

EVALUATION OF THE INTERACTIONS OF A SILANE AGENT WITH DENTAL MONOMERS BY NEAR INFRARED SPECTROSCOPY

S.H. Dickens¹, J.M. Antonucci², B.O. Fowler²

¹American Dental Association Health Foundation
Paffenbarger Research Center, ²National Institute of Standards and Technology, Gaithersburg, MD 20899-8546

Introduction

The preparation and characterization by mid-infrared spectroscopy of oligomeric silsesquioxane monomers obtained through hydrolysis-condensation reactions of 3-methacryloxypropyltrimethoxysilane (MPTMS) and the formation of silyl ether derivatives of the hydroxylated dental monomer Bis-GMA with MPTMS have recently been reported.^{1,2} This study evaluated the applicability of near-infrared (NIR) spectroscopy to follow the reactions between MPTMS and water and between MPTMS and non-hydroxylated dental monomers, e.g., an ethoxylated bisphenol A dimethacrylate (EBPADMA) and a urethane dimethacrylate (UDMA; product of 2,2,4,4-trimethylhexyl diisocyanate and 2-hydroxyethyl methacrylate). The photo-polymerization kinetics of the reaction products were followed by real-time NIR spectroscopy. For comparison, the reactions of MPTMS alone, and MPTMS with Bis-GMA or a Bis-GMA/TEGDMA (triethyleneglycol dimethacrylate) mixture were studied under similar conditions.

Experimental*

The reactions for preparing the alkoxy silane-derived monomers are described in detail elsewhere.³ Briefly, the neat base monomers EBPADMA, UDMA, Bis-GMA and the Bis-GMA/TEGDMA mixture were combined at room temperature with MPTMS at a molar ratio of 1.5:1 of base resin to MPTMS. The mixtures were then stored at 60 °C in open vials until no further weight loss was observed. NIR spectra of the mixtures were acquired in the region between 4000 cm⁻¹ and 6500 cm⁻¹ coadding 64 scans at 4 cm⁻¹ resolution. The relative uncertainty of the NIR intensity measurements is approximately ± 0.3 %.

The water content in the neat monomers and in the base resin/MPTMS mixtures during and after the reaction was determined quantitatively. In addition, the water bands at about 5200 cm⁻¹ in MPTMS and OMPTMS (oligomeric silsesquioxanes) were analyzed qualitatively. The resins were activated with camphorquinone and ethyl-4-dimethylaminobenzoate and were then photopolymerized for 1 min with a dental light ($\lambda_{\text{max}} = 470 \text{ nm}$) at a power density of about 400 W/cm². For the polymerization kinetics, spectra were recorded continuously for 5 min after the start of polymerization averaging 4 scans at 8 wavenumber resolution. The photopolymerization kinetics were determined by following the decrease of the 1st overtone of the =CH₂ stretching band at 6167 cm⁻¹.⁴

Results and Discussion

From previous work⁵ it was shown that MPTMS can react in two ways: with water to form OMPTMS (Figure 1), or through the formation of silyl ethers when hydroxyl groups are present in the coreactant monomer.

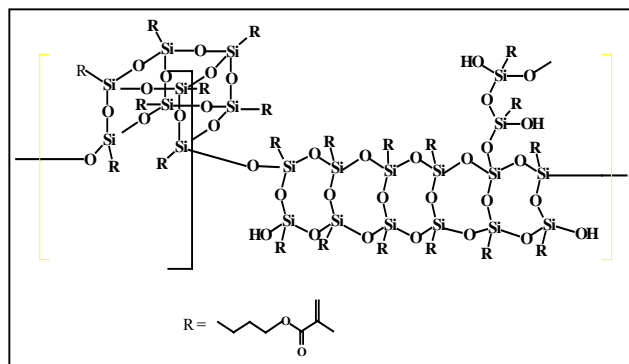
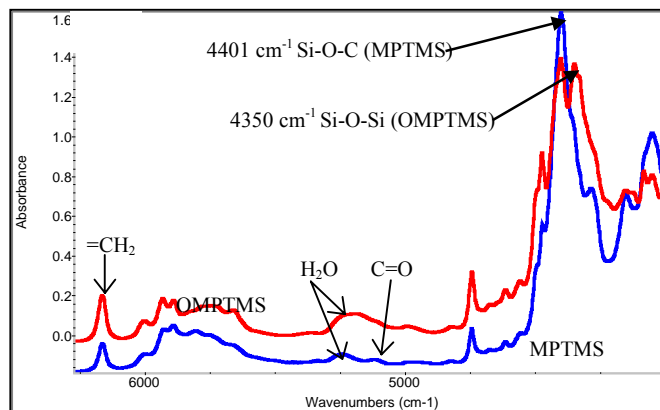


Figure 1. Silsesquioxane formation from MPTMS and water.

Various features related to the reaction can be seen in the MPTMS/OMPTMS NIR spectra in Figure 2. Due to the oligomerization, the quantity of double bonds increased by a factor of 1.5 over the amount of double bonds in MPTMS. The formation of the oligomeric product OMPTMS was indicated by a decrease in a band at about 4401 cm⁻¹ assigned to the alkoxy silane group (Si-O-C) and the appearance of a new band at 4350 cm⁻¹ due to the Si-O-Si bonds formed in the oligomer. The area around 5200 cm⁻¹ indicates that there is an apparent increase in the water content when MPTMS



reacts to form the oligomerized compound.
Figure 2. NIR spectra of MPTMS and the reaction product OMPTMS.

Deconvolution of the water bands in MPTMS (Figure 3a), OMPTMS (Figure 3b) and dried OMPTMS (Figure 3c), showed distinctly different features of water in MPTMS and OMPTMS. In MPTMS, water exists mostly (70 %) as free water (5250 cm⁻¹) and only a smaller fraction (5200 cm⁻¹) is bonded via one hydrogen bond. In contrast, this relationship is reversed in OMPTMS with 70 % of the water bonded with one hydrogen, while the rest exists as non-bonded water. Even in dried OMPTMS, half of the water molecules are bonded to polar groups with one hydrogen bond. The carbonyl position (5112 cm⁻¹) is unaffected by the changes in the water content and hydrogen bonding.

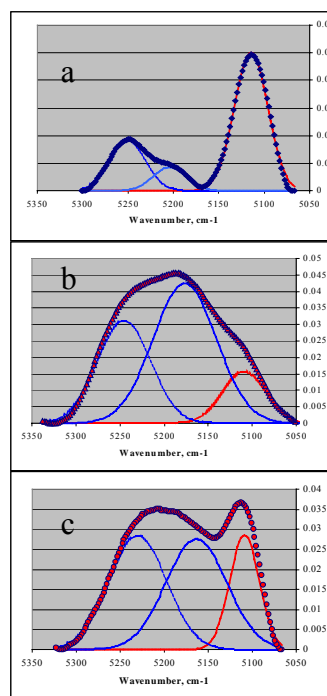


Figure 3. Deconvolution of the water bands in MPTMS (a), OMPTMS (b) and dried OMPTMS (c).

Following the reaction of MPTMS (Figure 4), to which a mass fraction of 2.6 % water was added, it was found that the water peak began to decrease within 2 min after mixing, indicating the immediate onset of hydrolysis of the alkoxy group to silanol groups (-Si-OH) and methanol (-C-OH).

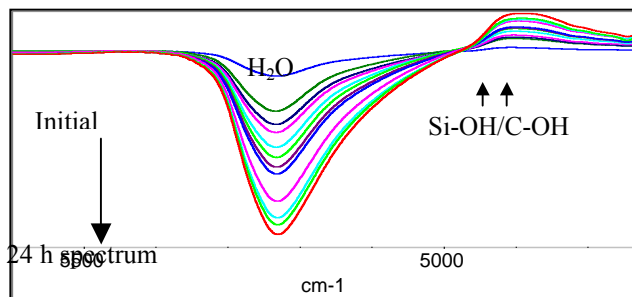


Figure 4. Difference spectra of the MPTMS/water reaction with time showing the amount of water lost and the increase in the Si-OH/C-OH band.

From a calibration curve obtained by mixing MPTMS and OMPTMS with known quantities of water, the amount of water in MPTMS, OMPTMS and the reacted dental resins was determined by measuring the water band after subtraction of the dry spectrum from the water-containing spectrum.⁶ As can be seen below in the table, the reaction products consistently contained slightly more water than the neat dental resins, presumably due to a slight increase in hydrophilicity from residual Si-OH groups formed during oligomerization (Figure 1). While the coefficient of variation of the water calibration curve was fairly high ($R^2 = 0.978$; standard error of the estimate = 5.60), the lowest quantity of water added to MPTMS was a mass fraction 0.25 %. Therefore, to calculate the small quantities of water in the monomers and monomer mixtures, the data had to be extrapolated and are estimates.

Table. H ₂ O (mass fraction %) in Neat Resins and Resin Mixtures		
	Neat resins	Resin mixtures (product)
MPTMS	< 0.1	0.7
EBPADMA	< 0.05	0.05
Bis-GMA	< 0.1	0.15
UDMA	< 0.1	0.15

A similar experiment as described for Figure 4 was performed in a 1 mm cell to allow quantitative evaluation of the more strongly absorbing region around 4401 cm⁻¹. From the difference spectra, subtracting the initial spectrum from the spectrum at each measured time, it is suggested that after 4 d changes occurred indicating that the oligomerization is proceeding (Figure 5).

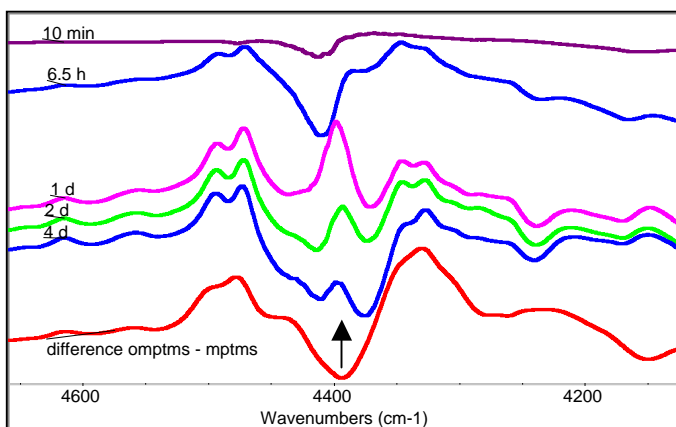


Figure 5. Difference spectra obtained by subtracting the initial spectrum of the MPTMS/water mixture from the spectrum at each measured time.

In comparison to the difference spectrum of OMPTMS/MPTMS, the disappearance of the peak above the arrow seems to indicate that the oligomerization reaction is proceeding towards the final product OMPTMS.

To this point, the discussion has dealt with the oligomer formation from MPTMS. As has been pointed out in previous work,^{3,5} these oligomers can form even in the presence of relatively small amounts of water in rather hydrophobic dental monomers, e.g., EBPADMA. Since the formation of such high molecular weight oligomers may severely affect the curing kinetics of the dental resin, real-time NIR spectroscopy was used to investigate the curing kinetics of the photoactivated reacted mixtures. In Figure 6 it is shown that reasonably high reactivities can be achieved, especially with comonomer mixtures prepared from MPTMS oligomerized in UDMA or Bis-GMA/TEGDMA. Neat UDMA monomer has the highest conversion⁷, followed by the OMPTMS free-Bis-GMA/TEGDMA resin. However, somewhat lower conversion of the OMPTMS containing monomer mixtures may be of lesser concern, because of the potential advantage of the high-molecular weight oligomers, which may increase the toughness of the resin based dental products, while reducing the polymerization shrinkage and shrinkage related stresses.

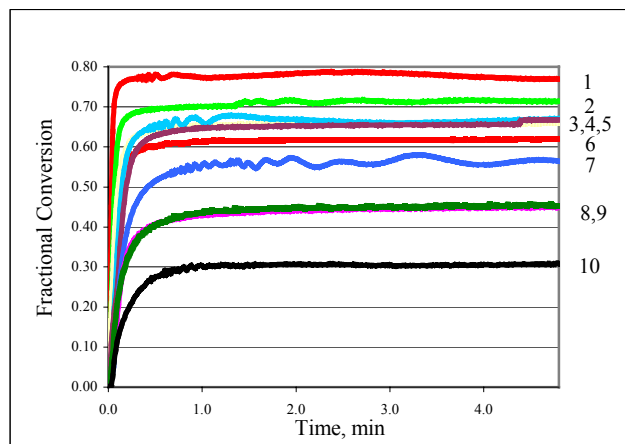


Figure 6. NIR cure profiles showing the extent of conversion vs. time for various base resin/MPTMS reaction products. For comparison, the reactivities of the base resins are also shown. 1 - UDMA, 2 - Bis-GMA/TEGDMA, 3 - Bis-GMA/TEGDMA with 14 % MPTMS; 4 - Bis-GMA-MPTMS/TEGDMA; 5 - EBPADMA; 6 - UDMA-MPTMS; 7 - EBPADMA-MPTMS; 8 - Bis-GMA; 9 - Bis-GMA-MPTMS; 10 - OMPTMS.

Conclusions

NIR spectroscopy has been shown to provide valuable insight into the polymerization kinetics and the effects of water on the in situ formation of MPTMS oligomers in dental monomer systems.

Disclaimer Certain commercial materials and equipment are identified in this paper for adequate definition of the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the ADA Health Foundation or that the material or equipment identified is necessarily the best available for the purpose.

Acknowledgements. Supported by ADAHF-PRC, NIDCR and NIST. The authors are grateful to Esstech for the donation of the monomers used in the study.

References

- (1) Antonucci, J.M. *Am Chem Soc*, **1997** *Polym. Prepr.* 38(2), 118.
- (2) Antonucci, J.M.; Fowler, B.O.; Stansbury, J.W. *J. Dent. Res.* **1998**, 77, 260.
- (3) Antonucci, J.M.; Fowler, B.O.; Dickens, S.H.; Richards, N.D. **2002**, *Polymer Preprints*.
- (4) Stansbury, J.W.; Dickens, S.H. **2001** *Dent. Mater.* 17, 71.
- (5) Antonucci, J.M.; Fowler, B.O.; Dickens, S.H. *J. Dent. Res.* **2002**, 81, 140.
- (6) Dickens, B.; Dickens, S.H. *J. Res. Natl. Inst. Stand. Technol.* **1999**, 104, 173.
- (7) Stansbury J.W.; Dickens S.H. *Polymer* **2001**, 42, 6363.