

Comparison of water sorption by methacrylate and dimethacrylate monomers and their corresponding polymers

S. Kalachandra* and R. P. Kusy

Dental Research Center, University of North Carolina, Chapel Hill, NC 27599-7455, USA
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Water sorption of some glycol dimethacrylate and methyl methacrylate monomers was determined by Karl Fischer analysis. After γ -irradiation, the corresponding polymers were characterized in terms of percentage water uptake (gravimetrically), diffusion coefficient (D), and contact angle (θ) measurements. Water sorption of the polymers approximated Fick's law. Ignoring the double bond contribution, the weight per cent oxygen content (WPO), which is indicative of hydrophilic character of these materials, was calculated and correlated with the total oxygen content present in each monomer molecule. A linear relationship between the WPO and percentage water uptake was observed in a series of four glycol dimethacrylate and eight linear methyl methacrylate monomers. Their corresponding polymers conformed to a linear correlation between the WPO and θ . On the basis of its WPO, one dimethacrylate monomer (BIS-GMA) sorbed less water than expected because an intramolecular hydrogen bond was present. The rapid initial rates observed in soft methyl methacrylate polymers were attributed to the water soluble impurities present in the matrix. The D values of the networks based on difunctional methacrylates were generally lower than methyl methacrylates, presumably because of the highly crosslinked nature of the former.

(Keywords: water uptake; diffusion coefficient; contact angle; oxygen content; hydrophilicity; intramolecular hydrogen bonding; methacrylates; dimethacrylates)

INTRODUCTION

Predicting the water sorption of a glassy polymer at a given temperature, based on its structure, has not been properly understood. Presumably one of the most important factors is the hydrophilicity of constituent groups of atoms and bonds. Hydrophilicity has been investigated in other contexts, because of its importance in biochemistry¹ and chemistry. From the study of several hundred organic compounds, hydrophilicity is, to a first approximation, an additive property. However, deviations can arise through interactions between groups of atoms². While these studies offer hope that general predictive principles will be developed, it would be more appropriate to study the solubility of water in organic compounds than to extend the solubility studies of organic compounds in water. Empirical affinities of organic compounds and functional groups for watery surroundings are of practical concern to researchers, who find it useful to refer to certain compounds or groups as being relatively hydrophilic or hydrophobic. In attempting to understand the origins of these differences in hydrophilic character, the relative numbers of atoms present in each solute that might be expected to form hydrogen bonds in water require consideration.

Pauling's simple hypothesis, that one molecule of water is sorbed per designated polar group, works only for undenatured globular proteins³⁻⁵. More general treatments, based on thermodynamics of mixing and on cohesion parameters⁶⁻⁸, are inadequate for glassy polymers. Moreover, additional factors must be considered, for example those which relate to molecular

packing^{9,10}. Crosslinking has produced a marked increase in water sorption in copolymers of methyl methacrylate and dimethacrylate^{11,12}.

The present work compares the water uptake and contact angle measurements of glycol dimethacrylate and methyl methacrylate monomers and polymers. The following two hypotheses have been proposed: (1) that the relative uptake of water by the polymers is determined primarily by the hydrophilicity of constituent atomic groups from the monomers; and (2) that the experiments involving determination of water uptake and water-polymer contact angle normally interpreted as indicative of hydrophilic interactions, can be correlated to a simpler index, namely the weight per cent oxygen content (WPO). This paper tests the second hypothesis, which is believed to be a new approach to the problem of hydrophilicity. The term hydrophilicity is used as an index to compare the observed increase in water uptake of monomers and polymers as well as the decrease in contact angle (θ) for water on polymeric surfaces with increase in the polar content, i.e. WPO.

EXPERIMENTAL

Some of the materials consisted of a series of diluting monomers (*Figure 1*). In all, 20 monomers were selected because of their potential use in biomaterials, especially in dental materials (*Table 1*). The purest monomers were sought from commercial sources, which contained <1% water and only minor amounts of hydrophilic impurities. Some of the monomers were purified with 5% solutions of sodium hydroxide to remove the inhibitors. The organic layer was separated, dried over anhydrous

* To whom correspondence should be addressed

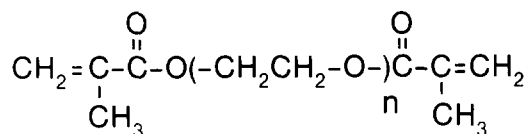


Figure 1 General structure of diluting difunctional methacrylate monomers

Table 1 Monomers investigated

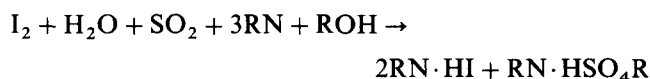
Monomer	Abbreviation	Source ^a
Ethylene glycol dimethacrylate	EGDM	A
Diethylene glycol dimethacrylate	DEGDM	A
Triethylene glycol dimethacrylate	TEGDM	B
Tetraethylene glycol dimethacrylate	tet-EGDM	C
Neopentyl glycol dimethacrylate	NPGDM	D
Trimethylol propane trimethacrylate	TMPTM	D
Bisphenol-A-bis(2-hydroxypropyl) methacrylate	BIS-GMA	C
Ethoxylated bisphenol A dimethacrylate	E-BIS-GMA	D
Methyl methacrylate	MMA	D
Ethyl methacrylate	EMA	B
n-Propyl methacrylate	n-PMA	C
iso-Propyl methacrylate	iso-PMA	D
n-Butyl methacrylate	n-BMA	B
iso-Butyl methacrylate	iso-BMA	B
t-Butyl methacrylate	t-BMA	C
n-Hexyl methacrylate	n-HMA	D
n-Decyl methacrylate	n-DMA	D
iso-Decyl methacrylate	iso-DMA	B
n-Tridecyl methacrylate	tri-DMA	D
n-Octadecyl methacrylate	octa-DMA	D

^aA = Esschem Co., Essington, PA, USA; B = Aldrich Chemical Co., Milwaukee, WI, USA; C = Polysciences, Inc., Warrington, PA, USA; D = Scientific Polymer Products, Ontario, NY, USA

calcium chloride, and finally distilled under reduced pressure to obtain fairly dry monomers. Constant proportions of dry monomers were equilibrated with triple distilled water. A portion of each monomer was polymerized by a 6 h exposure to a ¹³⁷Cs γ -ray source (dose rate = 0.8 Mrad h⁻¹; ambient temperature = 35°C) in nitrogen atmosphere.

Water uptake by monomers

The Model 447 Coulomatic K-F Titrimeter (Allied Fisher Scientific, Raleigh, NC) was used to determine the moisture content of monomer samples by automatic titration with coulometrically generated Karl Fischer reagent. In this technique, one molecule of iodine reacts with one molecule of water in the presence of sulphur dioxide, an organic nitrogen base, and an alcohol:



Liquid monomer (10 g) was thoroughly shaken with triple distilled water (50 g) and centrifuged after overnight storage at 37°C.

Samples (50–100 μl) were analysed to obtain reproducible values. In some mixtures, especially where the density of monomer was close to that of water, separation problems occurred. In such cases, measurements were made after saturation with water vapour at 37°C.

Water uptake by polymers

Water uptake by the corresponding polymers was

determined gravimetrically. The specimens (1.4 cm diameter \times 0.1 cm thickness) were placed at 37°C in triple distilled water. This temperature was selected in view of their possible use as biomaterials. As described in our earlier work^{13,14}, the specimens were periodically removed, mopped dry and weighed. This was continued until a constant weight was attained.

Samples immersed in triple distilled water increased in weight until apparently constant values were attained after a period of several days. Although such stationary values are used in the present work, a slow decrement in weight was detected upon prolonged immersion and attributed to the leaching out of residual monomer. This effect may also be a factor in accounting for the observation that estimates of water uptake by desorption are generally greater than values estimated by sorption. In the present work, uptake of water is estimated more reliably from desorption data. A sufficient number of samples (two or three) were tested, which gave values in satisfactory agreement, and the mean values were reported.

The rates of desorption and sorption were analysed using the conventional solutions to Fick's laws of diffusion for a plane sheet geometry¹⁵:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2\pi^2 Dt}{4l^2}\right] \quad (1)$$

$$\frac{M_t}{M_\infty} = 2(Dt/\pi l^2)^{1/2} \quad (2)$$

where M_t and M_∞ are the masses of water sorbed or desorbed at times t and ∞ , respectively, and $2l$ is the thickness of the specimen.

Measurement of contact angle

A contact angle goniometer (Model 100-00, Rome-Hart, Mountain Lakes, NJ) was used to measure the advancing contact angle (θ) of a droplet of triple distilled water on polymeric surfaces^{16–18}.

Weight per cent oxygen content

The weight per cent oxygen content (WPO), which is one indication of the hydrophilic character of the present monomers, was calculated on the basis of total oxygen content present in each monomer molecule. WPO content was chosen to correlate with weight per cent water uptake instead of another measure of oxygen content (such as mole per cent) so that the weight or number of atoms in that part of the monomer which does not bind water would not influence the results. The assumption was made that all of the oxygen atoms present in the molecule are involved in imparting the hydrophilic character to the monomer molecule. Additionally, the contributions from the double bonds in the monomers to the hydrophilicity are presumed to be insignificant.

Nuclear magnetic resonance

The n.m.r. spectra (¹³C and ¹H) were obtained on a General Electric GN-300 spectrometer. Deuterated solvents were used, chloroform-d (Isotec Inc.) and dimethyl sulphoxide-d₆ (Merck, Sharp, and Dohme).

RESULTS

The data conformed experimentally to equation (2) (Figure 2). The higher rate of desorption was similar to that reported previously in studies of poly(MMA) alone, at room temperature and was attributed to the dependence of the diffusion coefficient on water content¹⁹. In order to avoid complications arising from the leaching of residual monomer, more reliance was placed on values of *D* calculated from desorption data

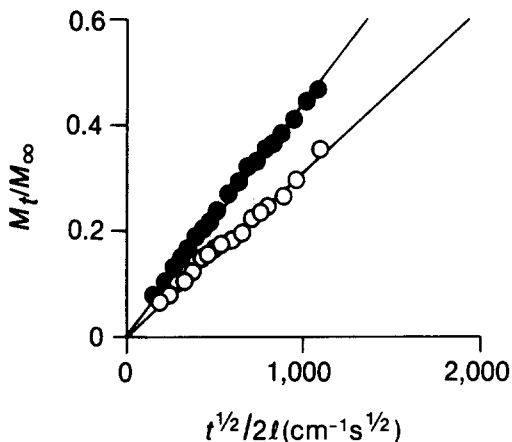


Figure 2 Kinetics of sorption (○) and desorption (●) of poly(TEGDM) at 37°C

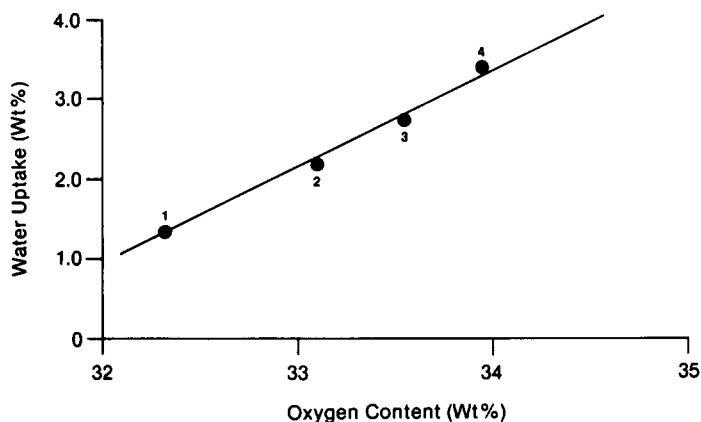


Figure 3 Linear relationship between oxygen content of glycol dimethacrylate monomers and their water uptake. 1, EGDM; 2, DEGDM; 3, TEGDM; 4, tet-EGDM

at 37°C, for which duplicate runs agreed within a few per cent. Figure 3 (columns 2 and 3 of Table 2) represented a linear relationship between WPO of four glycol dimethacrylate monomers and their per cent water uptake at 37°C. Figure 4 (columns 2 and 6 of Table 2) represents a linearity between WPO and the values of contact angle of water on the four glycol dimethacrylate polymer surfaces at 37°C. In Figure 5 (columns 2 and 3 of Table 3), all the eight normal monomers conformed to a linear relationship between their WPO and water uptake. A similar linear correlation was observed between the values of WPO and θ for the corresponding normal polymers (Figure 6). Table 4 compares the properties of n-PMA, n-BMA and n-DMA monomers and their polymers to their corresponding isomers.

DISCUSSION

In order to interpret the relationship between molecular structure and the WPO of monomers and corresponding

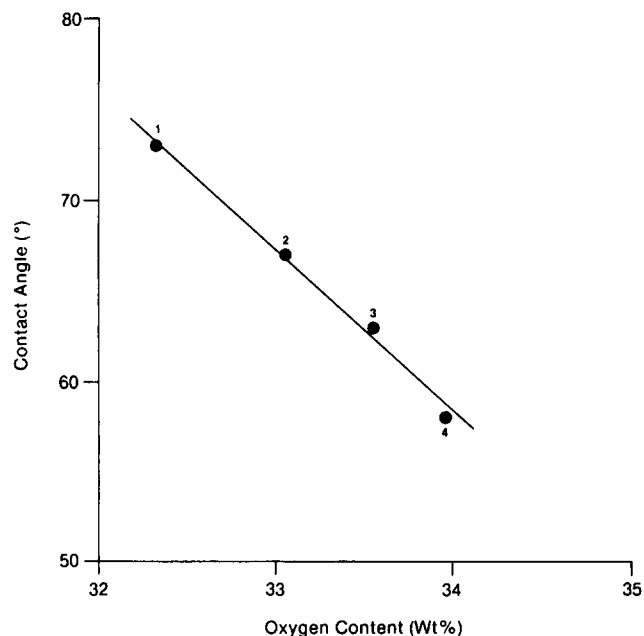


Figure 4 Linear relationship between oxygen content of glycol dimethacrylate polymers and their contact angle (θ) of water on the polymeric surfaces. 1, Poly(EGDM); 2, poly(DEGDM); 3, poly(TEGDM); 4, poly(tet-EGDM)

Table 2 Properties of some glycol dimethacrylate monomers and their corresponding polymers

Monomer	Weight per cent oxygen content (WPO)	Water uptake (%) ^a		Diffusion coefficient ^a $D \times 10^8$ (cm ² s ⁻¹)	Contact angle θ for water on polymer (degrees)
		Monomer	Polymer		
EGDM	32.3	1.03	3.21	9.3	73
DEGDM	33.1	2.24	5.32	5.6	67
TEGDM	33.5	2.74	6.22	3.6	63
tet-EGDM	33.9	3.39	7.75	3.3	58
NPGDM	26.7	0.63	1.38	8.4	61
TMPTM	28.4	0.74	1.44	5.5	54
BIS-GMA	25.0	2.35	1.40	3.3	66
E-BIS-GMA	21.2	2.60	0.50	8.4	55

^aMeasured in desorption at 37°C

polymers in quantitative terms, the per cent water uptake, diffusion coefficients (D) of water in polymers, and θ were measured. Although the WPO of monomers (or more specifically, the ratio of the weight of number of oxygen atoms to the total weight of the monomer unit) is an additive property, deviations are expected to occur through interactions between groups of atoms. For macromolecules, the amount of water taken up depends on the concentration of hydrophilic groups and their

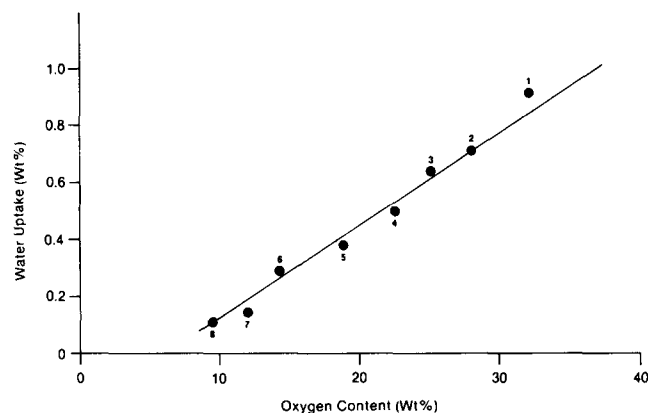


Figure 5 Linear relationship between oxygen content of normal methacrylate monomers and their water uptake. 1, MMA; 2, EMA; 3, n-PMA; 4, n-BMA; 5, n-HMA; 6, n-DMA; 7, tri-DMA; 8, octa-DMA

accessibility. Moreover, with glassy polymers, water may be accommodated by processes which are accompanied by little or no increase in volume of the polymer specimen. The nature of such processes has long been a matter of

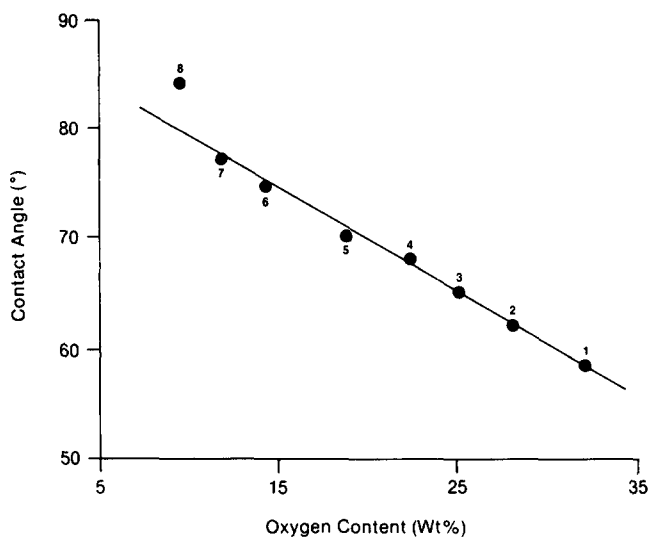


Figure 6 Linear relationship between oxygen content of normal methacrylate polymers and their contact angle (θ) of water on the polymeric surfaces. 1, Poly(MMA); 2, poly(EMA); 3, poly(PMA); 4, poly(BMA); 5, poly(HMA); 6, poly(DMA); 7, poly(tri-DMA); 8, poly(octa-DMA)

Table 3 Properties of some methyl methacrylate monomers and their corresponding polymers

Monomer	Weight per cent oxygen content (WPO)	Water uptake (%) ^a		Diffusion coefficient ^a $D \times 10^8$ ($\text{cm}^2 \text{s}^{-1}$)	Glass transition temperature T_g ($^{\circ}\text{C}$)	Contact angle θ for water on polymer (degrees)
		Monomer	Polymer			
MMA	32.0	1.03	2.3	5.1	105	58
EMA	28.0	0.71	1.0	13.9	65	62
n-PMA	25.0	0.64	0.7	18.4	35	65
n-BMA	22.5	0.49	0.9	114.0	21	68
n-HMA	18.8	0.38	6.9	519.0	-5	70
n-DMA	14.2	0.29	4.1	120.4	-60	75
tri-DMA	11.9	0.14	5.6	771.1	-43 ^b	77
octa-DMA	9.5	0.11	5.5	529.9	-100	84

^aMeasured in desorption at 37 $^{\circ}\text{C}$

^bDetermined by differential scanning calorimetry at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen in a DuPont 990 thermal analyser

Table 4 Comparison of properties of methacrylate monomers and polymers with their corresponding isomers

Polymer	Weight per cent oxygen content (WPO)	Water uptake (%) ^a		Diffusion coefficient ^a $D \times 10^8$ ($\text{cm}^2 \text{s}^{-1}$)	Glass transition temperature T_g ($^{\circ}\text{C}$)	Contact angle θ for water on polymer (degrees)
		Monomer	Polymer			
n-PMA	25.0	0.64	0.7	18.4	35	65
iso-PMA	25.0	0.83	6.9	3.9	81	75
n-BMA	22.5	0.49	0.9	114.0	21	68
iso-BMA	22.5	0.90	0.4	24.3	53	73
t-BMA	22.5	0.30	0.5	10.3	107	72
n-DMA	14.2	0.29	4.1	120.4	-60	75
iso-DMA	14.2	0.20	6.4	160.8	-44 ^b	89

^aMeasured in desorption at 37 $^{\circ}\text{C}$

^bDetermined by differential scanning calorimetry at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen in a DuPont 990 thermal analyser

discussion. More specific suggestions invoke Langmuir adsorption in 'holes' or microvoids²⁰, or saturation of a definite free volume fraction, which Adamson²¹ has estimated to be 0.025. In the case of poly(MMA) immersed in water at room temperature, swelling of the polymer only accounts for ~50% of the uptake of water. The overall mechanism of accommodation is not known²², but is believed to involve the accommodation of water in microvoids or excess free volume.

Equilibrium water uptake by dimethacrylate monomers and their polymers

The increase in water uptake by glycol dimethacrylate monomers (Figure 3 and Table 2) might be attributed to a linear increase in concentration of hydrophilic ethoxy groups, i.e. oxygen atoms. Interestingly, this increase in WPO has also resulted in a linear decrease in the θ value of the corresponding polymers (Figure 4 and Table 2). These observations are quite consistent with the expectations that the values of water uptake by monomers and their polymers and the values of θ vary with those of WPO.

Figures 3 and 4 clearly indicate an increase in water uptake with an increase in polar content. This trend breaks down, however, when the molecule is branched (with substituents) as in the case of NPGDM and TMPTM (Table 2). Branching with hydrophobic side chains probably prevents free access to water near the polar portions of the molecule. This can be a significant effect in systems of water-in-monomer in contrast to monomer-in-water.

The relative increase in water uptake by dimethacrylate polymers to their monomers (Table 2) may be attributed to the microvoids present in the polymer matrix. Similar observations were made with reference to NPGDM and TMPTM polymers although, not falling in the same homologous series, the increases in water uptake are less (Table 2). On the other hand, BIS-GMA sorbed less water than expected on the basis of its hydrophilicity. On comparing the water uptake values of the monomers BIS-GMA (WPO = 25.0%; water uptake = 2.35%) and E-BIS-GMA (WPO = 21.2%; water uptake = 2.60%), a reversal in the trend was observed which was contrary to our expectations (Table 2). Despite the fact that BIS-GMA contains a strongly hydrophilic group, that effect was reduced by the formation of an intramolecular hydrogen bond between the carbonyl oxygen and the hydrogen of the secondary hydroxyl group, (-CH-OH). This is consistent with the previous observation made with reference to hydrophobic side chains and conformational changes in proteins. The drastic reduction in the hydrophilic character of the peptide group was attributed to the formation of intramolecular hydrogen bonds, such as in the α -helical and parallel extended chain β -structures of the polypeptide chain²³.

N.m.r. was used to test the hypothesis that intramolecular hydrogen bonds are formed in BIS-GMA by identifying shifts in the ¹³C n.m.r. spectrum as a result of changes in the molecular conformation near the location of the hydrogen bond. The ¹³C n.m.r. spectrum of BIS-GMA was obtained in two deuterated solvents, dimethyl sulphoxide-d₆ and chloroform-d. The first solvent forms strong hydrogen bonds and thus suppresses intramolecular hydrogen bonding; the second solvent is water-insoluble and allows intramolecular hydrogen

bonds to form. Comparison of the n.m.r. spectra suggests that intramolecular hydrogen bonds do occur and that they form a seven-membered ring in several different conformations. A fuller account of the n.m.r. results is in preparation.

The decrease in water uptake by polymers (1.4% for BIS-GMA and 0.5% for E-BIS-GMA, Table 2) as compared to the monomers (2.35% for BIS-GMA and 2.60% for E-BIS-GMA, Table 2) may be attributed to inaccessibility of the hydrophilic groups during the water diffusion process and additional crosslinking probably due to intermolecular hydrogen bond formation involving -CH-OH groups between polymer chains.

The values of θ on BIS-GMA (66°) and E-BIS-GMA (55°) polymeric surfaces (Table 2) are not an expected trend based on their WPO. This suggests that the water uptake ability of BIS-GMA has been reduced by intramolecular hydrogen bond formation. Such a bond formation is not possible in E-BIS-GMA which exerts its own ability to absorb water (WPO = 21.2%).

Equilibrium water uptake by normal methacrylate monomers and their polymers

Linear trends, similar to that observed for glycol dimethacrylates, were seen in the series of normal methacrylate monomers (Table 3) and suggested a correlation between uptake of water and WPO of the monomers (Figure 5). This decrease in water uptake corresponds to the decrease in concentration of hydrophilic oxygen atoms in the series from MMA to octa-DMA. In addition, a linear relationship between θ of water on the corresponding polymeric surfaces and their WPO was observed (Figure 6). The enhanced water uptake by the polymers relative to the corresponding monomers (Table 3) may be attributed to the existence of microvoids, formed as a result of incompatible molecular packing, plus the WPO common to both monomers and polymers.

With the exception of poly(*n*-BMA), the water uptake by soft methacrylate polymers, which have T_g values well below the test temperature (37°C), was high compared with rigid methacrylates in the glassy state (Table 3). The relatively high water uptake could be attributed to the presence of water-soluble impurities that formed sites for the formation of water droplets^{24,25}. These water-soluble droplets grow in size until osmotic and elastic forces balance. This gives rise to an osmotic pressure gradient between the droplet solution and the external solution. Consequently, more water diffuses through the rubbery material into the impurity droplets. Enhanced values of D were observed in all soft methacrylate polymers with T_g values below the test temperature (37°C). Muniandy and Thomas²⁵ as well as Parker and Braden²⁴ pointed out that the natural rubber vulcanizates behave in a similar way to soft acrylics, suggesting that the phenomenon is characteristic of the elastomeric state rather than the chemical structure of the polymers.

Equilibrium water uptake by isomers of methacrylate monomers and their polymers

Analysis of the data (Table 4) reveals that structural changes seem to influence water uptake by the isomers *n*-PMA (0.64%) and *iso*-PMA (0.83%). The increased uptake by the latter suggests that it exists in a more

favourable conformation for sorption. A similar observation was made for n-BMA and iso-BMA (0.49 and 0.90% respectively, *Table 4*), suggesting that the structural changes do influence the water uptake. The lower water uptake observed for the t-BMA (0.30%) when compared with the other two isomers (0.90% for iso-BMA and 0.49% for n-BMA), might be attributed to the bulkiness of the hydrophobic t-butyl group. The n-DMA and iso-DMA isomers (0.29 and 0.20% respectively, *Table 4*) behaved contrary to the trends reported for either the PMA or BMA isomers.

Relative increases in water uptake by polymers compared with their monomers may be explained by invoking accessibility and the space filling properties of microvoids present in these polymers. Specifically, poly(iso-PMA) sorbed about 10 times more and had a diffusion coefficient (D) that was about five times less than its corresponding straight chain polymer (*Table 4*). The observed higher uptake (6.9%, *Table 4*) is perhaps due to the favourable conformation which gives better accessibility of the hydrophilic atoms. When poly(iso-PMA) and poly(iso-DMA) were compared with their normal forms, the iso-forms sorbed more water (6.9 and 6.4% respectively) than the normal forms (0.7 and 4.1% respectively). The higher water uptake by poly(iso-DMA) may be attributed to the greater swelling tendency of the matrix than that of the linear polymer and also to the presence of water-soluble impurities²⁴. The lower value of D in poly(iso-PMA) ($3.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, *Table 4*) than poly(n-PMA) ($18.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, *Table 4*) may be attributed to the tighter molecular packing of the former over the latter.

Based on this observation, θ measurements for water on the iso-forms are expected to be less than their corresponding normal forms, showing that they have more affinity for water molecules than the normal forms. Contrary to this expectation, the observed θ values for poly(iso-PMA) and poly(iso-DMA) (75° and 89° respectively) were greater than for their normal polymers (65° and 75° respectively). It is appropriate to point out here that, most often, the amount of water uptake by polymers depends on the concentration of hydrophilic groups, their accessibility to the water, the change in volume (swelling) of the polymer during sorption, and the presence of microvoids. In the cases of poly(iso-PMA) and poly(iso-DMA), the higher values of water uptake may be attributed to the swelling of the matrix. The reversal in the trend of θ values is perhaps due to the partial shielding effect of hydrophilic oxygen atoms by the folding of non-polar segments as a result of their conformational differences.

Kinetics of water sorption

Most commonly, diffusion in a glassy polymer is influenced by plasticization and by clustering of water molecules. Ample evidence shows that water does plasticize poly(MMA). For example, water depresses the glass transition temperature²⁶ in accordance with the Kelley-Bueche equation²⁷. Moreover, at room temperature considerable changes in mechanical properties occur which are consistent with a plasticizing action^{27,28}. Contrary to expectations that D should increase considerably by plasticization, the stepwise additions of water vapour to poly(MMA) specimens containing various stationary concentrations of water show that D

actually decreases. This decrease amounts to a change of a factor of ~ 0.5 as the concentration of water is increased from zero towards a saturation value of $\sim 2\%$. This trend is consistent with Crank's explanation for a rate of desorption being higher than sorption^{19,29}. Some suggest that diffusion in poly(MMA) is controlled predominantly by immobilization of water molecules in clusters^{30,31}.

The water uptake by difunctional methacrylate and methyl methacrylate polymers conformed to a diffusion-controlled process (*Figure 2* and *Tables 2, 3* and *4*). Analysis of the data in *Table 2* revealed that D values for the four glycol dimethacrylates decreased with increasing water uptake, which accounted for the protracted nature towards attaining equilibrium. This is consistent with previous findings reported by Braden *et al.*²⁹ with reference to water sorption of composite filling materials. The D values in the materials based on difunctional methacrylates (*Table 2*) were generally lower than those of methyl methacrylates (*Tables 3* and *4*) presumably because of the highly crosslinked nature of the former. Relatively larger values of D , which were observed in higher methacrylate polymers in the series (*Table 3*), may be attributed to the rubbery nature of the matrices as compared to those present in glassy polymers such as poly(MMA) ($T_g = 105^\circ\text{C}$), poly(EMA) ($T_g = 65^\circ\text{C}$), and poly(PMA) ($T_g = 35^\circ\text{C}$). The rapid initial rates observed in the case of soft methacrylates are consistent with the previous finding with reference to water sorption of methacrylate soft lining materials²⁴.

With regard to the methacrylate polymers (*Table 4*), the D values of poly(iso-PMA) ($T_g = 81^\circ\text{C}$), poly(iso-BMA) ($T_g = 53^\circ\text{C}$), and poly(t-BMA) ($T_g = 107^\circ\text{C}$) are less than their normal polymers with rubbery matrix. The observed D values may be attributed to the glassy nature of the matrix in which motion of the polymer chains in relation to each other is relatively sluggish. Since the matrix in both poly(DMA) ($T_g = -60^\circ\text{C}$) and poly(iso-DMA) ($T_g = -44^\circ\text{C}$) is in the rubbery state, changes in D values (*Table 4*) can only be attributed to their macromolecular conformation.

CONCLUSIONS

The series of four glycol dimethacrylate monomers (*Table 2*) and the eight normal methyl methacrylate monomers (*Table 3*) exhibited a linear relationship between the uptake of water and WPO.

A linear correlation was obtained between the values of contact angle (θ) and the WPO for the series of four glycol dimethacrylate polymers and for the series of eight linear methyl methacrylate polymers (*Tables 2* and *3*).

BIS-GMA monomer, which has a higher WPO (25%) than E-BIS-GMA (21.2%), sorbed relatively less water than expected (*Table 3*). This anomaly was explained on the basis of the existence of intramolecular hydrogen bonds between hydroxyl and carbonyl groups.

Water sorption of all polymers investigated conformed approximately to Fick's law of diffusion, although rapid initial rates were observed in the case of polymers having T_g values below the test temperature (37°C). This is perhaps due to the water-soluble impurities present in the matrix.

The diffusion coefficients (D) were generally lower for the networks based on difunctional methacrylates

compared with methyl methacrylates, presumably because of the highly crosslinked nature of the former (Tables 2 and 3).

Structural changes seem to influence the water uptake of certain isomers, namely n-PMA and iso-PMA (0.64% and 0.83% respectively, Table 4). A similar observation was made for the case of n-BMA and iso-BMA monomers (0.49% and 0.90% respectively, Table 4). The increased water uptake of certain isomers is perhaps due to the favourable conformation for water sorption.

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