MATERIAL INVESTIGATION OF A PHOTOPOLYMERIZED BIOMATERIAL

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Abstract

The objective of this study was to investigate the effects of different UV exposure time on the mechanical properties of a commercially available ORMOCER resin and relate these properties with the level of polymerization within the test samples. Coupons were tested in compression to obtain the mechanical properties as a function of light exposure time. The extent of resin crosslinking (degree of curing), at applied exposure times, was obtained using the recordings of a fiber optic sensor (FBG) embedded in freestanding block specimens.

Keywords: biopolymer, mechanical properties, UV-curing, exposure time, degree of curing

1. INTRODUCTION

Organic copolymers – defined as polymers from more than one species monomer – have found many applications as polymer materials. They are prepared by the sol-gel process starting from liquid precursors. This leads to molecular composite materials which cannot be prepared by conventional means. These materials have the potential to combine certain structural properties of different classes of materials in ways not accessible by mixtures of macroscopic phases as in the case of classical composites. ORMOCER® resins belong to the so-called hybrid materials while biological assays have shown that are nontoxic and biologically inert. Due to the possibility of UV-curing these resins can be used as dental materials. Their biocompatible nature has attracted a growing interest for microfabrication applications in biomedicine, sub-micron medical device structures and tissue engineering.

Photofabrication of functional components via the utilisation of advanced rapid prototyping systems has comprised a highly challenging task for the past decade. The technologies employed for the creation of such entities include techniques like stereolithography, three-dimensional printing, direct deposition etc. Concurrent technological evolution of micro-fabrication systems as well as custom engineered materials has lead research work into a whole new range of topics and applications [1, 2]. Many, well documented [3, 4], approaches utilising the aforementioned technologies rely upon the utilisation of prototype multifunctional materials within the context of specially developed rapid fabrication system apparatuses [5-10].

Experimental techniques capable of monitoring the curing shrinkage and mechanical changes during the polymerisation process are increasingly attracting attention. In recent years, the use of optical Fibre Bragg Grating (FBG) sensors has been considered as one of the most effective methods for in-process monitoring, as well as post-process determination of the micro curing strain state induced to the material. Apart from being inexpensive and electromagnetic interference resistant, fibre-optic sensors are extremely small possessing unique embedding characteristics in relation to a variety of host polymeric as well as composite materials. The fact that the mechanical behaviour of the glass fibre that contains the grating is not affected, leads to the conclusion that the technique is well suited for the determination of non-uniform axial Stains development due to the shrinkage of the resin during polymerisation. Scientific works have been reported
that use Fibre Bragg Grating sensors (FBG) for simultaneous monitoring of the fabrication strain and the cure temperature in epoxy resins and fibre reinforced composites [16 - 18].

This work investigates the photopolymerisation induced shrinkage strains in a commercial photopolymer commonly used in microfabrication. A fibre optic sensor is utilized for the effective determination of the resulted shrinkage strains throughout the consolidation process upon exposure to UV light of specific irradiation intensity. Another objective of the undertaken work was to report on the mechanical behaviour (as expressed by Young’s modulus) of the material as exposed to ultraviolet light (UV).

2. FIBER BRAGG GRATINGS PRINCIPLES

Fibre Bragg Gratings are specific regions along the length of an optical fibre’s core where spatial periodic (or quasi-periodic) modulation of the refractive index has been conducted [19]. The basic principle of operation of the FBG sensor is based upon the refractive signal’s (centre wavelength $\lambda_B$ of the back-reflected light from the Bragg grating) changes which depend upon the core’s effective refractive index ($n_{eff}$) and the periodicity ($\Lambda$) of the grating [20]. This means that Fibre Bragg gratings operate as wavelength selective filters [21]. Their main property is to reflect light transmitted from a broadband source over a narrow wavelength range and at the same time transmit without changing the remaining wavelengths giving a local steep reduction in the transmitted spectrum. Therefore, the Bragg wavelength is expressed by the following formula:

$$\lambda_B = 2n_{eff}\Lambda$$

When the FBG sensor in embedded into a host material and both experience temperature changes, the Bragg equation is modified to account for the thermally induced axial strains in the fibre as a result of the mismatch in the coefficients of thermal expansion between the optical fibre ($\alpha_f$) and the host material ($\alpha_m$). Therefore, a more generalized equation can be written as:

$$\frac{\lambda_B - \lambda_{B0}}{\lambda_{B0}} = \frac{\Delta \lambda_B}{\lambda_{B0}} = (1 - p_e)\varepsilon_Z + (1 - p_e)(\alpha_m - \alpha_f)\Delta T + (\alpha_f + \xi)\Delta T$$

In the case where the embedded sensor and the host material are not subjected to any temperature variations, the precious equation can be further simplified to the following form:

$$\frac{\lambda_B - \lambda_{B0}}{\lambda_{B0}} = \frac{\Delta \lambda_B}{\lambda_{B0}} = (1 - p_e)\varepsilon_Z$$

3. MATERIALS AND EXPERIMENTAL PROCEDURE

The investigated resin was an ORMOCER® photopolymer by Micro Resist Technology [20]. In general, ORMOCERS® consists of a highly crosslinkable organic network [21] as well as inorganic components which lead to high optical quality. The resin is used in two photon polymerisation [5, 10]. Several studies and experimental works [4] have been conducted incorporating ORMOCER® leading to the creation of a variety of components and structures. It has to be noted that the material’s biocompatibility in addition to its polymerisation effectiveness in the micro-scale contribute towards the continuous extension of micro as well as nano-scale research including applications in the medical sector [22].
Specimens of 10mm x 10mm x 40mm (width x height x length) were fabricated at room temperature in a custom made aluminum mould, where its open top surface was exposed to UV radiation. The mould cavity was coated with a thin layer of liquid release agent in order to minimize bonding of the solidified photopolymer to its surfaces. Furthermore, the mould design allowed for immediate and easy specimen removal at the end of the solidification process. The utilized UV source (UVP, Inc), produced a constant ultraviolet radiation of 365nm of wavelength and in order for the open surface of the cast resin to be uniformly exposed to UV radiation, a linear actuator (Instron 5848 Microtester), incorporating a small mechanical grip to hold the UV light probe, was also used. The grip's reciprocating travel along the length of the specimen was performed at a constant velocity of 5mm/sec. The experimental procedure incorporated intermediate Bragg wavelength measurements at the end of pre-selected time intervals of UV exposure, with the UV light source being switched off, as well as after partial and total demoulding of the solidified specimens. It is mentioned that specimen de-moulding took place only when the recorded wavelength maximum peaks and spectra did not change with additional specimen exposure to UV radiation. The contribution of any constraining effects from the mould on the FBG recordings was also investigated at the end of UV curing process.

4. RESULTS AND DISCUSSION

The evolution of the reflected spectrum at the selected time intervals during UV exposure is shown in Figure 1. Initially a single peak is obtained before photopolymer casting. Then, as the resin is exposed to UV radiation the recorded spectra exhibit multiple peaks demonstrating a non-homogeneous axial strain along the embedded FBG sensor. As the UV induced consolidation of the resin specimen advances, the wavelength value corresponding to the Bragg peak of the reflected spectra is subjected to additional changes. Using the calibrated value for $\lambda_{B0}(z) = \lambda_B = 1300.0 \text{ nm}$ and the maximum recorded wavelength value of $\lambda_B = 1297.22 \text{ nm}$, a compressive strain value of $2743 \mu\varepsilon$ is calculated. At this stage and as the resultant spectrum did not reveal any additional shift of the intensity peak value recorded at 20 min, the UV source was left switched-on overnight for 14.5 hours. It was found that specimen consolidation had advanced considerably leading to a calculated strain value of $4102 \mu\varepsilon$. Following the demoulding procedure, it is seen from Table 1 that casting of the Ormocer® resin into the used aluminum mould is associated with the introduction of considerable constraining effects on the recorded spectra.

![Figure 1](image-url)
Table 1. Measured maximum wavelength and corresponding calculated shrinkage strain at selected recording points for the ORMOCER® photopolymer.

<table>
<thead>
<tr>
<th>Recording Stage - ORMOCER®</th>
<th>Maximum Wavelength (nm)</th>
<th>Shrinkage Strain (µε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before FBG placement into mound</td>
<td>1300.00</td>
<td>-</td>
</tr>
<tr>
<td>After FBG alignment into mould</td>
<td>1300.00</td>
<td>0.0</td>
</tr>
<tr>
<td>After 20 min. of UV exposure</td>
<td>1297.22</td>
<td>-2743.0</td>
</tr>
<tr>
<td>After 30 min. of UV exposure</td>
<td>1297.22</td>
<td>-2743.0</td>
</tr>
<tr>
<td>After 15 h of UV exposure</td>
<td>1295.83</td>
<td>-4102.0</td>
</tr>
<tr>
<td>Demoulding - on base</td>
<td>1295.56</td>
<td>-4378.7</td>
</tr>
<tr>
<td>Demoulding - freestanding</td>
<td>1294.70</td>
<td>-5226.8</td>
</tr>
<tr>
<td>After thermal treatment at 75°C</td>
<td>1292.49</td>
<td>-7406.3</td>
</tr>
<tr>
<td>After 30 days in R.C.</td>
<td>1294.11</td>
<td>-8471.4</td>
</tr>
</tbody>
</table>

In a recent work, where a FBG sensor was embedded in an epoxy cylindrical specimen, it has been shown that after curing and at room temperature the only significant strain on the FBG is that due to shrinkage which gives the following equation form:

\[
\frac{\Delta \lambda}{\lambda_{B0}} = (1 - p_i) \alpha_{chem} \Delta \gamma
\]

where \(\alpha_{chem}\) is the chemical shrinkage coefficient and \(\Delta \gamma\) is the degree of curing at a given cycle. The \(\alpha_{chem}\) can be evaluated by assuming the volume change of a fully cured isotropic resin material, expressed as \(\alpha_{chem} = (\Delta V/V_0 + 1)^{1/3} - 1\) [34]. In this work a value of 5% volume shrinkage \((\Delta V/V_0)\), which leads to a value for \(\alpha_{chem} = 0.0164\), for Ormocer® was considered as drawn from the material’s specification sheet [20]. Actually, from the material provider a shrinkage range of 5 to 7% is given. In our calculations the smaller shrinkage percent (5%) was selected since in our experiment the speed of curing was slow (faster curing results in higher shrinkage). The results of the calculations for \(\Delta \gamma\) are presented in Table 2. It is noted that after demoulding the degree of conversion is small (~ 32%) which is supported by the observed sticky nature of the specimen surfaces when taken out of the mould. Thermal treatment resulted to an additional consolidation of 13.2%, corresponding to a total \(\Delta \gamma\) of 45.1%. Finally, after a month at room temperature and light conditions, an additional 6.5% consolidation is calculated. It is worth noticing that these calculated values for \(\Delta \gamma\) depend highly on the accuracy of the \(\alpha_{chem}\) data.

Table 2. Measured maximum wavelength and corresponding calculated degree of cure at selected recording points for the ORMOCER® photopolymer.

<table>
<thead>
<tr>
<th>Recording Stage - ORMOCER®</th>
<th>Maximum Wavelength (nm)</th>
<th>(\Delta \gamma) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demoulding - freestanding</td>
<td>1294.70</td>
<td>31.89%</td>
</tr>
<tr>
<td>After thermal treatment at 75°C</td>
<td>1292.49</td>
<td>45.10%</td>
</tr>
<tr>
<td>After 30 days in R.C.</td>
<td>1291.41</td>
<td>51.59%</td>
</tr>
</tbody>
</table>

The stress – strain curves and the measured Elastic Moduli for compressively loaded prismatic test specimens are presented in Figure 2 and Table 3. It is noted that the results correspond to two groups of prismatic specimens, been subjected to different durations of UV exposure, namely 40 min and 21 hours. It is seen that all group specimens demonstrate a repeatable behavior when compressively loaded. For the 40
For the min cured specimens the calculated mean value of the Elastic Modulus was \( E = 1.16 \text{ GPa} \) and corresponds to a 63% degree of polymerization. For the as considered fully cured specimens (21 hours of light exposure and 83% of curing degree) the calculated mean value of modulus was \( E = 1.6 \text{ MPa} \). It is worth noticing that the Young’s Modulus for the investigated Ormocer® resin was 36% lower than the Modulus reported in [23] for a non-biocompatible Ormocer hybrid polymer used in the micro-fabrication of cellular structures.

5. CONCLUSIONS
In this work, results are presented on shrinkage strain evolution during the UV-activated photopolymerisation and on the Elastic Modulus of a photopolymer commonly used in micro-fabrication. It is demonstrated that the followed experimental procedure based on the utilization of a fibre optic sensor can provide important information on the magnitude of cure-induced strains. It was found that the measured consolidation strains were of significant magnitude at the end of the curing process. The measured elastic modulus of the studied Ormocer® material was found to be 36% lower than the one reported in the literature.

LITERATURE


