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Water ageing of urethane dimethacrylate networks

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ABSTRACT

This work explores the process of water ageing of high-temperature high-pressure polymerized urethane dimethacrylate (UDMA) networks. UDMA samples polymerized under several pressures (0.1–300 MPa) and differing by the conversion degree of polymerization were aged in water at 37, 50 and 70 °C and followed by gravimetry. Diffusion was observed to obey Fick's law. The diffusion coefficient and water maximal uptake were observed to be almost independent of polymerization pressure, consistently with analysis of Dynamic Vapor Sorption data suggesting that external polymerization pressure has no effect on polymer affinity with water. This was ascribed to the fact that all materials have the same cohesive energy, as confirmed by ultrasonic measurements of elastic moduli. Polymerization pressure (used to improve conversion degree and mechanical properties) would thus have a minor influence on water ageing that is mainly triggered by polymer chemistry. When elevating the polymerization pressure, there is hence no compromise between the optimization of thermo-mechanical properties and the resistance to water ageing.

1. Introduction

Materials such as ceramics and organic matrix composites for dental applications have been developed to meet requirements of patients for aesthetic treatments. Dental resin composites formulations have been progressively improved since their introduction in the 1950s [1,2]. Bisphenol A Glycidyl Methacrylate [3] is still among the most used monomers. However, its high viscosity (1200 Pa s) due to its high molecular weight (512 g mol^{-1}), the presence of aromatic groups limiting mobility and OH groups creating hydrogen bond between chains [4] limits the incorporation of fillers aimed at improving mechanical properties, and makes necessary to mix it with diluents co-monomers such as Triethylene Glycol Dimethacrylate (0.011 Pa s viscosity). Urethane dimethacrylate (UDMA) offers an interesting alternative [5] with a lower viscosity (23.1 Pa s) despite its “high” molecular weight (470 g mol^{-1}). Its incorporation in reactive mixture was shown to delay the

vitrification, thus increasing the conversion degree and mechanical properties [6].

Progress and use of computer-aided design/computer-aided manufacturing (CAD-CAM) technology in dentistry [7–10] allows to have access in more efficient polymerization technique such as High Temperature – High Pressure (HT-HP) polymerization. This process permits to produce composite blocks with better machinability than ceramics blocks [11] and better mechanical properties than conventional photo-polymerized composites linked to higher conversion degree [12].

In the oral cavity, dental resins composites undergo water sorption usually causing color instability [13] and embrittlement [14]. Their durability is therefore at the heart of the concerns of practitioners and patients [15,16].

Studies on water ageing of light cured dental composites [17] suggest that UDMA presence reduces water sorption and improves mechanical properties of dental composites. This does not necessarily mean that long term properties will be better (a very nice example of detrimental effect in the case of epoxies can be seen in Ref. [18]).

It remains therefore to describe the ageing mechanisms in such

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thermoset networks containing ester groups. Water-polymer interaction mechanisms were extensively covered in comparable cases such as PMMA where hydrolysis of acrylate groups [19–21] was observed, together with a Fick mechanism for water diffusion a [22,23] and the existence of clustering [24]. The case of water ageing of UDMA used as matrices for HT-HP composite remains for us unclear and needs hence to be explored. Moreover, the effect of varying the conversion degree with external polymerization pressure on water ageing was also scarcely addressed for such networks.

The purpose of this preliminary work is hence to study the case of urethane-dimethacrylate networks polymerized at various pressures. For that purpose, water permeation will be measured from simple gravimetric curve during immersion in water, from which water diffusion coefficient and maximal water uptake can be easily extracted.

2. Materials and methods

2.1. Materials

Samples were obtained by bulk radical polymerization of UDMA (CAS 72869-86-4 supplied by Esstech, Germany) initiated by 0.5% Benzoyl Peroxide (ref 00213 - Sigma Aldrich) at 90 °C under atmospheric air (0.1 MPa) or under various pressures (100, 200 and 300 MPa) in custom built autoclave as described in Ref. [25]. The UDMA structure and the expected network structure are given in Scheme 1. Some of their initial characteristics are gathered in Table 1.

- conversion degree (DC) was measured from Near InfraRed spectroscopy as described in Ref. [25]. Experiments were repeated 10 times.
- T_g were measured by DMA as described later. Experiments were repeated 8 times.
- the soluble fraction was tentatively estimated from refluxing samples in ethyl acetate and was found to be close to 0 (within the range of experimental incertitudes).

Samples were cut to obtain 10 mm × 10 mm × 1 mm plates prior to ageing using an Isomet device (Buehler).

2.2. Ageing and characterization

2.2.1. Water uptake

UDMA samples polymerized under various pressures (square shaped of 10 mm, 1 mm thickness) were immersed in distilled water at several temperatures (three groups of six samples at 37, 50 and 70 °C ± 1 °C in ventilated ovens (AP60 supplied by SCS) and

regularly weighed using a XS105 DualRange balance (Mettler Toledo). 37 °C was chosen because it represents the value of in vivo use. The two other temperatures were chosen as a good compromise between acceleration and easy experimentation (to avoid water loss by evaporation). Measurements were performed almost every hour in the earliest ageing time (when mass increases quickly) and almost every week at high ageing times (when mass seemed to reach a plateau). Before water ageing, samples were dried at 50 °C under vacuum, and weighted until having a constant weight (the needed time was almost 4 weeks for 1 mm thick blocks). Those data were used to estimate the maximal water uptake and the diffusion coefficient as described in the ‘Discussion’ section. Experiments were repeated 6 times for each sample.

2.2.2. Dynamic vapor sorption (DVS)

The polymer affinity with water was measured by keeping about 20 mg samples in air at 0.1 MPa with fixed water partial pressures between 0 and 90% in a dynamic vapor sorption apparatus DVS-1000 from Surface Measurement Systems. Two UDMA samples were tested for each polymerization pressure (0.1, 100, 200 and 300 MPa). Sorption isotherms were performed at a constant temperature (70 °C) under varying water vapor partial pressures (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90%) with two cycles of sorption-desorption and 90 min steps at each partial pressure. Each experiment was duplicated.

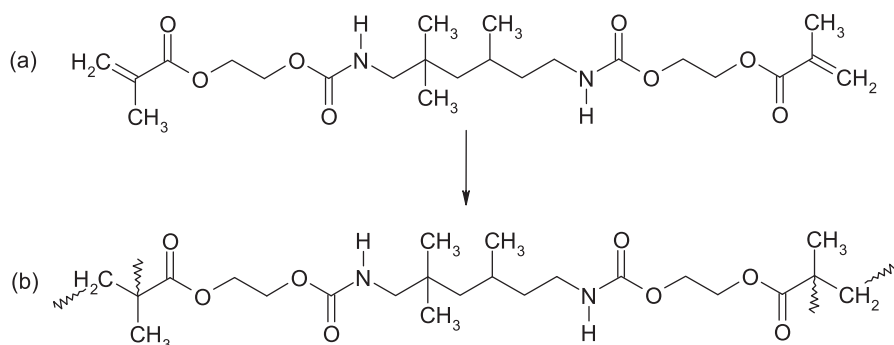
2.2.3. Ultrasonic measurements (US)

US were performed at 5 MHz using pulse method using a Sopranel ultrasonic source at room temperature on discoid samples of UDMA (18 mm diameter × 2 mm thick) for each polymerization pressure (0.1, 100, 200 and 300 MPa). The propagation velocities of longitudinal waves (v_L) and transversal waves (v_T) were recorded with an oscilloscope (LeCroy 9450 Dual 350 MHz). Density ρ (kg m⁻³) was determined by hydrostatic weighing for all samples (XS105 DualRange, Mettler Toledo, Switzerland). Each experiment was duplicated. The ultrasonic moduli E (Young) and G (shear) and ν (Poisson coefficient) were determined using the following relationships:

$$v_L^2 = \frac{E}{\rho} \frac{(1 - \nu)}{(1 + \nu)(1 - 2\nu)}$$

$$v_T^2 = \frac{G}{\rho} = \frac{E}{2 \cdot \rho(1 + \nu)}$$

Ultrasonic method was chosen here for its simplicity and reliability and particularly because it allows the best estimation of the “O K moduli” related to cohesive energy (compared to DMA where samples cannot be investigated at temperatures below –80 °C) as explained later. Experiments were repeated 3 times.



Scheme 1. UDMA monomer before (a) and after (b) polymerization.

Table 1Initial characterization (mean values and standard deviations) of UDMA samples (n = 10 for conversion degree, 8 for T_g , 3 for ρ , E, G and ν).

Polymerization pressure (MPa)	0.1	100	200	300
Conversion Degree (%)	89 ± 2	94 ± 1	96 ± 1	97 ± 1
T_g (°C)	118 ± 10	137 ± 2	143 ± 1	141 ± 2
ρ (kg m ⁻³)	1201 ± 0	1202 ± 0	1207 ± 0	1204 ± 0
E (GPa)	6.210 ± 0.052	6.190 ± 0.026	6.450 ± 0.062	6.437 ± 0.031
G (GPa)	2.293 ± 0.040	2.313 ± 0.012	2.403 ± 0.021	2.393 ± 0.015
ν	0.357 ± 0.010	0.347 ± 0.003	0.342 ± 0.003	0.345 ± 0.001

2.2.4. Dynamical mechanical analysis

Glass transition temperature (T_g) of each polymerized polymer block obtained were determined using dynamic mechanical analysis (DMA) in three-point bending mode using a Thermal Analysis Controller 7/DX instrument (PerkinElmer) from 8 rectangular specimens per group (4 mm width × 20 mm length × 1 mm thickness). Measurements were carried out using a static load of 0.3 ± 0.02 N, dynamic load of 0.2 ± 0.02 N was applied and a 2°C min^{-1} heating ramp from 30 to 180°C at a frequency of 1 Hz and a 15 mm spread of the three-point bending arrangement. T_g was determined as the maximum of damping peak.

3. Results

3.1. Ultrasonic characterization of virgin materials

Poisson ratio, shear and elastic moduli were measured from ultrasonic measurements at very high frequency. They express the behavior at very low temperature which is linked to the cohesive energy [26]. The measured values are presented in Table 1. It seems that they are very close irrespectively to the polymerization pressure (NB: this is also consistent with elastic moduli values at 30°C measured by DMA). In the absence of a much higher number of measurements and subsequent uncertainty estimations, this will not be commented in the following.

3.2. Sorption isotherms with DVS

The DVS shows that UDMA samples display the typical sorption isotherms at 70°C recorded by DVS [27]. They are overlapped in Fig. 1. The “toe” which is typical of Langmuir type sorption, expressing the existence of several kinds of molecular units with different level of interaction with water, is not witnessed here. Their shape is rather close:

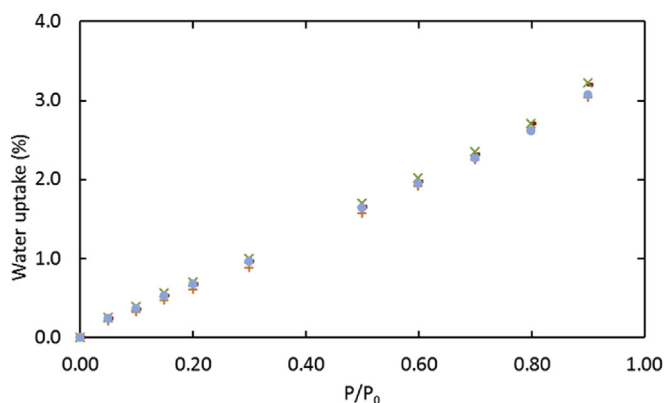


Fig. 1. Sorption isotherms at 70°C for UDMA polymerized under 0.1 (●), 100 (–), 200 (+), 300 (×) MPa.

- either to the Flory Huggins sorption isotherm [28].
- or by the sum of two contributions: ① Henry's law at low water activity where sorption curve is linear, expressing a random filling of polymer by water and ② a positive deviation observed at high water activity, and ascribed to the formation of clusters (i.e. groups of associated water molecules) which will be discussed later.

In the frame of the first hypothesis, the sorption isotherms can be described by the following equation:

$$\ln P/P_0 = \ln (1 - \phi_p) + \phi_p + \chi \cdot \phi_p^2$$

in which:

- P/P_0 is the RH%, the water activity in the external medium around the polymer.
- ϕ_p is the polymer volume fraction in the polymer + water mixture.
- χ is the polymer-water interaction defined by the following expression, in a first approximation:

$$\chi = \frac{V_m}{RT} \times (\delta_{polymer} - \delta_{water})^2$$

where $\delta_{polymer}$ and δ_{water} respectively are the solubility parameters for polymer and water, and V_m is the molar volume for water.

At low water activities, Flory Huggins equation can be simplified which gives:

$$\ln\left(\frac{1 - \phi_p}{P/P_0}\right) = \ln \alpha = -(1 + \chi)$$

We obtain χ values ranged from 2.4 to 2.8 regardless the polymerization pressure (Table 2). It seems, in a first approach, that this interaction parameter does not display any change with the polymerization pressure. The investigated materials have the same affinity with water. It takes intermediary values between highly hydrophilic polymers such as PA6 (0.9) [29] and moderately ones such as PLA (about 4.5) [30]. χ would take an almost common values for all the UDMA values irrespectively of the pressure under which they were polymerized. This suggests that they may have the same solubility parameter because they contain the same chemical groups (esters, urethane) as it will be discussed more in details below.

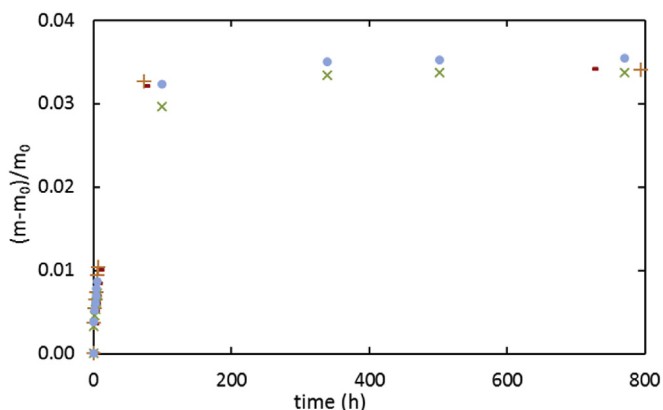
3.3. Kinetic curves for water uptake during immersion

The comparable water affinity of all UDMA networks under study was confirmed by performing sample immersion in water. Curves presented in Fig. 2 display the classical auto-decelerated shape [31]. It seems that:

- ① There is no evidence of a two stages diffusion process (also named Langmuir type diffusion attributed to the existence of

Table 2Flory interaction parameter derived from DVS isotherm sorption by DVS and calculated from UDMA samples (n = 2 for α and χ_{70} , 6 for water uptake).

Polymerization pressure (MPa)	0.1	100	200	300
α	0.0265 ± 0.0072	0.0320 ± 0.0004	0.0303 ± 0.0011	0.0274 ± 0.0039
χ_{70}	2.65 ± 0.28	2.45 ± 0.01	2.50 ± 0.04	2.60 ± 0.15
Water maximal uptake (%) at 70 °C	3.5 ± 0.0	3.4 ± 0.0	3.4 ± 0.1	3.4 ± 0.5
Water maximal uptake (%) at 50 °C	3.6 ± 0.2	3.4 ± 0.1	3.4 ± 0.0	3.4 ± 0.1
Water maximal uptake (%) at 37 °C	3.5 ± 0.1	3.4 ± 0.0	3.4 ± 0.0	3.5 ± 0.1

**Fig. 2.** Mass uptake curves for UDMA immersed in water at 70 °C polymerized under 0.1 (●), 100 (–), 200 (+), 300 (×) MPa.

sites generating strong bonding with diffusing water [32–35]), consistently with the shape of sorption isotherms recorded by DVS (see above). It suggests that the unpolymerized methacrylate group (structure a in Scheme 1) and its polymerized saturated analogue (structure b in Scheme 1) have the same “interaction” with water, despite the possible donor group of >C=C< double bond on the ester group suspected to increase the interaction with water.

- ⊗ Despite the possible hydrolysis of urethane [36] and esters [37], there is no effect of water hydrolysis and lixiviation (contrarily for example to [38]) in the investigated timescale, suggesting that UDMA undergo here mainly a physical ageing by water permeation.

For 1 mm thick samples, the maximal water uptake was observed at about 3 weeks at 70 °C, 5 weeks at 50 °C, and 8 weeks at 37 °C. The mean values of maximal water uptakes are also given in Table 2. According to statistical analysis, there is no effect of polymer pressure or of temperature on maximal water uptake. Those trends will be commented in the ‘discussion’ section.

The maximum water uptake values (w_m) range between about 3.4% to about 3.6%. This result is consistent with discussion of DVS results. This confirms that there are no major differences in water affinity between each kind of samples under investigation. From an applied point of view, it is noteworthy that UDMA materials display an affinity with water much lower than Triethylene Glycol Dimethacrylate (almost 6%) and slightly lower than Bisphenol A Glycidyl Methacrylate (almost 3.6–3.9%) [13,14] which makes them a suitable choice for matrices of dental composites. Moreover, since ageing by immersion can induce a loss of soluble compounds (unreacted monomers, initiator byproducts, hydrolyzed molecules ...) contrarily to DVS experiment (where water can only migrate into the polymer), this confirms that soluble fraction in UDMA networks was truly negligible.

4. Discussion

This discussion is aimed at explaining why, according to our experimental results, there is a minor effect of the polymerization pressure on the water-UDMA interactions, and gives a precise description of the water permeation mechanism in link with polymer structure and architecture.

4.1. Solubility

According to DVS results, it seems that the polymer-water interaction parameter is almost constant, irrespectively of the polymerization pressure. This result is worth to be discussed since polymerization pressure was shown to influence the conversion degree of samples [25], and their subsequent structure at “molecular” and macromolecular level.

The water affinity of a given polymer can be expressed as the number of water molecules absorbed per monomeric unit [39]:

$$H = \frac{w_m \cdot M}{1800} = \sum n_i H_i$$

Where:

- M is the molar mass of repetitive unit,
- n_i is the number of groups able to bind with H_i molecules of water.
- w_m is the equilibrium water absorption (wt. %).

H_i can be estimated from several polymers or chemicals (ideally with only one kind of functional group). For example, data for PMMA ($w_m = 1.5\%$) [27] suggest that $H_{\text{ester}} \sim 0.1$. Hence, the contribution of urethane groups H_{urethane} would be about 0.35 i.e. that urethanes would be greatly hydrophilic consistently with data on polyester-urethane networks published elsewhere (with w_m ranging from 1.5 to 8%) [36,37,40]). However, this simple theory is not robust enough to discuss on the effect of curing degree on water uptake in UDMA networks.

Based on Hildebrand’s approach, Van Krevelen suggested that the solubility of a given polymer in solvent is mainly determined by its chemical structure [41]. The solubility parameter (δ) of a given polymer with a given solvent can be defined as the square root of the cohesive energy density (CED) in the amorphous state at room temperature:

$$\delta = (\text{CED})^{1/2}$$

$$\text{CED} = \frac{E_{\text{coh}}}{V_m}$$

Where E_{coh} is the cohesive energy (J mol^{-1}), V_m is the molar volume ($\text{cm}^3 \text{mol}^{-1}$) and CED is the density of cohesive energy ($\text{MPa}^{1/2}$).

It was suggested that E_{coh} was an additive property for low molecular weight compounds and polymers [42–44] and that this “additivity method” makes it possible to obtain a good prediction of

the cohesive energy of a polymer at room temperature. E_{coh} and V_m can be calculated according to the incremental method based on additive group contribution proposed by Van Krevelen [26] as shown in Table 3 for a totally polymerized (Conversion degree = 100%) UDMA unit.

Based on degree of conversion (DC) of UDMA polymerized at 0.1, 100, 200 and 300 MPa (Table 1), the solubility parameters can be calculated. They increase from 24.97 MPa^{1/2} (UDMA polymerized under 0.1 MPa, DC = 89%) to 25.01 MPa^{1/2} (UDMA polymerized under 300 MPa, DC = 97%). This is consistent with their very close values of elastic moduli measured from ultrasonic measurements (Table 1) as expected since both values are correlated [26]. Let us note that a very nice correlation between the water maximal uptake and elastic moduli was earlier suggested by Morel et al. [45], certainly because both values are linked to the chemistry of the material.

In conclusion, our results mean that the polymerization pressure does not significantly change the cohesive energy, polymer polarity and later affinity with water which is expressed by the maximal water uptake. It remains possible however that some difference in water uptake exists in the case of samples displaying a wider range of conversion degree [13] but this is not the case for pure UDMA samples [25] where conversion degree always are higher than 90%.

Let us now discuss on the absence of temperature effect on the maximal water uptake. Alternatively to the description by Flory Huggins isotherms, the water sorption can be modeled using Henry's law describing water permeation in polymer when no clusters are formed (as it will be better justified below). This simple theory for water dissolution is associated to a very dilute solution behavior in which dissolved water molecules are few and far. It assumes that maximal (equilibrium) water uptake is directly proportional to the external water partial pressure:

$$C = s.P$$

Where C is solubility expressed for example in cc(STP)/cc(polymer), and s is the solubility coefficient (expressed in mol l⁻¹ Pa⁻¹) expected to obey Van't Hoff law:

$$s(T) = s_0 \cdot \exp\left(-\frac{\Delta H_S}{RT}\right)$$

P is the water partial pressure (expressed in Pa) obeying to Clapeyron's law:

$$P(T) = P_0 \cdot \exp\left(-\frac{\Delta H_{\text{vap}}}{RT}\right)$$

The apparent activation energy for water equilibrium concentration is thus given by:

Table 3
Estimation of cohesive energy for UDMA (DC is the degree of conversion of monomer).

Quantity	Group	E_{coh} (J/mol)	V (cm ³ /mol)
1	>CH-	3430	-1
5	CH ₃ -	4710	33.5
2 × (100-DC)/100	CH ₂ =	4310	28.5
2 × (100-DC)/100	>C=	4310	-5.5
1 + 2 × DC/100	>C<	1470	-19.2
2	-COO-	18000	18
8 + 2 × DC/100	-CH ₂ -	4940	16.1
2	COONH	26370	18.5
		169530	342.9

$$E_S = -\Delta H_S - \Delta H_{\text{vap}}$$

with ΔH_{vap} is close to -43 kJ mol⁻¹ [31]. Here, the absence of temperature dependence of water solubility means that E_S is close to 0 and that ΔH_S must be close to ~43 kJ mol⁻¹ in UDMA, which is consistent for example with the case of PMMA [46]. From a practical point of view, it means that immersion in water at temperatures higher than 37 °C can be a simple and efficient way for screening the water affinity of a polymer with the advantage of shorter testing times. We will now focus on the effect of polymerization pressure on the water penetration kinetics.

4.2. Water diffusion mechanism

Kinetic curves for water uptake can be plotted versus the square root of time, which is the most common method for investigating if diffusion obeys Fick's law [47,48]. As it can be seen in Fig. 3, plot is almost linear in the earliest immersion time showing that diffusion obeys Fick's, which is characteristic of diffusion regime where the diffusion rate of water is slower than the relaxation rate of polymer (i.e. that motions polymer segments are faster than jumps of water molecules and layer that penetration of water does not cause a change in the state of the polymer [49]).

Crank [50] proposed solutions for Fick law in case of an infinite plane like sample (length and width ≫ thickness) with a thickness of 2e and a mass m at time t, D is the diffusion coefficient:

$$\frac{m(t) - m_0}{m_\infty - m_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{4e^2}\right)$$

In other words, if the relative mass uptake increases linearly with square root of time, diffusion obeys Fick's law and D can be calculated from the slope. This equation actually admits an approximate solution for low levels of water sorption ($m/m_\infty < 0.6$):

$$\frac{\Delta m(t)}{\Delta m_\infty} = \frac{4}{e} \sqrt{\frac{D \cdot t}{\pi}}$$

D is here an apparent diffusion coefficient, for which a geometric correction can be made [51]:

$$D_{\text{real}} = \frac{D_{\text{app}}}{\left(1 + \frac{2e}{L} + \frac{2e}{l}\right)^2}$$

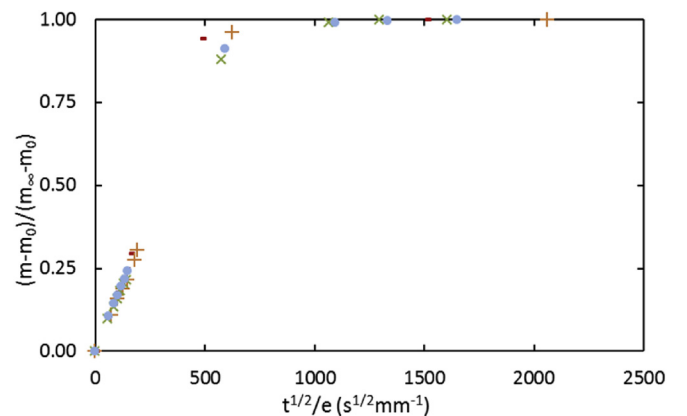


Fig. 3. Relative mass uptake curves for UDMA at 50 °C polymerized under 0.1 (●), 100 (–), 200 (+), 300 (×) MPa.

The following values of water diffusivity given in Table 4 are obtained from 6 samples per polymerization pressure:

The coefficient D does not seem to depend on the polymerization pressure in a first approach. This suggests that the DC and maybe the structure of the polymerized UDMA network have a minor influence on water diffusion. This might be unexpected since thermomechanical properties are shown to depend on the polymerization pressure [52]: for example T_g increases by more than 20 °C when increasing the polymerization pressure from 0.1 to 300 MPa (Table 1).

To propose an explanation, there are two main theories for explain the diffusion mechanism:

- ① “free volume approach” according to which the penetrant jumps from empty holes to another and is triggered by the size and the quantity of those free volume holes. This theory was developed by Cohen and Turnbull [53] in the 50’s and later developed by Vrentas and Duda in the 70’s [54,55] and is shown to describe the diffusion of apolar chemicals in almost apolar polymers [56].
- ② theories according to which hydrophilicity is related to the existence of specific interactions between the water molecules and polar groups of the polymer. Merdas et al. [31] observed an inverse correlation between the water diffusion coefficient and its equilibrium solubility for a wide series of epoxy diamine systems. It lead them to propose the following mechanism:
 - I. $[P1 \dots W] \rightarrow P1+W$ Dissociation of the polymer/water complex
 - II. $W \rightarrow$ Jump from P1 to P2
 - III. $W + P2 \rightarrow [P2 \dots W]$ Formation of the polymer/water complex, that water is retained by some groups of the polymer structure slowing down its diffusion kinetics.

They justified their reasoning from the inverse correlation between the diffusion coefficient and the water equilibrium solubility for a wide series of epoxy diamine systems.

In the present study, samples differ by their initial glass transition value, and possibly mobility. The fact that D does not change despite differences in T_g values (Table 1) leads to reject the “free volume theory” (or at least to consider it is not valid for glassy samples). Water diffusion is studied here at glassy state in polymer containing the same concentration in polar groups which justifies, for us, why mechanism 2 seems obeyed. From a practical point of view, it means that the use of an enhanced polymerization pressure pay permit to improve the initial mechanical properties [25] but the “ageing” behavior will remain almost the same.

Last, the chemical properties of the polymer would be the preponderant factor. D was shown to obey Arrhenius law:

$$D = D_0 \cdot \exp(-E_D/RT)$$

E_D takes a value close to 50 kJ mol⁻¹ for each material under study, in good agreement with those observed in other thermosets networks [57].

Table 4 Water diffusivity values obtained from immersion curves, corresponding average activation energy (values between brackets correspond to minimal and maximal values) and mean cluster size (MCS) values obtained from DVS.

Polymerization Pressure (MPa)	D (m ² s ⁻¹) at 37 °C	D (m ² s ⁻¹) at 50 °C	D (m ² s ⁻¹) at 70 °C	E_D (kJ mol ⁻¹)	MCS at 90% RH
0.1	$(9.2 \pm 0.9) \times 10^{-17}$	$(1.6 \pm 0.1) \times 10^{-16}$	$(7.2 \pm 0.5) \times 10^{-16}$	56 (48–62)	~1.2
100	$(8.5 \pm 0.7) \times 10^{-17}$	$(1.8 \pm 0.4) \times 10^{-16}$	$(5.3 \pm 0.7) \times 10^{-16}$	49 (41–54)	~1.2
200	$(7.0 \pm 0.7) \times 10^{-17}$	$(1.3 \pm 0.1) \times 10^{-16}$	$(4.5 \pm 1.1) \times 10^{-16}$	50 (39–61)	~1.2
300	$(6.7 \pm 2.0) \times 10^{-17}$	$(1.6 \pm 0.4) \times 10^{-16}$	$(4.9 \pm 0.9) \times 10^{-16}$	53 (33–64)	~1.4

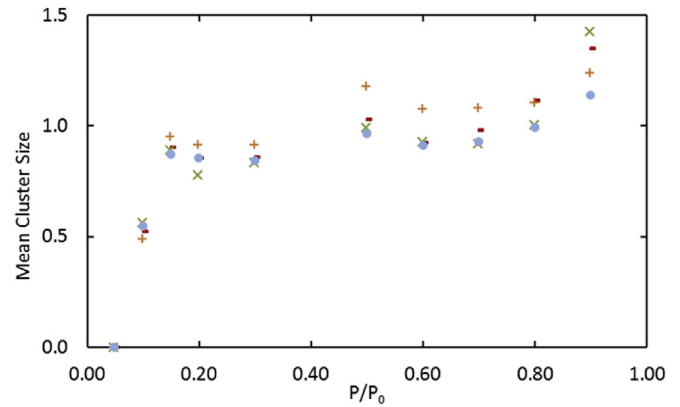


Fig. 4. MCS curves as function of %RH obtained from DVS at 70 °C for UDMA polymerized under 0.1 (●), 100 (○), 200 (+), 300 (×) MPa.

4.3. On the presence of clusters

The positive curvature in the DVS (Fig. 1) can be explained by the presence of water clusters (i.e. groups of associated water molecules) within the UDMA [58], meaning that water-water interactions are stronger than polymer-water. Those later can be evidenced by dielectric spectroscopy [59]. To explore this assumption, the MCS (mean cluster size) was numerically determined by the method of Zimm Lundberg [60,61]. The clustering function was defined as:

$$f_{ZL} = \frac{G_{11}}{v_1} = -(1 - \phi_1) \left[\frac{\partial a_1 / \phi_1}{\partial a_1} \right]_{T,P} - 1$$

G_{11} is a cluster integral for the water and v_1 and ϕ_1 are the partial molecular volume and volume fraction of water, respectively. When f_{ZL} is below a value of -1 , no clustering occurs. Means Cluster Size (MCS) is given by:

$$MCS = 1 + \phi_1 \cdot G_{11} / v_1$$

Table 4 shows that the MCS is almost similar for the different pressures (values from about 1.2 to about 1.4). The MCS tends to increase slightly with the polymerization pressure of UDMA. Fig. 4 shows that water molecules are associated to form “dimers” when water external partial pressure is up to 80% (MCS greater that 1).

This shows a certain tendency of water to aggregate at higher water activity, which can modify the mechanisms of water diffusion and solubility, and possibly the mechanical properties of wet UDMA samples [62].

5. Conclusions

This paper addresses the water ageing of polyurethane dimethacrylate networks obtained by radical polymerization in autoclave under several pressures. Samples were studied by classical gravimetric method. The sorption isotherms were monitored by Dynamic Vapor Sorption. This paper clearly shows that the maximal water uptake is about 3.5% irrespectively of the polymerization pressure with no influence of temperature (at least in the range 37–70 °C). The diffusion was observed to obey Fick's law and diffusivity values also seem to be constant for all the samples under investigation. In other words, the external polymerization pressure has a strong effect on initial mechanical properties but the rate at which these later decrease during water ageing should be the same. The case of UDMA based dental composites, where interfacial phenomena are expected to play an important role on water diffusion [47,48], remains now to be addressed.

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References

- [1] J.L. Ferracane, Resin composite—state of the art, *Dent. Mater.* 27 (2011) 29–38.
- [2] A.P.P. Fugolin, C.S. Pfeifer, New resins for dental composites, *J. Dent. Res.* 96 (2017) 1085–1091.
- [3] R.L. Bowen, Dental filling material comprising vinyl silane treated fused silica and a binder consisting of the reaction product of bis phenol and glycidyl acrylate, US Patent US3066112A (1962).
- [4] I.M. Barszczewska-Rybarek, Structure-property relationships in dimethacrylate networks based on Bis-GMA, UDMA and TEGDMA, *Dent. Mater.* 25 (2009) 1082–1089.
- [5] J. Foster, R. Walker, *Dental Filling Materials*, 1974.
- [6] E. Asmussen, A. Peutzfeldt, Influence of UEDMA BisGMA and TEGDMA on selected mechanical properties of experimental resin composites, *Dent. Mater.* 14 (1998) 51–56.
- [7] R. Giordano, Materials for chairside CAD/CAM-produced restorations, *JADA (J. Am. Dent. Assoc.)* 139 (137 Suppl) (2006) 14S–21S.
- [8] A.K. Mainjot, N.M. Dupont, J.C. Oudkerk, T.Y. Dewael, M.J. Sadoun, From artisanal to CAD-CAM blocks: state of the art of indirect composites, *J. Dent. Res.* 95 (2016) 487–495.
- [9] T. Miyazaki, Y. Hotta, J. Kunii, S. Kuriyama, Y. Tamaki, A review of dental CAD/CAM: current status and future perspectives from 20 years of experience, *Dent. Mater. J.* 28 (2009) 44–56.
- [10] R. van Noort, The future of dental devices is digital, *Dent. Mater.* 28 (2012) 3–12.
- [11] N.D. Ruse, M.J. Sadoun, Resin-composite blocks for dental CAD/CAM applications, *J. Dent. Res.* 93 (2014) 1232–1234.
- [12] J.F. Nguyen, V. Migonney, N.D. Ruse, M.D. Sadoun, Resin composite blocks via high-pressure high-temperature polymerization, *Dent. Mater. Off. Publ. Acad. Dent. Mater.* 28 (2012) 529–534.
- [13] A.S.Q.S. Fonseca, A.D. Labruna Moreira, P.P.A.C. de Albuquerque, L.R. de Menezes, C.S. Pfeifer, L.F.J. Schneider, Effect of monomer type on the CC degree of conversion, water sorption and solubility, and color stability of model dental composites, *Dent. Mater.* 33 (2017) 394–401.
- [14] C. Bastioli, G. Romano, C. Migliaresi, Water sorption and mechanical properties of dental composites, *Biomaterials* 11 (1990) 219–223.
- [15] J.L. Ferracane, Hygroscopic and hydrolytic effects in dental polymer networks, *Dent. Mater.* 22 (2006) 211–222.
- [16] I.D. Sideridou, M.M. Karabela, Sorption of water, ethanol or ethanol/water solutions by light-cured dental dimethacrylate resins, *Dent. Mater.* 27 (2011) 1003–1010.
- [17] I. Sideridou, V. Tserki, G. Papanastasiou, Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins, *Biomaterials* 24 (2003) 655–665.
- [18] N.D. Daniele, E.R. Long Jr., Effect of curing on the glass transition temperature and moisture absorption of a neat epoxy resin, *J. Polym. Sci. 1 Polym. Chem.* 19 (1981) 2443–2449.
- [19] W.N. Ayre, S.P. Denyer, Samuel L. Evans, Ageing and moisture uptake in polymethyl methacrylate (PMMA) bone cements, *J. Mech. Behav. Mater. Biomed. Mater.* 32 (2014) 76–88.
- [20] U. Ali, K.J.B.A. Karim, N.A. Buang, A review of the properties and applications of poly (MethylMethacrylate) (PMMA), *Polym. Rev.* 55 (2015) 678–705.
- [21] J. Semen, J.B. Lando, The acid hydrolysis of isotactic and syndiotactic poly(methyl methacrylate), *Macromolecules* 2 (1969) 570–575.
- [22] P. Dhanpal, C.K.Y. Yiu, N.M. King, F.R. Tay, N. Hiraishi, Effect of temperature on water sorption and solubility of dental adhesive resins, *J. Dent.* 37 (2009) 122–132.
- [23] I. Sideridou, D.S. Achilias, C. Spyroudi, M. Karabela, Water sorption characteristics of light-cured dental resins and composites based on Bis-EMA/PCDMA, *Biomaterials* 25 (2004) 367–376.
- [24] E.M. Davis, Y.A. Elabd, Water clustering in glassy polymers, *J. Phys. Chem. B* 117 (2013) 10629–10640.
- [25] A.C. Phan, P. Béhin, G. Stoclet, N.D. Ruse, J.-F. Nguyen, M. Sadoun, Optimum pressure for the high-pressure polymerization of urethane dimethacrylate, *Dent. Mater.* 31 (2015) 406–412.
- [26] J.-P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, *Thermosetting Polymers*, Marcel Dekker, Inc., 2002. Chap. 11.
- [27] L.S.A. Smith, V. Schmitz, The effect of water on the glass transition temperature of poly(methyl methacrylate), *Polymer* 29 (1988) 1871–1878.
- [28] J.A. Barrie, in: J. Crank, G.S. Park (Eds.), *Diffusion in Polymer*, Academic Press, London, 1968 chap 8 p.p. 260.
- [29] M. Broudin, V. Le Saux, P.Y. Le Gac, C. Champy, G. Robert, P. Charrier, Y. Marco, Moisture sorption in polyamide 6.6: experimental investigation and comparison to four physical-based models, *Polym. Test.* 43 (2015) 10–20.
- [30] E. Gaudichet-Maurin, Characterization and Ageing of a Water Ultrafiltration Membrane, *Arts et Metiers ParisTech*, 2005.
- [31] I. Merdas, F. ThomINETTE, A. Tcharkhtchi, J. Verdu, Factors governing water absorption by composite matrices, *Compos. Sci. Technol.* 62 (2002) 487–492.
- [32] H.G. Carter, K.G. Kibler, Langmuir-type Model anomalous moisture diffusion in composite resins, *J. Compos. Mater.* 12 (1979) 118–130.
- [33] A. Tcharkhtchi, P.Y. Bronnec, J. Verdu, Water absorption characteristics of diglycidylether of butane diol–3,5–diethyl–2,4–diaminotoluene networks, *Polymer* 41 (2000) 5777–5785.
- [34] S. Popineau, C. Rondeau-Mouro, C. Sulpice-Gaillet, M.E.R. Shanahan, Free/bound water absorption in an epoxy adhesive, *Polymer* 46 (2005) 10733–10740.
- [35] P. Gilormini, J. Verdu, On the role of hydrogen bonding on water absorption in polymers, *Polymer* 142 (2018) 164–169.
- [36] P.Y. Le Gac, D. Choqueuse, D. Melot, Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions, *Polym. Test.* 32 (2013) 1588–1593.
- [37] E. Richaud, P. Gilormini, M. Coquillat, J. Verdu, Crosslink density changes during the hydrolysis of tridimensional polyesters, *Macromol. Theory Simul.* 23 (2014) 320–330.
- [38] G. Capiel, L.A. Muccio, P.E. Montemartini, G.A. Schwartz, Water diffusion and hydrolysis effect on the structure and dynamics of epoxy-anhydride networks, *Polym. Degrad. Stabil.* 143 (2017) 57–63.
- [39] E. Morel, V. Bellenger, J. Verdu, Structure-water absorption relationships for amine-cured epoxy resins, *Polymer* 26 (11) (1985) 1719–1724.
- [40] Y.-J. Yu, K. Hearon, T.S. Wilson, D.J. Maitland, The effect of moisture absorption on the physical properties of polyurethane shape memory polymer foams, *Smart Mater. Struct.* 20 (2011) 085010.
- [41] D.W. Van Krevelen, K. Te Nijenhuis, Chapter 7-cohesive properties and solubility, in: *Properties of Polymers*, fourth ed., Elsevier, Amsterdam, 2009, pp. 189–227.
- [42] R.A. Hayes, The relationship between glass temperature, molar cohesion, and polymer structure, *J. Appl. Polym. Sci.* 5 (1961) 318–321.
- [43] A.T. DiBenedetto, Molecular properties of amorphous high polymers. 1. A cell theory for amorphous high polymers, *J. Polym. Sci.* 1 (1963), 3459–2476.
- [44] R.F. Fedors, A method for estimating both the solubility parameters and molar volumes of liquids, *Polym. Eng. Sci.* 14 (1974) 147–154.
- [45] E. Morel, V. Bellenger, M. Bocquet, J. Verdu, Structure-properties relationships for densely cross-linked epoxide-amine systems based on epoxide or amine mixtures, *J. Mater. Sci.* 24 (1989) 69–75.
- [46] J.A. Barrie, D. Machin, Diffusion and association of water in some poly-alkylmethacrylates. Part 1 – equilibrium sorption and steady state permeation, *Trans. Faraday Soc.* 67 (1971) 244–256.
- [47] Y. Joliff, L. Belec, J.F. Chailan, Modified water diffusion kinetics in a unidirectional glass/fibre composite due to the interphase area: experimental, analytical and numerical approach, *Compos. Struct.* 97 (2013) 296–303.
- [48] A. Chateauinois, L. Vincent, B. Chabert, J.P. Soulier, Study of the interfacial degradation of a glass-epoxy composite during hydrothermal ageing using water diffusion measurements and dynamic mechanical thermal analysis, *Polymer* 35 (1994) 4766–4774.
- [49] L. Masaro, X.X. Zhu, Physical models of diffusion for polymer solutions, gels and solids, *Prog. Polym. Sci.* 24 (1999) 731–775.
- [50] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, 1979.
- [51] C.H. Shen, G.S. Springer, Moisture absorption and desorption of composite materials, *J. Compos. Mater.* 10 (1976) 2–20.
- [52] A.C. Phan, M.-L. Tang, J.-F. Nguyen, N.D. Ruse, M. Sadoun, High-temperature high-pressure polymerized urethane dimethacrylate-mechanical properties and monomer release, *Dent. Mater.* 30 (2014) 350–356.
- [53] M.H. Cohen, D. Turnbull, Molecular transport in liquids and glasses, *J. Chem. Phys.* 31 (1959) 1164–1169.
- [54] J.S. Vrentas, J.L. Duda, Diffusion in polymer–solvent systems. I. Reexamination of the free-volume theory, *J. Polym. Sci. Polym. Phys. Ed* 15 (1977) 403–416.
- [55] J.S. Vrentas, J.L. Duda, Diffusion in polymer–solvent systems. II. A predictive

- theory for the dependence of diffusion coefficients on temperature, concentration, and molecular weight, *J. Polym. Sci. Polym. Phys. Ed* 15 (1977) 417–439.
- [56] M.P. Tonge, R.G. Gilbert, Testing models for penetrant diffusion in glassy polymers, *Polymer* 42 (2001) 501–513.
- [57] G. Pitarresi, M. Scafidi, S. Alessi, M. Di Filippo, C. Billaud, G. Spadaro, Absorption kinetics and swelling stresses in hydrothermally aged epoxies investigated by photoelastic image analysis, *Polym. Degrad. Stabil.* 111 (2015) 55–63.
- [58] E.M. Davis, Y.A. Elabd, Water clustering in glassy polymers, *J. Phys. Chem. B* 117 (2013) 10629–10640.
- [59] L. Garden, R.A. Pethrick, A dielectric study of water uptake in epoxy resin systems, *J. Appl. Polym. Sci.* 134 (2017).
- [60] B.H. Zimm, J.L. Lundberg, Sorption of Vapors by high polymers, *J. Phys. Chem.* 60 (1956) 425–428.
- [61] J.L. Lundberg, Clustering theory and vapor sorption by high polymers, *J. Macromol. Sci. Part B* 3 (1969) 693–710.
- [62] A. Serrano-Aroca, M. Llorens-Gómez, Dynamic mechanical analysis and water vapour sorption of highly porous poly(methyl methacrylate), *Polymer* 125 (2017) 58–65.