

# Aging Studies of a Radiopaque Light-Cured Dental Composite in Food-Simulating Liquids

V. KALLIYANA KRISHNAN, V. YAMUNA

Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences & Technology, Poojappura, Thiruvananthapuram, India 695 012

Received 16 May 1997; accepted 22 June 1997

**ABSTRACT:** Sorption behavior and changes in physical properties of an indigenously developed radiopaque light-cured dental composite upon aging in citrate buffer (pH 4.0), 50% ethyl alcohol and saline for a total period of 80 days, have been studied. Water uptake into the composite reaches saturation within 14 days in all media, whereas solubility values show an upward trend even after storage for 80 days. Solubility in alcohol medium is found to be high compared to saline and citrate media. Compressive strength and diametral tensile strength measurements tend to increase initially and then decrease gradually with time due to degradation of the composite upon storage. However, this reduction is not appreciable, as indicated by the strength values after 80 days, which are higher than the mandatory 220 MPa for CS and 34 MPa for DTS. Microhardness increases with time in all three cases, although alcohol medium tends to soften the material, resulting in an initial sharp decrease. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1153–1158, 1998

**Key words:** radiopaque; light-cured dental composite; solubility and water sorption; aging

## INTRODUCTION

Composites using radiopaque fillers have been developed recently, especially for posterior applications. Due to the stresses to which such materials are subjected to in the oral cavity, great demands are required on the quality of these materials.<sup>1,2</sup> However, in addition to the stress situations, the environment also plays an important role in determining the final properties of the material.

Water or other chemicals present in the oral cavity have been known to cause a filler–matrix debonding with time, thereby reducing the strength properties as well as wear resistance of the dental composite.<sup>3,4</sup> In addition, the filler par-

ticles can leach out ions such as silicon, barium, etc., as a result of this debonding.<sup>5</sup> The mechanism of the debonding and the resultant loss in properties are highly dependent upon the medium to which the composite is exposed to. The phenomena of leaching and the swelling of the composite that takes place simultaneously determines the final clinical performance of the composite.

Food simulating liquids are solvent media recommended by the Bureau of Food, Food and Drug Administration, USA (BFFDA, 1976). Pilliar et al. have reported that aging in ethyl alcohol increased the fracture toughness of dental composites.<sup>6</sup> McKinney and Wu investigated the effect of alcohol upon the surface hardness and wear of dental composites.<sup>1</sup> They have found that 75% ethanol caused the greatest softening and increase in wear. In the present study, the changes in strength characteristics such as compressive strength, diametral tensile strength, and micro-

---

Correspondence to: V. K. Krishnan.

*Journal of Applied Polymer Science*, Vol. 69, 1153–1158 (1998)  
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/061153-06

hardness of an indigenously developed light-cured dental composite after aging in three food simulating liquids such as citrate buffer (pH 4.0), 50% ethyl alcohol, and normal saline solution have been monitored with time. The sorption behavior and the solubility of the composites were also studied as a function of time during aging in these liquids.

## EXPERIMENTAL

### Materials

Bisphenol A–Glycidyl methacrylate (BIS-GMA) developed in the laboratory using a reported method<sup>7</sup> was used in preparing the composite paste. A radiopaque glass powder (Grade GM 27884, Schott, Germany) of particle size 0.7  $\mu\text{m}$  was used as the filler material after silanating it with 3-(trimethoxysilyl) propyl methacrylate to ensure strong binding between resin and the filler. To reduce the viscosity of the BIS-GMA resin and to act as a crosslinker, nearly 30% by weight of triethylene glycol dimethacrylate (Aldrich Chemicals, Milwaukee, WI) was added to BIS-GMA resin. A photoinitiator (–) Camphorquinone (99%, Aldrich) was also incorporated into the resin mixture to propagate the polymerization reaction. The final composite paste was used for preparing all the composite samples.

### Methods

#### Aging Studies

*Microhardness measurements.* Composite paste was packed in a stainless steel mold of 6 mm diameter and 3 mm thickness, covered both ends with glass slides and exposed to a dental cure visible light source having a constant wavelength of 460–480 nm range (Caulk the Max, Canada) for 60 s each. As each specimen was fabricated, each was taken out, stored in either 10 mL each of citrate buffer (pH 4.0), 50% ethyl alcohol, or saline (0.9% NaCl in distilled water) at 37°C for different time periods. Samples were taken out after 1, 14, 28, 45 and 80 days, and changes in properties studied.

The surface microhardness of the composite samples was measured on each side using a Vickers microhardness tester (Carl-Zeiss, Jena). At least eight measurements for each specimen were taken, and the mean and standard deviation cal-

culated. The specimen was placed flat on a glass slide and mounted on a holder on the microscope stage. The specimen surface was examined microscopically, and the indenter was then moved into position and the microscope stage was raised steadily until the required load was applied by the indenter upon the specimen. In all cases, a load of 100 g was used. The load was held for 15 s before the microscope stage was steadily lowered. The indenter was then replaced with the objective lens and the image of the indentation was focused. The contrast of the image was optimized using differential filtering, and the size of the diagonal of the indentation was measured. The Vickers microhardness ( $H_V$ ) was calculated using the following equation:

$$H_V (\text{Pa}) = 1854.4 P \times 9.80 \times 10^6 / d^2$$

where  $P$  is the load applied in grams and  $d$  is the length of diagonal in microns.

#### Compressive Strength Measurements

Specimens of size 3 mm diameter and 6 mm height were prepared for compressive loading by curing the composite specimens in cavities of appropriate size in a brass mold kept between two glass plates and held using a C-clamp. Each specimen was exposed to the light source for 60 s each on both ends for curing. Subsequently, the samples were released from the mold and the inner surfaces of the cured composite were exposed to the light source for a further 20 s to ensure uniform curing within the core of the material. At least 10 specimens of each paste were cured and stored at 37°C for 1, 14, 28, 45, and 80 days in the three media. The samples were subsequently taken out and the force at break was determined using a Universal mechanical tester (INSTRON, Model 1011, UK) while maintaining a crosshead speed of 10 mm/min. Knowing the force at break, the compressive strength was calculated using the equation

$$\text{CS, MPa} = P / \pi r^2$$

where  $P$  is the force applied in newtons,  $r$  is the radius of the specimen in mm.

#### Diametral Tensile Strength Measurements

DTS specimens of size 6 mm diameter and 3 mm height were prepared using a stainless steel mold

as was done for microhardness measurements. Paste packed in the mold between glass slides was cured using the visible light source as before. Exposure time was maintained at 60 s for all the samples. The cured specimens were taken out and stored at 37°C in the three media for 1, 14, 28, 45, and 80 days before testing. A minimum of 10 specimens were stored in each medium for each time period and tested accordingly.

A universal testing machine was used to determine the load at break. A reported procedure<sup>8</sup> was followed for DTS measurements. The crosshead speed of 10 mm/min was maintained for all tests. The load at which break occurred was noted and DTS was calculated using the equation

$$\text{DTS, MPa} = 2P/\pi DL$$

where  $D$  is diameter of specimen in mm and  $L$  is the height of the specimen in mm. The mean and standard deviation was then calculated.

### Water Sorption and Solubility Studies

Water sorption of the composite samples stored in citrate buffer, 50% alcohol, and saline at 37°C were determined at intervals of 1, 14, 28, 45, and 80 days. Specimens of 10 mm diameter and 2 mm thickness were prepared as described above. They were subsequently washed with soap water and distilled water in an ultrasonic cleaner to remove any impurities that may be adhering to them. The samples were dried in a vacuum oven at 60°C until dry weight was achieved ( $W_1$ ). After storage in the three media for different periods at 37°C, the samples were weighed again after removing the surface adherent water ( $W_2$ ) by gently wiping the surface of the composite samples with tissue paper. The specimens were then stored in a vacuum oven at 60°C until final dry weight was again achieved ( $W_3$ ). The solvent uptake (water sorbed) and solubility (amount of leachants) were determined using the following equations:

$$\text{Solvent uptake (\%)} = \frac{(W_2 - W_3)}{W_1} \times 100$$

$$\text{Solubility (\%)} = \frac{(W_1 - W_3)}{W_1} \times 100$$

### SEM Studies

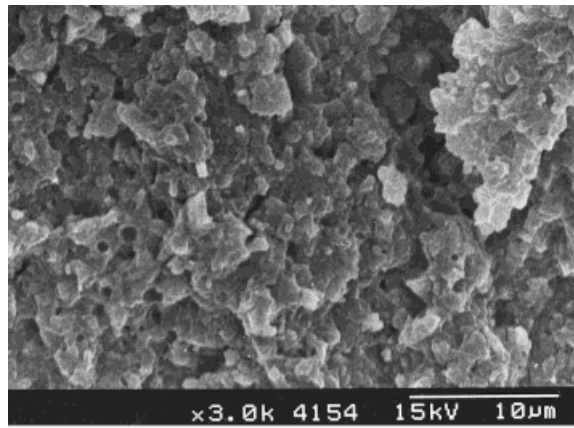
Samples aged for 80 days in the three different media were subjected to mechanical testing and

the surface of the fractured samples were coated with a layer of gold using a vacuum-sputtering machine (E-101, Hitachi ion sputter) and then subjected to scanning electron microscopic studies at a magnification of 1000–3000× using a scanning electron microscope (Hitachi Model S-2400, Japan).

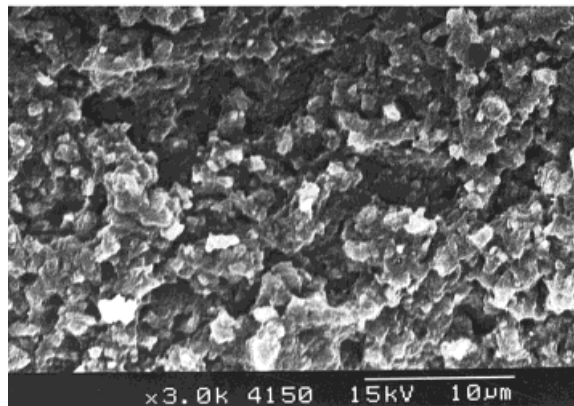
## RESULTS AND DISCUSSION

The filler particle is encapsulated by the resin matrix as is evidenced from the scanning electron photographs [Fig. 1(a–c)]. The silanation of the filler using the trimethoxy silane helped to stabilize the resin/filler paste through the interlocking chemical bonding between the methoxy groups in the silane and the filler hydroxyl molecules on one end and the free radical polymerization initiated by the photoinitiator through the unsaturated bonds at the other end.

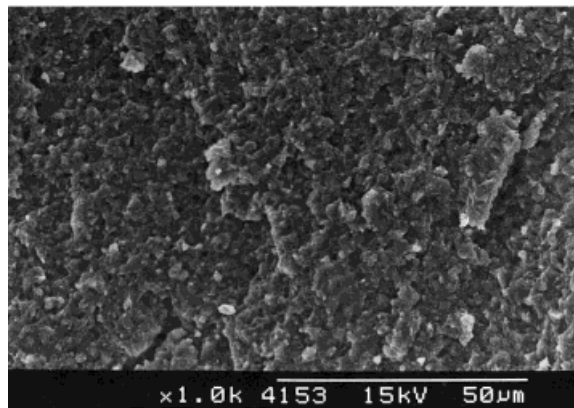
The variation in microhardness with time for the dental composite stored in the three food simulating media is shown in Figure 2. It is interesting to note the difference in variation in hardness values during the first few days. The sample in a highly polar low molecular weight volatile medium such as 50% alcohol tends to swell very fast, and the surface is softened considerably so that the hardness drops to nearly  $25.5 \times 10^7$  Pa from  $35.3 \times 10^7$  Pa, which is the hardness of the dry freshly prepared composite. In saline, this effect is absent as the swelling rate is very slow, and the hardness, in fact, increases to nearly  $39.23 \times 10^7$  Pa within the first 24 h and then stabilizes with a slow and steady increase over a period of 80 days. In the case of the citrate buffer, the microhardness does not show considerable change in the beginning, but tends to increase slowly upto  $47 \times 10^7$  Pa after a storage period of 80 days. Both citrate and saline media does not affect the strength of the composite adversely, and the values tend to lie in the same range over the time periods studied. It also indicates that the composite material tends to be harder in aqueous media such as saline and citrate buffer with time, whereas a volatile low molecular weight medium such as alcohol tends to soften the material and lower the hardness, which may lead to easy wear and degradation in the oral cavity. Softening of the composite in alcohol medium is also enhanced due to the easy dissolution of the resin rich layer at the surface of the composite in the solvent due



(a)



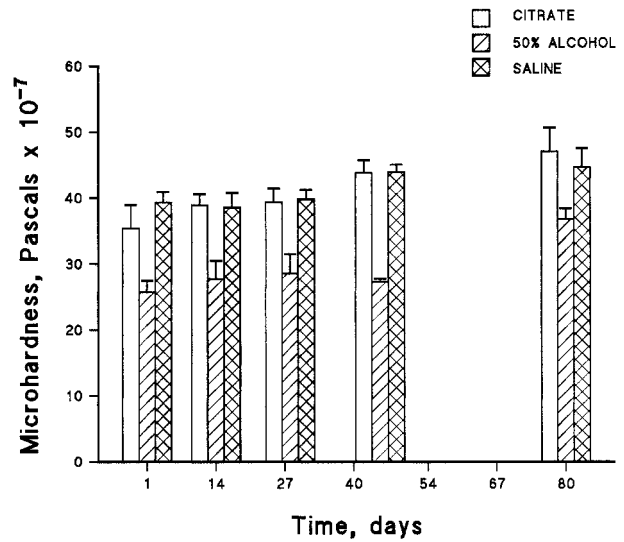
(b)



(c)

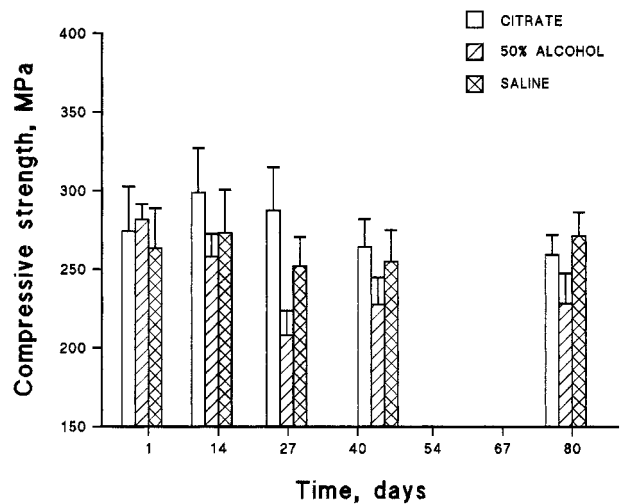
**Figure 1** SEM photomicrograph of the fractured surface of dental composite aged in (a) citrate, (b) 50% alcohol, and (c) saline for 80 days.

to its better solubility characteristics and is decided, to a great degree, by the solvent parameters.

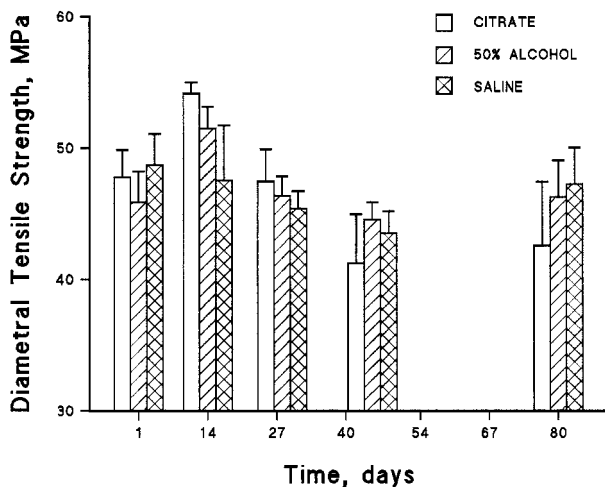


**Figure 2** Variation in microhardness (Pa) with time (days) for dental composite stored in three different food-simulating media.

Dental composites are subjected to high compressive stresses in the oral cavity especially during mastication of food material. That is why the study of compressive stress in different orally simulating media assumes importance. It can be seen from Figure 3 where variation in compressive strength over a period of 80 days has been plotted that a sharp initial increase in strength values is noticed for the composite stored in all three media, which then tends to



**Figure 3** Variation in compressive strength (MPa) with time (days) for dental composite stored in three different food-simulating media.



**Figure 4** Variation in diametral tensile strength (MPa) with time (days) for dental composite stored in three different food-simulating media.

fall slowly. It can also be seen that the time taken to reach the maximum for all three media are different. The sample exposed to alcohol medium shows a sharp increase in strength followed by citrate and then by saline. However, the rate of loss of strength over the aging period is also highest in alcohol medium. There is no change in strength values in saline after 80 days, whereas the composite stored in citrate tends to decrease slowly after the initial sharp rise in compressive strength. It is to be noted that there is no considerable difference in strength values of composites in saline and citrate after 80 days when compared with the values of the dry sample. Crosslinking within the

composite accompanied by swelling in the media and simultaneous elution of unreacted components from within the composite play an important role in determining the final strength values to a considerable extent. However the composite sample contacting the alcohol medium deteriorates in strength quite rapidly with time.

The diametral tensile strength values of the composite material in alcohol do not show considerable variation from the values of the dry sample as well as that of samples aged in citrate and saline. All the samples invariably show an initial increase in DTS during the first 10 days (Fig. 4). This was very similar to the behavior shown in case of compressive strength. This may be quite likely due to the polymerization reaction and subsequent crosslinking happening in the composite. A drop is noticed in the strength values after 10 days of aging, probably due to degradation resulting from the breakage of secondary forces (intermolecular interactions) present in the molecular structure. However, the values are seen to stabilize after nearly 20 days, and there is no considerable deterioration in the values of composites in the three liquids even after 80 days of storage.

Swelling of polymer matrices due to water sorption is likely to reduce stresses caused by shrinkage as well as reduce marginal leakage but they may have certain deleterious effects within the composite material. The water sorption and solubility of the composite over 80 days has been monitored and given in Table I. It can be seen that there is a sharp rise in solvent up-

**Table I** Solvent Uptake and Solubility Values of the Light-Cured Composite Aged in the Three Food-Simulating Media

Time (Days)	Medium					
	Citrate		50% Alcohol		Saline	
	Solvent Uptake (%) <sup>a</sup>	Solubility (%)	Solvent Uptake (%)	Solubility (%)	Solvent Uptake (%)	Solubility (%)
1	0.7040 ± 0.10 <sup>b</sup>	0.1128 ± 0.02	1.0254 ± 0.23	0.2436 ± 0.03	0.9247 ± 0.44	0.0561 ± 0.03
14	2.0664 ± 0.37	0.1233 ± 0.05	2.3981 ± 0.41	0.2428 ± 0.13	1.9629 ± 0.31	0.0867 ± 0.02
28	1.833 ± 0.15	0.1651 ± 0.04	2.206 ± 0.18	0.3918 ± 0.12	1.916 ± 0.24	0.161 ± 0.09
45	1.9144 ± 0.04	0.2956 ± 0.09	2.358 ± 0.1	0.5204 ± 0.02	2.0817 ± 0.04	0.1718 ± 0.04
80	1.71 ± 0.16	0.11 ± 0.01	4.81 ± 1.47	0.37 ± 0.09	1.91 ± 0.12	0.16 ± 0.07

<sup>a</sup> All percentage values expressed are weight percentages.  
<sup>b</sup> Standard deviation.

take during the first 7 days, which subsequently reaches a saturation level within a short time and then tends to stabilize. However, in the case of solubility, the values tend to show an increase at a slow rate even after 80 days of storage. The solubility values are low at first, because the rate of elution from the inside of the composite tends to increase only after the swelling phenomena happens to a large extent resulting in the relaxation of the molecular entanglement in the matrix. The solubility is higher in alcohol medium, as expected, probably due to the high degree of swelling in that medium.

In conclusion, it can be said that the final performance of dental composite depends to a large extent upon the oral environment to which it is exposed and, therefore, has a simultaneous effect upon the life of the composite in the oral cavity. Alcohol medium is found to have a deleterious effect on the properties of the composite upon aging, whereas saline and citrate does not seem to affect the strength characteristics to a great extent.

The authors wish to thank the Director and Head, BMT Wing, SCTIMST for providing facilities for carrying out the above work. They also wish to express their gratitude to Mr. K. Sreekumar for the SEM photographs.

## REFERENCES

1. W. Wu and J. F. McKinney, *J. Dent. Res.*, **61**, 1180 (1982).
2. R. A. Draughn, *J. Biomed. Mater. Res.*, **15**, 730 (1981).
3. K. J. Soderholm, M. Zigan, M. Ragan, and W. Fischlschweiger, *J. Dent. Res.*, **63**, 1248 (1984).
4. K. J. Soderholm, *J. Dent. Res.*, **60**, 1867 (1981).
5. H. Oysaed and I. E. Ruyter, *J. Dent. Res.*, **65**, 1315 (1986).
6. R. M. Pilliar, R. Vowles, and D. F. Williams, *J. Dent. Res.*, **66**, 722 (1987).
7. M. S. Sheela, K. T. Selvy, V. Kalliyana Krishnan, and S. N. Pal, *J. Appl. Polym. Sci.*, **42**, 561 (1991).
8. ADA Specification No. 27 for direct filling resins, Reports of Councils and Bureaus, *JADA*, **94**, 1191 (1977).