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ORIGINAL ARTICLE

Shrinkage strain – Rates study of dental composites based on (BisGMA/TEGDMA) monomers

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Abstract The viscosity of the initial monomer mixture and the chemical structure of the monomers are both important variables in the kinetic behavior of resin composites. This paper aims to determine the effect of opaque mineral fillers and monomer ratios on the shrinkage strain-rate and time at maximum shrinkage strain (S_{max}) rate, of experimental composites based on (BisGMA/TEGDMA) monomers. Polymerization shrinkage and the degree of conversion (DC) of resin composites are closely related manifestations of the same process. The proportionality of these two properties was also investigated by studying the variation of the ratio: (total shrinkage strain/degree of conversion): (S_{max}/DC), as a function of mineral filler contents and monomer ratios.

Resin composites were prepared by mixing different monomer ratios of (BisGMA/TEGDMA) with camphoroquinone and dimethyl aminoethyl methacrylate (DMAEMA) as photo-initiator system. Five different radiopacifying filler agents: La_2O_3, BaO, $BaSO_4$,·SrO and ZrO_2 at various volume fractions ranging from 0 to 80 wt.% were added. The samples were cured at ca. 550 mW/cm^2. The shrinkage strain-rate, was calculated from the derivative of shrinkage strain using numerical differentiation. The shrinkage strain was measured by the bonded-disk technique at room temperature. Degree of conversion was calculated using FTIR/ATR spectroscopy.

The results revealed that the fraction of opaque filler had no significant effect on the shrinkage strain-rate and on the time at maximum shrinkage strain-rate but these two parameters are closely related to the monomer ratios and viscosity of the organic matrix. The results have confirmed the proportionality of the shrinkage strain and DC and showed that the filler contents and monomer ratios would not affect this proportionality.

1. Introduction

The viscous aromatic dimethacrylate monomer: 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane, Bis-GMA, is the main part of the organic matrix of dental resin composites due to its low contraction rate when compared to other similar monomers (Lovell et al., 1999; Asmussen and

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Peutzfeldt, 1998). The matrix when used unfilled for the restoration of teeth shows a poor wear resistance (Sideridou et al., 2002). This can be improved by the incorporation of mineral fillers. The high viscosity of BisGMA indicates that there is less degree of freedom in the BisGMA molecule, which kinetically leads to a low degree of conversion, and results in a low shrinkage. Due to this high viscosity, it requires dilution with a low viscosity dimethacrylate such as TEGDMA (triethylene glycol dimethacrylate) (Lovell et al., 1999; Peutzfeldt, 1997). BisGMA has a greater viscosity than TEGDMA and a chemical structure with stiff central core and hydroxyl groups which can reduce the mobility of the BisGMA chains and hence the final conversion. The relative concentration of each monomer can have an important effect on the mobility of molecules and the kinetics of the reaction. Since these monomers form cross-linked networks, the mobility of the reaction system decreases as the reaction progresses. Therefore, the conversion of the network is also a significant parameter in the mobility of polymer chains. As a consequence, the initial monomer ratio plays an important role in the kinetics of the Bis-GMA/TEGDMA system (Lovell et al., 1999; Atai and Watts, 2006; Atai, 2005). As the network forms, the movements of the macro-radicals are restricted and the termination step, becomes diffusion limited (Kloosterboer, 1988; Soh and Sundberg, 1982). A decrease in the termination rate leads to an increase in the polymerization rate which is known as the gel effect or auto-acceleration that commonly occurs in dimethacrylate systems. During the phase of gelation, as the polymerization progresses, the system becomes more cross-linked and the environment becomes more restricted, so the propagation step becomes diffusion-controlled (Gayosso et al., 2004; Hay and Shortall, 1988). This decline in rate is called the auto-deceleration effect. A balance between diffusion-controlled propagation which decreases the rate of polymerization, and diffusion-controlled termination, which increases it, results in a maximum in the rate of polymerization (Lovell et al., 1999; Cook, 1992). This complex behavior is due to the fact that the mobility of the reacting system decreases as the polymerization proceeds. The unreacted double bonds may either be present in free monomer or as pendant groups on the network (Lovell et al., 1999). It has been shown (Sideridou et al., 2002; Braga, 2005) that physical and mechanical properties of dental resin composites are influenced by the level of conversion attained during polymerization (Sideridou et al., 2002; Gayosso et al., 2004; Stansbury and Dickens, 2001). At low levels of conversion, when the resin is transformed from a liquid to a solid three-dimensional network, dramatic property changes are expected. Because of limitations imposed by vitrification of the polymer network, typical levels of DC in photo-cured composite restorative materials are of the order of 55–75% (Baroudi et al., 2007; Silikas et al., 2000; Ferracane and Greener, 1984). The purpose of this work was to study the effect of the nature, volume and concentration of five radiopacifying fillers: La_2O_3, BaO, $BaSO_4$, SrO and ZrO_2 on the shrinkage strain-rate and time at maximum shrinkage strain-rate of experimental composites based on the mixture (BisGMA/TEGDMA) at different ratios: (50/50), (25/75) and (75/25). The importance of resin matrix viscosity on the network forming kinetics has also been deducted. This work was also focused on the effect of opaque mineral fillers and monomer ratios on the proportionality of the shrinkage strain and the DC of experimental resin composites.

2. Materials and methods

2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA), were obtained from Aldrich (France). Camphoroquinone (CQ) and N,N′-dimethyl aminoethyl methacrylate (DMAEMA) were purchased from Fluka (Germany). Five different radiopacifying agents were used: lanthanum oxide (La_2O_3), Barium oxide (BaO), Barium sulfonate ($BaSO_4$), Zirconium oxide (ZrO_2), and strontium oxide (SrO). They were obtained from Aldrich (France).

Experimental composites were prepared by mixing (BisGMA/TEGDMA) at different ratios by weight: (50/50), (75/25) and (25/75) as matrix phase 0.5 wt.% CQ and 0.5 wt.% DMAEMA, as photo-initiator system. The radiopacifying filler powders were then added, in various proportions, into the mixture to provide loadings ranging from 0 to 80 wt.%. Each experimental composite was well blended to obtain a homogenous mixture.

The shrinkage strain was measured at room temperature using the Watt's bonded-disk technique (Watts and Cash, 1991a,b). The specimen was light-cured for 40 s, using a visible light source (LA 500 Blue light curing light, 500 mW/cm^2, 450–490 nm, Aposa Enterprise). The shrinkage strain was measured continuously and total shrinkage strain data of each sample were recorded during 1 h. Three repetitive tests ($n = 3$) were carried out per sample. The shrinkage strain-rate of samples, was calculated from the derivative of shrinkage strain data using numerical differentiation.

The degree of conversion (DC%) was measured using FTIR spectroscopy (Nicolet 360 Avatar 360 FTIR spectrometer) with an attenuated total reflectance (ATR) sampling accessory (type Pike miracle ATR, Diamond/ZnSeW/Pike technology).

Each sample was light polymerized for 40 s using a visible light source (LA 500 Blue light curing light, 500 mW/cm^2, 450–490 nm, Aposa Enterprise). The spectrum of each sample before end after curing was than obtained.

The DC of each specimen was determined from the ratio of absorbance intensities of aliphatic (C=C) peak at 1638 cm^{-1} and aromatic (C=C) peak at 1608 cm^{-1} considered as internal standard. It was calculated using the following expression:

$$\mathrm{DC}(\%) = \left[1 - \left\{\left(\mathrm{C}_{\mathrm{aliphatic}}/\mathrm{C}_{\mathrm{aromatic}}\right)/\left(\mathrm{U}_{\mathrm{aliphatic}}/\mathrm{U}_{\mathrm{aromatic}}\right)\right\}\right] \times 100$$

where $\mathrm{C}_{\mathrm{aliphatic}}$ is the absorption peak at 1638 cm^{-1} of the cured specimen, $\mathrm{C}_{\mathrm{aromatic}}$ is the absorption peak at 1608 cm^{-1} of the cured specimen, $\mathrm{U}_{\mathrm{aliphatic}}$ is the absorption peak at 1638 cm^{-1} of the uncured specimen and $\mathrm{A}_{\mathrm{aromatic}}$ is the absorption peak at 1608 cm^{-1} of the uncured specimen.

3. Results and discussion

The maximum shrinkage rate (%/s) and time at the maximum shrinkage strain-rate (s) with standard deviations (SD) of experimental composites based on (BisGMA/TEGDMA): (50/50), (75/25), (25/75), containing photo-initiator system and mixed with five different radiopacifying agents: La_2O_3, BaO, $BaSO_4$, SrO, ZrO_2 at different weight fractions, ranging from: 0 to 80 wt.% are summarized in Tables 1 and 2. Figs. 1 and 2 illustrate, respectively, typical shrinkage strain-rate

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