Water sorption and mechanical properties of acrylic based composites

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Four commercial bisphenol-glycidilmethacrylate based composites used mainly for dental applications have been investigated. Differential thermal analysis performed on samples aged in water for different times indicated a small residual monomer reactivity which disappeared after ageing. A further crosslinking reaction facilitated by water plasticization and a monomer loss could be the main reasons for such a phenomenon. The embrittlement of these materials with ageing time has been detected from flexural mechanical properties. Water sorption/desorption experiments have been performed on all the materials studied at different temperatures. The decrease of diffusion coefficients with increasing water content together with the microscopic analysis of the fracture surfaces demonstrated good filler/matrix adhesion for all the four composites. The decrease of water diffusion coefficients with time for Miradapt, Silar and Adaptic has been explained on the base of the presence in the polymeric networks of different density regions due to inhomogeneous polymerization. This hypothesis is also in line with the Miradapt, Silar and Adaptic hysteresis phenomena observed in the sorption/desorption cycles.
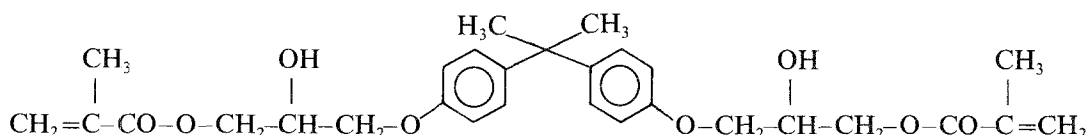
1. Introduction

Since their introduction [1] the bis-GMA (bisphenol-glycidilmethacrylate) based composites have gained increasing applications as restorative materials in dentistry.

Most of the commercial products consist of the same basic resin, different diluents and fillers of various nature, geometry and content in order to obtain the following main specifications:

1. long term dimensional stability [2]
2. low water sorption
3. low polymerization shrinkage [3]
4. reduced release of low molecular weight substances [4]
5. good surface finishing and colour stability [5].

The high viscosity of the basic monomer (1500 poise)

However fillers of different nature, geometry, size and content are used. Different classes of composite materials can be distinguished:

1. conventional composites which contain 70 to 85 wt % quartz, silica or silicates having dimensions around $20 \mu m$ [6],
2. microfine composites, containing up to 50 wt % pirolytic silica of very fine particle size ($< 1 \mu m$) [7],
3. hybrid composites, containing microsize (0.04–0.2 μm) and macrosize (8–25 μm) particles,
4. intermediate composites with fillers with dimension 1–5 μm.

In spite of their excellent finishing properties, the microfine show properties strongly dependent on the resin behaviour, such as high water sorption (about 2 wt %) [8] and lower mechanical properties compared

necessitates the use of diluents such as polyethylenglycoldimethacrylates, bisphenoldimethacrylate, methylmethacrylate etc.

They reduce the high viscosity of the basic monomer and increase the final degree of conversion of the thermosetting resin.

On the other hand, diluents increase the already high water sorption characteristics of bis-GMA resin together with the release of low molecular weight molecules.

In most of the commercial composites about 30 wt % diluents are used.

with conventional composites. Many papers on water sorption in dental filling materials have been published. Water sorption has been studied in terms of diffusion coefficients, equilibrium uptake and solubility in the unfilled polymer [9] and in the composites (i.e. [8, 10–12]).

More, effects of water such as dimensional change of composites [13], leaking and degradation of fillers [14, 15] have been investigated.

In this paper, the water ageing of several composites has been studied and a model to explain the parameters obtained has been proposed. The exposure of the resin

and composites to water at different temperatures induces modifications in the mechanical properties. The loss of low molecular weight components initially present in the resins, plays a role in the embrittlement of the samples.

2. Experimental details
2.1. Materials
In Table I the compositions of the tested dental composites are reported with commercial names and producers. From thin layer chromatography analysis it has been found that all the products contain bis-GMA as base resin. The diluents belong to the class of polyethylenglycoldimethacrylates [16]. The composition, content, surface area and size distribution of inorganic fillers were determined, respectively, by means of emission spectrometry, ashes analysis, BET tests and sedigraph methods.

Each commercial product is supplied in two components: the catalyst and the activator. The catalyst contains matrix, filler and a peroxide (benzoyl peroxide), the activator contains matrix, filler and an aromatic amine as N, N-diethanoilparatoluidine. To polymerize the product the two components have to be mixed in a $1:1$ ratio. The setting time ranges between 4 to 6 min at room temperature.

2.2. Methods
DSC measurements have been performed by using a differential scanning calorimeter Perkin Elmer DSC-7 with a scanning rate of $10°C\,min^{-1}$. Water sorption and desorption kinetics have been determined on samples of $0.045 \times 3 \times 0.5\,cm^3$ prepared with the following procedure.

The mixture of the two components was polymerized in a "Mylar" mould at room temperature for 15 min. All the samples had a first conditioning cycle in distilled water at $60°C$ followed by desorption under vacuum at $60°C$, until constant weight was attained.

Sorption and desorption experiments have been performed on the previous samples first immersed in water up to constant weight and then suspended on silica gel, at temperatures ranging between 37 and $60°C$.

The fracture surfaces of these samples have been analysed by using a scanning electron microscopy Cambridge Stereoscan model 604.

The flexural mechanical properties have been measured in air at room temperature ($25°C$, 50% R.H.) by using an Instron machine on samples previously aged in water at $37°C$ for 3, 15 and 60 days. Tests were performed on samples $4 \times 0.5 \times 0.2\,cm^3$ at a crosshead speed of $0.1\,cm\,min^{-1}$.

3. Results and discussion
3.1. Calorimetric analysis
DSC diagrams of Miradapt, after different times of immersion in water at $37°C$ are shown in Fig. 1. The results obtained with the other materials investigated are very similar.

The sample aged for 10 min (Curve a) shows a wide exothermic peak associated with the residual curing of the unreacted low molecular weight components. The exposure in a liquid environment at $37°C$ for 60 days (Curve c) strongly reduced the exothermic peak and increased the temperature of molecular mobility of the resin in the composites [17]. The shift of the molecular mobility temperature may be related to both the residual curing of the resin achieved during the ageing, and to the desorption of partially bonded or free low molecular weight components, which may be initially present in the resin acting as plasticizers.

3.2. Diffusion
In Fig. 2 the quantities M_i, M_o, M_g, M_{ga}, M_1, M_{la}, M_r, used in this work are defined.

In Figs 3 to 6 data related to the water sorption and desorption experiments are reported for the four materials Miradapt, Profile, Silar and Adaptic. The data are plotted against the square root of time

TABLE I Composition and characteristics of tested composite resins

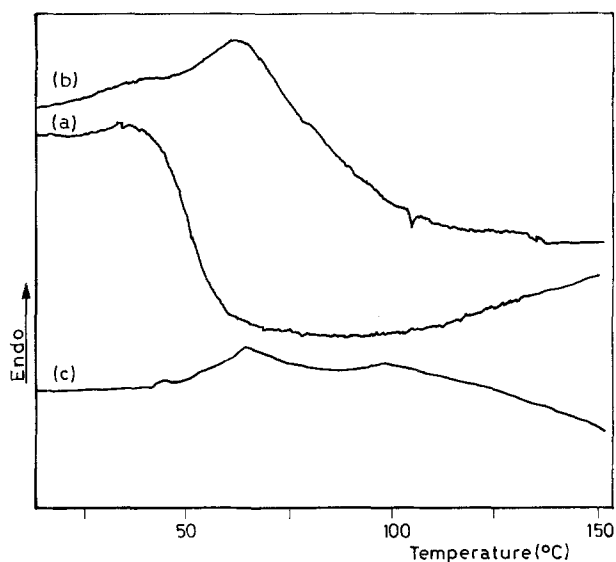|	Product name			
	Adaptic	Miradapt	Profile	Silar
Manufacturer	Johnson & Johnson	Johnson & Johnson	S. S. White	3M Company
Filler type	Quartz	Barium aluminium silicate	Strontium silicate	Pyrolitic silica
Filler content (wt %)	77.4	81.0	81.7	50.0
Surface area ($m^2\,g^{-1}$)	0.92	0.37	0.97	–
Average diameter (μm)	17.9	17.0	15.8	–
Filler size (μm)				
S 95	40	40	26	–
S 60	25	20	18	–
S 10	6	16	14	–

Figure 1 DSC thermograms for Miradapt after (a) 10 min, (b) 24 h and (c) 60 days of immersion in water at $37°C$.
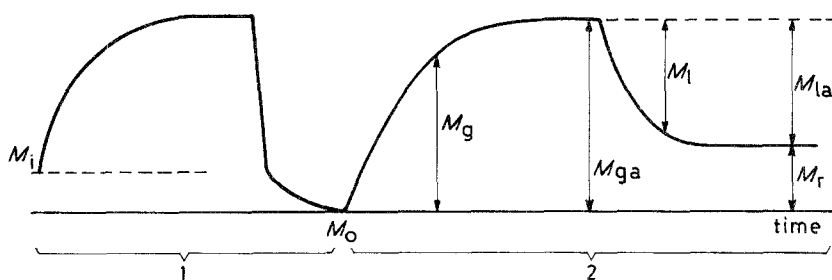
Figure 2 Schematic diagram of the sorption and desorption kinetics showing the nomenclature used. (1) First sorption/desorption cycle at 60° C, (2) second sorption/desorption cycle at different temperatures.

divided by the thickness ($\sqrt{t}/l$) and in all diagrams, an initial linear behaviour is evident. This suggests that both sorption and desorption phenomena are controlled by the Fickian diffusion [18].

In Tables II and III sorption (D_s) and desorption (D_d) diffusion coefficients and M_{ga}, M_{la} and M_r values are reported for the four materials studied.

Assuming a constant diffusion coefficient and by means of Crank's methods an apparent diffusion coefficient D_a, was obtained from the initial slope of the sorption curves and the equilibrium value of the water uptake. On the basis of equation [19]:

$$\frac{M_g}{M_{ga}} = 1 - \frac{8}{\pi^2} \sum_0^\infty \frac{1}{(2m + 1)^2}$$
$$\times \exp\left\{ - \frac{D(2m + 1)^2\pi^2 t}{l^2} \right\} \quad (1)$$

an analytical curve was obtained, where l is the thickness of the specimen and D is the constant diffusion coefficient.

For $M_g/M_{ga} > 0.5$ Equation 1 can be simplified as follows:

$$\frac{M_g}{M_{ga}} = 1 - \exp\left[-7.3 \left(\frac{Dt}{l^2}\right)^{0.75} \right] \quad (2)$$

with $D = D_a$.

The theoretical curves are reported with experimental data in Figs 3 to 6.

They indicate:

1. no deviations from ideality are observed as a consequence of filler/matrix debonding. In fact this last phenomenon would be characterized by an increase of water uptake with increasing of sorption temperatures. On the contrary a decrease of water uptake with temperature has been observed. Furthermore the electron micrographs of samples sections after the sorption cycles at 60° C do not show any evidence of filler/matrices debonding for all the four materials (Fig. 7).

2. Silar, Miradapt and Adaptic sorption diffusion coefficients are concentration dependent. This phenomenon is more evident at low temperatures (diffusion coefficients decrease with increasing water concentration).

3. Theoretical curves fit perfectly Profile experimental data over all the sorption isotherms at 37, 48 and 60° C.

4. The desorption isotherms at the different temperatures give a completely Fickian behaviour.

5. Hysteresis phenomena ($M_{la} < M_{ga}$) are evident for Silar, Miradapt and Adaptic sorption/desorption cycles particularly at 37° C.

As reported in the experimental section, all the materials studied differ in the filler nature (Silar also differs in filler content) while are similar in the matrix composition. They are constituted in fact of about 70% (w/w) of bis-GMA and 30% (w/w) of diluents
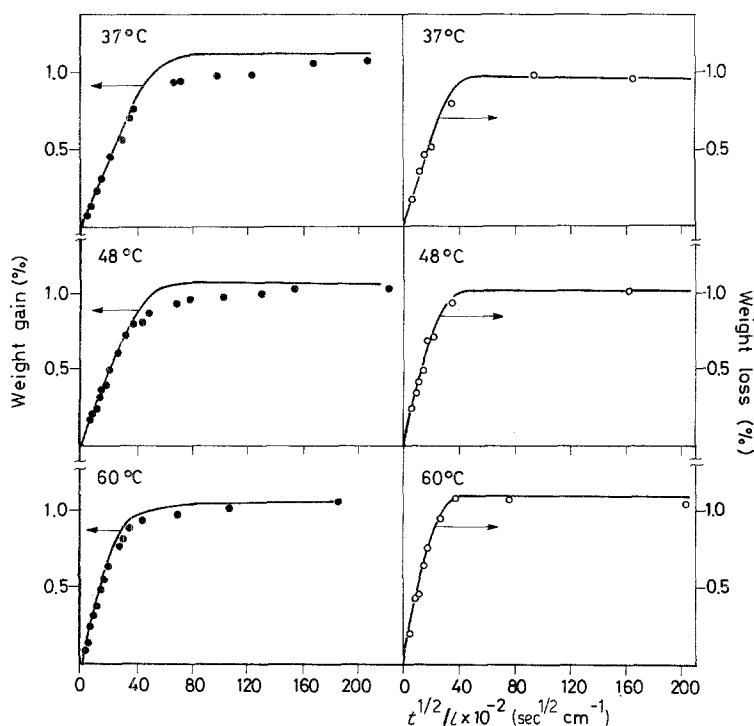

Figure 3 Miradapt sorption (●) and desorption (○) kinetics at different temperatures.

TABLE II Sorption (D_s) and desorption (D_d) diffusion coefficients for composite dental materials at different temperatures

	$D_s \times 10^8$ cm^2 sec^{-1}			$D_d \times 10^8$ cm^2 sec^{-1}		
	37° C	48° C	60° C	37° C	48° C	60° C
Adaptic	0.497	1.11	2.06	–	1.16	2.57
Miradapt	0.711	1.02	2.55	1.58	2.30	3.20
Profile	0.440	0.989	2.94	0.827	1.19	3.29
Silar	0.875	1.74	3.25	1.11	2.00	3.52

of the class of polyethylenglycoldimethacrylates; therefore the methacrylic matrix is highly crosslinked. The sorption kinetics reported are similar to those relative to PMMA [20, 21].

Various interpretations can be found to explain the decrease of diffusion coefficient with increasing water content.

For example Barrie and Platt [20] attributed such a behaviour to two possible phenomena:

1. cavities normally present in glassy polymers in which penetrant molecules are sorbed preferentially with little disturbance of the surrounding polymer matrix. Clustering of the water molecules in this case may be expected to develop easier in these cavities than in the denser regions of the matrix where some degree of expansion would be necessary.

2. Polar groups which may act as nuclei for clusters formation.

Roussis [21] also noticed the concentration dependence of water vapour diffusion coefficient in PMMA. He observed that of all sorption kinetic models tested, the most successful was that based on molecular relaxation. This model however cannot explain satisfactorily the behaviour of the matrices studied in the present work.

The dependence of the diffusion coefficient on water content does not seem to be related to the chemical nature of the matrices. The Profile sorption curves suggest motivations not intrinsic to the matrices nature but could be tied to their physical state which is influenced by the conditions used during the radical polymerization.

In fact, extremely short setting times, variable filler nature that affects the reaction heat dissipation, probable inhomogeneity in catalyst distribution etc., could easily result in differently crosslinked distribution in the examined matrices. That means that for both t and $M_g \to 0$ the experimentally measured diffusion coefficient approaches the average value of the diffusion coefficients of the region of low crosslinking density and successively decreases when water molecules start to penetrate the highly crosslinked regions.
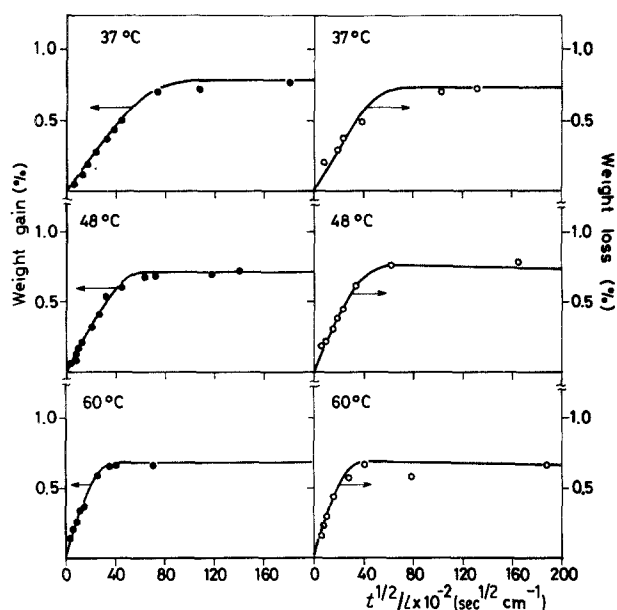

Figure 4 Profile sorption (●) and desorption (○) kinetics at different temperatures.

As an example, it is possible to apply a model utilized by Wong and Broutman [22, 23] to explain the diffusion mechanism of water in glassy epoxy resins on the basis of a free volume change. The model considers only two different regions:

Region 1, is a region with a lower crosslinking density characterized by D_1 diffusion coefficient.

Region 2, is a region of high crosslinking degree characterized by D_2.

In a sorption process, assuming that the molecular populations sorbed into the two regions are always in local equilibrium, then the total concentration, M_g, and the total flux, J, may be written as:

$$M_g = M_{g1} + M_{g2} \qquad (3)$$

$$J = -D_1 \frac{\partial M_{g1}}{\partial x} - D_2 \frac{\partial M_{g2}}{\partial x} \qquad (4)$$

with D_1 and D_2 constant. If $M_{g1} = F(M_g)$

$$D_s = D_1 F'(M_g) + D_2[1 - F'(M_g)] \qquad (5)$$

where D_s is the resulting diffusion coefficient.

Assuming that at low concentration, water molecules are predominantly concentrated in the region of lower crosslinking density, this implies:

$F'(M_g) = 1$ at low concentrations ($M_g \to 0$)

$F'(M_g) < 1$ at high concentrations when the contribution of the dense region becomes significant
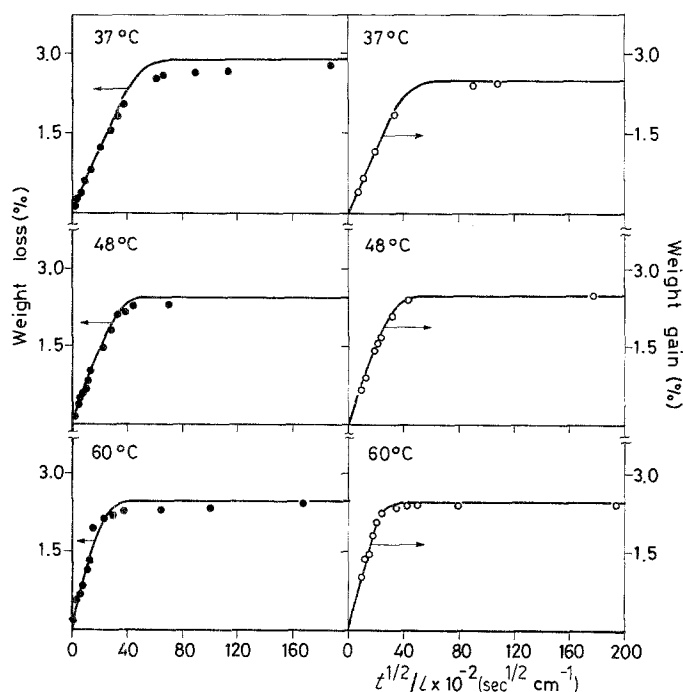
Since $D_1 > D_2$ from Equation 5 it can be deduced

TABLE III Equilibrium water gain (M_{ga}) equilibrium water loss (M_{la}) and water content (M_r) at different temperatures

	M_{ga} (%)			M_{la} (%)			M_r (%)		
	37° C	48° C	60° C	37° C	48° C	60° C	37° C	48° C	60° C
Adaptic	1.10	1.04	1.04	–	0.89	1.03	–	0.15	0.01
Miradapt	1.11	1.08	1.00	0.95	1.01	1.00	0.16	0.07	0
Profile	0.79	0.73	0.70	0.73	0.77	0.70	0.06	−0.04	0
Silar	2.89	2.44	2.46	2.42	2.40	2.41	0.47	0.04	0.05

that D_s should be almost constant one, $D_s \approx D_1$ at low concentrations and subsequently decreases with increasing water concentration.

This model is obviously a simplified one because it assumes only two differently crosslinked zones for the examined matrices; while a realistic model should take into account a wide distribution of crosslinking density. However it qualitatively explains the kinetic curves of materials characterized by regions of different crosslinking density.

This assumption is in accordance with the different behaviours of the examined products during the sorption process.

In particular the ideal behaviour of Profile sorption curves at all the temperatures studied can be attributed to a higher crosslinking homogeneity.

Desorption kinetics, as above indicated, show hysteresis phenomena ($M_{la} < M_{ga}$) [24] more evident for the products which give pseudo Fickian diffusion curves strongly deviating from the ideal behaviour. The assumption of materials not homogeneously crosslinked containing high density regions able to trap residual water can well explain this behaviour.

In desorption experiments for all the four examined materials an excellent fitting of the experimental data with Crank equation (Equation 1) is obtained using the apparent asymptote M_{la}.

That means that regions at low crosslinking degree start to desorb water while the water M_r trapped in the high crosslinked regions is released much more slowly.

Moreover the four examined materials give residual water contents M_r ranging between 0 and 20% not-
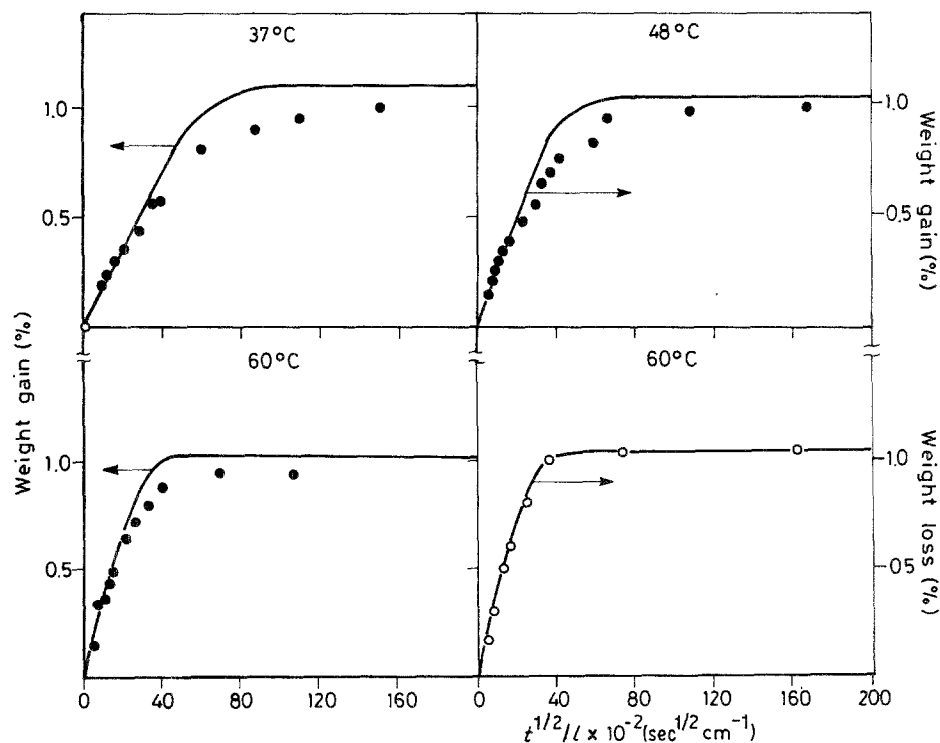

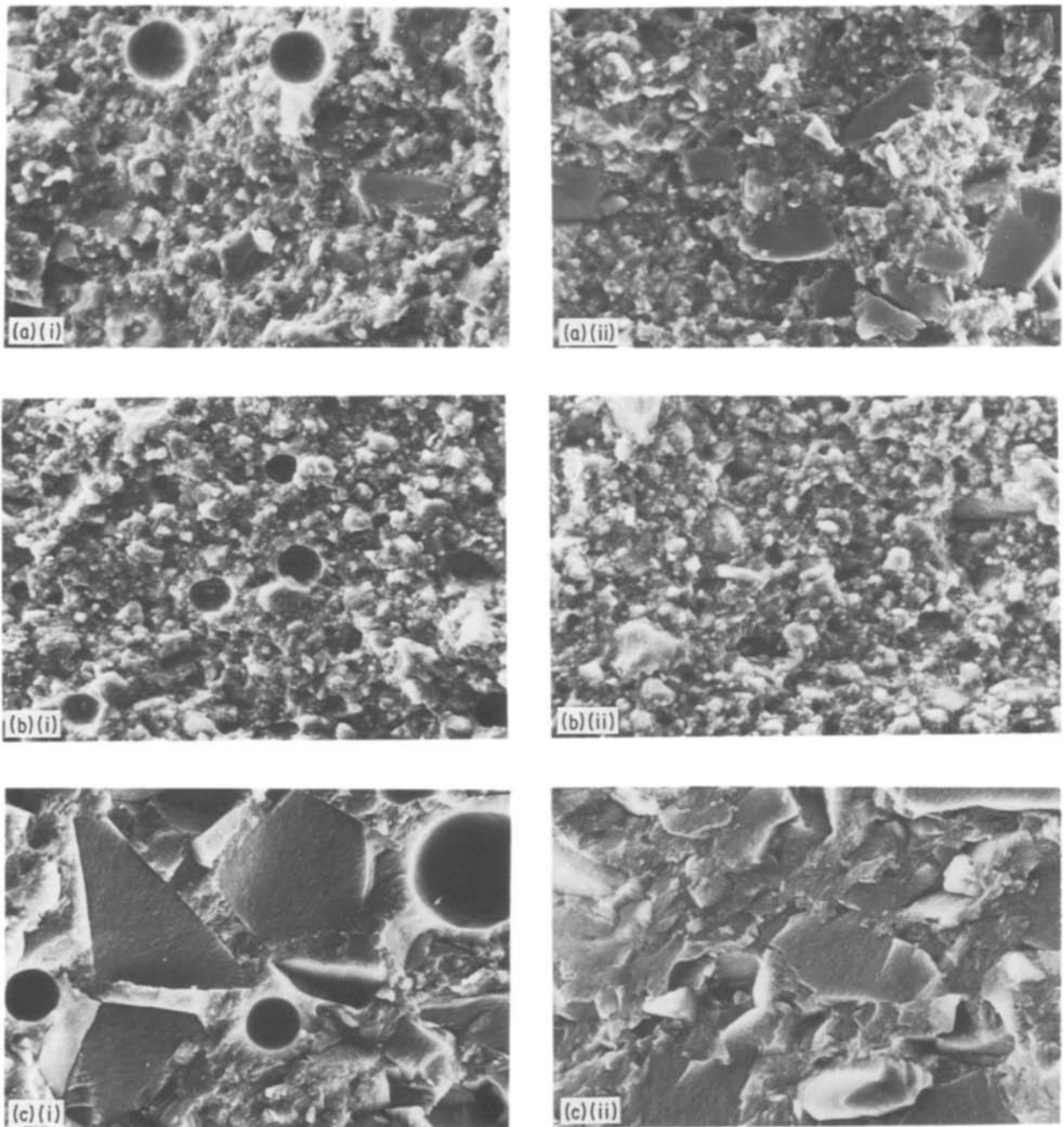*Figure 6* Adaptic sorption (●) and desorption (○) kinetics at different temperatures.

Figure 7 Electron micrographs of samples sections before and after sorption at 60°C. (a) Miradapt samples, (b) Profile samples, (c) Silar samples, (i) as-prepared, (ii) water aged.

withstanding the similar matrices, the comparable filler amounts, thickness and desorption times.

The activation energies of water transport in the different materials have been calculated, from D against temperature data, through the Arrhenius equation (Fig. 8 and Table IV).

In sorption experiments the activation energies of water transport are practically the same for Silar, Adaptic and Miradapt; the activation energy of Profile results higher. Because the activation energies (E_{as}) are calculated by D_s values obtained from the early-stage of the sorption curves, Silar, Miradapt and Adaptic activation energies refer to the less densely crosslinked regions.

Due to the ideal behaviour of Profile, the experimental D_s corresponds to the average value of the homogeneous region.

Therefore the higher Profile activation energy for water transport can reasonably suggest that the cross-linking degree of its homogeneous region is higher than the crosslinking degrees of the less dense regions 1 of Silar, Miradapt and Adaptic.

The desorption diffusion coefficients D have been calculated from the apparent asymptotic values M_{la}. Substituting M_{la} with M_{ga} the desorption coefficients sensibly decrease particularly for the products at high sorption/desorption hysteresis.

The activation energies of water desorption have been obtained by means of D_d calculated from the apparent asymptotic value M_{la}.

Desorption activation energy for Profile is lower than sorption activation energies. In fact in this case an overestimation of D_d is excluded because M_{la} always coincides with M_{ga} in all the range 37 to 60° C.

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TABLE IV Water sorption (E_s) and water desorption (E_d) activation energies

	E_s (kcal mol^{-1})	E_d (kcal mol^{-1})
Adaptic	12.36	–
Miradapt	11.52	6.27
Profile	15.75	12.27
Silar	11.36	10.40

It is possible to explain qualitatively this behaviour with small plasticization effects due to an increased segmental mobility of the acrylic network upon sorption of water. All the experimental data above related are in accordance with the assumption of polymeric matrices constituted by a different density regions distribution created from a not homogeneous crosslinking.

Such an hypothesis however does not exclude cavities normally present in glassy polymers in which penetrant molecules are absorbed preferentially with little disturbance of the ambient polymer matrix [20].

3.3. Mechanical properties
Flexural mechanical properties have been determined in samples aged in water at 37° C for 3, 15 and 60 days. Data are reported in Table V.

TABLE V Flexural modulus, E (kgcm^2), at different immersion times in water at 37° C and weight loss (ml) and water uptake (mt) after 60 days

	Immersion time (days)			ml (%)	mt (%)
	3	15	60		
Adaptic	84 000	95 000	104 000	0.76	0.85
Miradapt	62 000	86 000	121 000	0.60	1.07
Profile	135 000	93 000	99 000	1.40	1.09
Silar	43 000	54 000	59 000	2.35	2.97

In the same table values of weight loss and water uptake after 60 days are also indicated. The values of water uptake do not coincide with those of Table III. Data of Table III in fact have been determined at 37° C, after a first cycle in water at 60° C on thin samples, those of Table V instead have been measured directly immediately after immersion in water at 37° C on thick samples used for the mechanical tests.

All the products examined show a dependence of Young modulus, flexural strength and elongation at break on ageing time. Adaptic, Miradapt and Silar show an increase of all those parameters.

In accord with sorption kinetics and DSC measurements the embrittlement of the materials can be related mainly to an antiplasticization effect due to incoming water and outcoming monomers [17].

4. Conclusions
Four commercial dental composites have been studied. They consist of a matrix based on bis-GMA resin incorporating fillers of different types.

Differential scanning calorimetric diagrams of the examined materials after different times of immersion in water show a small residual monomer reactivity which disappears after 60 days of immersion.

Water plasticization and monomer loss could be the two reasons for such a phenomenon. The embrittlement of these materials on ageing time in water has been detected from flexural mechanical properties. This behaviour has been explained with the loss of low molecular weight components initially present in the resins.

Water sorption/desorption experiments have been performed on the four materials at three different temperatures. On the basis of the decrease of M_{ga} values (Fig. 2) with increasing of temperature and of the microscopic analysis of the fracture surfaces, the filler/matrix debonding effect has been excluded.

Acknowledgement

Figure 8 Arrhenius plots. Water sorption (●), water desorption (○). (a) Miradapt, (b) Profile, (c) Silar.

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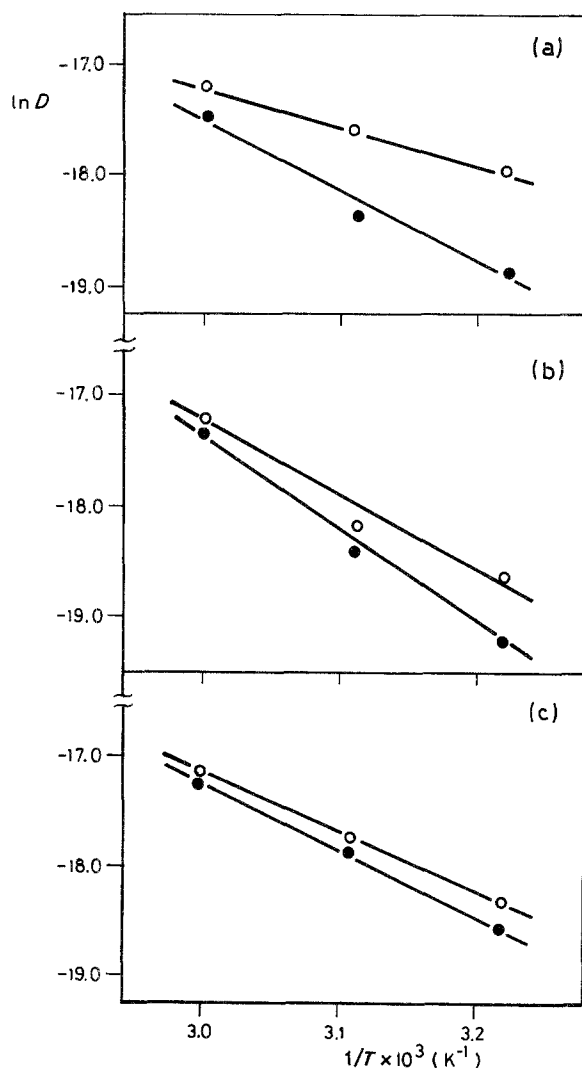
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