Penetration of restorative resins into acid etched enamel. I

Viscosity, surface tension and contact angle of restorative resin monomers

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It has been a controversial question whether an intermediate layer of low-viscous, non-composite resin between composite restorative and etched enamel is beneficial. It was the purpose of the present work to investigate some of the factors that govern the penetration of resins into the capillary pores of etched enamel surfaces. Viscosity, surface tension and contact angle on human enamel were measured using monomer mixtures similar to those found in commercial restorative resins. Employing a cylindrical model of relevant dimensions of the capillary pores, and on the basis of Poiseuille's equation the time of penetration was calculated for a relatively high-viscous and a relatively low-viscous monomer mixture. It was concluded that viscosity as such is not a limiting factor for the penetration of restorative resin monomers into the pores of etched enamel surfaces.

Key-words: Dental materials; physical properties

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Since the introduction of the acid etch technique it has been a controversial question whether an intermediate layer of low-viscous, non-composite resin between composite restorative and etched enamel is beneficial. The influence of the low-viscous resin has been treated in studies on adaptation, retention strength and marginal leakage. In the following a few examples of the contradictory results will be given: *Jørgensen & Shimokobe* (1975) demonstrated that composite resins adapt themselves to etched enamel surfaces equally well as do low-viscous resins. *Mitchem & Turner* (1974) and *Adipranoto, Beech & Hardwick* (1975) found that a coating of the etched enamel with a low-viscous resin prior to application of the composite did not increase the bond strength. *Ortiz et al.* (1976) found that the application of a low-viscous resin was an insignificant factor in marginal leakage. On the other hand *Dogon* (1976) showed that the frequency and the length of tags penetrating into the etched enamel increased as the viscosity of the resin

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decreased. *Draughn* (1976) found that the application of low-viscous resin caused a 50% increase in retention. Finally, *Hembree & Andrews* (1976) and *Dogon* (1975) demonstrated that microleakage was greatly reduced or prevented only by the use of an intermediary resin of low viscosity.

To obtain a basis for an explanation of the contradictory results given above, the physical factors that govern the penetration of restorative resins into the capillary pores of the etched enamel have to be investigated. Viscosity, surface tension and contact angle are such factors. It must be emphasized that tags from composite resins never contain filler particles (*Jørgensen & Shimokobe*, 1975). This means that the penetration is mainly dependent upon the properties of the monomer component of the composite material. Accordingly, it was the purpose of the present work to measure viscosity, surface tension and contact angle on human enamel of restorative resin monomers.

MATERIALS AND METHODS

The selection of the monomer mixtures used in the investigation was based on a quantitative analysis of monomers in brands of restorative resins (*Asmussen*, 1975 and unpublished results). From the results of this analysis the monomer composition at the moment of mixing was calculated. It was found that many brands contain BIS-GMA diluted with varying amounts of TEDMA. Table I shows the composition of the monomer mixtures used in the present investigation. Where possible, the corresponding brands are given.

The study was divided in three parts in which viscosity, surface tension and contact angle, respectively, were investigated.

Viscosity

The viscosity of the monomer mixtures listed in Table I was investigated by means of a Haake-Kugelfall-Viskosimeter, type CH. The viscosimeter was described by *Höppler* (1933) and used in accordance with the instructions given by the manufacturer (Gebrüder Haake, Siemensstrasse 27, Berlin-Steglitz). For each mixture the viscosity was determined at four temperatures in the range from 22 to 37 °C. The temperatures were accurate within ± 0.1 °C. At each temperature the time of fall of the appropriate ball was measured five times by means of a stop watch with 0.1 s divisions. The mean of the five readings was used in the calculation of the viscosities. To check the possibillity of incipient polymerization during the measurements the times of fall were remeasured at the initial temperature. A possible polymerization could then be detected by an increase in the time of fall.

In order to calculate the viscosities the dentisity of each monomer mixture was determined at six temperatures in the range from 22 to 37 °C. The densities were measured by means of a 50 ml graduated flask that had been calibrated with water. The densities were estimated to be accurate within ± 1‰. The densities were plotted against temperature, and from the regression line the densities at the appropriate temperatures were obtained and used in the calculation of the viscosities.

A monomer mixture consisting of 46 mole% TEDMA and 54 mole% BIS-GMA was found to be a Newtonian liquid by means of a temporarily available rotational viscosimeter. On this basis all the investigated monomer mixtures were assumed to be Newtonian liquids.

Surface tension

The surface tension against air of the monometer mixtures A-J, L and M was measured. The surface tension of mixture N was measured under cover to minimize evaporation of MMA. In addition surface tension measurements were carried out on monomer F in which either 3% by weigth of BPO (benzoyl-peroxide) or 0.5% by weigth of

Table I. *List of monomer mixtures used in the investigation*

Code	Composition (mole %)	Corresponding brand
A	100 % BISGMA 0 % TEDMA	
B	80 % BISGMA 20 % TEDMA	
C	60 % BISGMA 40 % TEDMA	
D	40 % BISGMA 60 % TEDMA	
E	20 % BISGMA 80 % TEDMA	
F	0 % BISGMA 100 % TEDMA	
G	64 % BISGMA 24 % TEDMA 12 % BISMA	Adaptic
H	46 % BISGMA 40 % TEDMA 14 % BISMA	Adaptic Glaze
I	31 % BISGMA 61 % TEDMA 8 % BISMA	Adaptic Bonding Agent
J	30 % BISGMA 42 % EDMA 28 % UPMA	AlphaFil
K	29 % BISEMA 38 % TEDMA 33 % UEMA	Compocap
L	26 % BISGMA 41 % TEDMA 33 % UPMA	Cosmic
M	34 % BISGMA 42 % TEDMA 24 % DEDMA	Finite
N	41 % BISGMA 59 % MMA	Nuva Seal

BISGMA: Bisphenol-A-glycidyl-dimethacrylate
BISEMA: Bisphenol-A-ethoxy-dimethacrylate
BISMA: Bisphenol-A-dimethacrylate
EDMA: Ethylene-glycol-dimethacrylate
DEDMA: Diethylene-glycol-dimethacrylate
TEDMA: Triethylene-glycol-dimethacrylate
UEMA: Trimethyl-hexamethylene-diurethane-ethylene-methacrylate
UPMA: Trimethyl-hexamethylene-diurethane-propylene-methacrylate
MMA: Methyl-methacrylate

DPPT (di-isopropyl-p-toluidine) had been dissolved. Furthermore, the surface tension of the brand Delton® (Johnson & Johnson) was determind. This fissure sealant has a composition of monomers (25% BIS-GMA, 9% BIS-MA, 66% TEDMA *Asmussen,* unpublished results) that is close to that of Adaptic Bonding Agent (Mixture I).

The surface tension was measured by means of a Krüss interfacial-tensiometer. The tensiometer was described by *Du Noüy* (1925), and used in accordance with the instructions given by the manufacturer (A. Krüss, Gertigstrasse 31, Hamburg). For each mixture the surface tension was determined at four temperatures in the range from 22 to 37 °C. The temperatures were accurate within ± 0.5 °C. At each temperature the surface tension was taken as the mean of three measurements. The surface tensions were re-measured at the initial temperature. In order to estimate the degree of inaccuracy of the surface tension determinations, repeated measurements were carried out on water at 24.0 °C.

Contact angle

The contact angle was measured on cariesfree enamel surfaces of human teeth. Following extraction and prior to use the teeth had been stored in demineralized water for not longer than 24 hours. Before use the teeth were cleaned with an aqueous slurry of pumice by means of a toothbrush, rinsed with demineralized water, and dried by compressed air. In one series of experiments the teeth were unetched, in another series the

teeth were etched with 35% phosphoric acid. The acid was applied with a cotton pellet for one minute, whereafter the teeth were rinsed with demineralized water and dried again. The teeth were then mounted longitudinally on an object glass with the appropriate tooth surface in as near a horizontal position as possible. With the unetched teeth the monomers A–D were investigated, with the etched teeth the monomers A and B. A small drop of monomer was applied to the surface of the enamel by means of a pointed toothpick. The spread of the drop was observed in a stereo microscope at a nominal magnification of 8 x 18. When the drop had ceased to flow, the point of the drop that protruded most in the direction of the long sides of the object glass (= the x-direction) was located. By means of a probe a spherical alloy particle was placed on the enamel close to the periphery of the drop at this point. The glass plate was then placed on the table in front of a horizontally positioned microscope with the x-direction perpendicular to the optical axis of the microscope. The microscope had a nominal magnification of 10 x 12. The table could be moved up and down and rotated around the x-direction. A beam of light was aimed at the drop, and after passing the microscope, reflected perpendiculary by means of a plane mirror onto a piece of paper. The table was now adjusted in such a manner that the contours of the alloy particle, the drop and the enamel all appeared sharp on the paper. By means of a ruler tangents to the contours of the enamel and the drop were drawn at the point of contact. The contact angle was measured with a protractor graduated in degrees. The experiments were carried out at a room temperature of 23 ± 2 °C. The relative humidity varied between 30 and 50%. For each monomer mixture the contact angle was measured on five teeth. For each tooth the angle was measured at two points at opposite sides of the drop.

RESULTS

Viscosity

For each monomer mixture the logarithm of the calculated viscosities was plotted against the reciprocal of the temperature in °K. Assuming a linear relationship the regression line was determined, and from this the viscosities at 23 and 35 °C were obtained. The coefficient of correlation was in all cases larger than 0.999. In Fig. 1 the logarithm of the viscosities (η) in cP is plotted against the content of TEDMA in mole % of the monomer mixtures A–F. The upper curve gives the viscosities at 23 °C, the lower curve the viscosities at 35 °C. Table II presents the results obtained with the monomer mixtures G–N. The variance about the above mentioned regression lines was used to calculate an estimate of the inaccuracies of the viscosities. The inaccuracy thus obtained was about 7% for monomer A, below 5% for monomers B–F, and is given in absolute numbers for monomers G – N in Table II. The differences between the viscosities determined initially and finally at the same temperature reading could in all cases be explained by a temperature difference of less than 0.2 °C.

Table II. *Viscosity of monomer mixtures G-N*

Monomer mixture	Viscosity (cP)	
	23 °C	35 °C
G	13700 ± 600	2740 ± 120
H	1670 ± 40	490 ± 10
I	197 ± 2	85 ± 1
J	1520 ± 50	440 ± 20
K	258 ± 7	104 ± 2
L	1090 ± 30	353 ± 9
M	181 ± 4	79 ± 2
N	450 ± 6	168 ± 2

By interpolation in Fig. 1 the viscosities of the monomers in BIS-GMA/TEDMA-based brands can be obtained. This was done for a number of brands with known compositions of monomers (*Asmussen*, 1975), and the results are presented in Table III.

Table III. *Viscosity of some BISGMA/TEDMA mixtures*

Composition (mole %)	Corresponding brand	Viscosity (cP)	
		23 °C	35 °C
64 % BISGMA 35 % TEDMA	Concice	5100	1210
53 % BISGMA 47 % TEDMA	Concise Cap-C-Rynge	1490	450
43 % BISGMA 57 % TEDMA	Prestige	520	190
37 % BISGMA 63 % TEDMA	Concise Enamel Bond	280	110

Surface tension

For each monomer mixture the surface tension was plotted against temperature. Assuming a linear relationship the regression line was determined, and from this the surface tensions at 23 and 35 °C were obtained. The coefficient of correlation was in all cases larger than 0.98. In Fig.2 the surface tension (γ) in dyne/cm is plotted against the content of TEDMA in mole% of the monomer mixtures A–F. The upper plot gives the surface tension at 23 °C, the lower one the surface tension at 35 °C. The straight lines were fitted by the method of least squares. The remainder of the results are shown in Table IV. The values presented in Fig. 2 and Table IV were estimated to be accurate within ± 0.2 dyne/cm. The differences between the surface tensions determined initially and finally at the same temperature were in all cases less than 0.2 dyne/cm.

Table IV. *Surface tension of monomer mixtures*

Monomer mixture	Surface tension (dyne/cm)	
	23 °C	35 °C
G	42.3	41.2
H	40.3	39.3
I	39.5	38.4
J	37.9	37.0
L	38.9	37.9
M	39.0	38.0
N	36.5	35.4
F + 3 % BPO	37.3	36.1
F + 0.5 % DPPT	37.0	35.9
Delton cat	39.6	38.4
Delton uni	39.5	38.3

Contact angle

For each of the unetched teeth the cosine of the mean of the two measured contact angles was calculated. For each monomer mixture A–D the mean and the standard error of the mean of these cosines were calculated. The results are presented in Fig. 3 in a «Zisman diagram» (*Zisman*, 1961). The mean of the cosines ($\cos \theta$) is plotted against the surface tension at 23 °C of the monomer mixtures. The surface tension of the monomers were taken from the upper straigth line in Fig. 2. The vertical lines represent the standard error. Assuming a linear relationship the regression line was determined. The coefficient of correlation was −0.99. The intercept of the regression line with the line $\cos \theta = 1$ defines the critical surface tension, γ_c, of enamel under the conditions described (*Zisman*, 1961). γ_c was found to be 37.7 dyne/cm.

With the etched teeth the monomer drops continued to spread until the contact angle was essentially zero.

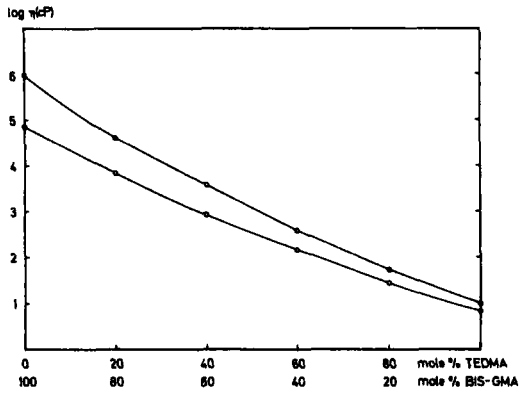

Fig. 1. Logarithm of viscosity (centipoise) in relation to composition (mole%) of BIS-GMA/TEDMA mixtures. The upper curve gives the viscosities at 23 °C, the lower curve the viscosities at 35 °C.

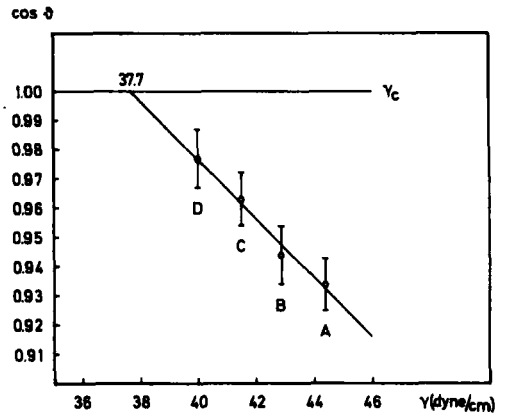

Fig. 3. Cosine of contact angle in relation to surface tension (dyne/cm) of BIS-GMA/TEDMA mixtures.

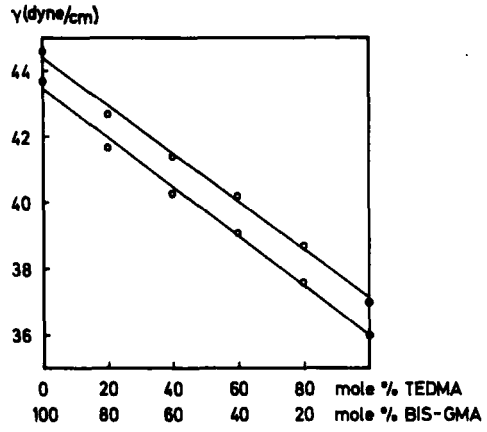

Fig. 2. Surface tension (dyne/cm) in relation to composition (mole%) of BIS-GMA/TEDMA mixtures. The upper curve gives the surface tensions at 23 °C the lower curve the surface tensions at 35 °C.

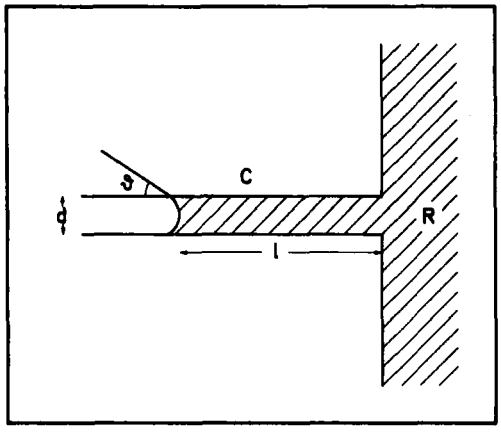

Fig. 4. Schematic presentation of the penetration of resin into the pores of an etched enamel surface. The pores are represented by the capillary cylinder C, of diameter d. The resin R, has penetrated to the depth 1. θ is the contact angle.

DISCUSSION

The foregoing has demonstrated that a wide range of viscosities can be obtained by mixing the high-viscous BIS-GMA with varying amounts of low-viscous monomers. Very little quantitative information on the viscosity of restorative resin monomers can be obtained from the litterature: *Dogon* (1975) found the viscosities of Concise Enamel Bond and Nuva Seal to be 185 cP and 236 cP, respectively. The temperature was not specified. These values are in fairly good agreement with the values listed in Table II and III.

The surface tensions of the investigated monomers lie in the range 35–45 dyne/cm. The results obtained with monomer F + 3% by

weigth of BPO, monomer F + 0.5% by weight of DPPT and the commercial Delton suggest that the addition of catalysts to restorative resin monomers does not significantly influence the surface tension.

The contact angle formed by various liquids on bovine or human enamel has been the subject of a number of publications. *Uy & Chang* (1966) reported values for γ_c of 31.5 dyne/cm at 100% relative humidity and 38.5–40.0 dyne/cm at 50% relative humidity. This contrasts with the results of *Glantz* (1969) who found γ_c in the range 42–64 dyne/cm, and that contact angle recordings did not vary with the relative humidity in the range 50–100%. *Alter & Fookson* (1971) gave values for γ_c of 26–32 dyne/cm in the 12–97% relative humidity range. In addition, these authors found that etching of the enamel for 1 min. with 50% formic acid did not influence γ_c. On the other hand *Snyder et al.* (1967) and *Retief* (1973) showed that the contact angle formed by various liquids was about halved by etching with H_3PO_4. *Newman & Sharpe* (1966) found that after etching with H_3PO_4 essentially zero contact angles were obtained with water and epoxy resins. In the present study natural enamel surfaces were used, whereas in the cited investigations plane ground surfaces were employed. The surface enamel is richer in fluorine than the subsurface layers (e.g. *Munksgaard & Bruun*, 1973). The critical surface tension of organic polymer surfaces decreases with increasing F-content of the surface (*Zisman*, 1961). Furthermore, *Glantz* (1969) demonstrated that γ_c decreased to about 37 dyne/cm after treatment with aqueous solutions of certain metal fluorides. This value is in good agreement with that found in the present study.

A complete explanation of the contradictory results reported in the above mentioned studies on contact angles is probably not possible. Differences in relative humidity, surface roughness and surface chemistry may all contribute to the discrepancies.

The foregoing has provided a basis for a description in physical terms of the penetration of monomers into the pores of etched enamel surfaces. In Fig. 4 the process is shown in a diagrammatic form. The pores in the etched enamel are represented by the cylindrical capillary C, of diameter d. The resin, R, has penetrated to the depth 1. The relation between time, t, and 1 can be obtained by integration from Poiseuille's equation as

$$t = \frac{4 \cdot \eta}{\gamma \cdot \cos\theta \cdot d} \cdot l^2$$

As examples, consider the relatively high-viscous Adaptic monomer and the relatively low-viscous Concise Enamel Bond. Assuming a temperature of 35 °C of the etched tooth, to which the resin is applied, the relevant constants for the two monomer mixtures are obtained from Tables II, III and IV, and Figs. 2 and 3:

Adaptic monomer: $\eta = 27.40$ Poise
$\gamma = 41.2$ dyne/cm
$\cos\theta = 0.966$

Concise Enamel Bond: $\eta = 1.10$ Poise
$\gamma = 38.8$ dyne/cm
$\cos\theta = 0.990$

Assuming a pore length of 50 μm and a pore diameter of 0.4 μm, the penetration time can be calculated as 1.7 s for Adaptic monomer and 0.072 s for Concise Enamel Bond. Even allowing for the uncertainty in the values of η, γ and $\cos\theta$, it may be concluded that viscosity as such is not a limiting factor for the penetration of restorative resin monomers into capillaries of the type and dimensions mentioned above. There is, however, a factor in the process of penetration into the capillaries of an etched enamel surface which has not been taken into account in the above calculations of penetration times: The capillary in Fig. 4 is open which is not the case with the pores of etched enamel surfaces. This means that air is undoubtedly trapped in the pores when the restorative resin is applied, whereby the monomer penetration may be retarded or even prevented. It is, however, possible that the entrapped air will dissolve in

the monomer. The monomer is saturated with air at a pressure of one atmosphere. As the resin is drawn by the capillary forces into the pores, the pressure of the entrapped air will increase. According to Henry's law the solubility of air in the monomer will hereby also increase. Consequently, it may be that the rate of dissolution of air into the monomer determines the depth of penetration into the pores of the etched enamel. This problem has been further investigated (*Asmussen*, 1977)

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