Rheological Investigation of the Gel Time and Shrinkage in Hybrid Organic/inorganic UV Curable Films

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Inorganic silane oligomer based on tetraethoxysilane was synthesized via sol-gel under acidic condition. UV curable organic-inorganic hybrid coatings were then prepared using the synthesized inorganic oligomers and tetraethylene glycol diacrylate. The effect of organic/inorganic content ratio on gelation and shrinkage of samples was investigated by photorheometry. It was revealed that incorporating higher amount of inorganic component in the samples improves the system mobility and postpones gelation. It also reduces the final film shrinkage that is stemmed from photopolymerization induced phase separation.

Keywords: photopolymerization, photorheometry, hybrid materials, shrinkage

1. Introduction

In last decades, photopolymerization technology attracts lots of researchers all around the world, because of their fascinating properties [1-5]. Photocurable polymer technology presents different advantages. For instance, rapid curing, low VOC, high energy efficiency, low temperature curing process can be highlighted. These properties make it capable to be utilized in wide range of applications such as coatings, printing inks and adhesives. On the other hand, another kind of coatings that are called “hybrid coatings”, have been investigated widely because of their specific properties. These coatings can combine the robustness of organic polymers (such as low temperature processing condition, flexibility and ductility) with the interesting properties of ceramics (such as hardness, high mechanical strength, and low coefficient of thermal expansion) [6-10]. In this context, developing hybrid coatings that can be cured by light becomes an attractive field of research [11].

One of the most important concerns about preparation of hybrids is the low affinity between organic and inorganic network. This concern can cause serious problems for dispersion of inorganic phase through the organic phase before solidification and also maintaining domain size in the desirable range. On the other hand ceramic processing condition is usually so severe that can completely degrade the organic phase. The most convenient way to overcome these challenges is to take advantage of the sol-gel chemistry to introduce the inorganic moieties in a polymeric material. In this approach the
building block of the inorganic part has the general composition of \( R-\left[SiX_3\right]_n \). In this structure, \( n \) is the number of \([SiX_3]\) hydrolysable groups in which, \( X \) is O-CH\(_3\) or O-CH\(_2\)-CH\(_3\). \( R \) can be either an organic group that is covalently attached to the Si atom or another hydrolysable group [12-13]. The sol-gel polymerization proceeds with hydrolysis and sequential condensation and eventually affords a Si-O-Si network [14]. While the sol-gel process takes place under mild conditions, it can be utilized to prepare wide range of hybrid materials with different polymers [15]. On the other hand, since this process can occur in situ, the problems associated with the dispersion of inorganic phase in the organic polymer network can be almost completely resolved [8].

Rheology is a great tool to investigate the UV curing. Changes in the rheological properties of a material can reflect the formation and extent of the crosslinking [16]. Monitoring the rheological properties of UV curable materials as they evolve from a liquid through the gel point to a solid can be carried out with a conventional rheometer modified to accept a light source [17-21]. Thus, rheological properties measured during photopolymerization reflect the microstructure changes which result from the photoinduced crosslinking. This latter determines final mechanical properties of the cured material [22]. Hence, evaluating the effect of different formulation aspects—such as the amount of inorganic moieties in UV curable hybrid materials—is of great importance in order to optimize the coating formulation.

In addition to chemical and mechanical properties, dimensional aspects of the film are also changed during photopolymerization. The extent of photoinduced shrinkage is significant especially for acrylate monomers and oligomers that are widely used in UV curable coatings. Shrinkage is caused by the replacement of weak and long distance van der Waals interactions by strong and short length covalent bonds that are formed during photocuring. The shrinkage can cause several problems for photopolymers, such as poor adhesion, delamination, insufficient flatness and also development of microcracks [23]. In UV curable restorative materials, buildup of stress can lead to mechanical failure of the composite-tooth interface and formation of gaps [24]. All these concerns are of prime importance in the coating area. Therefore, there is an increasing interest for monitoring the shrinkage during photopolymerization and proposing methods to reduce it [25-27]. Recently, Schmidt and coworkers proposed a new method for real time investigation of shrinkage during photopolymerization by implementing photorheometry [23]. The results were found in good agreement with previously reported studies achieved by different methods such as shrinkage evaluation using buoyancy force.

Meanwhile, limited efforts have been devoted to investigate the dimensional and rheological changes in hybrid photopolymers under light curing. In this project, silane based oligomers were prepared and incorporated into acrylate monomeric systems to provide UV curable hybrid coatings. The effect of incorporating the inorganic part on the rheological and dimensional properties evolution was investigated using photorheometer.

2. Experimental
2.1. Materials

The chemical structure and abbreviations of the mentioned materials are represented in Scheme 1.

![Scheme 1. Chemical structure of TtEGDA, TEOS and IR 184.](image)

Tetraethoxysilane (TEOS) and hydrochloric acid (32%) were purchased from Aldrich. Ethanol was supplied by Merck and Tetraethylene glycol diacrylate (TtEGDA, Sr 268)
was obtained from Sartomer. The photoinitiator (1-hydroxy-cyclohexyl phenyl ketone) IR 184 was provided by BASF. All the reagents were used as received.

2.2. Synthesis of silane oligomer

In a first step, partial hydrolysis and condensation of TEOS precursor was carried out under acidic conditions [13, 26-28]. For this purpose, 0.12 mol (25 g) tetraethylorthosilicate was dissolved in 0.48 mol ethanol in a round-bottom flask. 0.115 mol distilled water was then added into the mixture. After the mixture was homogeneous, 1.2 mmol hydrochloric acid (32 wt%) was added with mechanical stirring. The reaction mixture was carried out at ambient temperature for 72 h. The solvent was then removed by a rotary evaporator at 50 °C to afford the TEOS oligomer (16.8 g, 67.2% yield based on TEOS monomer). Since the time scale for condensation of TEOS precursor was carried out in the linear viscoelastic (LVE) regime, amplitude sweep tests have been conducted for all samples prior measurement.

In order to in situ monitor the photocrosslinking process, the bottom plate was replaced by a glass plate. Samples were irradiated with a Mercury-Xenon arc source (Hamamatsu L8282) which is linked to the rheometer by a light guide. The intensity of UV light was 0.155mW/cm².

During the experiment, continuous readjustment of the normal force FN to the upper tool of the rheometer to FN=0 was achieved, a fact that compensated changes in thickness due to sample shrinkage. The shrinkage extent was determined from the ratio between the actual gap and the gap before the reaction [23].

3. Results and Discussion

3.1. Real-time photorheometry

The time evolution of complex viscosity is shown in Fig. 1. After a short time, the complex viscosity starts to grow up rapidly which is an evidence of the polymerization process [28].

![Complex viscosity of the hybrid formulations.](image)

3.2. Gel time

The initial plateau part of the curve at the very beginning stage of polymerization has also been observed in other studies [19,29,30]. At the initial stage of the curing, the modulus of the formulation is too low and cannot be measured accurately. After a few seconds, the modulus increases enough for the system to be measured accurately [30].
Gel point is the most important parameter that affects the processing condition of thermoset materials. Transition from liquid state to solid state takes place at gel point and the flow becomes restricted. So, as mentioned previously, determining gel point is very important for optimizing the curing conditions [31]. According to Winter and Chambon, the gel point is the point at which, tanδ (loss factor) becomes independent of the frequency. In other words, it corresponds to the intersection of tanδ curves at different frequencies [32,33]. However, for many samples, it is reasonable to assume the intersection of G’ and G” curve (the point at which tanδ becomes equal to 1 as gel point [17].

In this study it was found that the gel times for aforementioned methods are in good agreement with each other. So the point at which loss factor becomes tanδ=1 was assumed as gel point.

Fig. 2. Evolution of tanδ with irradiation time.

\[
\text{tanδ} \quad \text{I0} \quad \text{I05} \quad \text{I10} \quad \text{I15}
\]

\[
0 \quad 5 \quad 10 \quad 15 \quad 20
\]

Fig. 2. Evolution of tanδ with irradiation time.

\[\text{tanδ} \text{ plotted against curing time in Fig. 2. As it can be seen, samples with higher inorganic content reach gel point later. This can be attributed to the fact that this nonreactive oligomer improves the mobility of the growing polymeric chains. So the sample is undergone gelation at higher monomer conversion. This effect has also been reported in the literature [34,35]. All the data are summarized in Table 2.}\]

3.3 Shrinkage

The changes in sample thickness and resulting shrinkage can also be monitored by photorheometry during the photopolymerization. The corresponding results are shown in Fig. 3 and Fig. 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel time (s)</th>
<th>Final shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I0</td>
<td>10.2</td>
<td>16.7</td>
</tr>
<tr>
<td>I05</td>
<td>10.9</td>
<td>14</td>
</tr>
<tr>
<td>I10</td>
<td>11.7</td>
<td>13.3</td>
</tr>
<tr>
<td>I15</td>
<td>12.1</td>
<td>11.3</td>
</tr>
</tbody>
</table>

It is obvious from these curves that the shrinkage is reduced by increasing the amount of inorganic oligomer content in the samples.

Fig. 3. Change in the sample thickness as a function of irradiation time.

Fig. 4. Shrinkage change during photopolymerization process for different inorganic contents.

In general, dimensionally stable fillers are added to the coating formulations to reduce
final shrinkage [23,36]. Another creative approach for reducing film shrinkage is the addition of another component which is miscible with the UV curable resin prior to radiation but undergoes photopolymerization induced phase separation (PIPS) at higher conversions. When phase separation occurs, film volume expands and compensates a portion of the shrinkage that arises from photopolymerization [25,37]. Herein, all the samples were completely transparent and homogenous before irradiation but formulations that contained inorganic oligomers became turbid after photopolymerization. This result was attributed to phase separation that occurs during photopolymerization.

4. Conclusion

Inorganic oligomer based on TEOS precursor synthesized via sol-gel process was introduced to an organic matrix to prepare UV curable organic-inorganic hybrid coatings. The effect of the amount of inorganic content on gelation and shrinkage was investigated by real-time photorheometry. The results showed that samples containing higher amount of nonreactive inorganic content, undergo a delayed gelation. It can be arisen from the improved molecular mobility in the samples at higher inorganic contents. In addition, increasing the portion of inorganic moieties in the coating formulation reduced the final film shrinkage. It can be attributed to the photopolymerization induced phase separation.

References