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THE WETTABILITY OF COMPOSITE RESINOUS FILLING MATERIALS

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The adhesive properties of the composite resins Adaptic®, Addent 12®, Blendant®, Dakor® DFR®, and TD 71® and of the non-composite resin Sevriton Simplified® have been studied by measurements of contact angles between solid surfaces of the resins and drops of six different test liquids.

The results indicate that all the materials studied have low energy surfaces with very similar critical surface tensions. An analysis of variance showed the presence of statistically significant differences between the recorded angles of the different materials. These differences were, however, found to be smaller and probably have no appreciable effect on the adhesive properties of the studied materials.

The inorganic phases of the composite resins were not found to have any influence on wettability.

The free surface energy of all the resins studied was consisted of generally both van der Waal's dispersion forces and polar forces and/or hydrogen bonds.

The influence on the retention of resinous fillings of the shrinkage during setting is discussed with reference to the adhesive forces found to form the free surface energies of the studied materials.

The force of adhesion or reversible work necessary to separate two adhering compounds is equal to the sum of their free surface energies (*Dupré*, 1860). In the oral cavity among other things this means that the amount of dental plaque which can adhere to tooth surfaces (*Glantz*, 1969) and the retention of fillings and crowns partly depends on the adhesive properties of enamel, dentine and restorative dental materials.

Studies concerned with attempts to determine or measure the adhesive forces between resins and enamel/dentine have been reported by e.g. *Buonocore* (1955), *Rose et al.* (1955), *Swartz and Phillips* (1955), *Buonocore et al.* (1956), *Schoubee et al.* (1956), *Swanson* and *Beck* (1960), *Myers et al.*

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(1963), and *Bowen* (1965 a, b, c, d). The adhesive properties of amalgam and silicate cements have been determined by *Glantz* (1969).

This investigation concerns the wettability and the adhesive properties of composite resinous restorative materials as judged from their critical surface tensions according to the method described by *Zisman* (1964).

MATERIAL AND METHOD

The material consisted of 4 test pieces of each of the following composite resins: Adaptic®, (Johnson & Johnson, New Brunswich), Addent 12®, (Minnesota Mining and Mfg. Co. St. Paul), Blendant® (Kerr Mfg Co. Detroit), Dakor®, (L. D. Caulk Corp., Milford), DFR®, (Surgident Ltd., Los Angeles), and TD 71® (Dental Fillings Ltd., London). To enable comparison of the registered adhesive properties of these materials the wettability of an older type of resinous filling material, Sevriton Simplified®, (De Trey Freres S.A., Zürich) was studied simultaneously and served as reference.

All the materials were prepared in accordance with the manufacturer's instructions. The test pieces were cylindrical with a diameter of 10 mm and a height of 5 mm. All the test pieces were made in a Teflon-mould by one and the same operator, who handled the different materials in a random order.

As *Wenzel* (1936) has found that both small and large irregularites of solid surfaces influence the values of contact angles recorded against these surfaces, the resins were allowed to set in contact with clean smooth glass plates. In a study with a Perth-O-Meter type S4 Bd, at 3 recordings on each of 3 randomly chosen glass plates, their surfaces were found to have a mean CLA-value of 0.0003 μm (range 0.002—0.003) and a mean R_{MAX}-value of 0.024 μm (range 0.021—0.028).

For measurement of the contact angles the following 6 liquids were used: water, glycerol, formamide, thiodiglycol, methylene iodide, and 1-bromonaphtalene. These liquids, which were chosen because of the differences between their surface tensions, have commonly been used in determinations of the critical surface tensions of low energy solids. (*Fox & Zisman*, 1950, *Ellison et al.*, 1953; *Jarvis et al.*, 1964).

The water was redistilled, and the other liquids, all highly purified by their respective manufacturers, were examined with a Krüss-tensiometer, type T 52, for impurities capable of affecting their surface tensions. The purity of the test-liquids, according to the manufacturers, and the means and standard deviations of 6 surface tensions determinations of each liquids

Table I.

Liquids used for measurement of contact angles.

Liquid	Formula	Manufacturer	Purity (according to manufacturer)	Surface tensions (dynes/cm)		
				Mean	S.D.	Ref.
Water	H_2O			72.2	0.3	72.6[1]
Glycerol	$C_3H_8O_3$	Merck A.G. Darmstadt	Pro Analysi	64.6	0.5	63.4[1]
Formamide	$HCONH_2$	Merck A.G. Darmstadt	Für die Chromatographie	58.0	0.3	58.2[1]
Thiodiglycol	$S(CH_2CH_2OH)_2$	R. Grave A.B. Stockholm	A 9831 (För kromatografi)	54.2	0.4	54.0[2]
Methylene iodide	CH_2I_2	Merck A.G. Darmstadt	Zur Trennung von Mineralgemischen	50.2	0.4	50.8[1]
1-bromonaphthalene	$C_{10}H_7Br$	KEBO Stockholm	S 1616 (Purum)	44.3	0.3	44.6[2]

[1] Hodgman, C.D., 1962
[2] Jarvis, N. L., et al., 1964

are given in Table I, together with previously recorded surface tensions of the same liquids (*loc.cit.*).

The equipment used for measuring contact angles has been described in detail by *Glantz* (1969).

The contact angles were measured when the liquid drops had ceased to spread over the solid surface and had reached a state of mechanical equilibrium. The volume of a given drop of liquid varies with the viscosity of the liquid and in this study it ranged between about 0.0004 ml for water and about 0.0012 ml for glycerol. Such variations have, however, no influence on the magnitude of contact angles (*Zisman* ,1964).

A separate AGLA-syringe was used for each of the 6 liquids. Before each experiment the syringes were taken apart and cleaned with fresh dichromatic sulphuric acid, absolute alcohol, and distilled water (twice). Then they were steam-washed and dried at a temperature of $96\pm3°C$ in an oven (Elektro-Helios 284 52 C).

All the contact angles were measured by the one and the same person in an air-conditioned room with a temperature of $20.0\pm0.1°C$, and a relative humidity of 55 ± 5 per cent. The humidity consisted of water vapour. The temperature and the relative humidity were recorded on a thermohygrograph type Lambrecht 252.

10 angles were measured between each liquid and each of the 4 test pieces of each solid studied.

For studies of the errors of the method used see *Glantz* (1969).

RESULTS

The mean values of the recorded contact angles (Θ) between the test liquids and plane surface of various front tooth resins are given in Table II together with their numbers, cosines, and standard deviations.

The results given in Table II indicate first, that all the tested restorative materials had surfaces consisting of low energy materials and, second, that they were similar in wettability.

Because of the observed similarities between the wetting properties of the tested materials the critical surface tension (γ_C) has only been reported graphically for one of the tested resins (Adaptic) (Fig. 1).

The critical surface tension was gained by plotting a graph of cos Θ against the surface tensions of the liquids (γ_{LV}). From the intercept at cos $\Theta = 1$, γ_C was read of. The two straight lines of Fig. 1 were drawn parallel to the

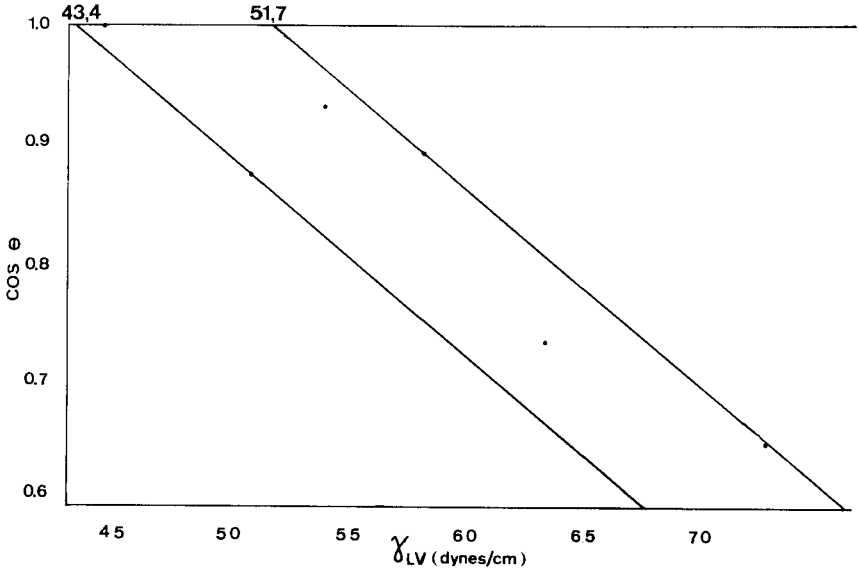

Fig. 1. Relation between the surface tension of liquids (γ_{LV}) and the cosines of contact angles between these liquids and the plane surface of a composite resinous filling material, Adaptic, (cos Θ), and range of the calculated surface tension of this material.

Table II.

Advancing contact angles with some composite and non-composite resinous restorative materials

	Water (γ_{LV} = 72.6 dynes/cm)			Glycerol (γ_{LV} = 63.4 dynes/cm)			Formamide (γ_{LV} = 58.2 dynes/cm)			Thiodiglycol (γ_{LV} = 54.0 dynes/cm)			Methylene iodide (γ_{LV} = 50.8 dynes/cm)			1-bromonaphthalene (γ_{LV} = 44.6 dynes/cm)	
Material	n	Θ	S.D. cos	n	Θ	S.D. cos	n	Θ	S.D. cos	n	Θ	S.D. cos	n	Θ	S.D. cos	n	Θ
Addent 12	40	50.7°	1.68° 0.6334	40	42.9°	1.62° 0.7322	40	26.8°	2.27° 0.8926	40	20.9°	2.16° 0.9342	40	28.8°	1.84° 0.8763	40	Spreads
Adaptic	40	49.5°	1.55° 0.6494	40	42.8°	1.44° 0.7340	40	26.4°	2.02° 0.8961	40	21.4°	2.96° 0.9312	40	28.9°	2.71° 0.8753	40	»
Blendant	40	51.1°	2.25° 0.6286	40	43.4°	1.64° 0.7269	40	25.9°	1.61° 0.9000	40	23.3°	1.51° 0.9182	40	29.8°	2.04° 0.8682	40	»
Dakor	40	48.2°	1.99° 0.6665	40	43.8°	1.65° 0.7224	40	26.0°	2.00° 0.8992	40	20.9°	2.31° 0.9343	40	26.6°	2.40° 0.8945	40	»
DFR	40	49.1°	1.51° 0.6544	40	42.0°	1.83° 0.7428	40	26.2°	1.85° 0.8940	40	21.2°	2.32° 0.9327	40	30.6°	1.26° 0.8611	40	»
TD 71	40	50.1°	2.22° 0.6418	40	43.1°	1.91° 0.7305	40	27.9°	1.77° 0.8836	40	21.0°	3.04° 0.9334	40	27.3°	3.07° 0.8886	40	»
Sevriton Simplified	40	50.9°	1.77° 0.6310	40	42.5°	1.45° 0.7375	40	27.9°	1.96° 0.8838	40	21.9°	2.76° 0.9276	40	30.3°	2.64° 0.8638	40	»

regression line of the test liquids containing not only dispersion forces but also polar and hydrogen bonding forces (water, glycerol, formamide and thiodiglycol). As only one of the liquids only containing dispersion forces (methylene iodide) was forming a lens on the test pieces no regression line could be drawn for these liquids.

According to Fig. 1, the critical surface tension of the studied material was 43.4—51.7 dynes/cm.

Statistical analysis

On the recorded values an analysis of variance for factorial design was made according to the program BMD 02 V (Univac Data Processing Centres' version of May 4 1965).

In Table III the sums of squares, the degrees of freedom, the mean squares, and the F-ratios are given.

The result of the analysis indicates that, for each of the test liquids, with which contact angles greater than 0° were recorded, there were statistically significant differences between the values recorded on the different materials. Further, from the values of Tables II and III, it appears warranted to conclude that these significant differences are not caused entirely by the result of the recordings against the non-composite resin, Sevriton Simplified, but to an equal extent by the recordings against the composite resins.

DISCUSSION

Judging from the results of a reported methodological study (*Glantz*, 1969), the contact angles were measured with satisfactory accurracy when the described method was used.

Whether or not the contact angles are dependent entirely on the thermodynamic properties of the adherents is of little or no importance in the evaluation of the results of this study and will therefore not be considered.

The contact angle determinations showed that both composite and non-composite resinous filling materials have low energy surfaces with surface tension values, which implies that they comprised of organic material. All the materials studied consisted of a polymeric organic compound or compounds and all of them except one also had an inorganic component viz. ceramic, silica, or a similar compound acting as a filler. All the materials of which these inorganic fillers were made had high free surface energies per unit of area (*Livey & Murray*, 1956; *Wolf*, 1959; *Krupp et al.*, 1960).

Table III.

Results of analysis of variance on the contact angles recorded between some composite and non-composte resinous restorative dental materials and test liquids

Test liquids	Sources of variance	Sums of squares	Degrees of freedom	Mean squares	F-ratios
Water	Between materials	263.5	6	43.9	12.5
	Within materials	960.2	273	3.5	
	Total	1223.7	279		
Glycerol	Between materials	77.6	6	12.9	4.7
	Within materials	750.3	273	2.7	
	Total	827.9	279		
Formamide	Between materials	183.3	6	30.5	8.2
	Within materials	1021.8	273	3.7	
	Total	1205.1	279		
Thiodiglycol	Between materials	185.0	6	30.8	5.0
	Within materials	1687.0	273	6.2	
	Total	1872.0	279		
Methylene iodide	Between materials	534.3	6	89.0	16.2
	Within materials	1504.4	273	5.5	
	Total	2038.6	279		

The statistical analysis of the results showed significant differences between the wettability of the tested materials, which were probably due to minor differences in the composition of the materials. However, the results also showed that the differences between the materials were small and probably had no appreciable effect on their adhesive properties.

Many composite resins consist of filler particles precoated with an organic film by their respective manufacturers. Even if this is not the case, the observation that the high energetic components generally have no influence on the adhesive properties of these composite resins is readily understood from the fact that when the materials are beeing mixed the organic parts is in a viscous state. By a mechanism that can be explained by the second law of thermodynamics (*Clausius*, 1865) the energetic differences between the organic and inorganic phase will under such conditions result in a coating of the high energetic filler particles with the low energetic resin.

The results of the wettability-studies also indicate that the free surface energy of the materials tested was generated by van der Waals-dispersion forces and by polar forces and hydrogen bonds. This is demonstrated in

Fig. 1, where the test liquid, methylene iodide, which has a surface tension made almost entirely of dispersion forces, formed comparatively greater angles that the other liquids, which are capable of using dispersion forces as well as polar and hydrogen bonding forces in their adhesion to the solid surfaces.

The adhesive properties per unit of area was found to be approximately the same for all the tested materials including Sevriton Simplified ®, which represented the older type of resinous filling materials and was used as reference. These findings imply that the true adhesive properties of the composite resinous materials do not differ considerably from the non-composite ones. However, as with the type of materials tested in this study, the absolute majority of relevant adhesive forces decreases by the sixth or seventh power of the distance between the adherents they will practically cease to have any effect when there is not a true, molecular contact between the adherents. Thus, the problems of adhesion is not only confined to the adhesive properties of the adherents per unit of area but also to their ability to maintain a large area of contact with their adherents. One of the main problems is thus to maintain, i.e. after the material was set, the intimate contact established between the cavity walls and the filling material on insertion of the latter. The composite resinous materials shrink less than the non-composite ones, but it is still probable that the shrinkage of the composite materials is too great to maintain a sufficient area of contact with the cavity walls. In order to minimize the influence of the shrinkage on the total work of adhesion between the cavity and the resinous filling perhaps the introduction of an elastic liner adhering well to the cavity wall also after setting and capable of forming primary chemical bonds with the filling material might provide a solution to the problem of getting a material with a good adhesion to tooth surfaces.

Compared with the adhesive properties of silicate cement (*Glantz*, 1969) the composite resins have smaller free surface energy per unit of area. The reason to this is the fact that silicate cement is a filling material entirely consisting of inorganic compounds.

The amount of dental plaque capable of adhering to fillings varies with the type of materials studied depending on the free surface energy of it as well as on micro-biological and other physico-chemical factors than the free surface energy. Therefore the results of wettability studies alone, allow no conclusion as to determine whether the composite resins group of materials under standardized conditions are more or less susceptible to the growth of dental plaque than is e.g. silicate cement.

REFERENCES

Bowen, R. L., 1965 a: Adhesive bonding of various materials to hard tooth tissues. I. Method of determining bond strength. J. Dent. Res. *44*:690.

—»— 1965 b: Adhesive bonding of various materials to hard tooth tissues. II. Bonding to dentin promoted by a surface-active comonomer. J. dent. Res. *44*:895.

—»— 1965 c: Adhesive bonding of various materials to hard tooth tissues. IV. Bonding to dentin, enamel and fluorapatite improved by the use of a surface-active comonomer. J. dent. Res. *44*:906.

—»— 1965 d: Adhesive bonding of various materials to hard tooth tissues. V. The effect of a surface-active comonomer on adhesion to diverse substrates. J. dent. Res. *44*:1369.

Buonocore, M. G., 1955: A simple method of increasing adhesion of acrylic filling materials to enamel surfaces, J. dent. Res. *34*:849.

Buonocore, M. G., W. Wileman and *F. Brudevold*, 1956: A report on a resin composition capable of bonding to human tooth structure. J. dent. Res. *35*:846.

Clausius, R., 1865: Abhandlung über die mechanische Wärmetheorie 1—2, Braunschweig.

Dupré, M. A., 1860: Théorie mécanique de la chaleur. Gauthier-Villars, Paris.

Ellison, A. H., H. W. Fox and *W. A. Zisman*, 1953: Wetting of fluorinated solids by hydrogen-bonding liquids. J. phys. Chem. *57*:622.

Fox, H. W. and *W. A. Zisman*, 1950: The spreading of liquids on low-energy surfaces. I. Polytetrafluoroethylene. J. Colloid Sci. *5*:514.

Glantz, P.-O., 1969: On Wettability and Adhesiveness. A study of enamel, dentine, some restorative dental materials, and dental plaque. Odont. Revy 20, suppl. 17.

Hodgman, C. D. (ed.), 1962: Handbook of chemistry and physics. Ed. 44. Chemical Rubber Publishing Company, Cleveland.

Jarvis, N. L., R. B. Fox and *W. A. Zisman*, 1964: Surface activity at organic-liquid air interfaces. V. Effect at partial fluorinated additives on the wettability of solid polymers. In: Contact angle, wettability and adhesion. Gould, R. F. (ed.), Adv. Chem. Ser. no. 43, Amer. Chem. Soc., Washington D.C.

Krupp, H., G. Sandstede and *K.-H. Schramm*, 1960: Zur Physik des Haftens fester Körper. Dechema Monogr. *38*:115.

Livey, D. T. and *P. Murray*, 1956: The surface energies of solid oxides and carbides. Atomic energy research establishment M/R 1846, Harwell, Berks.

Myers, C. L., G. Ryge, J. B. Heyde and *J. F. Glenn*, 1963: In vivo test for bonding strength. J. dent. Res. *42*:907.

Rose, E. E., J. Lal, N. B. Williams and *J. P. Falcetti*, 1955: The screening of materials for adhesion to human tooth structure. J. dent. Res. *34*:577.

Schoubee, P. J., G. C. Paffenbarger and *W. T. Sweeney*, 1956: Resin cements and posterior-type direct filling resins. J. Amer. dent. Ass. *52*:584.

Swanson, L. T. and *J. F. Beck*, 1960: Factors effecting bonding to human enamel with special references to a plastic adhesive. J. Amer. dent. Ass. *50*:172.

Swartz, M. L. and *R. W. A. Phillips*, 1955: A method of measuring the adhesvie characteristics of dental cement. J. Amer. dent. Ass. *50*:172.

Wenzel, R., 1936: Resistance of solid surfaces to wetting by water. Ind. Engng. Chem. *28*:988.
Wolf, K. L., 1959: Physik und Chemie der Grenzflächen. Springer Verlag, Berlin.
Zisman, W. A., 1964: Relation of the equilibrium contact angle to liquid and solid constitution. In: Contact angles, wettability and adhesion. Gould, R. F. (Ed.), Adv. Chem. Ser. no. 43, Amer. Chem. Soc., Washington D.C.

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