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A numerical tool for studying photopolymerization inside thick composites: Influence of optical properties on the conversion profiles for a silica/TEGDMA-BisGMA formulation

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ABSTRACT

Photopolymerization of composite materials is not trivial. Indeed, the main drawback of this process is the light energy attenuation within the material, resulting in limited photopolymerized thicknesses. This light attenuation with depth relates to light absorption and scattering within the reaction mixture. Furthermore, the light scattering is influenced by the gap between filler and polymer refractive indices. In order to understand the influence of these parameters on both process and homogeneity of the resulting photocomposites, we present here a numerical model that provides access to data that are not experimentally accessible as the evolution of scattering coefficient or conversion gradient inside thick composite material during and after photocuring. To exemplify the model, three different cases representative in terms of optical properties will be discussed.

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1. Introduction

Nowadays, photopolymerization of composite materials have emerged in a range of numerous applications such as dental resins [1–4], paints [5–8], patterned substrates and manufacturing of ceramics by stereolithography [9–12]. The main shortcoming of the photopolymerization process applied to composite formulations is the limited curing light penetration within these suspensions that jeopardizes the depth of cure. The curing light attenuation in suspensions is a result of photoinitiator absorption, surface reflection, and above all of scattering by fillers and filler-matrix interface when refractive indices of the different components are not identical. To minimize this scattering or to elaborate transparent composite materials, two approaches were explored. The first one is to reduce the filler size below the critical scattering length, typically less than 200 nm [13]. The second one is to match filler and organic matrix refractive indices. Indeed, theoretical and experimental results showed that, when the refractive index difference between resin and filler narrows, the scattering phenomenon decreases and the transmission efficiency is enhanced [14–16]. If this approach seems very attractive, its implementation is still a challenge. Indeed, during photocuring, the refractive index of filler is supposed to be constant while the refractive index of the organic matrix increases versus medium density that is linked to both reactive group conversion and matrix volume shrinkage [17–19].

The purpose of this work is (i) to develop a numerical tool for obtaining data that are not readily accessible, and (ii) to predict the cure light transmission evolution and its influence on conversion profiles and cure depth inside a standard composite formulation during its photocuring. This simulation will take into account several phenomena inherent in the implemented photopolymerization reaction: the increase of the sample temperature due to the reaction exothermicity, as well as the variation of the light intensity consecutive to the physicochemical changes of the medium during the reaction. Different experimental measurements will be required to set up this simulation. Firstly, the evolution of reactive group conversion versus irradiation time will have to be determined on unloaded formulations for different incident light intensities and reaction temperatures. Secondly, the evolution of the optical properties of each component of the studied formulation will have to be known versus conversion, i.e. the refractive index and the absorption coefficient of both resin and filler. Lastly, the evolution of the composite medium optical properties versus conversion will have to be determined, i.e. the absorption and scattering coefficients. All these measurements will be carried out on a standard formulation composed of:

- two dimethacrylate resins (TEGDMA/Bis-GMA) typically used in dental materials; these resins exhibit low absorptivity, which

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does not significantly vary with methacrylic double bond conversion;
- a photoinitiating system (CQ/DMAEMA) also typically used in dental materials; the CQ photoinitiator is known to exhibit no photobleaching and to absorb in visible wavelength field [20];
- a micrometric silica filler chosen for its refractive index close to the methacrylic matrix one; the filler amount in the final composite is arbitrarily set at 33 vol-%.

From these experimental data, a phenomenological model [21–23] will be used to mathematically describe the evolution of the polymerization rate versus time as a function of irradiation conditions (temperature and incident light intensity). Furthermore, the medium temperature evolution will be calculated by means of the general heat equation [24]. At last, a four-flux model [25,26] making use of the optical parameters will be applied to describe the changes of light intensity inside the composite system.

Once this numerical model established and experimentally validated, three possible cases will be presented from an optical point of view considered at the end of the photocuring process: (i) the matrix and filler refractive indices are equal; (ii) the matrix refractive index is lower than the filler one; (iii) the matrix refractive index is higher than the filler one. For each case, temporal conversion profiles versus sample thickness will be presented and discussed.

2. Materials and methods

2.1. Materials

Bisphenol A glycidyl dimethacrylate (Bis-GMA, Sigma-Aldrich, 99%), triethylene glycol dimethacrylate (TEGDMA, Sigma-Aldrich, 95%), camphorquinone (CQ, Sigma-Aldrich, > 98%) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA, Sigma-Aldrich, 99%) were used as received. Silica particles with spherical form and a 30–50 μm average diameter were purchased from Biovalley. Their refractive index was determined with an uncertainty of 0.01 thanks to a series of refractive index matching oils (Bellingham + Stanley).

Bis-GMA and TEGDMA were mixed in various weight proportions with 1%-wt of CQ/DMAEMA (1/1) used as photoinitiating system. As required, 33 vol-% of silica particles were added in the acrylic matrix. The mixture was homogeneized with a Speedmixer.

2.2. Conversion and refractive index measurement

The polymerization progress was monitored by real time infrared spectroscopy using a Vertex 70 FTIR spectrometer (Brüker, Germany). An attenuated total reflection accessory fitted with a thermocouple (ATR MKII Golden Gate, Specac, Eurolabo, France) was used. A drop of the photocurable mixture was spread out over the ATR crystal and covered by a polyethylene film and a quartz plate in order to assure uniform exposed surface and to avoid the reaction inhibition caused by oxygen. By measuring the absorbance of the methacrylic double bond band at 1636 cm^{-1} comparing to the absorbance of an inert function band (used as reference) corresponding to the aromatic cycle at 1607 cm^{-1} for Bis-GMA or to the C—O band at 1452 cm^{-1} for TEGDMA, the conversion χ was calculated as follows:

$$\chi(t) = \frac{\frac{A_0^{function}}{A_0^{ref}} - \frac{A_t^{function}}{A_t^{ref}}}{\frac{A_0^{function}}{A_0^{ref}}} \times 100$$

where A_0 is the initial absorbance and A_t is the absorbance at t time.

The matrix refractive index evolution was followed at 656 nm by real time refractometry using an Arago refractometer (Cordouan Technologies, France). The formulation was spread out over the Sapphire prism without adding any high refractive index interfacial contact agent. Measurements were carried out at the selected temperature.

Whatever the analytical technique used, similar experimental conditions (temperature, light intensity, sample thickness) were applied for a given sample batch. The irradiation source was a 465 nm light emitting diode that perfectly matched with the maximum absorption of the photoinitiating system [20]. The light intensity was measured at the sample surface using a luxmeter (465 nm, Amprobe LM-100, Germany).

2.3. Absorption and scattering coefficients measurement

Absorption and scattering coefficients were measured using a UV–vis spectrophotometer (Varian Cary 100, USA) and an experimental device constituted of an integrating sphere and a QP 300-1-UVISR spectrophotometer from Ocean Optics (I.D.I.L. Fibres Optiques, Lannion, France) [27], respectively.

3. Determination and calculation of the parameters necessary to the modeling

3.1. Kinetic data

An autocatalytic model was applied to describe the reaction kinetics in a purely mathematical way [21–23]. According to this model, the polymerization rate $\frac{d\chi}{dt}$ (depending on the sample temperature T and on the light intensity I) is expressed as follows for the studied formulation:

$$\frac{d\chi(T,I)}{dt} = k(T,I).\chi^{0.8}(T,I).[\chi'(T,I)-\chi(T,I)]^2 \quad (1)$$

where χ is the methacrylic double bond conversion, χ' is the final methacrylic double bond conversion and k is the rate constant usually assumed to observe the Arrhenius law.

3.2. Temperature

The polymerization exothermicity and the low thermal conductivity of the sample can induce an increase of the sample temperature. If this variation can be considered as uniform at any place of the sample for thin layers [28], a temperature gradient can be observed in the case of thick samples [29]. As this variation cannot be experimentally measured in a direct way, this one must be calculated.

Whatever the studied photocurable system is, numerical calculations are based on the general heat equation with two location-dependent heat sources [25]:

$$\nabla^2 T - \frac{1}{a}\frac{\partial T}{\partial x} + \frac{S}{k_c} + \frac{\Delta H_0^{theor} d\chi(T,I)}{aC_p dt} = 0 \quad (2)$$

a (10^{-7} m^2 s^{-1}) and k_c (0.17 Wm^{-1} K^{-1}) are the thermal diffusivity and the thermal conductivity of the sample, respectively. These parameters are assumed to be constant during all the process.

S is the first location-dependent heat source corresponding to the light intensity absorption, $\frac{\Delta H_0^{theor} d\chi(T,I)}{aC_p dt}$ is the second location-dependent heat source induced by polymerization with ΔH_0^{theor} (−54.7 kJ mol^{-1} for a methacrylic double bond) [30] the theoretical

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