Role of oral environment upon the life of dental composites

V. Kalliyana Krishnan* and Sini T. Jayan

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

The life of a dental composite restoration inside the oral cavity is very much dependent upon the environment to which it is exposed. Deleterious changes in its properties with time have often been reported resulting in shortening of its life expectancy. This phenomenon is dependent to a great extent on the food habits, including liquid diet of an individual. Our study examines the changes in properties of an indigenously developed urethane-based radiopaque dental composite aged in orally simulating liquids up to 30 days. Micro-hardness changes along with compressive, transverse and diametral tensile strengths of a light cured composite have been monitored at intervals of 1, 7, 15 and 30 days after ageing in 75% alcohol, citrate buffer and phosphate buffered saline (PBS). The effect of the media and time of storage on the properties have been estimated using statistical calculations. Sorption of solvent media into the composite (adsorption process) and extent of solubility of unreacted components from the composite (desorption process) into the ageing media have also been studied.

DENTAL composites are generally used for restoring damaged teeth or to fix orthodontic appliances inside the oral cavity. Currently they are the most popular materials used in these applications as they have been able to overcome the shortcomings of conventional materials such as silicates, acrylics and amalgams[1]. They possess excellent strength permitting their use on both anterior and posterior tooth surfaces, good aesthetics, low shrinkage and thermal expansion. Glass ionomers in spite of their excellent adhesion to teeth suffer from poor strength compared to composites limiting their use to non-load bearing surfaces[2–3]. Dental composites generally exist in the form of a paste which when exposed to a visible light source having a wavelength of 440–480 nm cure into a hard solid within 20–60 sec. Basically the composite paste is composed of a resin matrix (20–40%), either bisphenol A-glycidyl methacrylate (commonly known as BIS-GMA) or urethane methacrylate resins reinforced with fillers such as quartz or glass having a particle size of < 20 microns. A photo-initiator incorporated in small amounts is responsible for the polymerization reaction and subsequent curing of the paste into a hard solid.

*For correspondence. (e-mail: bmwing@md2.vsnl.net.in)

The success of any dental restorative material depends largely on its physical, chemical and mechanical properties. Interaction with many substances inside the oral environment may be a determining factor contributing to the durability of restorations. Dental composites are subjected to extremely fluctuating oral conditions in the day-to-day life of an individual. Previous reports have indicated that the food habits of an individual influence the life of a restorative considerably[4,5]. On exposure to the organic acids of plaque and to certain food constituents, the resin matrix tends to become soft[6]. Its surface layer can be softened by chemicals with a solubility parameter ranging from 1.82×10^4 to 2.97×10^4 $(J/m^3)^{1/2}$. This range of solubility parameter embraces a wide variety of chemicals including substances[7] like alcohol and other organic buffers. The nature of the food taken also normally tends to alter the pH within the oral cavity. High intake of citrus fruits or hot food tends to increase the acidity in the oral cavity. Food trapped between cavities also tend to produce bacteria which in turn produce lactic acid that attacks and degrades the restorations over a period of time. Hence, all these phenomena contribute in decreasing the life of the material to various extents.

We have reported earlier the development and evaluation of chemical curing[8], light curing[9] and radiopaque[10] composites based on BIS-GMA and a radiopaque light curing material based on a urethane resin matrix[11]. Due to the high viscosity and difficulty in processing of BIS-GMA, urethane resins have been gaining importance during recent years. In this study, we are reporting changes in properties of a dental composite based on a urethane tetramethacrylate resin developed in our laboratory after storing them in three-food simulating media for a maximum period of 30 days. Sorption and solubility studies have also been carried out.

Materials and methods

Urethane tetramethacrylate resin is a reaction product of 1,3-bis(methacryloxy)2-hydroxy-propane (2 moles) and 1,6-hexamethylene diisocyanate (0.96 moles) in the presence of a basic catalyst. The resin was synthesized and characterized by spectroscopic techniques such as IR, UV and NMR and the purity checked using refractive

index measurements and HPLC having a UV detector at 254 nm. The synthesis and characterization of the resin has been reported earlier[11]. Radiopaque glass filler (240–260 parts per hundred of resin matrix, Schott Glaswerke, Germany) of particle size less than 5 microns was used as the filler material during the composite paste preparation. Before use, the filler particles were silanated as per established procedure[12] to ensure strong adhesion between the resin matrix and the filler. (–) Camphorquinone and triethylene glycol dimethacrylate (99% purity, Aldrich Chemicals, Milwaukee, USA) were used as the photo-initiator and diluent respectively. Dimethyl *p*-toluidine was used as the activator and traces of inhibitors were also incorporated in the paste.

The paste was cured by exposing it to a visible light source (Caulk the Max, Canada) for times varying from 20 to 60 sec. The photo-initiator undergoes dissociation resulting in free radicals and subsequent polymerization of the methacrylate resin. The diluent added also acts as a crosslinker participating in the polymerization.

Ageing studies

75% ethyl alcohol, phosphate buffered saline (pH 7.4) and citrate buffer (pH 4.0) were chosen as the food simulating media used for storing the composites. Their preparation was as per standard established procedures. Cured samples were aged in these media at 37°C and were withdrawn after 1, 7, 15 and 30 days of storage and tested for changes in various properties.

Cylindrical specimens, 2.5 mm in diameter and 6 mm in height were fabricated using a split brass mould for compressive strength (CS) studies. Composite paste was packed tightly inside the mould, both ends were covered with cellophane sheets and exposed to the visible light source for 60 sec on each side. The samples in the mould were kept in an incubator at 37°C for 15 min and after opening the mould, they were exposed to the light source for a further 20 sec each to ensure curing of the bulk. A minimum of 12 samples was prepared for each time-period and for each medium. These samples were subsequently stored in 10 ml of the ageing media at 37°C. They were kept between the platens of a universal testing machine (Instron Model 1011, UK) and the load at break was determined. A cross-head speed of 10 mm/min was maintained. Compressive strength in Mega Pascals was calculated for each sample using the formula $P/\pi r^2$. The best six values were chosen, and their mean and standard deviation calculated.

Samples (3 mm height × 6 mm diameter) for diametral tensile strength (DTS) measurements were prepared as stipulated[13] in ADA specification no. 27. The cured samples were aged in 10 ml of ageing media for 1, 7, 15 and 30 days at 37°C and tested between the platens of a universal testing machine at a cross-head speed of 10 mm/min. Samples were placed on the platens in such a way that the longitudinal axis was parallel to the axis of the platens. Load at break was noted and the DTS in Mega Pascals was calculated using the formula

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

where P is the load in Newtons at break, D is the diameter in mm and L is the height or thickness of the sample. A minimum of 8 samples were tested for each ageing period and the mean of the best six values and standard deviation were calculated.

Specimens for Vickers micro-hardness measurements were prepared as was done for DTS using the same mould. For each testing, two specimens were used. The surface micro-hardness was measured on each side using a Vickers micro-hardness tester (Carl–Zeiss, Jena). At least 8 measurements for each specimen were carried out and the average and standard deviation calculated for the six best values. A diamond indentor is a square based pyramid suitable for Vickers hardness measurements. 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 indentor was then moved into position and the microscope stage was raised steadily until the required load was applied by the indentor on the specimen. In all cases, a load of 100 g was used. The load was held for 15 sec before the microscope stage was steadily lowered. The indentor 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 micro-hardness (H_v) was calculated using the following equation:

$$H_v\ (\text{kg/mm}^2) = 1854.4\, P/d^2,$$

where P is the load applied in g, d is the length of the diagonal in microns.

Transverse strength (TS) test specimens were prepared as specified[14] in ISO specification no. 4049 (25 mm length, 2 mm depth and 2 mm thick). The cured bar samples were aged at 37°C in the respective media for 1, 7, 15 and 30 days, taken out and kept horizontally over two metal rods of 2 mm diameter and 20 mm apart fixed on a aluminium platen (base plate). A load was applied at the middle of the specimen from the top using a third metal rod fixed to a second platen. A cross-head speed of 1 mm/min was maintained in the universal testing machine during the experiment. The load at break was noted and the TS was determined using the formula:

$$\text{TS}\ (\text{MPa}) = 3PL/2bd^2,$$

where P is the load in Newtons, L is the length of the specimen between two metal rods at the base plate, b

is the thickness and d is the depth in mm. A minimum of 3 specimens were tested for each time-period.

Water sorption and solubility of the composite samples stored in distilled water at 37°C were determined at intervals of 1, 7, 15 and 30 days. Specimens of 10 mm diameter and 2 mm thickness were prepared by exposing composite pastes packed in stainless steel moulds to a visible light source for 60 sec each on either side. The surface of the specimens was polished initially using 240 grit silicone carbide paper. They were subsequently washed with soap water and distilled water in an ultrasonic cleaner to remove any dirt or oil that may be sticking to them. The samples were dried in a vacuum oven till dry weight was achieved (W_1). After storage in citrate, PBS and 75% alcohol for different periods at 37°C, the samples were weighed again after removing the surface adherent water (W_2). The specimens were then stored in a vacuum oven till final dry weight was again achieved (W_3). The solvent uptake (water sorbed) and solubility (amount of leachants) were determined using the following equations:

$$\text{Water sorption } (\%) = \frac{W_2 - W_3}{W_1} \times 100,$$

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

The 30 day storage medium used for sorption and solubility studies was carefully transferred and made up into 25 ml in volumetric flasks. A specific volume of the extracts was injected into a C_{18} column of a high pressure liquid chromatograph (Waters Associates, USA) using acetonitrile/water (90/10 v/v) as the mobile phase at a flow rate of 1 mm/min. Components having an absorption at 254 nm were detected using a UV detector unit and the resulting chromatogram was compared with control chromatograms of unreacted components to estimate the elutant values after 30 days of storage.

Analysis of variance (single factor ANOVA) statistical method was used to calculate the probability (P) values while comparing changes in properties of the dental composite in different media with time. Changes where P values were reported to be less than 0.05 were taken as significant.

Results and discussion

The urethane tetramethacrylate adduct (UTMA) synthesized and purified in a rotary evaporator was found to be a colourless waxy paste, more free flowing than BIS-GMA. Its refractive index was 1.4830 and this was found to correspond with previous reported values[15]. Radiopaque glass particles (< 5 microns particle size) along with a small amount of pyrogenic silica could be incorporated into the resin easily. The choice of a hybrid filler system was to provide optimum properties compared to microfine fillers (< 0.4 microns) or conventional filler systems (20–50 microns). The paste prepared was of a high aesthetic quality compared to conventional BIS-GMA based composites.

Samples stored in the three ageing media were taken out and tested for CS at specific intervals of time (1, 7, 15 and 30 days). Ageing seems to affect CS to different degrees in each medium though the variations in each medium were found to be within standard deviation limits even after 30 days of storage. Apparently an improvement in CS values could be noted (Table 1), especially for samples stored in citrate and PBS whereas in alcohol medium CS values do not seem to show appreciable change with time. Earlier reports have shown

Table 1. Mechanical properties for urethane composites aged for specific periods of time in three oral simulating media*

Property →	Compressive strength (MPa)			
Period, days → /medium ↓	1	7	15	30
Citrate	335.1 ± 11.6	356.1 ± 13.5	361.4 ± 16	387.0 ± 14.7
PBS	346.5 ± 22.7	329.3 ± 17	336.1 ± 20.7	357.5 ± 17.6
75% Alcohol	339.9 ± 24.4	367.1 ± 26.2	353.2 ± 20.6	339.1 ± 21.19
Property →	Diametral tensile strength (MPa)			
Citrate	43.7 ± 2.4	35.1 ± 4.3	30.8 ± 4.9	24.2 ± 2.5
PBS	40.8 ± 3.4	33.9 ± 5.1	32.9 ± 7.0	30.1 ± 6.6
75% Alcohol	39.0 ± 3.6	42.2 ± 2.6	40.8 ± 2.9	38.6 ± 3.5
Property →	Vickers micro-hardness (kg/mm^2)			
Citrate	44.8 ± 4.4	38.8 ± 4.0	40.5 ± 2.0	46.7 ± 4.9
PBS	40.6 ± 3.1	33.0 ± 2.5	40.3 ± 3.3	36.5 ± 2.2
75% Alcohol	38.9 ± 1.9	33.9 ± 3.7	40.7 ± 3.3	33.6 ± 2.1

*Values joined by the same vertical line are statistically significant ($P < 0.05$).

that BIS-GMA based composites tend to lose their CS steadily upon ageing in these media[5].

Table 1 indicates the CS values obtained for composite samples aged for different time periods. Statistical analysis helped considerably in evaluating the effect of the media upon strength values and values joined by the same straight line ($P < 0.05$) show that significant changes in strength has been affected only in these cases by the change in media. It can be seen that improvement in CS values of the composite is also statistically significant for citrate and PBS with time compared to alcohol medium and it can be concluded that the behaviour of the composite in citrate and PBS is different from that in alcohol. This may be quite likely due to a high degree of swelling of the composite in the alcohol medium due to the easier softening of the urethane molecules in alcohol resulting in the higher degree of elution of components from the composite into the medium upon storage compared to that into citrate and PBS. These components may be unreacted monomer units and degraded filler particles present within the matrix of the composite which have a higher solubility in alcohol compared to other media. The rate of diffusion of the leached components into alcohol is expected to be considerably high compared to the rate of diffusion into citrate and PBS. This theory has been substantiated by the solubility values. However, as far as CS is concerned, the effect of swelling seems to play a dominant role compared to the degree of degradation of the filler particles.

The CS values recorded during the study ranged from 350 to 430 MPa for most of the composites which is quite appreciable compared to the minimum required value of 220 MPa recommended for the successful functioning of the composite in the oral cavity. A value of nearly 400 MPa makes it feasible for the composite to be safely used for posterior restorations and the fact that a radiopaque filler has been used is doubly advantageous from a clinical point of view.

It is interesting to note the sharp deterioration in DTS values of the composite samples stored in citrate and PBS compared to those stored in alcohol which do not seem to affect DTS values even after 30 days of ageing. This is in sharp contrast to the trend in CS values. It can be concluded that the nature of the media is highly significant in determining the DTS and the final performance of the composite. Data shown in Table 1 also ratify the above observations. Changes in DTS are found to be statistically significant in each medium and performance is highly dependent on the medium in which it is stored or exposed to in the oral cavity. Citrate and PBS have been known to attack the glass particles, resulting in degradation of filler particles[16], which may be the factor resulting in deterioration of the DTS values. Swelling does not seem to be significant in DTS specimens as evidenced by the retention of DTS in alcohol aged samples. Another observation is that the degree of swelling only has an insignificant role in determining the composite strength with ageing though the degree of degradation and elution of filler particles seems to affect the strength sharply.

Surface hardness of the composite does not seem to be affected considerably with time upon ageing in all the media. Differences observed were within standard deviation limits. Alcohol tends to soften the surface more than citrate and PBS and hence a small reduction in hardness values was noticed in all cases for composites stored in alcohol. Statistical data support this case (Table 1). However, most of the composites showed values above 34 MPa which is the minimum required value for satisfactory performance of the composite in oral cavity. In this case, only the nature of the surface mattered and so the degree of degradation and elution of filler particles did not seem to have any significant effect upon the micro-hardness.

TS values are affected considerably with time upon ageing of urethane composites in all the media (Figure 1), though the values were above 50 MPa (minimum stipulated value for dental composites) for samples stored in citrate and PBS media even after 30 days. Alcohol medium is found to affect the TS adversely in contrast to what was observed for compressive and diametral tensile strength.

Sorption of solvent molecules into the composite and desorption of unreacted components and degraded filler particles from the composite into the surrounding medium are parallel processes happening simultaneously. Sorption

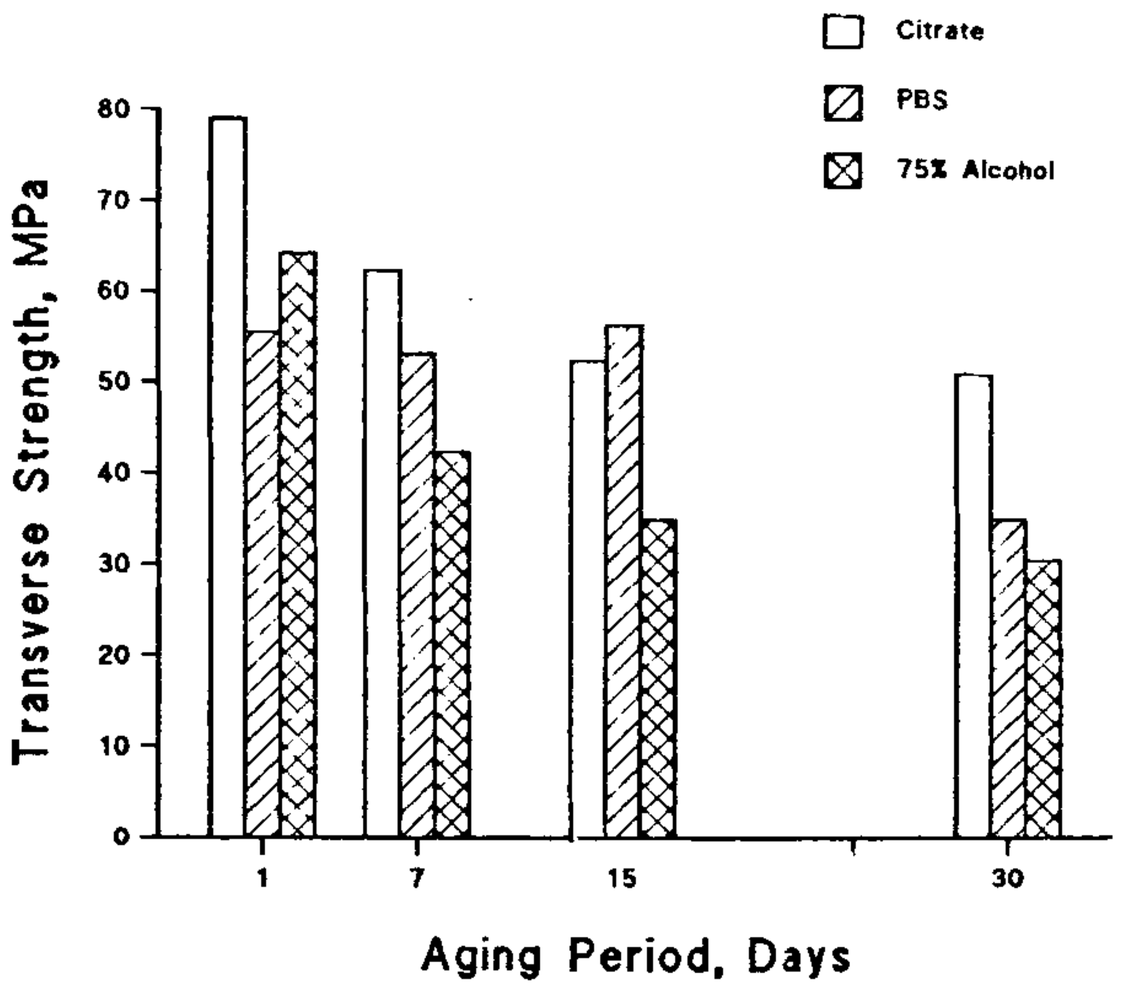

Figure 1. Variation in TS of dental composites with time of ageing in three oral simulating media.

values tend to increase with time as shown in Figure 2. Degree of sorption seems to be independent of the media concerned. Urethane composites studied here show higher sorption values (~ 2%) compared to BIS-GMA composites. This is in accordance with the previously reported values. Increased water sorption is expected to compensate for shrinkage of the composite in the dental cavity, thereby reducing marginal leakage. Increased sorption is likely due to the presence and higher degree of swelling of aliphatic cross-linked urethane linkages compared to aromatic cross-linked network of BIS-GMA. Sorption values tend to reach a maximum within 30 days with 40–50% of the total sorption having been completed within the first 24 h. Therefore it can safely be assumed that the first few hours of exposure of the composite to the surrounding medium is the critical and rate determining step.

Solubility is the process by which the degraded filler particles and unpolymerized monomer units elute out of the swollen composite with time into the surrounding medium. It is found from Figure 3 that the solubility values also tend to increase with time when monitored for 30 days in all the three media. The degree of elution apparently seems to be independent on the surrounding medium. A maximum of 0.8–0.9% was noticed in all the three media after 30 days of storage.

The amount of eluted components after 30 days of storage was estimated, as shown in Table 2, using HPLC (Figures 4–6). It can be seen that MHP is eluted into alcohol medium as it is more soluble and elution is faster. The presence of MHP is due to the fact that an excess of this chemical was used during its reaction with HMDI to synthesize UTMA. Other components eluted are likely to be unreacted UTMA, its dimethacrylate unit, methacrylic acid. Individual components other than MHP were not analysed due to paucity of time

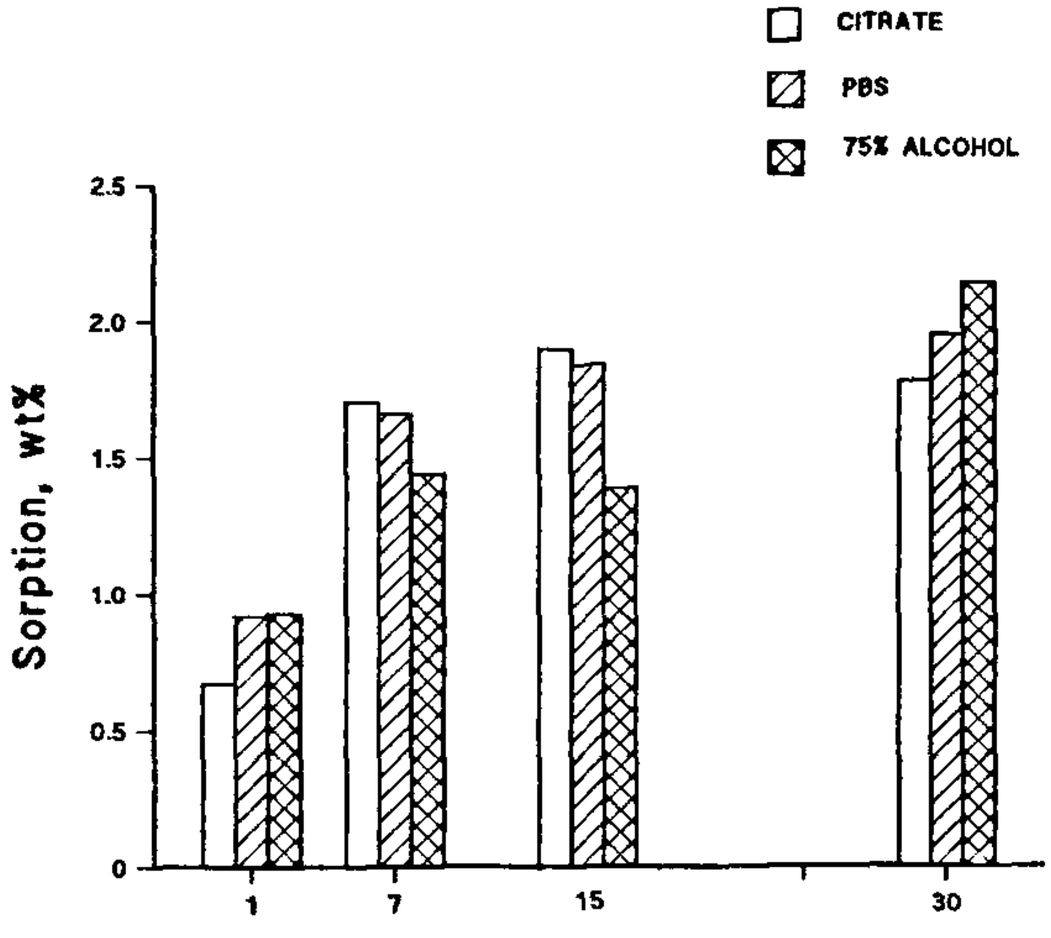

Figure 2. Sorption changes with ageing time in three media for urethane dental composite.

Table 2. Amount of leachants from polyurethane composite present in three oral simulating media after 30 days of storage

Medium of storage	Period of storage (days)	MHP eluted ($\mu g/mm^2$)	Other components ($\mu g/mm^2$)
Citrate	30	—	49.37
PBS	30	—	1.945
75% Alcohol	30	0.5968	1.596

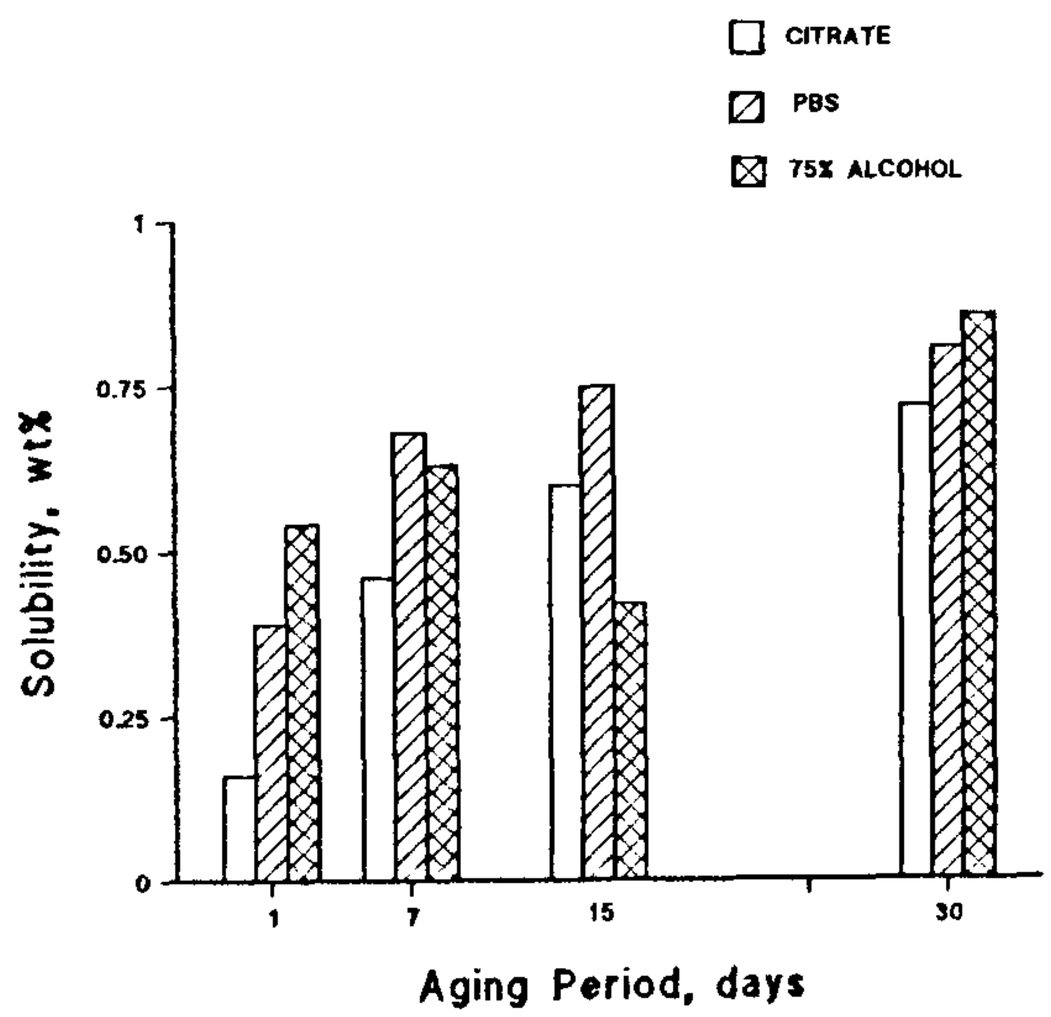

Figure 3. Solubility changes with ageing time in three media for urethane dental composite.

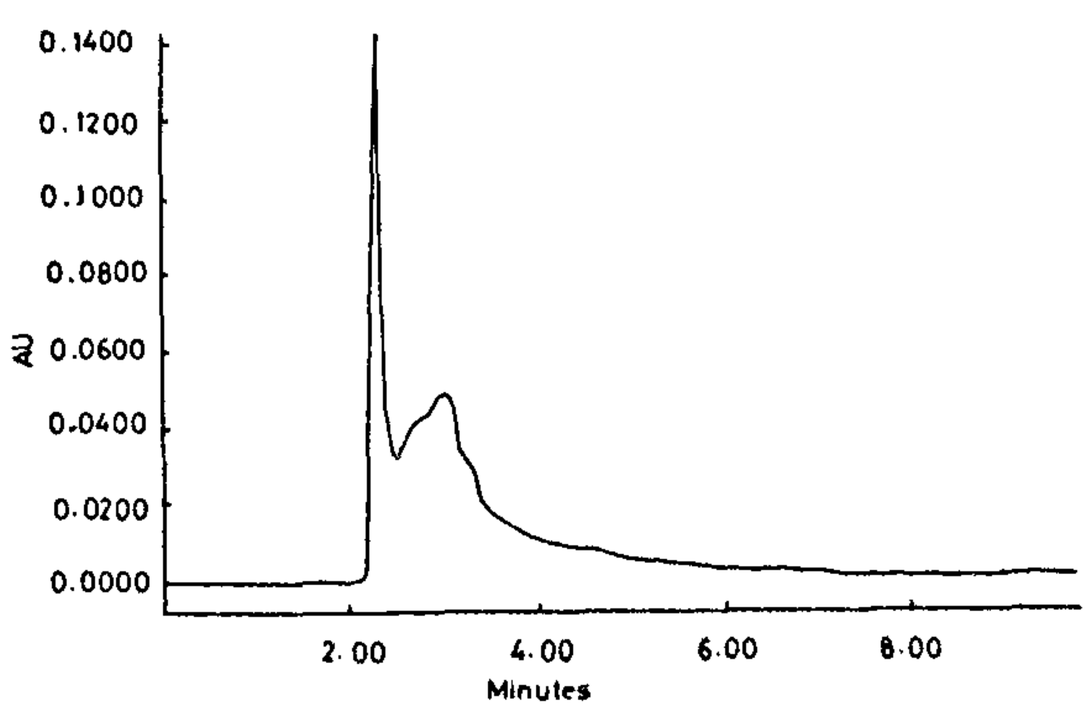

Figure 4. HPLC chromatogram of composite extract (citrate) after ageing for 30 days.

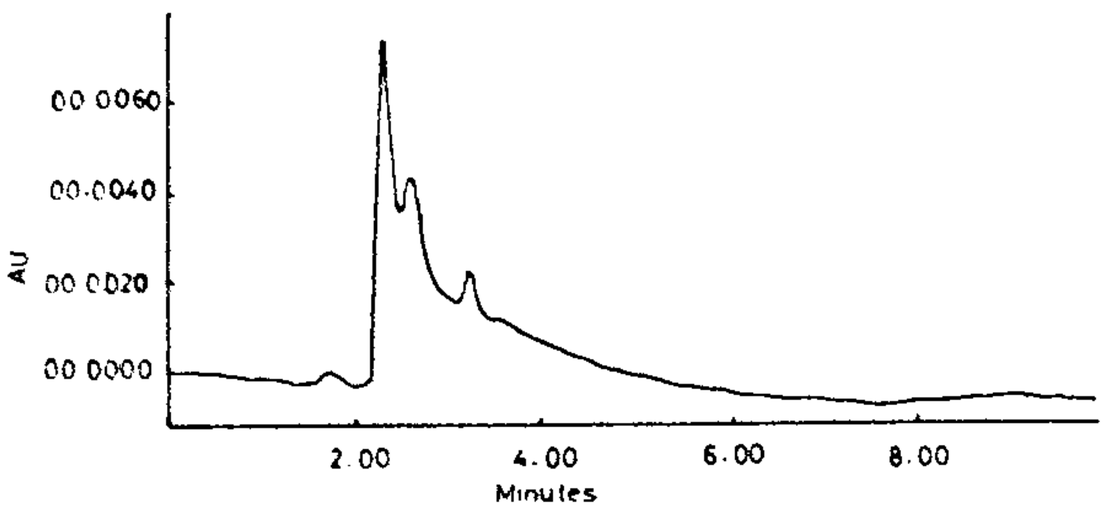

Figure 5. HPLC chromatogram of dental composite extract (PBS) after ageing for 30 days.

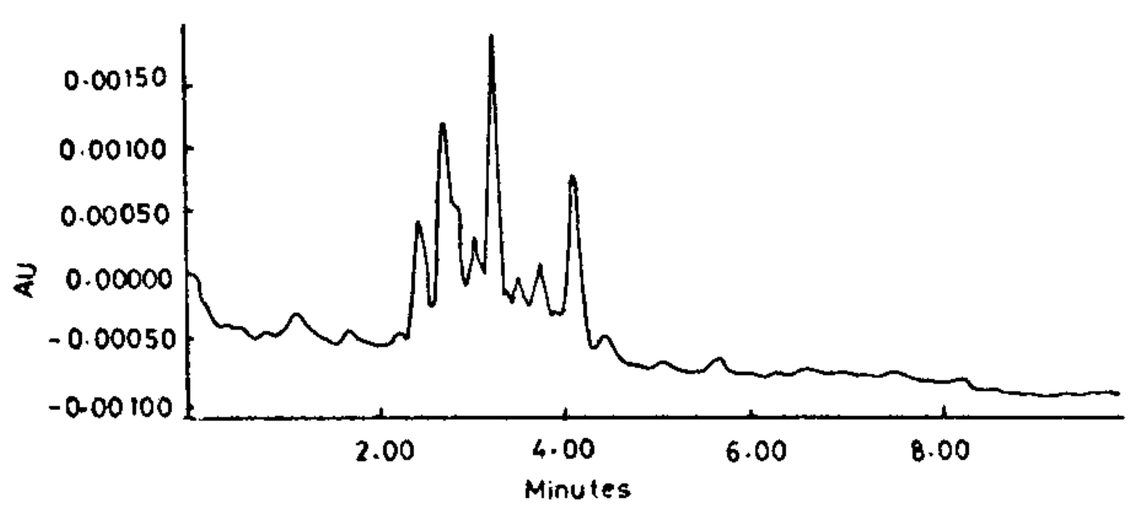

Figure 6. HPLC chromatogram of dental composite extract (75% alcohol) after ageing for 30 days.

and standard chemicals. Migration of unsaturated monomer elutants apparently seem to be complete within 30 days. It should be kept in mind here that a UV detector was used to identify the elutants and only unsaturated compounds having an absorption at 254 nm has been detected. The degraded filler particles do not come under the purview of this study for which an ion plasma mass spectroscopy technique has to be used to quantify the elements.

Conclusion

Ageing of UTMA composite in oral simulating media such as citrate, PBS and 75% alcohol is found to affect its physical properties and sorption characteristics to a significant extent. CS of samples stored in citrate and PBS are found to improve with ageing whereas there is no significant change for samples stored in alcohol. Samples aged in citrate and PBS show a deterioration in DTS values with ageing whereas alcohol medium does not seem to affect the property of the urethane composite. Changes in micro-hardness values are not significant in all three media with ageing whereas TS is adversely affected in all media though alcohol media is found to affect it the most. Statistical calculations support the above observations. It can be concluded that citrate and PBS tend to attack the glass filler which tends to migrate out into the surrounding medium. However, unpolymerized MHP and other components are found to be more soluble in alcohol medium. These elution processes combined with the sorption of the solvent molecules affect the physical properties significantly. It can therefore be assumed that the oral simulating media play a dominant role in determining the properties of the dental composites and in their final performance. UTMA-based composites are aesthetically more acceptable, retain their CS, handling characteristics and processing are made easier compared to BIS-GMA-based composites. However, ageing of these composites to longer periods of time in various oral simulating media is essential to have a fair idea about their long-term performance.

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