoretical determination of the thermal expansion of free volume by means of lattice-hole theory.^{15,16}

In this work, we investigate the impact of the regulation of photopolymerization via chain transfer agent (CTA) and of differently cured 2M, as a model material, by direct irradiation and via mask on the microstructure. 2M is an equimolar mixture of two dimethacrylates (urethane-based dimethacrylate UDMA and 1,10decanediol dimethacrylate D3MA). Modified mixtures of 2M with addition of dithiol (poly2M-co-EDDT) and two differently cured poly2M networks were investigated in terms of void volume and void fraction. Here, we try to find information on the shape of the free volume voids and their expansion behaviour in a model dimethacrylate-based material. In addition, we also determined the influence of irradiation via mask on the crosslinking behaviour and the microstructure in pillars, which determine the material properties of final cured materials, for example in 3D lithography. These directly illuminated areas by light guides with different properties will be called pillars in this work, which have significantly larger dimension than micropilars. This study helps to extend the knowledge about thermal expansion in dimethacrylates and the impact of differently cured dimethacrylates on their microstructure.

2. Experimental

2.1. Material

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The two dimethacrylate-based monomers, i.e. urethane dimethacrylate (UDMA, isomeric mixture, CAS: 72869-86-4, $M_w = 470.57$ g mol⁻¹) and 1,10-decanediol dimethacrylate (D3MA, $M_w = 310.44$ g mol⁻¹), kindly provided by lvoclar Vivadent AG, were mixed in equimolar ratio with 0.1 mol % of ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate (TPO-L, CAS: 84434-11-7, from Lambson Ltd HQ, $M_w = 316.3$ g mol⁻¹) as a photoinitiator (see Fig. 1). 2,2'-(Ethylenedioxy)diethanethiol (EDDT, CAS:465178) was purchased from Sigma-Aldrich. The average molar mass (M_s) for poly2M and poly2M-co-EDDT formulations is 390.51 g mol⁻¹ and 338.45 g mol⁻¹,

2.2. Resin preparation

The reference mixture of two dimethacrylates (2M) and the CTAbased sample containing 20 mol % of EDDT (2M+EDDT) were poured into a chamber with a diameter of 15 mm and a thickness of 3 mm. Samples were irradiated via PMMA-based diffusor by a series of 12 diodes (violet LED OSV5YL57E1A, a flux density of ~ 4.65 m W cm², photon emission at λ = 405 nm) for four hours. The second

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measurements are performed at the laboratory temperature of 296.2 K

2.3.2. Near-infrared spectroscopy (NIR)

The spectra were measured on BW Tek detector (Sol. 2.2) using light source BPS 2.0 of spectral range (350 to 2600 nm) and optical-fiber cables of diameter 100 um. At the registration of spectra, the integration time of 1000 $\ensuremath{\mu s}$ and the wavenumber range of 4442 - 9431 cm⁻¹ were applied. The liquid monomers were measured in quartz cuvettes and the cured samples were fixed in a fiber coupled cuvette holder BW TEK. In the case of mapping of poly2M-B samples, the reflex probe was used.

2.3.3. PALS

Time annihilation spectra were measured on a conventional fastfast coincidence spectrometer with a time resolution of about 340 ps FWHM. The resolution function of the spectrometer as well as the correction for annihilation in the positron source were made by measuring the lifetime spectrum of defect-free AI sample with a single lifetime of 166 ps. Activity of the ²²Na source enclosed between two Kapton films (DuPont[™]) with a thickness of 8µm was about 1 MBq. A standard sample-source-sample sandwich arrangement was used. Temperature measurements were made in a closed-cycle cryogenerator from Janis Co., Model CCS-450 with a temperature stability of 0.5 K. All measurements were conducted in vacuum. The LT program was used to evaluate the lifetime spectra.17

2.3.4. Specific volume measurements

Measurements of the specific volume in the two dimethacrylatebased samples, i.e. poly2M-A and poly2M-B, were performed using a capillary dilatometer, which contained the sample immersed in mercury (purity > 99.999 %, Fluka) used as a reference liquid. The volume of the bulb was 2.306 cm³, the length and section of the capillary were 30 cm and 0.0143 cm², respectively. For the cooling runs, the dilatometer was immersed in a thermostatic bath to grant a uniform temperature; the circulating liquid was water in the temperature range 343 - 280 K and ethanol from 280 to 258 K. The height reached by the mercury meniscus in the capillary at each temperature was determined by means of a digital

cathetometer. The temperature was stable within 0.5 K. The measurements started from the highest temperature: the cooling rate to reach a new temperature was 0.1 K min⁻¹. Then, the sample remained in the new temperature state for 15 min before starting the measurements. Three runs were carried out for each sample.

In the case of thiol-based sample poly2M-co-EDDT, dilatometric behaviour was investigated via high pressure dilatometry using a commercial confining fluid type pressure dilatometer (Gnomix Inc.) revamped with a new acquisition system (NI) and control software. The confining fluid was mercury. The material dilatometric behaviour was investigated through a series of isothermal compressions: starting from 10 MPa, the pressure is increased by 10 MPa, then a 5 min waiting stage at constant pressure allows

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Based on the known sample mass the bulk density is computed. All temperature re-equilibration before the measurement is made. The maximum pressure in each compression is 200 MPa. Temperatures ranged between 298.15 K and 368.15 K, performing an isobaric compression every 10 K. Specific volume at atmospheric pressure was extrapolated from experimental data via the Tait equation.¹⁸

3. Results and Discussion

3.1 NIR

3.1.1 Uncured D3MA, UDMA, 2M and dithiol-based 2M mixtures

The investigation of hydrogen bond donor groups of monomers, their structure and their self- or intermolecular interactions between the same monomers (self-association) or between different monomers or the chain transfer reagent (CTA) has a great impact on a better understanding of photopolymerization and final material properties. The polar N-H groups in urethane dimethacrylates (UDMA) have the tendency to form hydrogen bonds with carbonyl (C=O) and ether (C-O-C) groups which preferentially yield linear structures but HN·····HN bonding is less favourable.¹⁹ In addition, interactions between urethane groups can form more stable dimers or oligomeric structures, which are limited due to competing formation of cyclic dimers.²⁰



Fig. 2 NIR spectra of monomers: D3MA (- - -) and UDMA (----), dithiol EDDT (-----) and of the mixtures: 2M (---), 2M+EDDT (---).

In Figure 2, highly viscous UDMA monomers exhibit pronounced absorption peaks of the N-H stretch first overtone in the region (6498 - 6890 cm⁻¹) and the peak maximum of the C-H second overtone lies at around 8444 cm⁻¹. The vibrations of these groups greatly reflect even slight changes in molecular interactions. After addition of D3MA, the 2M and 2M+EDDT mixtures showed the appearance of a shoulder of the C-H 2nd overtone at lower frequency (8307 cm⁻¹), which can be ascribed to strong C-H interactions.

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strongly associated and the weakest H bond structures are influenced by the weak hydrogen bonds of S-H groups.

3.1.2. Cured samples

The NIR spectra of both directly cured poly2M-A, poly2M-co-EDDT and cured via mask poly2M-B samples, obtained after PALS and dilatometry experiments, were measured at four different disc areas (Fig. S3 in SI) or the directly irradiated middle and shaded parts (Fig. 5, Fig. S4 in SI), respectively.



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The wavenumber region of the N-H absorption band (6498 – 6890 cm⁻¹) may be decomposed into three constituent contributions, as seen by the Gaussian fits in Figure 3. The fit curve in the lower wavenumber region (6683 - 6695 cm⁻¹) for three uncured samples can be assigned to the strong self-associating species; and two less intense fit curves (2 and 3) lying at around 6750 $\rm cm^{\text{-}1}$ and 6800 $\rm cm^{\text{-}1}$ come from weak H bonded structures or free NH groups, respectively.

In the case of the mixture of the two studied monomers UDMA and D3MA in a ratio 50:50 (2M), the addition of D3MA causes formation of weak hydrogen bonds within self-associated species and given by the lowering of intensities and by the shift to high wavelengths. The strength of the H bonds weakens due to the lower polarity of D3MA monomers. It was revealed that UDMA monomers have higher electrical permittivity and conductivity compared to triethylene glycol dimethacrylate (TEGDMA),²¹ which has two ether oxygen groups more than D3MA. In addition, the increase of the intensity of the $\mathbf{3}^{rd}$ overlapped absorption band, lying at around 6800 cm⁻¹, suggests the formation of free N-H groups in the structure (Figure 3, Figure S2 b).



Fig. 3 N-H 1st overtone region for uncured UDMA (---), 2M (---), 2M+EDDT (---) samples, with the decomposition of the absorption peak into three Gaussian fit curves, given by the dash lines, lying at a wavenumber of peak maxima: 6883-6695 cm⁻¹, 6756 - 6765 cm⁻¹, and at around 6800 cm⁻¹.

In the case of uncured 2M+EDDT sample, thiol S-H groups with lower electronegativity (χ = 2.589) than N-H groups (χ = 3.04) are slightly polar and have moderate formation of H bonds with other molecules. In Figure 3, the adding of 25 mol% of dithiol-based chain transfer (EDDT) reagent again showed a decrease of 1st and 3rd N-H band intensities at 6695 cm⁻¹ or ~ 6800 cm⁻¹, respectively, but the 2^{nd} peak at $\sim 6765~\text{cm}^{\text{-1}}$ is almost unchanged. This implies that only

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Fig. 4 N-H 1st overtone region for selected cured a) poly2M-A (—), b) poly2M-B (—) and c) poly2M-co-EDDT (—) samples, measured in the irradiated middle part of disc, with the decomposition of the broad band into three Gaussian fit curves given by the dash lines (1-3). Red arrow implies the shift of wavenumber after curing of the mixture and the blue arrow marks the formation of free N-H groups in the network structure.

In Fig. 4 a) and b), in the region of the N-H 1st overtone, the main 1st peak of the selected cured poly2M-A and poly2M-B samples has a shift to higher wavenumbers compared to the monomer mixture (given by the red arrow) and an increased intensity of $3^{\mbox{\scriptsize rd}}$ peak assigned to the formation of free N-H groups in the network structure (marked by the blue arrow). Both findings suggest weak H-bond interactions after network formation. Moreover, the increased conversion and larger shift to the higher wavenumber for poly2M-A sample than for poly2M-B sample, in Figure 5 a 4 a), imply weakening of H bond interactions due to increased heterogeneity of the network structure. On the other hand, the poly2M-co-EDDT sample displays a broad $\mathbf{1}^{st}$ peak and an overlap with two additional weaker H-bonded structures without formation of free N-H groups that may point out the homogeneous H-bond interactions in the network. Moreover, the slight shift in the 1st peak to lower wavenumbers of cured poly2M-co-EDDT sample (given by the red arrow in Fig. 4 b)) implies the formation of stronger H-bond interactions after curing of the sample.

The conversion of monomers, reflected in the disappearance of the double bond, i.e. >C=CH₂ groups (6172 cm⁻¹) did not show complete conversion (Figure 5). The published conversion of monomers determined by real-time near infrared (RT-NIR)-photorheology for the mixture 2M and dithiol-based sample was 71 % or 99%, respectively.¹⁰ In Fig. 5, a less intense >C=CH₂ band of poly2M-co-EDDT also implies higher double bond conversion compared to the poly2M samples.



Fig.5 NIR spectra of selected cured poly2M-A (—), poly2M-B (—) and poly2M-co-EDDT (—) samples from Figs. S3 and S4 in SI, measured in the irradiated middle part of disc, with the inset: the region of double bonds.

3.2. Bulk density

The bulk density (ρ_p) or a related parameter packing density reflect the structural arrangement given by the conversion of monomers, packing ability of chains and local free volume. In Table 1, two differently cured poly2M samples show that directly irradiated poly2M-A sample had a little higher ρ_p compared to poly2M-B irradiated via mask. In comparison with the regulated photopolymer poly2M-co-EDDT, higher ρ_p of poly2M-co-EDDT compared to poly2M implies a more densely packed network structure. This finding is in agreement with the published ρ_p^{-11}

Moreover, more or less packed network structure of cured samples poly2M-A and poly2M-co-EDDT according to their bulk density is in agreement with the NIR findings of the position of N-H 1st overtone and to the conversion of >C=CH₂ groups in Fig. 4 a), 4 b) or Fig. 5, respectively.

Table 1 Bulk density (ρ_p) for three differently cured samples at 298 ν

Samples	(g/cm ⁻³)
poly2M-A	1.146 ± 0.001
poly2M-B	1.144 ± 0.001
poly2M-co-EDDT	1.170+-0.001

3.3. PALS

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Three-component analysis of annihilation lifetime spectra was gerformed. The shortest component is attributed to the annihilation of *p*-Ps, the intermediate component originates from direct electron-positron annihilation in bulk, the longest *o*-Ps is lifetime component is related to defects and free volumes. Only this last component is subject to further discussion because the lifetime of *o*-Ps is directly dependent on the size of the cavities in the investigated material according to the different models. The very frequently used semiempircal Tao-Eldrup model^{13,14} assumes spherical holes with the effective radius, *r*_h for *o*-Ps annihilation with lifetime *r_o*-*p*_s. The relationship is given by the equation:

$$\tau_{o-Ps} = 0.5 \left\{ 1 - \frac{r_h}{(r_h + \Delta R)} + \left(\frac{1}{2\pi}\right) sin\left[\frac{2\pi r_h}{r_h + \Delta R}\right] \right\}^{-1}$$

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where ΔR is the empirical constant 0.166nm.²² The relative intensities of *p*-Ps and *o*-Ps annihilation processes were fixed at the theoretical ratio of 1/3 at which a good fit with a normalized chi square $\chi 2$ in the range of 0.95-1.05 was obtained. The *o*-Ps lifetimes, used for direct comparison with the dilatometric measurements, are shown for the selected temperature range (260 – 370 K) in Fig. 6, and for the whole temperature range in Fig. S5 in SI.The fitted data were from the second cooling cycle measured after fast cooling from RT down to low temperatures with the rate 2.5 K min¹ and next the first heating of the sample to 370 K. In Fig. S5, τ_{o-Ps} exhibited the hysteresis above room temperature after the first heating suggesting network rearrangement. The subsequent heating/cooling cycles were reproducible. Therefore, the PALS data from the second cooling cycle are suitable for comparison with dilatometric data.



Fig. 6 Temperature dependence of the *o*-Ps lifetime ($\tau_{o,Ps}$) and the size of free-volume cavities of spherical shape (V_h) for poly2M-A (\blacksquare), poly2M-B (\star) and poly2M-co-EDDT (\blacktriangle) samples; T_g^{PALS} determined by the intersection point of two linear regions.

The temperature dependence of $\tau_{o,Ps}$ from the PALS experiments shows the following: The lifetimes for sample poly2M-A below the

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glass transition temperature (T_g) are lower than for poly2M-B. Above $T_g,$ poly2M-A has a higher expansion of the free volume of cavities compared to poly2M-B. The dithiol-based sample poly2M-co-EDDT has a lower T_g^{PALS} than the poly2M-A sample and steep free volume expansion above T_g^{PALS} .

Table 2 Characteristic PALS glass transition temperatures T_g^{PALS} and thermal expansion coefficients of free-volume voids, below and above of T_g^{PALS} (α_{r1} , α_{r2}) for the series of studied samples

Samples	Tg ^{PALS} (K)	α _{F1} (10 ⁻⁴ K ⁻¹)	α _{F2} (10 ⁻⁴ K ⁻¹)	α _{F1} - α _{F2} (10 ⁻⁴ K ⁻¹)
poly2M-A	317	47.27	97.23	49.96
poly2M-B	290	43.38	63.87	20.49
poly2M-co-EDDT	291	52.24	92.66	40.42

The thermal expansion coefficients of free-volume voids α_{FI} , α_{F2} , calculated by spherical model of holes, and their difference $(\alpha_{F2} - \alpha_{F1})$ can be relevant characteristics for these investigated samples. It was published that dithiol-based samples form regulated and less crosslinked structures, ¹¹ which supports the finding of lower Tg^{PALS} and high expansion in the glassy state (Table 2).¹² It suggests that true crosslinking structure is reflected by Tg^{PALS} and the expansion of flexible linkers and unreacted monomers is reflected.

3.4 Dilatometry

(3)

Specific volume results, as obtained from dilatometry, are shown in Fig. 7 for the three polymers. Although the data displays a linear trend, a slight change in the slope is observed towards 300 K for poly2M-A and poly2M-B, which is in agreement with the PALS results.



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Fig. 7 Temperature dependence of the specific volume in the three investigated polymers: poly2M-A (■), poly2M-B (*) and poly2Mco-EDDT (▲). The uncertainties do not extend beyond the symbols. The arrows show the value of the specific volume (V) at 298 K, marked by the vertical line.

Specific volume data have a twofold function. First of all, they can be used to find the scaling parameters T^* and V^* needed to calculate the free volume fraction within the framework of the lattice-hole theory.23 This supplies an equation for the state of amorphous polymers at equilibrium, which is expressed in terms of reduced thermodynamic coordinates $\tilde{T} = T/T^*$ and $\tilde{V} = V/V^*$ at atmospheric pressure. By fitting such an equation (not reported here for simplicity, see e.g. Ref. 24) to the specific volume data, the scaling parameters are found. Alternatively, it is possible to use a simpler polynomial interpolation which gives the same results.²⁵ For the investigated polymer we found the values (Table 3):

Table 3 Scaling parameters calculated.

Samples	V [*] (cm ³ g ⁻¹)	<i>T</i> [*] (K)
poly2M-A	0.910	14833
poly2M-B	0.907	13783
poly2M-co-EDDT	0.846	10402

The Van der Waals volume (V_{VdW}) of poly2M-A and B polymers²⁶ is 410.47 Å³ molecule⁻¹, which corresponds to 0.633 cm³ g⁻¹. For poly2M-co-EDDT, V_{VdW} is 0.615 cm³g⁻¹. It is interesting to observe that the values found for V^* fit very well (within 5%) the relationship V^* = 1.45 V_{VdW} , noted for polymers obeying the Simha-Somcynsky equation of state.²⁷ Parameters T^* and V^* allow to find the dependence of the specific occupied volume V_{occ} on the temperature in the range of interest for each polymer by adapting a master curve.²⁸ Then, the free volume fraction (h) is calculated as

$$h = 1 - V_{occ} / V.$$

(4)

The temperature dependence of h for our series of polymers is shown as a solid line in Figs. 9 and 10. Knowledge of the specific volume. V. is also essential to build the free volume fraction (f) as determined from PALS data. Indeed, the specific free volume can be seen as the product of the number density of holes, N, times the average hole volume (v_h). Then, the free volume fraction results:

$$f = \frac{Nv_h}{V} = \frac{Nv_h}{Nv_h + V_{occ}}$$
(5)

By plotting V versus v_h , the number density of holes, N, is found. We point out that the result is model dependent, since the transformation from o-Ps lifetime to v_h implies a guess on the adopted geometry for the holes. In Fig. 8, the correlation between V and v_h is shown for poly2M-A, poly2M-B and poly2M-co-EDDT, assuming spherical holes according to the Tao-Eldrup model (eq. 2). The correlation coefficients for poly2M-A, B and poly2M-co-EDDT

are 0.996, 0.989 and 0.995, respectively, which imply that N (the slope of the straight lines interpolating the data) can be assumed to

be a constant in the range of investigated temperatures. It results in $N = 5.0 \cdot 10^{20} \text{ g}^{-1}$ and $6.5 \cdot 10^{20} \text{ g}^{-1}$ for poly2M-A and poly2M-B, respectively, and in $N = 6.1 \cdot 10^{20} \text{ g}^{-1}$ for poly2M-co -EDDT. The finding of N for poly2M-A is in agreement with the published value for poly2M 5.7 $\cdot 10^{20}~g^{\text{-}1.^{12}}$ In addition, the comparable trend, that poly2M-co-EDDT contains a higher number density of voids (N) and lower specific occupied volume (Vocc) than the poly2M-A sample (Table 4), was already published.12



Fig. 8 Dependence of the specific volume, V, on the hole volume, v_{h} . for the three investigated polymers: poly2M-A (■), poly2M-B (*) and polv2M-co-EDDT (**▲**).

The new finding, a higher hole fraction for polv2M-co-EDDT than or poly2M, suggests that this parameter is sensitive regarding the curing parameters, i.e. type and amount of photoinitiator and reaction conditions. This is the object of further study.

Table 4 PALS characteristics from Tao-Eldrup spherical model, i.e. void volume v_h at RT, the specific occupied volume V_{occ} , at room temperature (RT, 298 K), the free volume number density per unit mass N, and free volume fraction at RT for two differently cured 2M samples and thiol-based sample.

Samples	v _{h, 298K} (nm ³)	V _{occ} (cm ³ g ⁻¹)	N (10 ²⁰ g ⁻¹)	f _{298К}
poly2M-A	0.077(0.002)	0.865	5.0	0.045
poly2M-B	0.082(0.002)	0.863	6.5	0.062
poly2M-co-EDDT	0.092(0.002)	0.745	6.1	0.066

Fig. 9 reports the dependence of f on the temperature. It is evident that, by using the spherical approximation for the holes, the *f* data for the polymers are systematically above the theoretical behaviour

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of h. Concerning poly2M-A and -B, the issue was to investigate cuboids and cylinders (flattened as well as elongated) as other possible shapes for the holes, but the discrepancy remained. On the other hand, a satisfactory fit was obtained with 'anisotropic' cylindrical holes. The usual implicit assumption for the growth of the holes with temperature is an isotropic increase: $v_h \propto s^3$, where s is a typical size (e.g. the radius of spherical holes). Nevertheless, it is conceivable that physical or chemical constraints hinder the expansion of the holes in specific directions, with the result that their volume can scale with a power law with $s: v_h \propto s^t$, with t < 3. Just as a naive example, volumes of cylindrical holes with fixed height would scale with the square of the radius. In this sense, we use the word 'anisotropic'. In order to quantitatively test the assumption, we considered cylindrical holes, whose aspect ratio (that is, the ratio between the height and the radius of the cylinder) changed by increasing the temperature.

If we call *q* the initial aspect ratio, r_0 the initial radius of the cylindrical hole, *p* a parameter accounting for the anisotropy (*p* = 1 for isotropic cylinders), the height *a* of the cylinder is:

$$a = qr_0^{1-p}r^p$$

It follows that the volume is:

 $v_{anis\,cyl}=\pi q r_0^{1-p} r^{2+p}$







Fig. 9 Temperature dependence of the free volume fraction as evaluated from the hole-lattice theory (*h*, continuous line) and from experimental data, *f*, assuming spherical holes (*f*, full symbols) for the three investigated samples: a) poly2M-A, b) poly2M-B and c) poly2M-co-EDDT. The arrows show the corresponding value of *f* at 298 K.

The procedure to determine the parameter p was the following: First, *o*-Ps lifetime r_3 was transformed into the radius of the cylinder r using the following pertinent equations,²⁹ suitably modified to take to account for (eq. 5):

$$\frac{1}{3} = \lambda_0 (1 - P_1 P_2)$$
 (8)

where

τ

(6)

(7)

$$P_1 = \frac{a}{a + \Delta a} + \frac{1}{\pi} \sin\left(\frac{\pi a}{a + \Delta a}\right) \tag{9}$$

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 $\int_0^{a_1 r/(r+\Delta r)} x J_0^2(x) dx$

 $P_2 = \frac{\int_0^{a_1} x \int_0^{a_1} x \int_0^{a_1} x \int_0^{a_2} (x) \, dx}{\int_0^{a_1} x \int_0^{a_2} (x) \, dx}$

 $J_0(x)$ being the Bessel function of the first kind of zero order, $a_1 = 2.4048$ the first zero of $J_0(x)$, $\lambda_0 = 2 \text{ ns}^{-1}$ and $\Delta r (= \Delta a)$ have the same meaning as in eq. 3.

(10)

Then, the hole volume v_h was calculated according to eq. 7, for a fixed p. Fitting the specific volume V versus v_h for each p supplied parameter N, which was used in (eq. 5) to calculate the fractional free volume f. Finally, this last parameter was compared with the theoretical quantity h (Fig. 10). Elongated cylinders (q > 1) did not produce a satisfactory fit; on the contrary, flattened cylinders give good fits. For q = 0.3 p = 0.24 was found and 0.15 for poly2M-A or poly2M-B, respectively. In the case of poly2M-co-EDDT, for q = 0.23 p = 1 was attributed. It means the polymer holes in this last network expand isotropically.

The finding of the cylindrical-flattened shape of the holes, which expand 'anisotropically' with temperature for both poly2M photopolymers (A, B), can be the basic structural characteristics for the highly crosslinked inhomogeneous networks formed by the irregular chain growth process. 2M-based resin was thus included in the group of polymers with anisotropic thermal expansion of holes found in perfluorinated oligomers,³⁰ low molecular weight polypropylene glycols,³¹ and thermoplastic polyesterurethane.³² In these materials, parameter *p* ranged between 0 and 0.40.

However, small but measurable differences were found between the two poly2M samples. Directly irradiated sample poly2M-A has slightly lower average volume, number density of holes and free volume fraction than the poly2M-B sample cured via mask. In the case of dithiol sample, the obvious reduction of free volume size (V_h), large increased number of density of holes (*N*)¹² and free volume fraction could be set as the key structural characteristics for regulated crosslinking structure. In particular, both the average volume as well as the number density of holes are slightly smaller in the poly2M-A than in poly2M-B sample, using the anisotropic model for evaluation.



Fig. 10 Free volume fraction f evaluated according to the 'anisotropic' model for cylindrical flattened holes $(\Box, *)$ and to the 'isotropic' model for cylindrical flattened holes (Δ) compared to the analogous theoretical quantity h (line) and to spherical model (\blacksquare ,

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*, \blacktriangle) for a) poly2M-A, b) poly2M-B and c) poly2M-co-EDDT. The arrows show the corresponding value of *f* at 298 K.

Table 5 Characteristic PALS parameters determined from the flattened cylindrical model. The void volume v_h , the free volume number density per unit mass *N*, and the free volume fraction at RT for two differently cured 2M samples and the thiol-based sample.

Samples	v _{h,298K} (nm³)	N (10 ¹⁹ g ⁻¹)	f _{298К}
poly2M-A	0.39	4.1	0.019
poly2M-B	0.43	4.4	0.022
poly2M-co-EDDT	0.16	29.5	0.054

Moreover, the free volume fractions also showed tiny differences, as it is evident from the comparison of the specific volumes in Fig. 7. In fact, the occupied volumes in the two samples are almost identical (Table 4). We point out that a simple analysis of the two specific volumes as supplied by dilatometry would not reveal the peculiarities of the free volume at microscopic level in the two samples. In this connection, PALS plays a valuable role; on the other hand, the two techniques act synergistically since only their combination allows one to deduce the number density of holes in a structure, and if such a number remains constant with temperature. The most important finding of the isotropic expansion of the free volume in the dithiol-based sample is a valuable contribution to the knowledge of the behaviour of regulated dimethacrylate networks. Similar results were found in polystyrene¹⁴ and in an amorphous polyether-polyseter polyurethane.¹⁵

In the case of the poly2M sample illuminated via mask, the double bond conversion by NIR and the free volume characteristics by PALS were measured for the local illuminated and shaded areas. The details about the determination of measured irradiated and shaded areas can be found in Fig. S6 in SI. NIR measurements revealed small but measurable differences in the conversion of monomers between both areas. In Fig. 11, direct illuminated areas of poly2M-B sample exhibit the shift to higher wavenumber and lower absorption band of terminal $C=CH_2$ groups compared to the shielded ones implying higher conversion of monomers. The small differences were also found in the microstructural PALS data of the poly2M-B sample. Despite certain limitations of the PALS experiment with larger active area of the positron source of about 3 mm than the illuminated areas of 1 mm on the mask, it can be stated that the directly illuminated areas containing pillars show a higher intensity of o-Ps than the shielded areas, which means that a higher number of holes exist in this region (Fig. 12 c). This finding is in agreement with higher DBC from NIR (Fig. 11). Similarly, the lower dispersion of o-Ps lifetimes for directly irradiated areas implies that formation of highly cross-linked pillars leads to a more homogeneous free volume size distribution (see Fig. 12 b).



Fig. 11 NIR spectra of poly2M-B sample illuminated via mask measured in irradiated ($\Phi,$ 1 - 3) and shaded areas (I-III).

But, the pillar containing areas have in some places higher *o*-Ps lifetime that could be due to higher shrinkage stress during formation of pillars than in the shielded areas. Another explanation can be that in less cross-linked shaded areas the chains are closer to each other due to less crosslinks. However, these issues are already outside the scope of the main topic of the article and will be studied in more detail in the future. The volume properties in the shielded areas were also influenced by microstructural properties of the interface of non-irradiated regions and pillars, where molecular diffusion also plays an important role in the boundary between the irradiated and unirradiated regions.³³ These qualitative findings contribute to a better understanding of the differences in the microstructure of the inhomogeneously illuminated sample volume of copolymer 2M during photopolymerization.



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Fig. 12 a) *o*-Ps lifetimes, b) their dispersion, and c) relative intensity I_{Ps} for poly2M-B sample, measured in directly illuminated areas (\bullet) and shielded areas (\circ) on mask. Radius from the middle part of sample (zero point) is the number above the symbols (in mm). The highlighted areas correspond to the mean values with standard deviation.

Conclusions

In the present work we investigated the microstructure of dimethacrylate-based mixture (2M) light-cured in two different ways, i.e. direct irradiation (poly2M-A) or via mask (poly2M-B), and of the regulated dimethacrylate sample poly2M-co-EDDT by combining dilatometry and positron annihilation lifetime spectroscopy. In spite of the thermal expansion of the specific volume, which is very similar in the first two investigated polymers, the combination of the two techniques allowed us to evaluate the free volume fraction and in particular the number density of holes. The comparison with the analogous quantity estimated by the lattice-hole theory supplied valuable information about the shape of sub-nanometer cavities forming the free volume. Although the

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result is only approximate, since real cavities are obviously irregular, we found that a cylindrical flattened shape is a better approximation with respect to the usually assumed spherical geometry.

Furthermore, the simple idea of isotropic expansion of the cavities, implicit in the spherical guess, brings about systematic differences with the theory for the poly2M samples. Such a discrepancy can be eliminated when the holes are set to expand anisotropically: growth along the axis of the cylinder occurs slower than the lateral expansion, as it is deduced by the fact that the parameter p < 1 in both polymers. At RT, the poly2M-A sample has smaller voids and lower number density of voids compared to poly2M-B. In addition, the relative comparison of the different regions in the poly2M-B sample irradiated via mask revealed higher conversion of monomers in volumes with pillars than shielded ones, which is in relation to the higher number of voids and reduced dispersion of void sizes. Moreover, the larger void size in pillar containing areas than in directly irradiated areas can be due to formation of higher shrinkage stress or more crosslinks where the chains are not close to each other. Although the differences in the free-volume behaviour of the two investigated poly2M samples are not so large, this work suggests the need to study these curing processes in dimethacrylate based samples in more detail in the future, as they may have implications for many material properties. The herein developed method with PALS has proven to be a promising tool for this purpose.

Also, in the case of the regulated dimethacrylate, thiol-based 2Msample (poly2M-co-EDDT), the cavities forming the free volume can be better approximated as flattened cylinders. However, during their expansion with temperature, our results show that the aspect ratio remains constant, in contrast to the other two dimethacrylates. Moreover, the regulated dithiol-based network structure forms increased number density of reduced voids resulting in obviously higher void fraction than in poly2M samples. Therefore, the developed PALS analysis could be employed to determine network homogeneity of regulated radical polymerization. Finally, the NIR spectra of cured poly2M-A and poly2M-co-EDDT samples revealed that the formation of N-H groups and the positon of the main 1st peak of NH absorption band can be used additionally to evaluate the homogeneity of the network structure. Studying the relationships between the factors influencing the microstructural free volume behaviour, i.e. free volume characteristics, of dimethacrylate-based samples and mechanical properties can bring valuable knowledge about improved material properties.

Author Contributions

Conceptualization (H.Š.), Data curation(G.C., O.Š.), Formal Analysis (G.C, O. Š.), Funding acquisition (H.Š.), Investigation (G.C., F.Q., F.B, E.Y., O.Š., R.L., H. Š), Methodology (G.C.), Project administration (H.

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Š.), Resources (H. Š, K.E.), Supervision (G.C., H.Š.), Writing – original draft (G.C., H.Š.), Writing - review & editing (G.C., F.Q., F.B., E.Y., O.Š., K.E., H. Š.).

Acknowledgements

This work was supported by Ivoclar Vivadent AG as well as by the VEGA and the SRDA, Slovakia under Grants No. VEGA 2/0029/20 or APVV-19-0338, respectively.

Conflicts of interest

There are no conflicts to delcare.

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