Photopolymerizable Acrylic Resin: Effect of Curing Time and Temperature

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ABSTRACT: A photopolymerizable resin was closely examined for its capacity as an adhesive via cure advancement in submerged water at cold temperatures. The effects of curing time and temperature were studied by bond strength measurements and extracted monomer quantification with high pressure liquid chromatography. In both cases the cure was performed under water, and there was one wet interface. Both methods showed the progression of the photopolymerization with time and had similar characteristic times. The adhesion strength was measured by lap shear and remained nearly constant over the entire temperature range studied (around 2 MPa for a 2-min cure), while a slight increase in the extracted uncured monomer quantity of one of the resin components was obtained for increasing temperatures. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 546–554, 2001

Key words: bisphenol A-diglycidyl ether dimethacrylate (bis-GMA); triethylene glycol dimethacrylate (TEGDHA); high pressure liquid chromatography; underwater cure; photopolymerization

INTRODUCTION

Light-activated resins are finding new uses where environmental conditions restrict the use of standard two-component or heat-activated resins. For example, in dentistry and other medical applications, light-activated resins are preferred because of their ease of application, less damaging effects on biological tissues, and binary response.[1,2] In cold environments, especially in highly dissipative media such as liquids, heat-activated resin processing suffers from high heat losses and the use of two-component adhesives is hampered by the difficulty to maintain constant mixing properties over the whole temperature range.

The ideal adhesive for use under water displaces water from the bondline, has a viscosity low enough to fill surface features, and is thick enough to not be dispersed by currents. An additional concern for a light cured resin is the requirement for line of sight. As a model study we investigated the underwater curing characteristics of a light cured resin using a transparent substrate, illuminating through it as a window. Strength measurements were performed on bonds assembled under water for several cure times and temperatures. Extraction experiments on cured specimens were performed, and the residual amount of each monomer constituent was tracked by high pressure liquid chromatography (HPLC).

EXPERIMENTAL

Materials

The resin studied here was a derivative of a dental composite restorative formulation.[3] It

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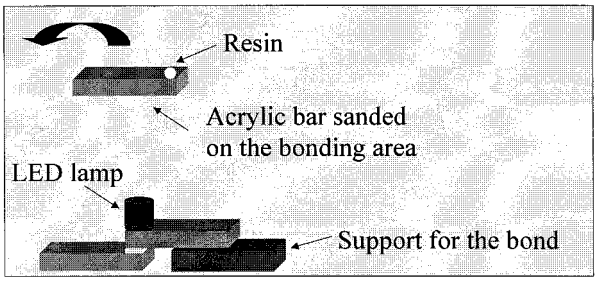

Figure 1 The bonding setup in the water bath.

was composed of bisphenol-A diglycidyl ether dimethacrylate (bis-GMA, Cook Composites and Polymers Co.) and triethylene glycol dimethacrylate (TEGDMA, Aldrich) with camphorquinone (Aldrich) and *N*,*N*-dimethyl-*p*-toluidine (Aldrich) as a photoinitiator package. The ratio of bis-GMA and TEGDMA was 2 to 1, which provided a resin with a thicker consistency that could still be dispensed with an eye dropper.

The photopolymerization was activated by blue illumination. The illumination lamp was composed of an array of 24 LEDs with an emission peak at 470 nm. The lamp was connected to a power supply, resulting in an overall intensity of 25 W/m^2. Preliminary measurements showed the mechanical strength evolution of the bulk resin cured under water at temperatures[4] between 1 and 38°C and good underwater bonding capability.[5]

Mechanical Experiments

The adhesion of the resin was evaluated by measuring the shear strength of bonds assembled under water in a lap shear configuration. All bonds were made using 0.25-in. acrylic substrates (clear cast acrylic, 8560-K148, McMaster–Carr) with the bonding area slightly sanded and methanol cleaned prior to bond assembly. The transparency of the substrates allowed the resin sandwiched between them to be illuminated. The bonding process included the following steps. A substrate was first immersed in the water bath (at about 2 cm below the waterline) at the chosen temperature. In a dark hood, one drop of resin was deposited on the other substrate, which was then also immersed in the water bath. The two substrates were then assembled in a lap shear configuration using an alignment guide and a bar support with some tape on it to control the bond thickness (see Fig. 1). The lamp was placed on the uncured lap and switched on for a designated curing time. Immediately after cure, the samples were stored in a freezer to prevent any further cure evolution.

The strength of the lap bonds was measured using a Texture Technologies Corp. (Scarsdale, NY) TA.XT2 texture analyzer (Stable Micro Systems, Godalming, Surrey, U.K.) in tension mode. Two bars of the same dimensions as the substrates were inserted in the device grips with the bond extremities to prevent any tilting during the deformation (Fig. 2). The applied load was recorded as a function of the displacement, and the breaking load divided by the bonding area yielded the tensile strength. The bond area was typically between 150 and 250 mm^2, and the bond thickness was around 200 μm.

HPLC Experiments

Following the construction of calibration curves, HPLC was used to derive the quantity of residual monomers extracted from the cured resin pieces.[6] For each extracted chemical identified by its characteristic retention time, its concentration in the extraction solution was related to the retention peak amplitude and area. As a way to verify the validity of measurements, the amplitude and area values were both recorded for each monomer peak in the calibration measurements, allowing for the construction of two calibration curves for each monomer. The results obtained by both methods should coincide.

Calibration solutions were prepared by diluting 1 g of bis-GMA and 1 g of TEGDMA, the two major components of the studied resin, each in

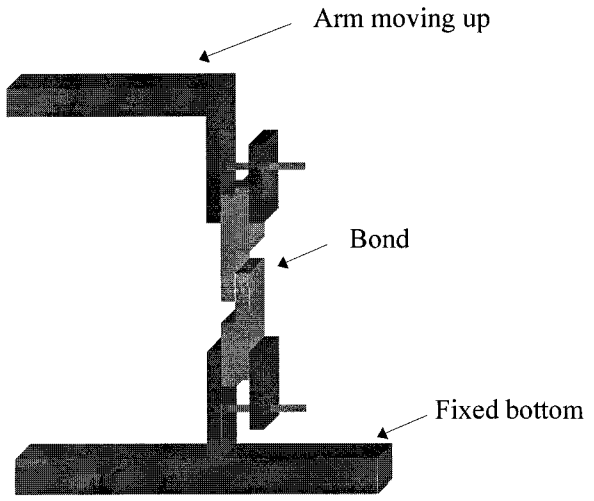

Figure 2 A schematic of the TA.XT2 with lap shear bond and antitilting bars.

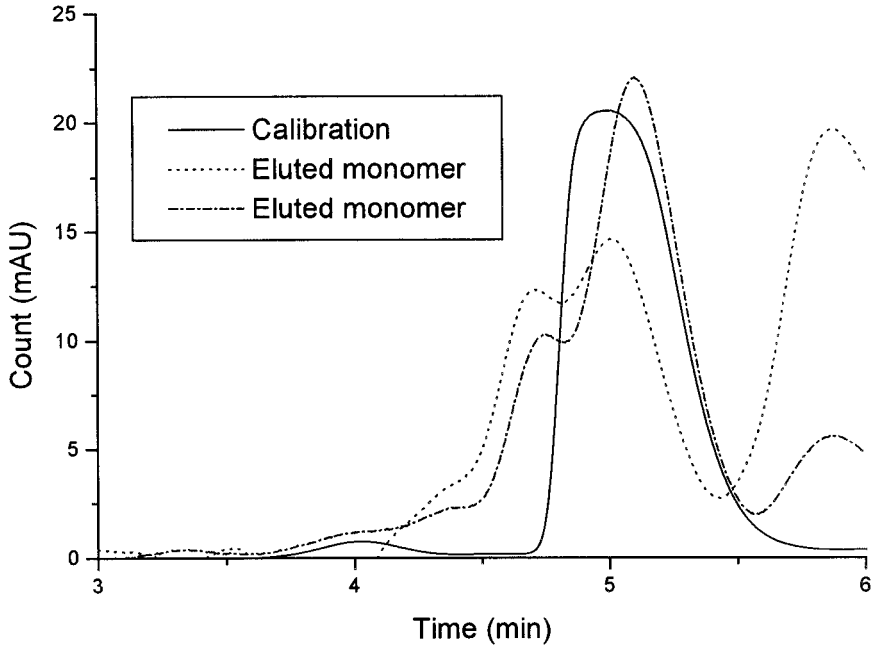

Figure 3 The detected signal for the TEGDMA monomer.

100 mL of a solution composed of 75% methanol and 25% water by volume, which is reported to be the best solvent formulation for this type of resin.[7] Then these two mixtures were successively diluted with the same 75MeOH/25H_2O solution, leading to a concentration range of the two monomers extending from 0.01 to 10 g/L.

To prepare the monomer extraction solutions, a drop of the resin was cured under water (one wet interface) between two glass slides at different temperatures and for different illumination times. Immediately after cure, the resin was detached from the slides, weighed, and immersed in 10 mL of the 75MeOH/25H_2O solution for 46 h in a shaking device (300 rpm). Then the cured piece was removed from the solution and aliquots were taken for analysis.

The HPLC unit was an autosampling 1050 Hewlett–Packard system with a deuterium variable wavelength detector and a diode array detector. Hewlett–Packard ChemStation software controlled the system parameters and collected the signal intensity from the detectors. The same experimental conditions were used for all the calibration and sample measurements: 1 mL/min for the mobile phase speed, 75% methanol and 25% water for the mobile phase composition, 100 μL for the injection volume, and 254 nm for the detected wavelength. Each peak area and height value was the average of four measurements, two replicates on two samples taken from the calibration or the extraction solution.

The bis-DGEMA and TEGDMA monomers were easily separable with a C18 column; bis-GMA was resolved at around 9 min and TEGDMA at 5 min. The remaining components of the resin system presented elution peaks at around 5 min, but they were in such a low concentration in the resin formulation that they were not considered as potential contaminants for the cured resin extraction spectrum. TEGDMA manifested itself as an isolated peak both for the calibration and for the cured resin extraction solutions as shown in Figure 3. On the other hand, in the vicinity of the bis-GMA retention time, three peaks of varying relative amplitudes and positions appeared for the cured resin extraction solutions (Fig. 4), leading to complications in the extraction of peak area values for bis-GMA. The drift in the retention times, which is visible in Figures 3 and 4, was caused by column degeneration but it did not affect the general shape of the signal. The comparison of the concentration results obtained from the peak area and height yielded a way to check the validity of the measurement.

RESULTS AND DISCUSSION

Extraction experiments were performed using samples fabricated with varying temperatures (1,

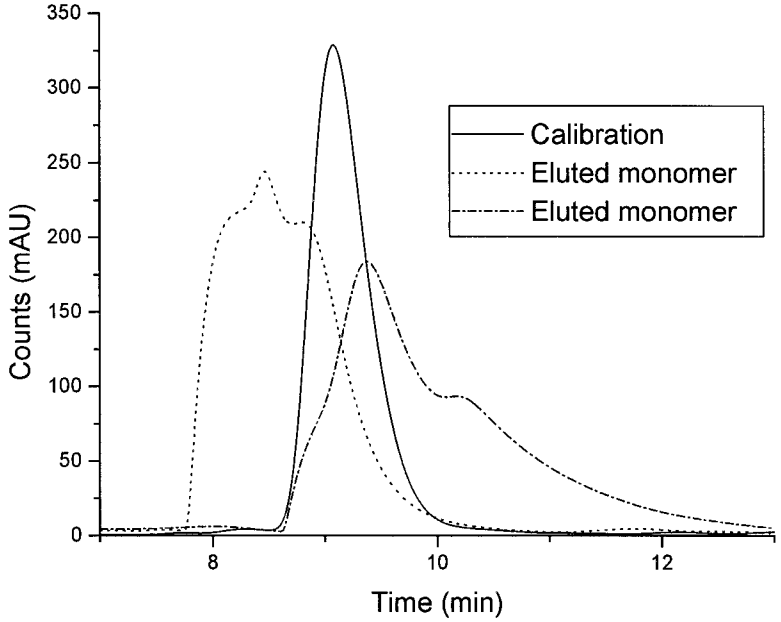

Figure 4 The detected signal for the bis-GMA monomer.

5, 10, 15, and 25°C) and illumination times (30 s and 1, 2, 3, 5, and 10 min) for the resin photopolymerization process, and aliquots from the extracted solutions were analyzed by HPLC. Using calibration curves, the uncured percentage of bis-GMA and TEGDMA as a function of the curing time and temperature was calculated from both the peak height and area.

For TEGDMA, the results extracted from the determinations of the peak height and the peak area generally coincided (Fig. 5) within the error bars (not provided for clarity purpose), proving

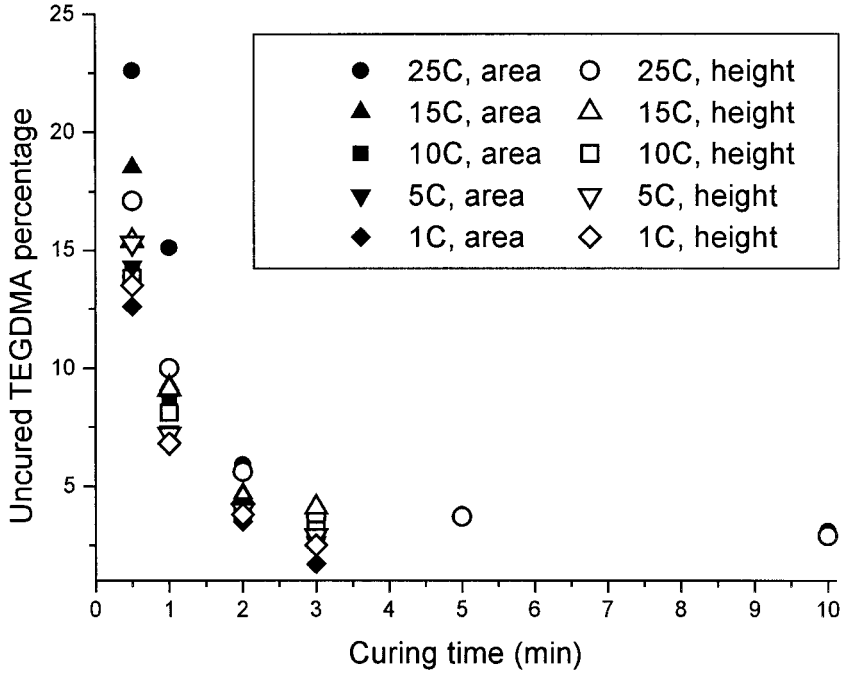

Figure 5 The eluted TEGDMA percentage measured with the peak height and area.

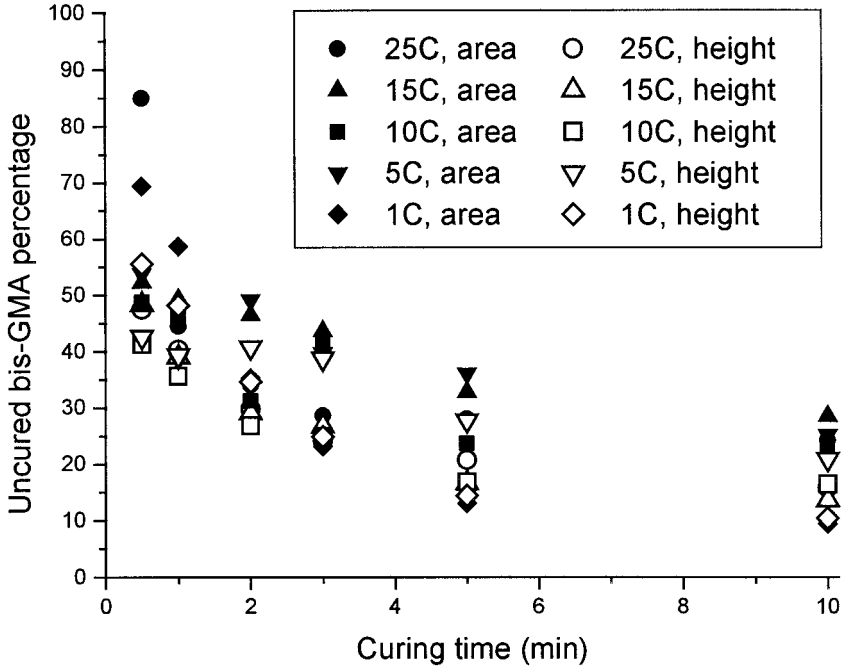

Figure 6 The eluted bis-GMA percentage measured with the peak height and area.

the validity of the measurements. On the other hand, for bis-GMA eluted from the cured resin, the presence of two other peaks in the vicinity of the major peak complicated the determination of bis-GMA elution characteristics (see Fig. 6). As a consequence, uncured percentages determined from the peak area and peak height often did not correspond. Two facts allowed us to consider the data extracted from the peak heights as closer to the truth than the ones obtained from the peak areas. As shown in Figure 4, the two additional peaks around the bis-GMA peak were very narrow and appeared mainly as shoulders on both sides of the main peak. As a consequence, their contribution to the main peak height was rather small while their separation from the main peak area was more subtle. In addition, a careful examination of Figure 6 reveals that the data points obtained from the peak heights (open symbols) follow a consistent trend, while the data extracted from the peak areas (solid symbols) are scattered between the peak height curve and much higher values. As a consequence of these observations, for the following data analysis, only the data obtained from the peak heights were considered for the bis-GMA elution.

The first result obtained from the measurements concerns the range of the percentages of uncured monomer found in the resin. The uncured TEGDMA monomer quantity was around 20% for a 30-s illumination time, and it was reduced to 2–3% after 10 min. For bis-GMA, more than 40% remained uncured after 30 s and about 15% after a 10-min illumination. Oxygen inhibition, which was observed with this resin at interfaces cured in contact with air,[8] could not be invoked because the resin drop was cured between two glass slides.

These results are quite different from those reported for dental resins of similar compositions.[6,7,9] The problem in the literature reports is that the uncured monomer quantity was normalized by the total weight of the resin, including the filler and the other additives, giving a very low percentage of eluted uncured monomer ($<2\%$). For the results reported here we normalized the results by the initial monomer quantity introduced in the resin formulation.

Another difference with the results reported in the literature[1,6,7,10] concerned the proportion of TEGDMA eluted versus that of bis-GMA. While these prior studies observed that most of the unreacted monomers were TEGDMA molecules, in our measurements for a 30-s illumination time for example the TEGDMA was cured 2 times more than the bis-GMA monomer and the gap in incomplete conversion between them increased with longer illumination times. Considering the fact

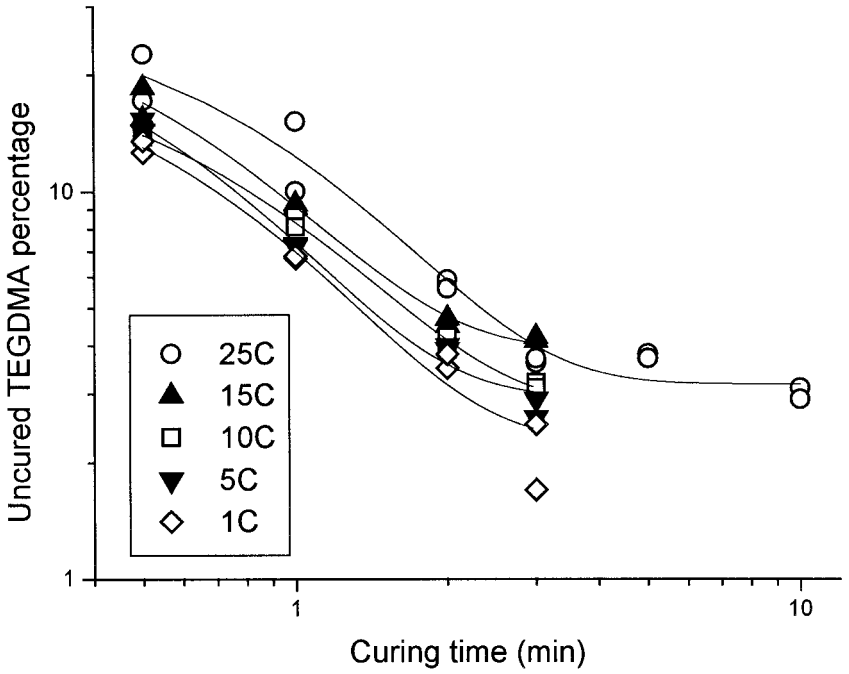

Figure 7 The effect of the cure temperature on percentage of the uncured TEGDMA.

that TEGDMA is smaller and more mobile than bis-GMA, we wondered if all the unreacted bis-GMA was eluted in these reported experiments. This diffusion difficulty was attributed in these other studies to the size of the specimens being at least a few millimeters thick, while our samples were thin films that were a few tens of microns thick. A nonoptimized match of the solubility factors between the resin and the extraction solution might also affect the rate of uncured bis-GMA extraction through the cured resin. Lee et al. reported that a 75% ethanol and 25% water by volume solution, which we used in our experiments, produces a maximum softening of the cured bis-GMA resin.[10]

This imperfect elution of bis-GMA uncured monomer may also explain why only about 10% of the uncured methacrylate (MA) reactive bonds (which represent 50–60% of the initial ones for a cure by illumination, according to some IR analysis of dental composites[7]) were measured in these studies. It also questions the hypothesis[7] that in these resin systems most of the uncured bonds are included in pendant MA groups. This hypothesis was proposed to account for the very low eluted monomer quantity.

A small but clear effect of temperature on the uncured TEGDMA percentage is shown in Figure 7. The values extracted from the heights and areas are not differentiated, and the fitting curves are only given as a guide for the eye. As the temperature increased from 1 to 25°C, the uncured TEGDMA percentage increased over the whole range of curing times between 30 s and 3 min. After 3 min and for temperatures lower than 25°C the limit of detection for the peak height and area thwarted their determination. Because an excellent inverse correlation between the degree of conversion and the monomer elution percentage was demonstrated for a bis-GMA/TEGDMA resin system,[11] the temperature appeared to adversely affect the cure of TEGDMA monomer over the studied range. Although an increase of conversion with increased temperature between 25 and 70°C was reported for some photocured diacrylate resins,[12] in a nonpure photochemical free-radical polymerization, the kinetics can lead to a reduced chain length with increasing temperature.[13,14] A practical way to think about it is that the additional free radicals provided by the thermal activation of the photoinitiator accumulate with those induced by illumination, which can cause the termination process to exceed its normal level.

With bis-GMA, a better separation of the peaks in the vicinity of the bis-GMA elution time is needed to better resolve the measured uncured percentages.

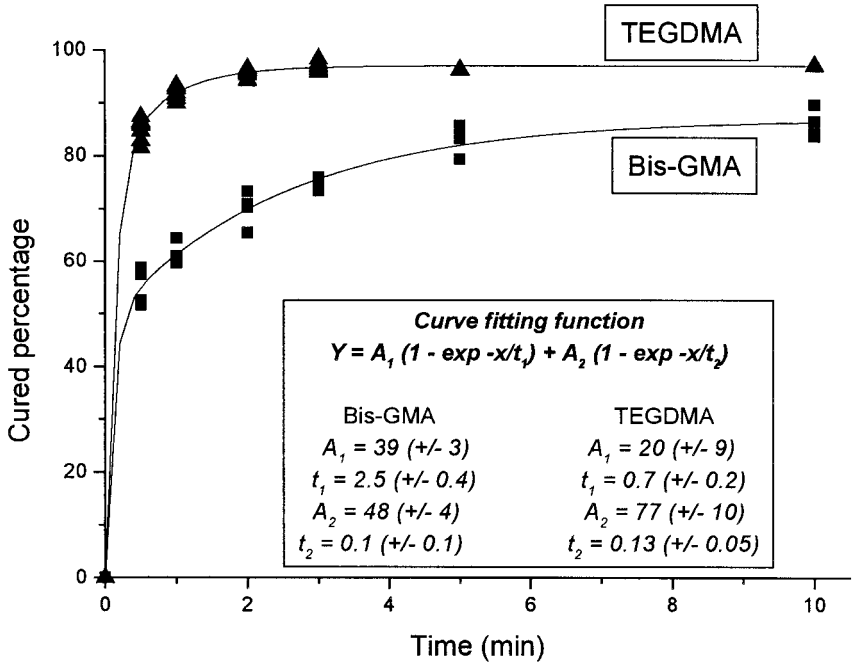

Figure 8 The eluted uncured monomers as a function of the curing time.

The time dependence of the cured fraction of both monomers was obtained, neglecting the effect of the temperature, and this is shown in Figure 8. Both sets of data are fitted by exponential association curves, and characteristic parameters are given in the inset in Figure 8 (A in % and t in min). The reaction kinetics for the photopolymerization of TEGDMA were much faster than those of bis-DGEMA: the cured TEGDMA percentage reached a plateau after about 5 min of illumination, but the cured bis-DGEMA percentage was still increasing after 10 min. This was attributed to the higher mobility and flexibility of the TEGDMA segments.

The maximum bonding strength of the resin is displayed in Figure 9 as a function of the temperature for different illumination times between 30 s and 10 min. Each data point is the average of three measurements and the error bars represent the standard deviation. The bonding strength was constant over the studied temperature range (1 to 40°C) and was quite high at between 2 and 4 MPa. As a comparison, the shear strength of barnacles[15] varies between 1 and 5 MPa and that of adhesive films used in the aerospace industry are between 2 and 7 MPa.[16]

The only observed effect of temperature was evident at very short illumination times (30 s) for temperatures higher than 15°C: the bonds were so weak that they broke while being inserted in the testing grips. This behavior was attributed to the increased uncured TEGDMA content with increasing temperature, which may have also plasticized the resin.

The dependence of the strength on the curing time is illustrated in Figure 10; only the strength values corresponding to 5 and 10°C are included. Because of the large error bars, the fit by the exponential association was not as precise as for the HPLC data. Nevertheless, the two characteristic times were comparable to that of TEGDMA and bis-GMA obtained by HPLC.

CONCLUSIONS

Two different techniques were used to characterize the conversion of a photopolymerizable acrylic adhesive based on TEGDMA and bis-GMA monomers; the influence of temperature and time were studied in particular. In one case, the lap shear strengths of bonds made under water were measured for different illumination times and water bath temperatures. The other technique used HPLC to evaluate the level of conversion of resin drops polymerized under water at different conditions of time and temperature.

Strength measurements and monomer extractions displayed the same type of time dependence, and time constants were shorter than 5 min. One

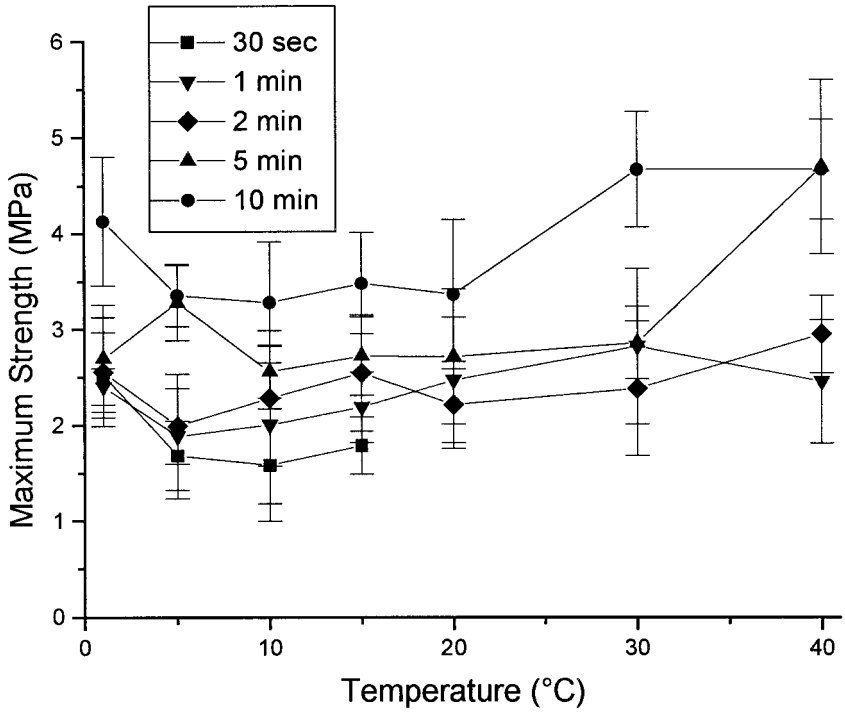

Figure 9 The effect of the temperature on the maximum bond strength.

clear temperature effect was obtained with TEGDMA extraction, where an increased temperature led to a slight decrease in the extent of photopolymerization. Better peak separation was needed to resolve the trend for bis-GMA extraction. In addition, for very short illumination times and

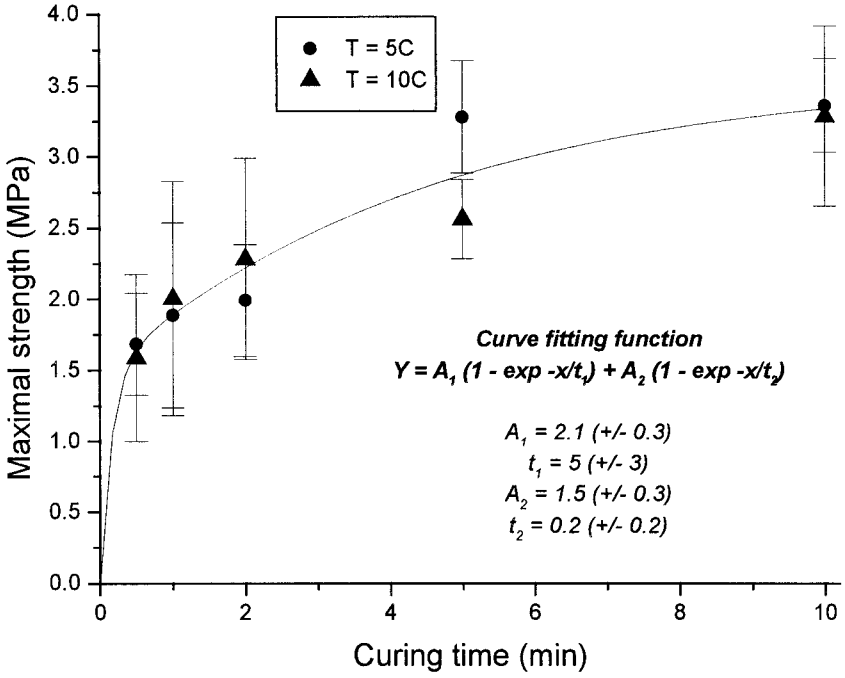

Figure 10 The effect of the cure time on the maximum bond strength.

high water bath temperatures, the bond strengths were too weak to even be measured. Otherwise, the bond strength remained constant over the whole range of studied time and temperature conditions. The characteristics of the bis-DGEMA/TEGDMA resin in terms of a rapid reaction rate and constant bonding strengths over a large range of temperatures position it as a potential candidate for a large number of applications, especially those involving cold temperature and marine conditions.

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REFERENCES

1. Tanaka, K.; Taira, M.; Shintani, H.; Wakasa K.; Yamaki M. J Oral Rehabil 1991, 18, 353.
2. Anseth, K. S.; Svaldi, D. C.; Laurencin, C. T.; Langer, R. Photopolymerization Fundamentals and Applications; Scranton, A. B.; Bowman, C. N.; Peiffer, R. W., Eds.; ACS Symposium Series 673; American Chemical Society: Washington, DC, 1997.
3. Davidenko, N.; Cohen, M. E.; Diaz, J. M.; Sastre, R. J Biomater Sci Polym Ed 1998, 9, 891.
4. Dolez, P.; Love, B. J. In Proceedings of the American Chemical Society, Division of Polymeric Materials: Science and Engineering; Ober, C., Ed.; 1999; Vol. 81, p 407.
5. Trenor, S.; Love, B. In Proceedings of the Adhesion Society Meeting, Myrtle Beach, SC, February 20–23, 2000; Anderson, G. L., Ed.; Blacksburg, VA.
6. Vaubert, V. M.; Moon, P. C.; Love, B. J. J Biomed Mater Res Appl Biomater 1999, 48, 5.
7. Ferracane, J. L. J Oral Rehabil 1994, 21, 441.
8. Ruyter, I. E. Acta Odontol Scand 1981, 39, 27.
9. Inoue, K.; Hayashi, I. J Oral Rehabil 1982, 9, 493.
10. Lee, S. Y.; Huang, H. M.; Lin, C. Y.; Shih, Y. H. J Oral Rehabil 1998, 25, 575.
11. Rueggeberg, F. A.; Craig, R. G. J Dent Res 1988, 67, 932.
12. Decker, C.; Decker, D.; Morel, F. In Photopolymerization, Fundamentals and Applications; Scranton, Bowman, Pfeiffer, Eds.; ACS Symposium Series 673; American Chemical Society: Washington, DC, 1997; p 63.
13. Rosen, S. L. Fundamental Principles of Polymeric Materials; Wiley: New York, 1993; p 145.
14. Cowie, J. M. G. Polymers: Chemistry & Physics of Modern Materials; Chapman & Hall: New York, 1991; p 74.
15. Bultman, J. D.; Griffith, J. R. In Recent Developments in Biofouling Control; Thompson, Nagabhushanam, Eds.; 1994; p 383.
16. Politi, R. E. In Handbook of Adhesives; Skeist, I., Ed.; Chapman & Hall: New York, 1990; p 713.