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# Relationships between refractive index change and light scattering during photopolymerization of acrylic composite formulations

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### ABSTRACT

Light scattering by filler particles is the main cause of the decrease in light intensity inside a photocurable composite material. This scattering phenomenon depends on the matrix and filler refractive index gap. This work aims to elaborate a non scattering photocured composite by minimizing this gap. Relationships between refractive index and conversion of unloaded acrylic formulations were first studied by real time infrared spectroscopy and refractometry. Refractive index of the final polymer was especially related to its monomers composition. These results allowed matching the matrix and silica refractive indexes, i.e., determining the suitable composite formulation which led to a non scattering material.

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## 1. Introduction

Nowadays, photocured resins are used in numerous application fields. Some applications such as dental resins [1–3], paints [4–7], patterned substrates and layered manufacturing of ceramics by stereolithography [8–11]... require the addition of fillers to improve some properties (aesthetical, mechanical, optical ...) [12]. Photopolymerizable composites generally consist of inorganic powder dispersed in an organic matrix composed of monomers and photoinitiators [13]. Epoxy or acrylic resins are usually used as organic matrix whereas inorganic fillers can be silica, alumina, zircon... depending on the ultimate application of the composite.

The low photocurable sample thickness is the main shortcoming of the photopolymerization applied to composite formulations. Light attenuation within the material due to absorption by monomers and photoinitiators, scattering by filler particles and refraction at the filler/monomer interface is the cause of this limitation. As preponderant phenomenon, the light scattering jeopardizes light transmission and consequently conversion and depth of cure [1,8,12].

Experimental results have demonstrated that the scattering coefficient decreases and the transmission efficiency improves when the refractive index difference between resin and filler narrows [14–17]. In such systems, the filler refractive index is constant while the organic matrix refractive index increases during the pho-

topolymerization process. Indeed, the index variation follows the medium density evolution (volume shrinkage), which is linked to conversion [18–20].

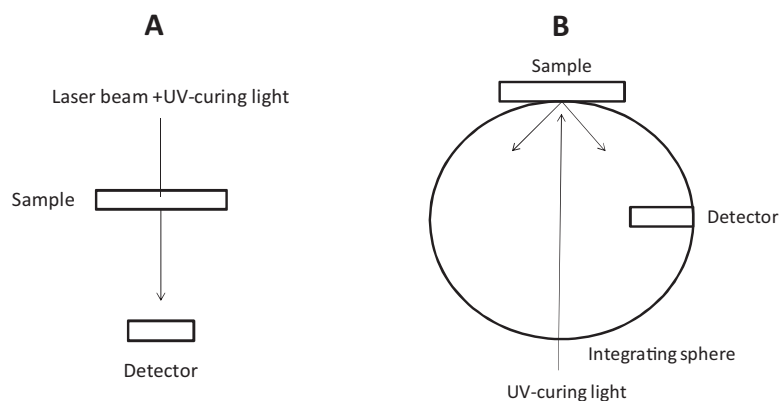
The goal of this paper is to elaborate a non scattering photocured composite material by minimizing the light scattering phenomenon, i.e., by adjusting both refractive indexes of filler and matrix. For that, we arbitrarily chose to work on a model system composed of an acrylic matrix and silica filler. This one could be used to produce ceramic objects by stereolithography [8]. The matrix conversion and refractive index evolution during photopolymerization will be first investigated by combining real time refractometry and infrared spectroscopy. This study will be carried out on unloaded acrylic formulations. Refractive index-conversion relationships will be determined as a function of reaction temperature, incident light intensity as well as acrylic formulation composition. These results will be secondly used to elaborate a non scattering composite material. In this aim, the organic matrix composition will be chosen so that refractive indexes of organic matter and silica particles match at the end of the reaction. Amelioration of light transmission and decrease of scattering coefficient will be confirmed by spectroscopic measurements.

## 2. Materials and methods

Bisphenol A glycidyl dimethacrylate (Bis-GMA, Sigma–Aldrich, 99%), triethylene glycol dimethacrylate (TEGDMA, Sigma–Aldrich, 95%), bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure® 819, BASF), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur® 1173, BASF), camphorquinone (CQ, Sigma–Aldrich,

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**Scheme 1.** Experimental devices for (A) transmitted light and (B) scattering coefficient measurements.

>98%) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA, Sigma–Aldrich, 99%) were used as received.

Silica particles with spherical form and a 30–50  $\mu\text{m}$  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).

The polymerization progress was monitored by real time infrared spectroscopy using a Vertex 70 FTIR spectrometer (Brüker, Germany). An attenuated total reflection accessory (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. The conversion  $\chi$  was calculated by measuring the absorbance of the acrylic double bond band at  $1636\text{ cm}^{-1}$  comparing to the absorbance of an inert function band (used as reference) corresponding to the aromatic cycle at  $1607\text{ cm}^{-1}$  for Bis-GMA or to the C–O band at  $1452\text{ cm}^{-1}$  for TEGDMA as follows:

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

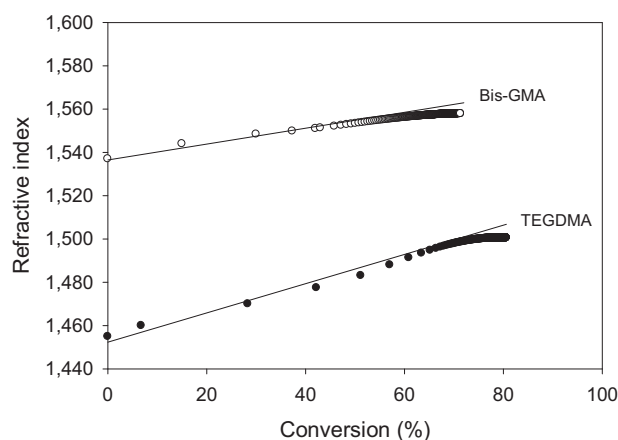
where  $A_0$  is the initial absorbance and  $A_t$  is the absorbance at  $t$  time.

The 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 each 2.3 s at the chosen temperature.

Whatever the analytical technique used, similar experimental conditions (temperature, light intensity, 20  $\mu\text{m}$  sample thickness) were applied for a given sample batch. Light intensity coming from either 365 nm or 465 nm light emitting diode was measured at the sample surface using a radiometer (365 nm, Vilber–Intraspec Oriol VLX-3W, France) or a luxmeter (465 nm, Amprobe LM-100, Germany).

Cylindrical samples (1 mm thick and 0.6 cm diameter) were prepared at different reaction temperatures using a  $20\text{ mW cm}^{-2}$  radiation intensity at 465 nm. Photocured samples were then analyzed by dynamical mechanical analysis (DMA Q800, TA Instruments) in compression mode using a stainless steel parallel plate probe (1 mm in diameter) at a 1 Hz frequency and a  $3^\circ\text{C/min}$  heating rate. The applied strain amplitude was 5  $\mu\text{m}$ . The mechanical transition temperature  $T\alpha$  was measured at the maximum of the  $\tan \delta$  curve.

Transmitted light and scattering coefficient were measured thanks to the experimental devices collected on Scheme 1. A QP



**Fig. 1.** Refractive index-conversion relationships for pure Bis-GMA and TEGDMA photopolymerized at  $T=30^\circ\text{C}$  in the presence of 1 wt-% Darocur 1173 ( $I_0 = 20\text{ mW cm}^{-2}$  at 365 nm).

300-1-UVISR spectrophotometer from Ocean Optics (I.D.I.L. Fibres Optiques, Lannion, France) was used as described in published works [21].

### 3. Results and discussion

#### 3.1. Refractive index-conversion relationship

1 wt-% of Darocur 1173 was first added in pure BisGMA or TEGDMA resin. Each unloaded formulation was then irradiated at  $30^\circ\text{C}$  with a  $20\text{ mW cm}^{-2}$  light intensity coming from a LED at 365 nm. The photopolymerization reaction was followed in real time by FTIR spectroscopy and refractometry. Temporal evolution of both double bond conversion and refractive index was then obtained. The combination of both curves allowed plotting the evolution of the relationship between conversion and refractive index, as shown in Fig. 1.

One can first notice that linear relationships were obtained at conversion lower than 70% for TEGDMA and 55% for Bis-GMA. These results are in agreement with similar works based on interferometric measurements [18,19], which showed that the refractive index increase during the photopolymerization was related to the increase in the material density, i.e., in the volume shrinkage. Above these conversion values, the reaction continued but the refractive index became constant. This could mean that no more volume shrinkage occurred.

Identical experiments were carried out by varying the incident light intensity or the photoinitiator type (Irgacure 819 and irra-

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