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Article

Curing, Monomer Leaching and Water Sorption of TEGDMA/BisGMA Photopolymerized Copolymers

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O objetivo deste trabalho é correlacionar o grau de conversão de copolímeros de 2,2-bis[4-(2-hidróxi-3-metacriloiloxipropóxi) fenil]propano (BisGMA) e dimetacrilato de trietilenoglicol (TEGDMA) (copolímeros TB) obtidos por fotopolimerização, usando o sistema fotoiniciador canforquinona/etil 4-dimetilaminobenzoato (CQ/EDB), com a eluição de monômeros e a absorção de água. A eluição de monômeros foi avaliada a partir da imersão dos polímeros em etanol/água e análise por CLAE (cromatografia líquida de alto rendimento). A absorção de água de saliva artificial foi determinada gravimetricamente. Os resultados mostram que a composição dos copolímeros TB influencia a cinética de polimerização, a quantidade de monômeros eluídos, o grau de conversão e a quantidade de água adsorvida. Uma boa correlação foi encontrada entre estas propriedades.

The aim of this work was to correlate the degree of conversion with residual monomer release and water absorption of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]propane (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA) (TB copolymers) obtained by photopolymerization, using canforquinone/ethyl 4-dimethylaminobenzoate (CQ/EDB) photoinitiator. The monomer release from the copolymers was evaluated by immersion in ethanol/water and HPLC (high performance liquid chromatography) analysis. Water absorption from artificial saliva was determined by mass variation. The results show that the composition of the TB copolymers influences the polymerization kinetics, the amount of the released monomers, the degree of conversion and the amount of adsorbed water. A clear correlation can be found between these properties.

Keywords: photopolymerization, degree of conversion, residual monomers, artificial saliva

Introduction

Photopolymerized dimethacrylate-based resins are extensively used in dentistry in a variety of applications, like fissure sealants, binding agents, resin cements and filling materials. The more commonly monomers used in the resin formulations are mixtures of dimethacrylate monomers such as 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]propane (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA).[1] These monomers form, after irradiation, three-dimensional networks by radical crosslinking polymerization of the C=C double bonds of the methacrylate end groups of the monomers. The formation of these networks results in various specific properties of the materials, like moderate degrees of conversion, existence of free radicals trapped within the materials and release of residual non-polymerized monomers during storage time. Thus, these materials will show changes in their properties at longer times.

During the polymerization, the monomers are initially incorporated into polymer chains as units containing pendant bonds. Afterwards, the propagation can proceed by addition of another monomer molecule or by intramolecular or intermolecular addition to the pendant double bond. Intramolecular attack results in cyclization reactions (intramolecular crosslinking), and the intermolecular process leads to crosslinking and the formation of a three-dimensional network. The network is inhomogeneous from the first stages of the polymerization reaction. In densely crosslinked poly(dimethacrylates), trapped radicals are stable even in the presence of large amounts of unreacted double bonds (monomeric and pendant) and have been observed for days or even months, depending on the temperature and other conditions, like the composition and

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structure of the monomers used in the photopolymerization reactions.[2-4]

Dental polymer networks are considered to be largely insoluble structures with relatively high chemical and thermal stability. However, these networks can absorb solvents and release unreacted monomers. These phenomena induce a variety of chemical and physical processes that in general will produce undesirable effects on the structure of the polymer, like volume changes, swelling, plasticization and softening of the material that might alter the performance of the polymer.

A significant number of studies indicates that monomers may be released from these copolymers to the environment.[4-6] The release of residual monomers, oligomers or degradation products may influence the biocompatibility and the mechanical properties of the material.[7] The process of elution is influenced by several factors like the extent of the polymerization reaction, i.e., degree of conversion to polymer for specific monomers, the solvent and the chemical nature of the released components.[4,8]

Solvents such as water, ethanol, methanol and artificial saliva have been used in different investigations related to the leaching of monomers,[6,9] and the excess water in the environment acts as a plasticizer in resin based materials.[10] On the other hand, it can cause some undesirable effects such as softening, degradation of the adhesive and reduction of the loading capacity of the resin matrix.[11]

The aim of this study is to correlate the absorption of solvents and of residual monomers from the copolymers with the degree of conversion of TB copolymers obtained by photopolymerization.

Experimental

Materials

The dimethacrylates TEGDMA and BisGMA, the photoinitiator camphorquinone (CQ) and the co-initiator ethyl 4-dimethylaminobenzoate 99% (EDB) (all from Aldrich) were used as received without further purification. Copolymers were prepared from mixtures of TEGDMA and BisGMA with weight ratios 30:70, 50:50, 70:30 and 20:80 (TB3070, TB5050, TB7030 and TB2080, respectively). To prepare the model adhesives, 100 μL of EDB (0.25%) were mixed with 100 μL of CQ (0.50%), both dissolved in dichloromethane and evaporated by flushing with nitrogen. The required amount of TEGDMA was then added to the residual mass and mixed with the corresponding amount of BisGMA. The mixtures were stored in the dark until the photocuring process was initiated.

Photopolymerization

10 mm diameter and 1 mm thickness discs were obtained in a Teflon mould covered with polyethylene film. The desired mixture of monomers, photoinitiator and co-initiator was inserted in the groove and irradiated for 60 or 100 s. The irradiation was carried out with a 600 mW LED Ultra Blue IS light emitting diode (DMC Instruments, Brazil) having a light unit tip of 7 mm diameter. The emitted radiation is predominantly in the 475 ± 15 nm range, in which CQ also absorbs (λ_{max} = 470 nm, $\varepsilon = 3.8 \times 10^4$ cm^2 mol^{-1}). Samples were placed at 3 mm of the radiation source.

The kinetics of polymerization were recorded using a Bomem 100 (MB Series) spectrometer with a Golden Gate™ single reflection diamond ATR (attenuated total reflection) unit (Specac Inc.), with spectral resolution of 8 cm^{-1}. One drop of the mixture of monomers was placed on the internal reflectance crystal where total internal refection occurs, and the irradiation was carried out for different times with the lamp described above. The degree of conversion[12,13] was determined from the ratio between the absorption peak areas of the aliphatic C=C absorption (ca. 1635 cm^{-1}) and the aromatic carbon-carbon absorption (ca. 1608 cm^{-1}) for the cured and uncured copolymers, according to equation 1:[14-16]

$$DC(\%) = 100 - \left\{ \frac{A_t(1635)}{A_t(1608)} \middle/ \frac{A_0(1635)}{A_0(1608)} \right\} \times 100 \qquad (1)$$

where $A(1635)$ and $A(1608)$ are the areas of the peaks at 1635 and 1608 cm^{-1}, respectively, and A_0 and A_t correspond to the areas before and after polymerization. The spectra were recorded immediately after the end of the irradiation.

Elution studies

After preparation, the TB copolymers were immediately immersed in 5 mL of a 75 wt.% ethanol/water solution, or artificial saliva, at 37 °C used as the extraction fluid. Samples were analyzed after immersion in the solution for up to 720 h. The released monomers were analyzed in a high performance liquid chromatography (HPLC) system (Shimadzu Corp.) with a refractive index detector (RID-6A). The peak areas of residual monomers on the HPLC trace were determined using the Class-LC10 software (Shimadzu Corp.).

The chromatographic analysis was performed using a 5 μm LiChrosorb® RP-18 column (Merck), water/methanol ratio 25/75, at a flow rate of 1.0 mL min^{-1}, and the injection volume was 20 μL.

Calibration curves were made using standard solutions containing known amounts of each of the evaluated monomers (TEGDMA and BisGMA). Solutions of various concentrations of each monomer were injected in the chromatograph and the peak areas were recorded and measured to obtain calibration curves. Thereafter, the sample solutions containing unknown concentrations of the monomers were injected and their concentrations were determined from the calibration curves.

Adsorption measurements

To perform the swelling experiments, the copolymers were kept in artificial saliva at 37 °C. At different times, over a period of 90 days, samples were withdrawn from the solution, dried over filter paper, left in air and weighted until constant weight. The amount of absorbed artificial saliva (S_t) was determined using equation 2:

$$S_t = \frac{m_t - m_0}{m_0} \quad (2)$$

where m_0 is of the mass of dry copolymer and m_t is the mass of the copolymer at time t.

The composition of the artificial saliva used was 4.5 g sodium chloride, 0.3 g potassium chloride, 0.3 g sodium sulfate, 0.4 g ammonium chloride, 0.2 g urea and 3.0 g lactic acid (all reactants from Synth) dissolved in 1000 mL distilled water adjusted to pH 6.5 to 7.0 using 5 mol L^{-1} sodium hydroxide.[17]

Results and Discussion

Degree of conversion of TB copolymers

The degree of conversion (DC) for the TB3070, TB5050 and TB7030 copolymers during the irradiation is shown in Figure 1. It can be seen that DC rises very rapidly during the first instants of the irradiation and tends slowly to a maximum after about 0.50 min. The mixtures with a larger proportion of TEGDMA reach larger DC. The extrapolated maximum values were 54, 46 and 40% for TB7030, TB5050 and TB3070, respectively.

This behavior can be associated to the higher mobility of TEGDMA, compared with BisGMA, in the crosslinked polymer network during photopolymerization. Even at very low conversions (4-6%), the propagation and termination rates become diffusion controlled due to the restricted movements of radicals, promoting a decrease in the termination rate and leading to the increase in the overall polymerization rate (gel effect). The balance between both events (rate diffusion-controlled termination and propagation) leads to a maximum in the polymerization rate. BisGMA is more viscous than TEGDMA due to the presence of the rigid aromatic rings and to the OH groups that promote strong hydrogen bonds. Thus, the lower degree of conversion of the copolymer with higher BisGMA monomer proportion can be traced to the higher viscosity of this material.

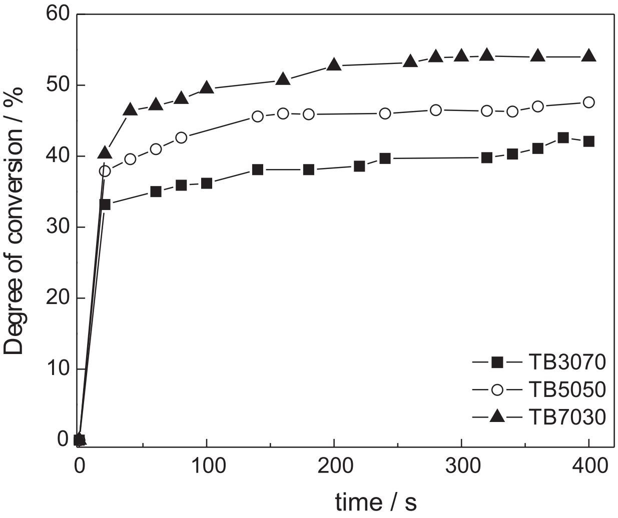

Figure 1. Degree of conversion of TB copolymers during irradiation.

Elution of residual monomers from TB copolymers

A correlation between the different degrees of conversion and rigidity of the polymer networks can be obtained from the elution of non-reacted monomers after the end of the polymerization process, shown in Table 1. Polymers irradiated for 60 and 100 s were immersed in 75% ethanol-water at 37 °C for different times. The amounts of eluted TEGDMA and BisGMA monomers were determined by chromatography. It can be observed that the larger the amount of a monomer in the feeding polymerizing composition, the more of it is eluted. Also, the amount of eluted TEGDMA monomers is always higher, or similar, than that of BisGMA monomers. This is probably due to the higher viscosity of the latter, which might hinder its elution because of the difficulty in flowing through the polymer network.

Figure 2 shows the monomer elution behavior for TB7030 photocured for 60 and 100 s. The increase in the irradiation time causes the decreased of the amount of eluted monomers. The same effect was found for all the copolymers studied. This effect is probably due to the higher degree of conversion, and therefore more rigid structure of the polymers cured for longer times.

Figure 2 also shows a fast release of about 80% of the residual monomers during the first hours of immersion,

Table 1. Amounts of eluted monomers from copolymers TB7030, TB5050 and TB3070 photocured for 60 and 100 s

Copolymer	time / h	60 s irradiation		100 s irradiation	
		[TEGDMA] / 10^{-4} (mol L^{-1})	[BisGMA] / 10^{-4} (mol L^{-1})	[TEGDMA] / 10^{-4} (mol L^{-1})	[BisGMA] / 10^{-4} (mol L^{-1})
TB7030	3	33.6	5.14	28.3	3.78
	168	40.0	6.58	34.3	4.82
	336	43.8	7.26	33.9	5.26
	720	41.8	6.94	35.0	5.70
TB5050	24	18.2	6.79	18.1	6.62
	168	22.0	7.97	19.1	7.32
	336	22.4	8.58	17.8	6.67
	720	21.8	8.16	19.5	7.58
TB3070	3	–	8.02	–	8.56
	72	11.3	10.2	8.13	7.94
	336	10.6	11.2	11.1	11.10
	720	10.3	10.1	11.8	11.00

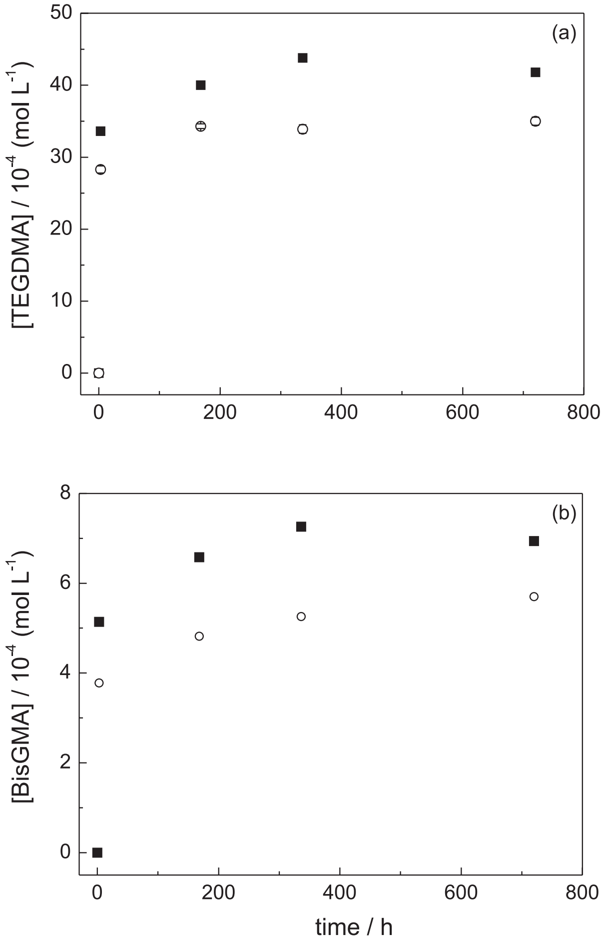

Figure 2. (a) Amount of TEGDMA eluted from TB7030 copolymers, and (b) amount of BisGMA eluted from TB7030 copolymers photopolymerized for (■) 60 s and (○) 100 s.

which levels off after about 200 h. The amount released after 720 h of immersion is not significantly different from that released after 200 h.

Saliva sorption

Artificial saliva sorption was evaluated for the TB2080, TB3070, TB5050 and TB7030 copolymers as function of the contact time (Figure 3). The maximum mass percentage of absorbed artificial saliva was 2.8, 3.0, 3.6 and 4.8%, respectively.

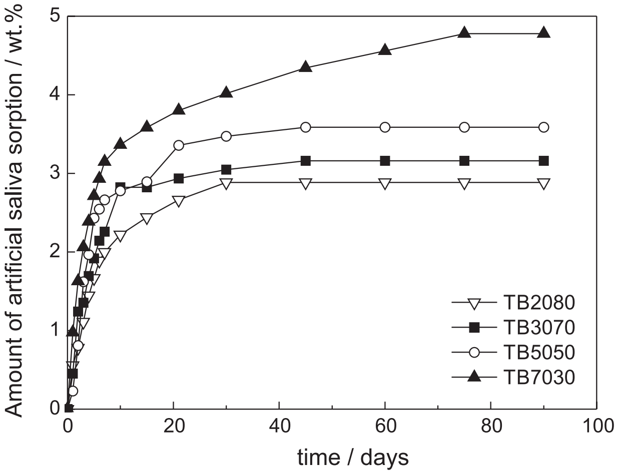

Figure 3. Amount of absorbed artificial saliva as function of immersion time.

As can be observed, the TB2080 copolymer absorbs less saliva that the other copolymers. This result must be associated with the structural differences of the copolymers and is consistent with the results obtained for the degree of conversion, as discussed above. The higher viscosity of the BisGMA led to a more crosslinked polymer network after polymerization when this monomer is present in higher proportions. The more compact structure avoids, in a certain degree, the absorption of the saliva and the swelling of the polymer. Furthermore, water sorption is highly dependent upon the chemical properties of the monomers. Thus, studies have shown that water sorption is larger for the polymers with higher concentrations of TEGDMA due to the presence of hydrophilic ether bonds.[18,19]

Water sorption by the polymer network occurs by three mechanisms: diffusion, capillarity and transport via microcracks. Among the three factors, diffusion is considered to be the major mechanism.[11] At an early stage, the rate of water absorption can be expressed according to Fick's law of diffusion:[20]

$$\frac{M_t}{M_\infty} = 2\left(\frac{D\,t}{\pi L^2}\right)^{1/2} \tag{3}$$

where M_t is the mass gain at time t, M_∞ the mass gain at equilibrium, L the thickness of the sample and D the diffusion coefficient.

Plots of M_t/M_∞ *vs.* $t^{1/2}$ were linear in the initial stages of the absorption indicating that the systems obey the Fick's law of diffusion. The values of the absorption diffusion coefficients calculated are in the range of 13×10^{-8}-23×10^{-8} cm^2 s^{-1}. These values are in the same order than those found for similar resins (11×10^{-8}-22×10^{-8} cm^2 s^{-1}).[21]

SEM analysis

Figure 4 shows typical SEM images of the TB7030 copolymers before and after immersion in 75% ethanol-water at 37 °C for 720 h after photopolymerization with LED Ultra Blue IS for 60 s and 600 mW power. A significant change in the appearance of the images can be observed, indicating that the surface of the polymer after immersion in the solvent is more homogeneous. This suggests that the solvent might, besides removing the unreacted monomers, also rearrange the superficial copolymer chain and, eventually, wash away shorter polymer chains.

Conclusions

A clear correlation can be found considering the three phenomena that were studied in this work, i.e., degree of conversion, monomer leaching and saliva absorption. The copolymer with the highest TEGDMA content (TB7030) showed the highest conversion, as well as the highest absorption of artificial saliva. It is also the copolymer from which the larger amount of TEGDMA remains unreacted after the photopolymerization, as shown in Figure 5.

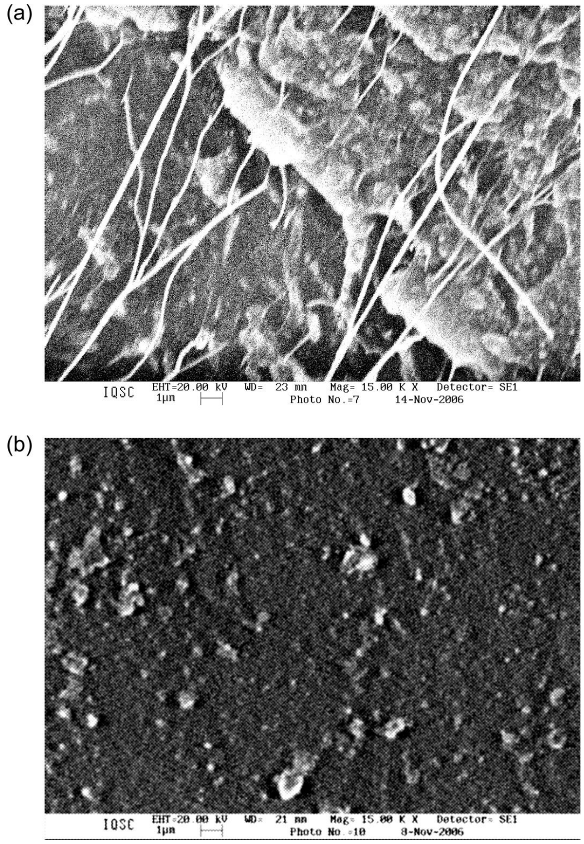

Figure 4. Scanning electronic micrographies of the copolymer TB 7030 (a) before and (b) after immersion in 75% ethanol-water at 37 °C for 720 h after photopolymerization.

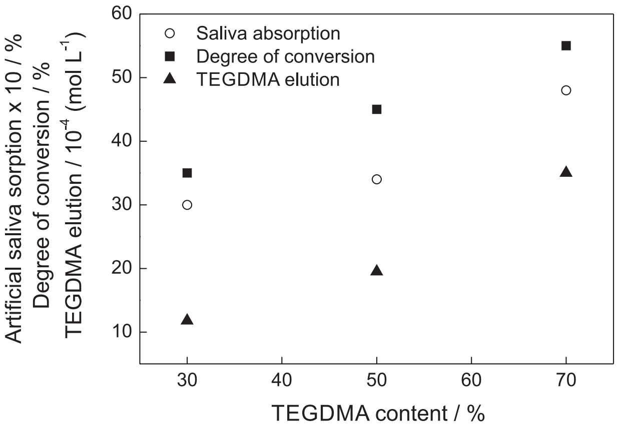

Figure 5. Saliva absorption, TEGDMA elution and degree of conversion of TD copolymers obtained by photopolymerization.

The higher photocuring conversion, which can be associated to a faster reaction rate, gives rise to a more irregular polymer network, so that it will be easier for the solvents to penetrate and remove unreacted monomers. At the same time, the fact that the copolymer network is looser allows the saliva to penetrate easier in the material.

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