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Effects of water on glass-filled methacrylate resins

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Composite materials have been prepared with up to 50 vol % glass beads in two methacrylate resins: polymethyl methacrylate and 64% bisphenol A di(glycidyl methacrylate) – 36% triethyleneglycoldimethacrylate. These composites were immersed in water at 60° C for up to six months and the changes in weight, elastic modulus and compressive strength were followed. In the polymethyl methacrylate composites the water uptake levels off after 5 days. The strength and modulus decrease over this period due to plasticization of the resin, but then increase again. The cross-linked methacrylate composites show the same decrease but no subsequent increase. Silane treatment of the glass beads reduces the water uptake by the resin and the decrease in modulus and strength.

1. Introduction

Water causes degradation in the properties of many composite materials with polymeric matrices. Many of the polymers used in composites, including epoxy resins and polyesters, take up several per cent of water on immersion or exposure to high humidities. This swells the polymer and plasticizes it, causing a reduction in modulus and strength. The interface between glass and polymer is very water sensitive because of the high surface energy of glass relative to the polymer and the permeability of the polymer allows water to reach the interface. Thus water attack severely reduces the strength of glass-reinforced polymers but this may be largely prevented by silane coupling agents which can provide a covalent bond between the reinforcement and the matrix. A recent review [1] discusses these effects in detail for glass fibre-reinforced epoxy resins.

During the last two decades glass-particle filled methacrylate composites have been developed as dental filling materials. They have the advantage over dental amalgam that they are colourless, and they are not subject to slow dissolution as are the silicates which were used previously to fill anterior teeth. However, the composites do wear rather rapidly if used in the heavily stressed occlusal faces of posterior teeth. They also tend to discolour with time. It seems that water uptake may play a significant role in both of these processes by adsorbing at the particle–matrix interface.

In a previous study Prasad and Calvert [2] found that abrasive wear of silica- and glass bead-filled polymethyl methacrylate (PMMA) was reduced by up to four-fold if a silane coupling agent (γ-methacryloxypropyl trimethoxysilane) was used. This present work investigates the effect of water absorption on glass bead-filled PMMA and on a filled copolymer used in dental composites. This latter was developed by Bowen [3] and is a mixture of bis-GMA, a condensate of bisphenol A and glycidyl methacrylate, with triethylene glycol dimethacrylate (TEDMA). Bis-GMA contains two hydroxyl groups per molecule and is highly viscous; the TEDMA serves to reduce the viscosity. The system is polymerized with a peroxide initiator and an amine accelerator and forms a heavily cross-linked polymer.

2. Experimental methods

PMMA samples were prepared with up to 50 vol % Ballotini glass beads (4 to 44 μm) as filler. 1 wt %

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benzoyl peroxide was used as catalyst and 0.3 wt% N,N-dimethyl–p-toluidine as accelerator. The mixture was slowly rotated to prevent sedimentation until polymerization rendered it viscous. It was then poured into 4 mm glass tubes, allowed to polymerize for one day, then cured for 12 h at 90° C and slowly cooled. Burn-off tests showed that no sedimentation had occurred in the sample and porosity was less than 1%.

Samples were also prepared with a matrix of 64 mol% bis-GMA and 36 mol% TEDMA, similar to the composition used in commercial composites. These were mixed and polymerized with 1% benzoyl peroxide at 60° C for 1 h without accelerator. They were then cured at 75° C for 1 h and 90° C for 4 h before cooling. In the samples containing 40 vol% silane-treated glass beads the porosity was high, about 5%; with untreated beads it was about 1%.

The fillers were dried for 4 h at 250° C and stored in a desiccator before use. Silane treatment was carried out for 24 h from a 2% solution of γ-methacryloxypropyl trimethoxysilane in toluene after which the particles were filtered and dried at 60° C for 12 h. It was shown previously [2] that this treatment produces roughly a monomolecular layer of silane on the glass surface.

Modulus and compressive yield strength at 0.2% strain were measured by axial compression of the 4 mm diameter, 8 mm long cylinders at 1.3 mm min^{-1} in an Instron testing machine. Water sorption was measured by weighing samples of about 1 g after storage in 10 cm^3 of distilled water at 60° C for up to six months.

3. Results

The Young's modulus of PMMA composites increases with volume fraction of filler roughly in agreement with the simple series equation

$$1/E_c = V_m/E_m + V_f/E_f \qquad (1)$$

where E_c, E_m and E_f are the Young's moduli of the composite, matrix and filler respectively; V_m and V_f are the volume fractions of matrix and filler. Composites containing silane-treated filler had moduli somewhat above the theoretical value while untreated particles were below (Fig. 1).

Fig. 2 shows that a short water immersion treatment at 60° C for six days reduces the modulus of the matrix and of the composites. The untreated bead composites lose proportionately more than the treated ones, which still follow the series Equa-

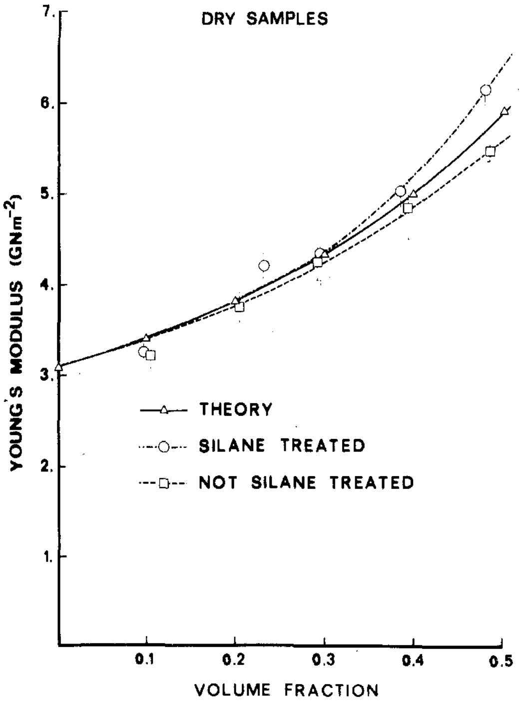

Figure 1 Modulus in compression against volume fraction of glass bead filler (silanated or untreated) in PMMA. Theory according to Equation 1, series model.

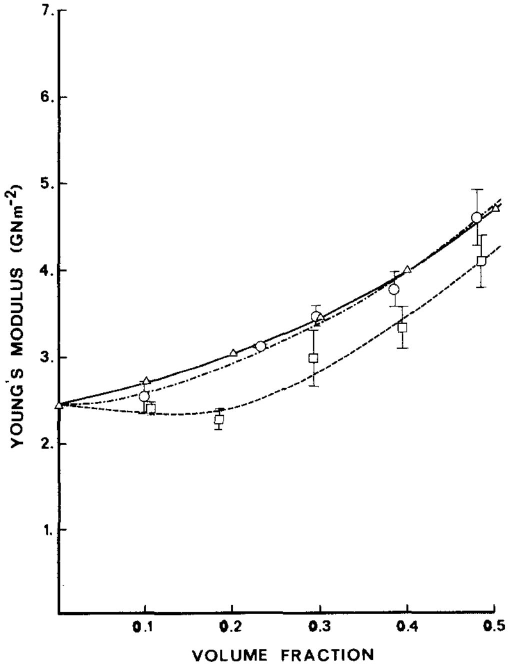

Figure 2 As Fig. 1 after six days immersion in water at 60° C.

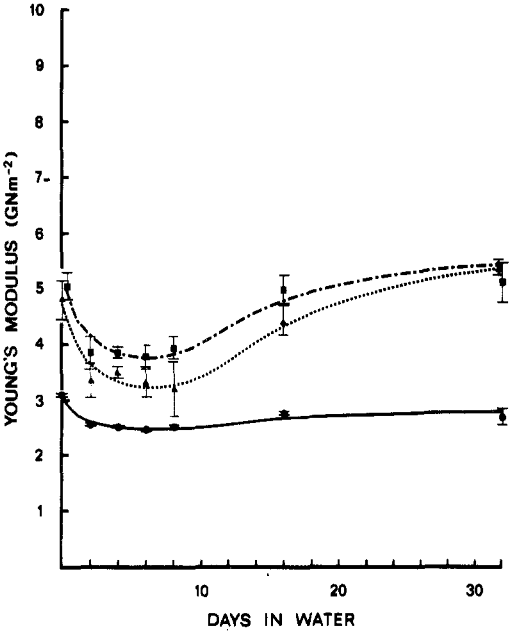

Figure 3 Moduli of PMMA and 40vol% filled PMMA composites as a function of treatment time in water.

tion 1. Fig. 3 shows this process as a function of time. The matrix goes through a 15% drop in modulus over about four days after which it barely changes. With the composites the modulus rises again after about eight days and regains its initial value. As seen in Fig. 4 this rise is not due to water sorption which stabilizes after 5 days.

The compressive strength of the PMMA composites increases slightly with the addition of treated filler and decreases with the poorly bonded untreated filler (Fig. 5). At six days the effect of water is to decrease all the strengths (Fig. 6) although with longer times there is again some recovery.

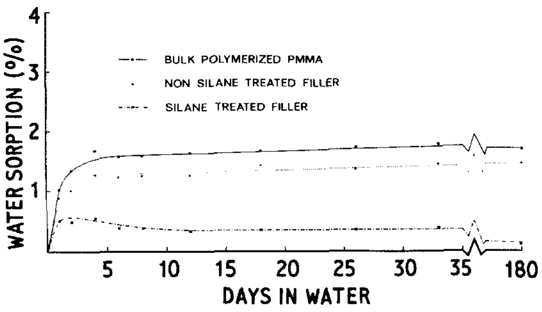

Figure 4 Water uptake by weight gain against immersion time at 60° C for PMMA and composites.

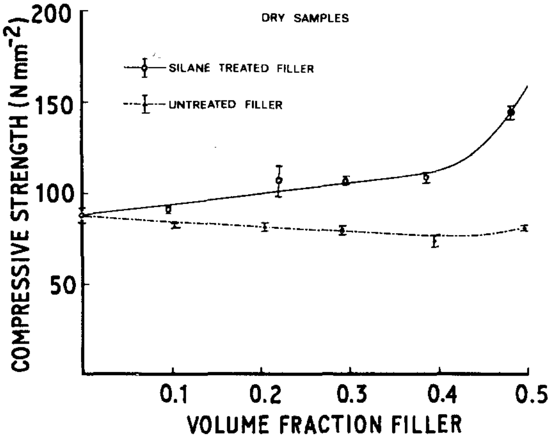

Figure 5 Compressive yield strength (0.2%) against filler volume fraction for dry PMMA composites.

As seen in Figs. 7 to 9 the story in the bis-GMA/TEDMA composites is similar although there is apparently no recovery in properties with longer term water treatment. The most porous samples, containing 40% silane-treated beads, show a continuing water uptake with time rather than levelling off.

Scanning electron micrographs of composites fractured after 16 or more days in water showed

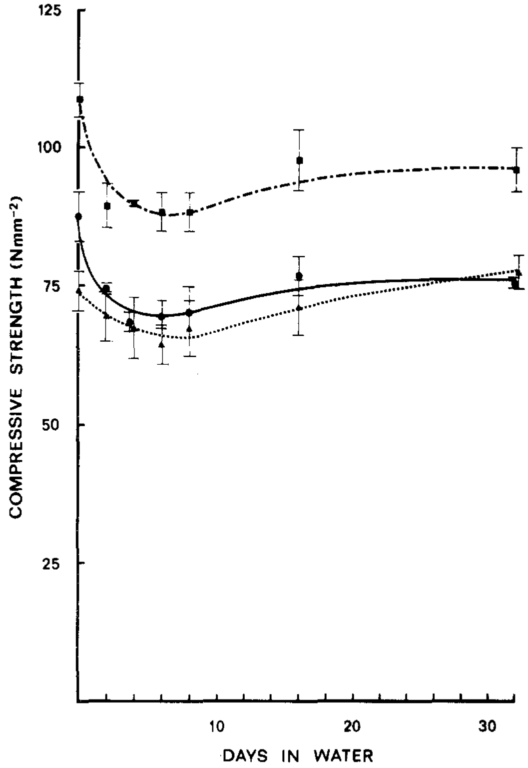

Figure 6 Effect of 60° C water immersion on compressive yield strength of PMMA and composites.

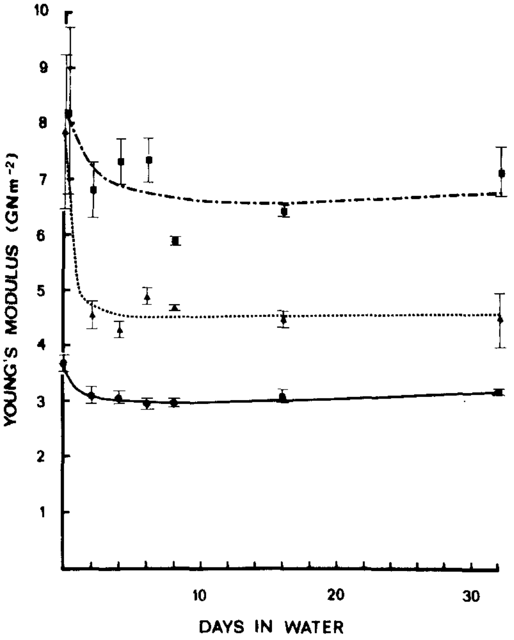

Figure 7 Moduli of bis-GMA/TEDMA and 40vol% glass bead composites as a function of immersion time in water.

that the filler particles were breaking up, shedding a surface layer whose thickness increased with time of exposure to water, reaching about 0.3 μm after 180 days (Figs. 10 to 12). This did not seem to occur in composites containing silane-treated beads and was more noticeable in PMMA matrix composites [4]. Similar effects have been described in glass fibre-reinforced resins [1].

4. Discussion

The prime effects of water are to swell and plasticize the polymer matrix which give a loss of modulus and strength. The bis-GMA/TEDMA resin is cross-linked, whilst PMMA is linear so the longer term responses of the two systems may differ.

The equilibrium water sorptions of the two resins, 1.5% in PMMA and 3% in bis-GMA/TEDMA are in agreement with literature values [5]. The measured diffusion coefficients of water in PMMA and bis-GMA/TEDMA at 60° C are 7.4×10^{-8} and

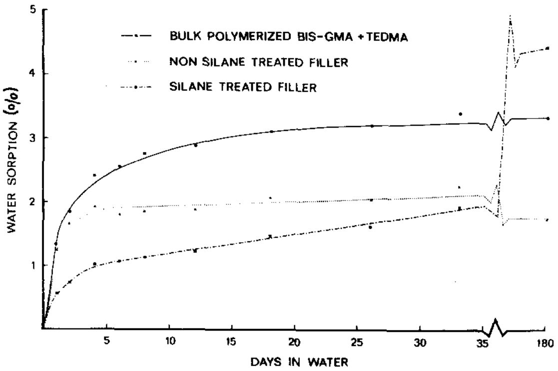

Figure 8 Water uptake by weight gain against immersion time at 60° C of bis-GMA/TEDMA and 40vol% composites.

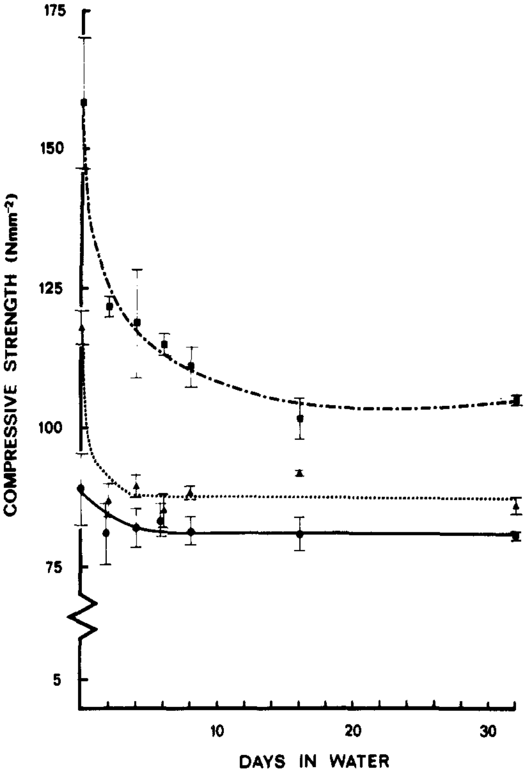

Figure 9 Effect of 60° C water immersion on compressive yield strength of bis-GMA/TEDMA and composites.

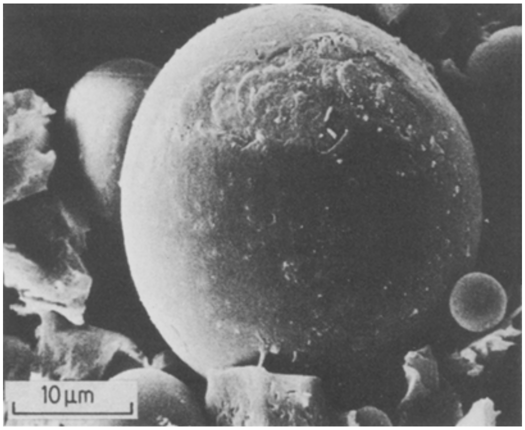

Figure 10 PMMA containing 40vol% untreated glass beads. Fractured after 32 days in water at 60° C.

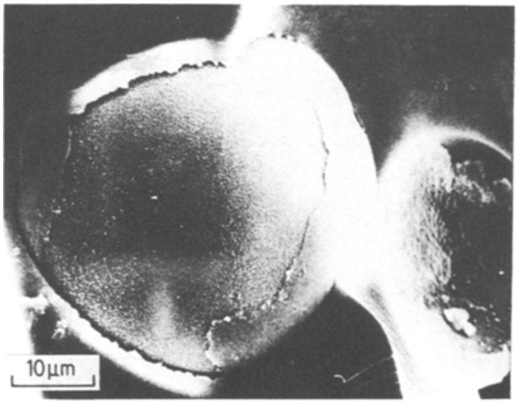

Figure 11 Bis-GMA/TEDMA containing 40 vol% untreated glass beads. Fractured after 180 days in water at 60° C.

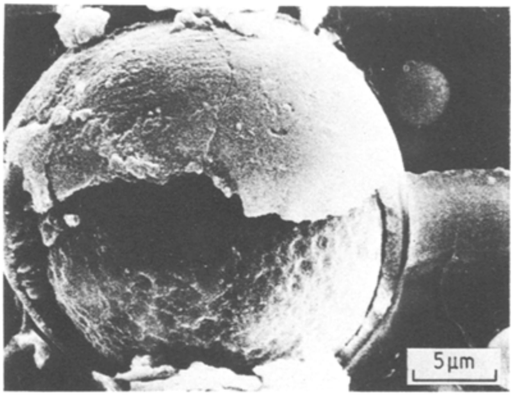

Figure 12 PMMA containing 40 vol% untreated glass beads. Fractured after 180 days in water at 60° C.

$1.6 \times 10^{-8} \text{cm}^2 \text{sec}^{-1}$ respectively [6]. The predicted time for 50% of the total final water uptake into 4 mm cylinders would then be 0.4 days for PMMA and 2 days for bis-GMA/TEDMA as compared to observed times of less than 1 day and 1.5 days respectively [7]. The expected water uptake for the 40 vol% filled polymers is 42% of that of the pure resin. For PMMA with treated filler the sorption is 22% of the matrix and for untreated filler 81% of the matrix sorption, see Table I. This suggests that with the treated filler the strong interfacial bond prevents the polymer swelling away from the filler while in the untreated case the matrix swells and voids open adjacent to the filler which fill with water. Bis-GMA/TEDMA behaves in a similar way. These water-filled voids apparently lead to corrosion of the beads whilst water-swollen but tightly bonded resin does not.

Table I shows the percentage drop in Young's modulus that would be expected on water immersion of the composite from Equation 1 and knowing the decrease that takes place in the matrix modulus. No attempt was made to correct for the different measured water sorptions of the composites. It can be seen that the untreated bead composites behave much worse than those with treated beads, which are moderately close to the expected values. In PMMA the compressive strength measurements on the composites change roughly in proportion to the changes in matrix strength. In bis-GMA/TEDMA the matrix and treated bead composites both lose strength with water immersion, whilst the untreated bead composite, which starts weak, does not get much worse.

PMMA composites show a longer term recovery of strength and modulus which is not reflected in any change in the water uptake and is not seen in bis-GMA/TEDMA. This is possibly due to annealing and relaxation in this matrix which does not occur in the cross-linked bis-GMA/TEDMA.

5. Conclusions

Water uptake by filled methacrylates leads to a plasticization of the matrix and a reduction of modulus and strength. The total water uptake is limited if a strong filler–matrix bond prevents the matrix swelling. Evidence of water-induced relaxation is seen in PMMA. In some circumstances the

TABLE I Observed and predicted effects of water on composites

	Resin observed	Composite predicted	Composite observed	
			Treated beads	Untreated beads
(a) Water uptake (wt/%)				
PMMA	1.6	0.7	0.35	1.3
bis-GEM/TEDMA	3.1	1.3	1.1	1.9
(b) Maximum modulus decrease on water immersion (%)				
PMMA	17	16	24	33
bis-GEMA/TEDMA	21	20	16	42

glass beads start to break up after long exposures to water.

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