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Wettability of poly(methyl methacrylate) surfaces in dental use

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Poly(methyl methacrylate) is widely used in dentistry. In contact with water, there is an increase in the polar surface free energy from 9.5 to 21 mJ m^{-2}. Various other surface modification treatments have been examined (chemical treatment, gold deposition and flaming), which also bring about a surface polar component increase and thus produce a better wettability in contact with water or saliva. The water modification seems to be the best treatment.

1. Introduction

Poly(methyl methacrylate) (PMMA) is widely used in density, particularly for dental prostheses. The wettability properties of PMMA surfaces can vary with contact time and temperature when in prolonged contact with a medium of different polarity. This continuous surface-energy modification may be due to the chain motions and orientation of functional end-groups and is a general property of polymers [1–4].

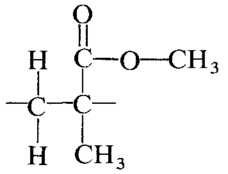
It is known that for PMMA films obtained from solution by solvent evaporation, in contact with substrates with either low or high surface energy, such as polytetrafluoroethylene or mercury, the surface free energy can vary between 44 and 50 mJ m^{-2}. This ability of PMMA surfaces to restructure as a function of the medium on which they have been prepared was observed by Carre and Schreiber [5].

One way to model the orientation characteristics at the interface is to study the evolution of surface properties as a function of the contact time with water at ambient temperature, as was done with 1% acrylic acid-grafted polyethylene in previous studies [3, 4]. The dispersive and polar components of the solid surface free energy, γ_S^D and γ_S^P, are determined by contact angle measurements using the now classical two-liquid-phase method [6]. The polar component is always increased. Acrylic acid-grafted polyethylene [3, 4] and maleic anhydride-grafted polypropylene [7], in contact with water, have been examined. This methodology was applied here to the case of PMMA surfaces.

2. Experimental

2.1. Materials

The PMMA used in this study was obtained commercially under the trade name Resarit (Resart). The repeating group is



$$-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle \overset{\displaystyle O}{\|}{C}-O-CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-$$

The PMMA was supplied in granular form and 1 mm-thick plates were prepared under a press by melting the polymer at 180 °C for 15 min against steel plates. Melting against polytetrafluoroethylene or steel plates showed no change in the surface properties. Using this method, smooth surfaces can be produced.

Evaporation and cathodic sputtering of gold, which can be used in dental applications, were also carried out on PMMA. Cathodic sputtering is achieved by applying a high voltage (2.5 kV) between the gold used as the cathode and the PMMA substrate holder, in an 8 Pa argon atmosphere.

The surface was also chemically modified by a 30 min treatment in 10% potassium hydroxide in ethanol solution. The samples were then washed with water, neutralized with 0.1 M hydrochloric acid for 10 min, washed with water again and dried for 48 h in an oven at 50 °C. For comparison a flame treatment was applied on the polymer surface, with a classical methane–air flame 8 mm from the PMMA surface and with successive crossings of 0.075 s.

2.2. Contact angle measurements

The classical two-liquid-phase method [6] was used: a drop of alkane was deposited on the polymer immersed in water (Fig. 1). The relationship between the

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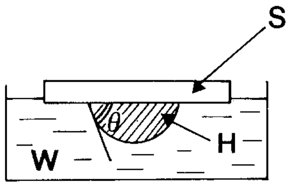

Figure 1 Two-liquid-phase method principle.

surface free energy components of the solid (S), the water (W) and the alkane (H) can be written as

$$\gamma_H - \gamma_W + \gamma_{HW} \cos\theta$$
$$= 2\gamma_S^{D\,1/2} (\gamma_H^{D\,1/2} - \gamma_W^{D\,1/2}) - 2\,(\gamma_S^P \gamma_W^P)^{1/2} \quad (1)$$

where θ is the contact angle of the alkane drop in water and each value is the quadratic mean of 20 contact angle determinations. γ_H, γ_W and γ_S are the surface free energies of, respectively, the alkane, water and polymer. γ_{WH} is the interfacial free energy between water and alkane. By using different alkanes it is possible to determine the dispersive component of the polymer surface, by plotting Y (left part) as a function of X $(\gamma_H^{D\,1/2} - \gamma_W^{D\,1/2})$ (in the right-hand part of Equation 1). A straight line is obtained by using the least mean squares method. Results are given with an accuracy of $\pm$ 2 mJ m^{-2} for each surface component and $\pm$ 4 mJ m^{-2} for the total surface energy. The slope of the straight line allows the determination of the dispersive component γ_S^D, and the intercept at the origin leads to the polymer surface non-dispersive or polar component γ_S^P.

Polymer samples were floated on the surface of distilled water at ambient temperature for several days before contact angle determination.

3. Results

The surface properties of the polymer before contact with water were $\gamma_S^D = 41 \pm 2$ mJ m^{-2} and $\gamma_S^P = 9.5 \pm 2$ mJ m^{-2}, so $\gamma_S = 50.5$ mJ m^{-2}. The change in contact with water was studied over 20 days at ambient temperatures. The contact angle measurements as a function of time showed a rapid change within 8 days, by comparison with polyethylene which needed 15 days [3]. The surface free energy component variations are shown in Fig. 2. The dispersive component showed a maximum after 3 days on water and then decreased again. The polar component also increased and attained the maximal value after the eighth day, when an equilibrium was reached. The final values were $\gamma_S^D = 41$ and $\gamma_S^P = 20$ mJ m^{-2}. There was a distinct increase in the polar component, the dispersive component being constant.

After a chemical treatment with alcoholic potassium hydroxide, the surface polar free energy was 21 mJ m^{-2}, and after a subsequent prolonged contact with water γ_S^P was 23 mJ m^{-2}. Taking into account the precision of $\pm$ 2 mJ m^{-2}, it was concluded that the polarity remained constant. The dispersive component at the polymer surface increased from 42 to 48 mJ m^{-2}.

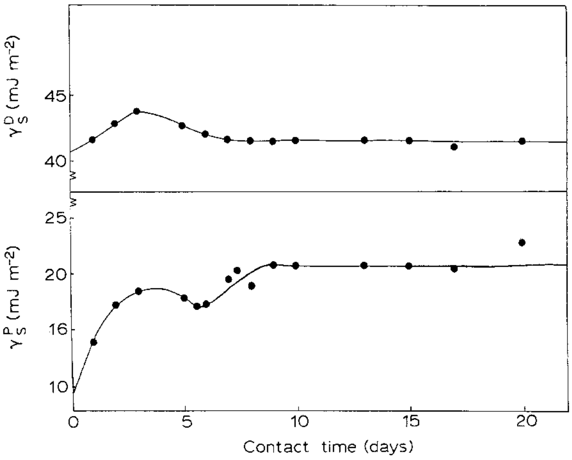

Figure 2 PMMA surface energy evolution as function of contact time with water.

Gold-covered surfaces were also examined. Gold alone has no polar component and a dispersive component of around 122 mJ m^{-2}. For gold evaporated on PMMA, γ_S^D was 128 mJ m^{-2} and γ_S^P around 1 mJ m^{-2}, very close to the value for pure gold. After contact with water for 24 h at 80 °C, γ_S^D was only 34 mJ m^{-2} and γ_S^P reached 28 mJ m^{-2}. A low adhesion of this evaporated gold on the polymer was observed.

For comparison, gold was deposited on a glass platelet. The surface properties were analogous to those observed with PMMA, and after being exposed to water γ_S^D attained 43 and γ_S^P 34 mJ m^{-2}. It can be concluded that these values are characteristic of the gold deposit and independent of the substrate. The sputtered gold on PMMA had a dispersive component of surface free energy of 86.5 mJ m^{-2} and a polar component of 35 mJ m^{-2}, close to those observed for evaporated gold. We can conclude that evaporation and sputtering do not give the same results on PMMA. However, the sputtered gold was not stable in contact with water, the surface becoming crazed.

For comparison, a flame treatment was also applied to PMMA, using a methane–air flame. After ten crossings of 0.075 s each, the polar component increased to 18 mJ m^{-2}.

With the help of these results, calculation of the work of adhesion (W) was possible for a solid (S) in contact with a liquid, according to Fowkes [8] and Owens and Wendt [9]:

$$W = 2(\gamma_S^D \gamma_L^D)^{1/2} + 2(\gamma_S^P \gamma_L^P)^{1/2} \quad (2)$$

The data after contact with water are given on Table I. These results obtained with pure PMMA were compared with dental PMMA, before and after 24 h contact with water at 80 °C. Corresponding results are given on Table II. The same limit appeared with nearly all of the samples, although they contained different types of additives or dyes.

All of these results are discussed below in view of the use of PMMA in dental applications [10].

4. Discussion

First, let us examine wettability. It was observed clearly that the polar component of free energy increased from 9.5 to 22 mJ m^{-2} after contact with water for nearly 10 days at ambient temperature. This increase may be due to surface reorientation and to water adsorption. Surface polarity can also be increased to 21 mJ m^{-2} after an alcoholic potassium hydroxide treatment and water rinsing. Carboxylic groups are then formed. A flame treatment in air led to 18 mJ m^{-2}, which is comparable with that observed after prolonged contact with water. Oxidized and nitrogenated groups are then usually created.

With evaporated gold, the high surface polarity (28 mJ m^{-2}) observed after contact with water seems not to be a function of the PMMA surface, because the same results were observed with gold evaporated on a glass substrate. It can be concluded that the surface polarity of PMMA is at the maximum 22 mJ m^{-2}, after orientation on water. With dental resins this value can increase to 27 mJ m^{-2}, probably because of additive migration to the interface. PMMA, like other polymers, shows an increase in the polar component of free energy due to a macromolecular chain reorientation at the interface with water [3, 4].

TABLE I Polar and dispersive components of surface free energy and adhesion energy with water for PMMA and modified surfaces

	γ_S^P (mJ m^{-2})	γ_S^D (mJ m^{-2})	W_{SL} (mJ m^{-2})
PMMA before contact with water	9.5	41	103
PMMA after contact with water	21	41	125
PMMA + KOH before contact with water	21	42	126
PMMA + KOH after contact with water	23	47.5	133
PMMA evaporated gold before contact with water	1	128	122
PMMA evaporated gold after contact with water	28	34	129
PMMA + sputtered gold	35	86.5	171

Adhesion properties with water or saliva are now discussed. Calculations were made with human saliva, whose total surface energy was determined in our laboratory by the Wilhelmy method, and whose dispersive component was obtained by contact angle measurements on a polytetrafluoroethylene substrate [10, 11]. The total surface energy was 47 mJ m^{-2}, γ_S^D was 31 mJ m^{-2} and γ_S^P near 16 mJ m^{-2}. Water has a surface energy of 72.6 mJ m^{-2}, γ_S^D being 21.6 and γ_S^P 51 mJ m^{-2}. Samples of dental resin were placed in the mouth for 36 h. Another group was first boiled in water for 24 h and then kept in the mouth for 36 h. The polar component was 11 mJ m^{-2} for the first sample and 27 mJ m^{-2} for the second. No pellicle formation was observed on the polymer surfaces. Therefore, as shown on Table III, modelling with water seems to be valid for the provision of in-mouth behaviour, and this can be attributed to the polar character of the two liquids.

The study on water has a good predictive capacity of what is happening in the presence of saliva, as shown by the constant proportionality coefficient of 1.15 between work of adhesion calculated in contact with water for saliva (Table III). The experiments in the mouth showed that for a non-equilibrated surface the non-dispersive component increased slowly to

TABLE II Surface energy polar and dispersive components of various dental PMMAs before and after contact with water

	Ortho-resin	SR 3/60	Auto 3/60	BA 606	SR 3/60 plus	3/60 PTFE[a]	23/07
Before contact with water							
γ_S^P (mJ m^{-2})	10	4	13	18	4	0.3	4
γ_S^D (mJ m^{-2})	40	40	39	42	40.5	38	40.5
After contact with water							
γ_S^P (mJ m^{-2})	23	24.5	21	27.5	25.5	25	21
γ_S^D (mJ m^{-2})	40	40	38.5	40.5	39	38	41

[a] PTFE, polytetrafluorothylene.

TABLE III Comparison of PMMA adhesion energy with water and saliva

	γ_S^P (mJ m^{-2})	γ_S^D (mJ m^{-2})	$W_{S/\text{water}}$ (mJ m^{-2})	$W_{S/\text{saliva}}$ (mJ m^{-2})
PMMA before contact with water	9.5	39.5	103	95
PMMA after contact with water	21	41	125	108
PMMA + KOH before contact with water	21	42	126	109
PMMA + KOH after contact with water	23	47.5	133	115

11 mJ m^{-2}, which is close to the surface energy component of saliva. The sample boiled in water showed an increase to 27 mJ m^{-2}, the maximum value observed with PMMA on water. It can therefore be concluded that a previous equilibration on water leads to a higher final value of surface polarity. This has an application in dental use in order to obtain the best saliva–denture adhesion [12] and immediately obtain the best performances. Equation 2 shows that the PMMA surface polar component increase is beneficial in improving adhesion.

A comparison can be made between the various treatments for dental application. The different surface treatments proposed here led to various surface properties and a theoretical work of adhesion could be calculated. After the flame treatment a polar component increase was observed, but the behaviour in contact with water was not examined. The higher work of adhesion against water associated with sputtered gold deposition on PMMA is unfortunately unusable because of the cracking of such a deposit in contact with water. It appears necessary to leave the prosthesis in water before putting it in the mouth in order to attain the highest surface polarity and to favour interactions between the PMMA surface and the saliva. All other treatments, such as chemical treatment, flaming or gold deposition, did not greatly improve the surface properties and deteriorate the surface mechanical properties.

5. Conclusion

Prosthesis retention in static and dynamic situations depends essentially on adhesion phenomena between the prosthesis material and saliva [12]. A good stability of the intrados surface state is hence desired and a metallic surface could be a solution, considering the surface properties. However, as can be seen, the metallization of PMMA is not at all satisfactory.

In order to improve adhesion between PMMA and saliva, previous contact with water is seen to be beneficial. The polarity increase after contact with water has a direct implication for dental use. Other chemical or physical treatments do not improve the adhesion with saliva, except for sputtered gold, but the quality of this type of deposit is poor.

Comparing the different treatments, it can be concluded that after contact with water, PMMA is in the best state to obtain good stability in the mouth. The PMMA can then be considered as a solid with high surface energy, so adhesion with saliva is increased. In fact, it is usually recommended before the first use of a PMMA denture to equilibrate the prosthesis in water, and this study gives a scientific explanation of this procedure.

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