

## Identification of Relationship Between the Synthesis/Process Parameters and Properties of a Sol-Gel-Derived Polymer Nanocomposite System

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**ABSTRACT:** A Ti-containing silicate-based epoxy-functional polymer nanocomposite system was synthesized by a sol-gel route with or without the introduction of a reflux process, which was followed by UV-induced epoxy polymerization. Influences of synthesis and process parameters, including Ti content, sol ageing, reflux process, and UV-irradiation on various properties of the system were detailed. It was demonstrated that the introduction of a reflux process during the sol-gel synthesis could significantly modify the chemical and physical properties of the resultant material system along with other parameters such as Ti content. Overall results showed that the synthesis and process parameters examined could be employed to modify the microstructure, and to tune the final properties of this polymer nanocomposite system. The technique described herein, therefore, could be used to develop a new process regime to obtain materials of this type with desired properties, which might potentially be employed in certain applications such as dental restoration. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3704–3709, 2013

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### INTRODUCTION

Through the combinations of different types of bonding (in terms of covalent/ionic character of bonds) and processing methods, materials with new properties can be produced for electrical, optical, structural, or related applications; inorganic–organic hybrid material systems, particularly organically modified silicates, offer significant opportunities in the context of development of materials for applications such as dental restoration, photonic interconnection/optical waveguiding, abrasion-resistant coating, etc.<sup>1–5</sup> The development of new hybrid materials is typically performed by combining metal alkoxides and organic oligomer/polymers via the general sol-gel approach.<sup>6–10</sup> Inorganic–organic hybrids with crosslinkable functional groups, such as acrylate/methacrylate or epoxy, can also be used in various applications such as electronics, dental restoration, etc. at present.<sup>1,3,11,12</sup> An advantage of epoxy-based systems is that the crosslinking of epoxy functional groups can be achieved either by a suitable catalyst or by irradiation with UV or visible light in the presence of a suitable photoinitiator.<sup>6,12</sup> In addition to Si-containing precursors, alkoxy compounds of transition metals such as Ti or Zr can also be involved in the sol-gel synthesis so that functional properties can be tuned.<sup>1,3,6,13</sup> For instance, Zr and/or Ti may be

incorporated into sol-gel-derived inorganic–organic hybrid material systems in order to improve their mechanical properties, which are of critical importance in dental restoration. Moreover, these species are known to be capable of catalysing epoxy ring opening reactions, which might thus facilitate the formation of polymeric ether species within the structure; and exposing these species to higher temperatures during the synthesis will normally promote the epoxy polymerization reactions.<sup>6,13</sup> The employment of these species in the sol-gel synthesis of inorganic–organic hybrid material systems, therefore, may result in changes in the microstructure of the material, and hence affect its functional properties. That is to say, elaborate analysis and characterization of the influences of synthesis and process parameters on the material properties are needed to be performed to help identify the structure–property relationship for this type of materials.

The aim of this study is to help explore the potential of certain types of polymer nanocomposites to be successful candidates in new fields such as dental restoration. Current commercially available dental restoration/adhesion materials are composed mostly of acrylate-/methacrylate-based composites. Major disadvantages associated with these composites include their lack of adhesion to dentine, and that they exhibit volumetric shrinkage

upon polymerization, which is an inherent feature of acrylates/methacrylates.<sup>11,12,14</sup> Moreover, it is well known that their monomers as well as some other chemicals associated with their chemical structure (e.g., Bisphenol-A) are potentially detrimental for human health. There is currently no superior replacement for these acrylate-/methacrylate-based composites, however. It is of therefore a great importance to find suitable alternatives to them. The potential advantage of using epoxy-based polymer nanocomposite material systems in the field of dental restoration would be the replacement of the existing composites without having their drawbacks (i.e., shrinkage upon polymerization, low-adhesion, health-related side-effects, etc.). In this regard, a detailed investigation of the comparative effects of synthesis/process parameters on the properties of an identical nanocomposite were discussed previously.<sup>15</sup> As was demonstrated in that article, the epoxy polymerization/cross-linking reactions were, to some extent, carried out by the catalytic effect of Ti species prior to the UV-irradiation (during the synthesis/sol-ageing). Also postulated was that UV-radiation might cause a change in the number of the Si—O—Ti species in the structure (bond cleavage). Further to that work, an identical inorganic-organic hybrid material system was synthesized in this study. In addition, a reflux process, applied at two different temperatures, was optionally employed during the synthesis. So-obtained sol-mixtures were also aged for various periods of time. Spectroscopical, thermal, and mechanical characterization of the sol-gel mixtures and the resultant materials were performed. Combinational influences of these synthesis and process parameters on various properties of the system were detailed.

## EXPERIMENTAL

### Synthesis

The following synthesis route was used in the case where the reflux step was not employed: a mixture of (3-glycidyloxypropyl)trimethoxysilane (GDPTMS) (Aldrich), tetraethoxysilane (TEOS) (Aldrich), and dimethyldiethoxysilane (DMDEOS) (Fluka) (the main inorganic structure formers) were prepared with a molar ratio of 18 : 1 : 1, respectively. Various amounts of a mixture of titanium(IV) iso-propoxide (Ti(OPr)<sub>4</sub>) (Aldrich), a network former, and a potential catalyst for epoxy crosslinking, and methacrylic acid (MAA) (Merck), a complexing agent, (with a molar ratio of 1 : 4 (Ti(OPr)<sub>4</sub>:MAA)) were added to the former mixture while stirring. After 15 min, iso-propyl alcohol (IPA) (Sigma-Aldrich) was added, which was followed by the addition of an aqueous solution of HCl (Merck) (1 N), with a molar ratio of 1 : 1 : 0.05 ((Si + metal):IPA:HCl), were added while stirring. After 2.5 h, triarylsulfonium hexafluoroantimonate salts (50 % mass in propylene carbonate) (Aldrich) were added as a photo-initiator to the resultant mixture with a mass ratio of 1 : 0.1 (GDPTMS:photo-initiator). After a further stirring of 1 hour, several samples were stored to investigate the effect of sol ageing at ambient conditions up to 10 days.

In the case of the synthesis with the reflux process, a similar synthesis route was followed with the following exceptions: only H<sub>2</sub>O rather than the aqueous HCl solution (H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>) was added after the addition of IPA. This was followed by the reflux process at either 60 or 85°C in an oil bath while stirring for 2.5

h. This mixture was then cooled down to room-temperature, which lasted for ~5 min. Then, the aqueous HCl solution (H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>) was added. The schematic representation of the synthesis routes followed, and the structures of the chemicals used are presented in Figure 1.

### Process

All sol-gel mixtures were transferred into Teflon moulds with various shapes and sizes. They were then placed in a laboratory oven (Memmert UNE 500) at 60°C for 30 min for partial drying. Following this step, the samples were irradiated with UV light for either 10 or 60 min. This UV-irradiation was carried out using a Philips 300 W-UV lamp whose wavelength and light intensity were 259 nm and 12,000 lm, respectively. The distance between the lamp and the sample was ~15 cm; and this area was cooled down using a fan since the lamp also emitted heat (the temperature at which the samples were irradiated was ~54°C).

### Characterization

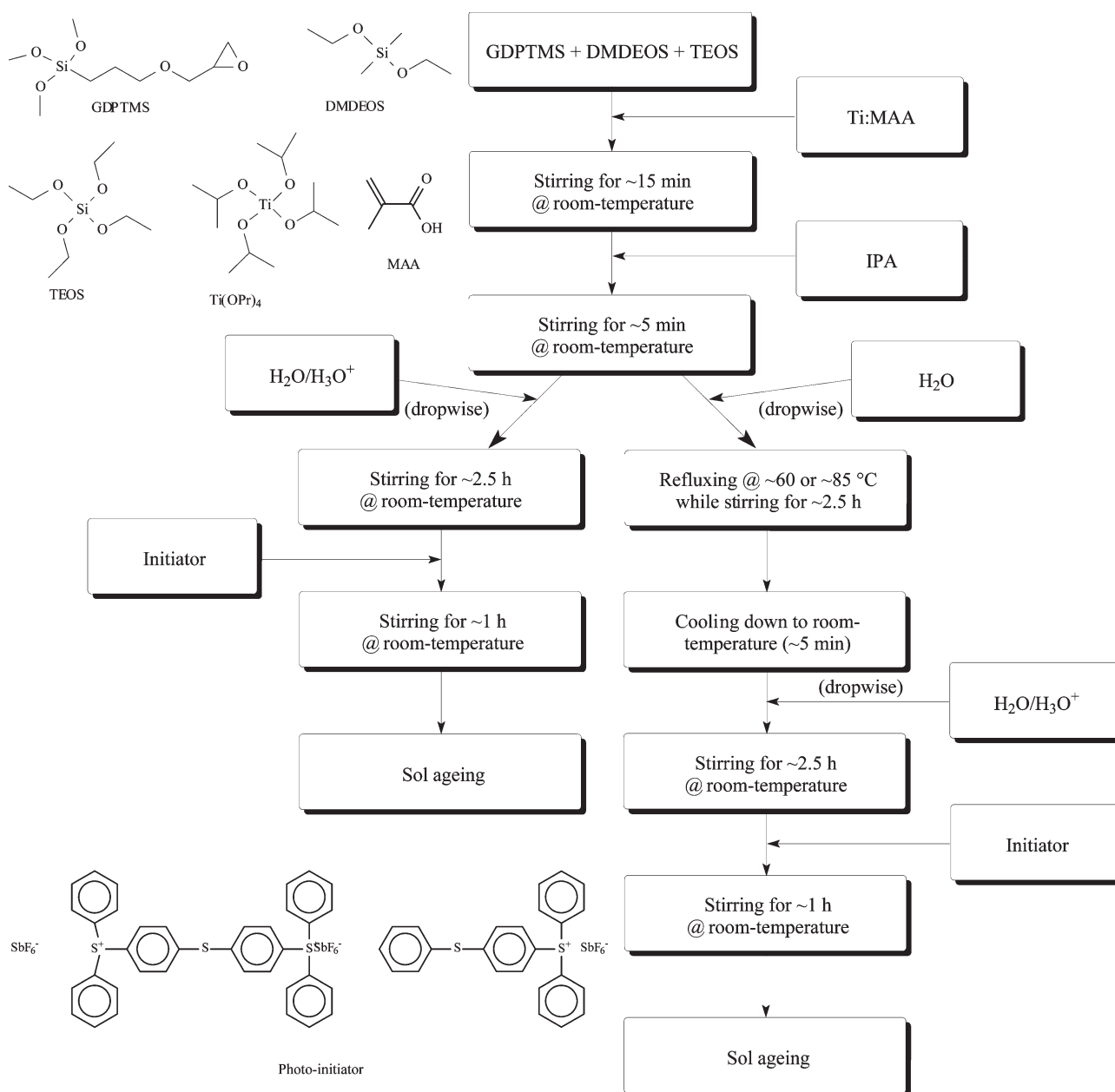
Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis were performed using a Nicolet 520-model FTIR spectrometer, and a Perkin Elmer Pyris 1-model thermogravimetric analyzer, respectively. N<sub>2</sub> atmosphere and a heating rate of 10°C min<sup>-1</sup> were used in the thermogravimetric analysis measurements. Shore-A-type-hardness tests were performed using a Devotrans D. V. T.-model durometer at ambient conditions; and a minimum five measurements were carried out for each sample, and the average of the values obtained from these five measurements was used in the evaluation of the results.

## RESULTS AND DISCUSSION

Both systems, refluxed or not, were successfully obtained with no precipitation, phase separation, etc. When the 25 mol % Ti-containing sol-gel mixtures synthesized through the reflux process were compared with that synthesized without the reflux process, it was observed that the refluxed mixtures were darker in colour than the one not refluxed. More strikingly, neither of the refluxed mixtures (60 or 85°C) gelled for very long durations of time (over a month and a half), which was observed in the nonrefluxed ones within 10 days during the sol-ageing.<sup>15</sup> To be able to shed some light on this issue and to demonstrate the relationship between the influences of the reflux process and those of other parameters, the following studies were carried out.

### FTIR Spectroscopy

An FTIR spectrum of a representative sample, which contained 25 mol % Ti, and was UV-irradiated for 10 min, is presented in Figure 2. Data processing was performed with appropriate baseline corrections. The assignments of the generic peaks were made as follows: the broad peak around 3400 cm<sup>-1</sup> was assigned to the O—H bonds in the structure; the features around 2800 and 3000 cm<sup>-1</sup> were assigned to the C—H bonds; the strong peak around 1000 cm<sup>-1</sup> was assigned to the Si—O—Si species. In addition, the peak around 910 cm<sup>-1</sup> was assigned to the epoxy rings in the structure,<sup>16</sup> and that around 950 cm<sup>-1</sup> to the Si—O—Ti species.<sup>17</sup> The presence of the latter in the samples containing Ti demonstrated that Ti did

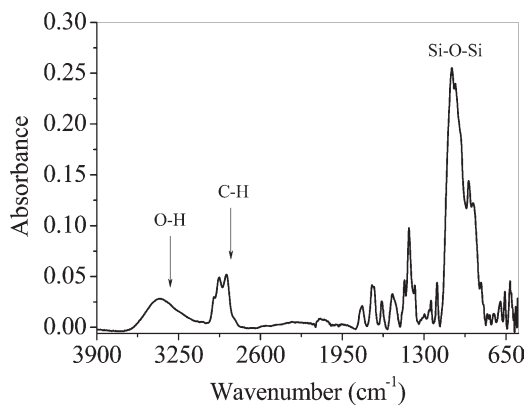


**Figure 1.** Schematic representation of the synthesis routes followed with or without the reflux step, and the structures of the chemicals used.

incorporate into the final structure of the materials. The polymeric ether groups were expected to exhibit an absorption band around  $1100\text{ cm}^{-1}$ <sup>18</sup>; but because it overlapped with that of the species associated with the Si—O—Si group, it revealed itself as a shoulder around  $1100\text{ cm}^{-1}$ .

FTIR spectroscopy was performed to identify the effects of sol ageing on the chemical structure of the system; and the results revealed that little or no change occurred in the chemical functionality of the system upon sol-ageing up to 10 days as seen from the evolution FTIR spectra taken using the sample sets with or without Ti (Figure 3). Nevertheless, in order to minimize any error that might arise, the remaining characterization studies were performed with the samples aged for 1 day.

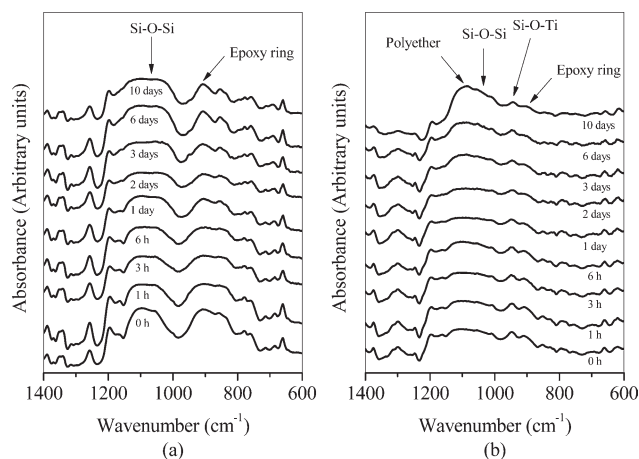
The FTIR spectra of the sol-mixtures (1-day-aged) that contained 25 mol % Ti, and were nonrefluxed or refluxed at either 60 or 85 °C were taken, and the spectral regions associated with the chemical changes thought to have taken place during the synthesis/sol ageing are shown in Figure 4. While there were no significant differences between the spectra in general, it was observable that the relative intensity of the absorption band belonging to the polymeric ether groups increased to some extent, and that of the one belonging to the epoxy rings decreased to nearly the same extent<sup>17–19</sup> as a result of the incorporation of the reflux process applied at either 60 or 85 °C. This observation indicated that the epoxy ring opening and cross-linking reactions in the refluxed systems took place to a greater extent in comparison with the nonrefluxed system. An increase



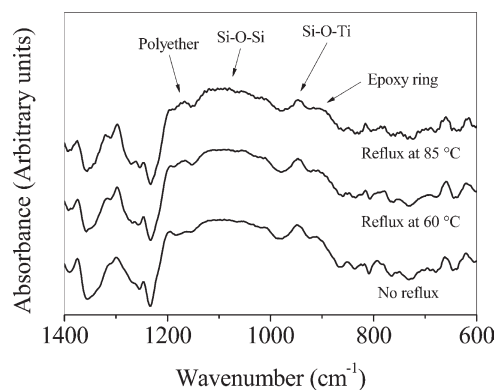
**Figure 2.** An FTIR spectrum of a representative sample, which contained 25 mol % Ti, and was UV-irradiated for 10 min.

in viscosity, expected to be observed in this type of situations (but at higher temperatures and for longer durations of reflux<sup>13,20</sup>), however, was not observed. On the contrary, as mentioned above, neither of the refluxed sol-gel mixtures aged for over 1.5 month became a gel whereas the nonrefluxed mixtures gelled within 10 days. This implied that the hydrolysis and condensation reactions, which were expected to occur during the sol-ageing, must have been impeded to some extent in the case of the refluxed system. The following postulations were therefore suggested to account for all these observations:

1. the polymeric ether groups, which were formed through the catalysis of Ti-containing species during the synthesis, sterically hindered the connectivity of the species that were to realize the hydrolysis and condensation (both homo and hetero) reactions, i.e., Si/Ti-OR (R: any of the alkyl groups) and Si/Ti-OH, to some extent; and the extent of this hindrance augmented by the inclusion of the reflux process in the synthesis since this process would promote the catalytic effect of the Ti-containing species on the epoxy ring opening as well as crosslinking reactions with respect to the nonreflux case;



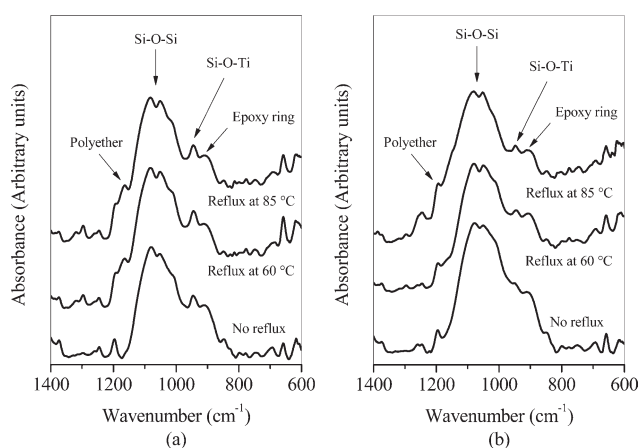
**Figure 3.** Evolution-FTIR spectra of the systems that contained either 0 or 25 mol % Ti [(a) and (b), respectively] for sol ageing. The numbers on the curves denote the duration of the sol ageing.



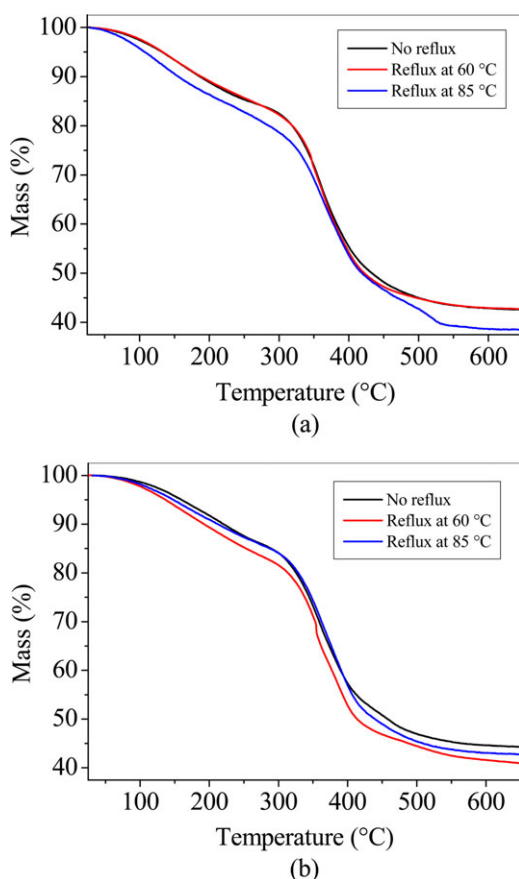
**Figure 4.** FTIR spectra of the 1-day-aged sol-gel mixtures that contained 25 mol % Ti, and were obtained with or without the incorporation of the reflux process at two different temperatures (60 or 85°C).

2. after they played their catalytic roles, Ti-containing species did not sufficiently take place in the hydrolysis and condensation (both homo and hetero) reactions;
3. a combination of these two factors.

Therefore, the significant differences in gelation time between the nonrefluxed and refluxed mixtures containing 25 mol % Ti might be attributed to the fact that the incorporation of the reflux process in the synthesis promoted the catalytic effect of the Ti-containing species on the epoxy ring opening as well as crosslinking reactions with respect to the nonreflux case. This then impeded the ongoing sol-gel reactions to some extent. To further probe this postulation, the FTIR spectra of the materials (nonrefluxed and refluxed) that contained 25 mol % Ti and were irradiated with UV light for 10 or 60 min were taken. Like in the case of the sol-gel mixtures, the relative intensity of the absorption band belonging to the polymeric ether groups in the sample materials, which were obtained via UV-irradiation, was observed to be higher in the refluxed samples than in the nonrefluxed ones as seen in Figure 5 [(a,b)]. The intensity of this band further increased when the reflux temperature was raised from 60 to 85°C. These observations were consistent with those



**Figure 5.** FTIR spectra of the systems obtained with or without the incorporation of the reflux process at two different temperatures (60 or 85°C): UV-irradiated for 10 (a), or 60 min (b).



**Figure 6.** Thermograms of the systems obtained with or without the incorporation of the reflux process at two different temperatures (60 or 85°C): UV-irradiated for ~10 (a), or 60 min (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

mentioned above. Moreover, when the spectra in Figure 5(a) are compared with those in Figure 5(b), it can be seen that the relative intensity of the absorption band belonging to the Si—O—Ti species is higher in all 10-min-irradiated samples than in all 60-min-irradiated ones. This might indicate that relatively long UV-exposure times could cause a decrease in the relative number of Si—O—Ti species in this type of material systems, which was also supportive of the previous results.<sup>15</sup> This was more likely due to the transformation of these species into different species (via bond cleavage) as a result of the absorption of the UV-light. To be able to explicate these observations and to clarify the influences of the synthesis and process conditions on the other properties of the system, the following studies were performed.

#### Thermogravimetric Analysis

Figure 6(a,b) shows the thermograms of the 1-day-aged system, refluxed or not, that contained 25 mol % Ti and was UV-irradiated for either ~10 or 60 min, respectively. The common points between these two figures were as follows: the mass loss up to ~100°C was due to the evaporation of the volatile species, i.e., water and alcohols, which was immediately followed by the decomposition of the species associated with the epoxy groups in the structure<sup>16,21</sup> between ~100 and ~350 °C. The mass loss

at higher temperatures was attributed evidently to the decomposition of the remaining organic structure. The residue (~40 % mass) was due to the presence of Si/Ti oxide and possibly of a carbonaceous material; the combustion was incomplete as the atmosphere used in the measurements was N<sub>2</sub>.

No significant change was observed in the thermal stability of either system (10- or 60-min-UV-irradiated) upon the incorporation of the reflux process demonstrating the ineffectuality of the employment the reflux process during the synthesis of this material system on its thermal stability. On the other hand, there was a slightly discernable difference between the thermal decomposition profile of the 10-min-UV-irradiated system and that of the one irradiated for 60 min. The thermal stability between ~100 and ~350 °C, in particular, was higher to a slight extent in the 60-min-UV-irradiated system in comparison with its 10-min-irradiated counterpart. This observation was in good agreement with the previously reported findings,<sup>15</sup> and supported the idea that the cleavage of some certain bonds associated with the Si-O-Ti species upon UV-irradiation in a material system of this type might form thermally more stable species.

#### Mechanical Properties

To assess the mechanical properties of the materials produced, Shore-A-type-hardness tests were carried out. Shore-A-type-hardness is not only important for practical applications of materials of this type, but can also be used to gain insight into the further mechanical properties such as elastic (Young's) modulus ( $E$ ) as reported in the literature.<sup>22,23</sup> As a result of the hardness measurements as well as the corrections/calculations presented in these publications, the values shown in Table I were obtained for some particular sample materials. As can be seen from the table, the incorporation of the reflux process in the synthesis route clearly improved the mechanical properties of the system, which was even more pronounced at the higher reflux temperature (85°C). These observations corroborated the postulations made above; that was, the incorporation of the reflux process in the synthesis must have promoted the catalytic effect of the Ti-containing species on the epoxy ring opening and crosslinking reactions. As a result, the final structure/network of the refluxed system must have had an organically more crosslinked/developed network than that of the nonrefluxed

**Table I.** Shore-A Hardness and  $E$  Values for the 1-Day-Aged System Containing 25 mol % Ti Obtained with or without the Incorporation of the Reflux Process at Two Different Temperatures (60 or 85°C), and UV-Irradiated for 10 or 60 min (The samples Had Various Thicknesses, Which Were Taken into Account While Calculating the Values of  $s$  and  $E$ )

Sample	Shore-A hardness	$E$ (MPa)
10-min-UV-exposed (no reflux)	64	4.2
10-min-UV-exposed (reflux at 60°C)	73	6.5
10-min-UV-exposed (reflux at 85°C)	79	8.6
60-min-UV-exposed (no reflux)	53	2.7
60-min-UV-exposed (reflux at 60°C)	64	4.3
60-min-UV-exposed (reflux at 85°C)	73	6.5



system. This organically more developed structure must thus have been responsible for the improved mechanical properties observed.

Furthermore, when the UV-irradiation time was raised from 10 min to 60, the mechanical properties of the system was observed to worsen to some extent. From the point of view of the role the Ti-containing species played in the sol-gel reactions (hydrolysis/condensation) and their catalytic involvement in the epoxy crosslinking reactions, this result was also consistent with the aforementioned observations and explanations as well as with the previously reported results.<sup>15</sup> This demonstrated the dominancy of the catalytic effect of Ti-containing species on the epoxy polymerization/crosslinking reactions over the epoxy crosslinking/curing effect of UV light.

The mechanical properties of this material system, moreover, were comparable with those reported in the literature.<sup>22-24</sup>

## CONCLUSIONS

A Ti-containing silicate-based epoxy-functional polymer nanocomposite system was synthesized by a sol-gel route with or without the introduction of a reflux process, which was followed by UV-induced epoxy polymerization. Influences of synthesis and process parameters, including Ti content, sol ageing, reflux process, and UV-irradiation on various properties of the system were detailed. Incorporation of the reflux process was shown to promote the catalytic effect of the Ti-containing species on the epoxy ring opening as well as crosslinking reactions with respect to the nonreflux case, which then impeded the ongoing sol-gel reactions to some extent. Further, the reflux process seemed to cause to the formation of an organically more crosslinked/developed network with respect to the nonrefluxed case, which thus improved the mechanical properties of the system. This improvement was more pronounced at the higher reflux temperature (85 °C). It was evidenced by the FTIR spectroscopy and thermogravimetric analysis results that relatively high UV-exposure doses (60 min of irradiation in this case) could decrease the relative number of Si-O-Ti species leading to a relatively weak mechanical properties. Nevertheless, the mechanical properties of this material system were comparable with those reported in the literature.<sup>22-24</sup> Therefore, the overall observations and results demonstrated that the synthesis and process parameters investigated herein could be capitalized on to tune the final properties of this polymer nanocomposite material system and thus to develop a new process regime to obtain materials of this type with desired properties in certain applications such as dental restoration. However, it is obvious that further investigations must be carried out to precisely identify the combinational influences of the synthesis/process parameters on the material properties. Research is thus underway to further examine the structure-property relationship for material systems of this type and to evaluate their applicability in the area of dental restoration.

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## REFERENCES

1. Lebeau, B.; Innocenzi, P. *Chem. Soc. Rev.* **2011**, *40*, 886.
2. Sanchez, C.; Belleville, P.; Popall, M.; Nicole, L. *Chem. Soc. Rev.* **2011**, *40*, 696.
3. Haas, K.-H.; Wolter, H. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 571.
4. Sharp, K. G. *Adv. Mater.* **1998**, *10*, 1243.
5. Zou, H.; Wu, S.; Shen, J. *Chem. Rev.* **2008**, *108*, 3893.
6. Çopuroglu, M.; O'Brien, S.; Crean, G. M. *J. Sol-Gel Sci. Technol.* **2006**, *40*, 75.
7. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, **1990**.
8. Pomogailo, A. D. *Colloid J.* **2005**, *67*, 726.
9. Wen, J.; Wilkes, G. J. *Chem. Mater.* **1996**, *8*, 1667.
10. Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.
11. Nicholson, J. W. *Int. J. Adhes. Adhes.* **1998**, *18*, 229.
12. Peutzfeldt, A. *Eur. J. Oral Sci.* **1997**, *105*, 97.
13. Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1986**, *82*, 31.
14. Kleverlaan, C. J.; Feilzer, A. J. *Dent. Mater.* **2005**, *21*, 1150.
15. Çopuroglu, M.; Şen, M. *Radiat. Phys. Chem.* **2012**, *81*, 1324.
16. Chiniwalla, P.; Bai, Y.; Elce, E.; Shick, R.; McDougall, W. C.; Allen, S. A. B.; Kohl, P. A. *J. Appl. Polym. Sci.* **2003**, *89*, 568.
17. Alaoui, O. T.; Nguyen, Q. T.; Rhlalou, T. *Environ. Chem. Lett.* **2009**, *7*, 175.
18. Weast, R. C. *CRC Handbook of Chemistry and Physics*, 53rd ed.; CRC Press: Cleveland, Ohio, **1972**.
19. Zeitler, V. A.; Brown, C. A. *J. Phys. Chem.* **1957**, *61*, 1174.
20. Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283.
21. Çopuroglu, M.; O'Brien, S.; Crean, G. M. *Polym. Degrad. Stab.* **2006**, *91*, 3185.
22. Meththananda, I. M.; Parker, S.; Patel, M. P.; Braden, M. *Dent. Mater.* **2009**, *25*, 956.
23. Siddiqui, A.; Braden, M.; Patel, M. P.; Parker, S. *Dent Mater.* **2010**, *26*, 560.
24. Lu, H.; Lee, Y. K.; Oguri, M.; Powers, J. M. *Oper. Dent.* **2006**, *31*, 734.