

ASSESSMENT OF THE IMPRESSION MATERIALS BY INVESTIGATION OF THE HYDROPHILICITY

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The wettability of 18 dental impression materials, commercially available, during their working time was investigated using the contact angle method, as a good wettability is desired to obtain a high fidelity impression. Polyetheric materials, A-silicones with added surfactants and C-silicones were found to have a good wettability. Alginate was found to be the most hydrophilic material, but this quality decreases in time. In the paper an explanation for the time dependence of the contact angle is advanced.

Keywords: impression materials, wettability, contact angle, hydrophilicity.

1. Introduction

Wettability is an important feature for accurate, void-free positive casts for the negative reproduction of the oral tissues. Therefore, wettability of cured impression surfaces have been intensively studied: Research has been made for the wetting by water of cured elastomeric impression materials [1], gypsum products [2–4] or die stone materials [5–7]. Further research refers to the alteration or optimization of the wetting properties by disinfecting agents [3, 8–10], extrinsic surfactants [9, 11, 12] and glow-discharge treatments [4, 13, 14].

For adhesion to occur, the adhesive must wet the substrate. The most common method of observing wetting is the measuring of the contact angle. The contact angle θ is the internal angle in a droplet of liquid in contact with a solid. It results from the equilibrium between the interfacial tensions of the solid, the liquid and the gas phases involved (figure 1) namely γ_{SV} , γ_{SL} , γ_{LV} with "S", "V," and "L" referring to the solid, liquid and vapour phases, respectively. The equation governing the force balance at an interface is Young's equation [15]:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

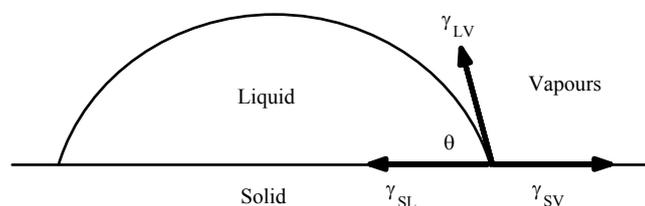


Figure 1: The balance of interfacial tension forces in the plane of the substrate surface.

Wetting proprieties of solid in contact with a liquid (usually water) are characterized by the contact angle of this liquid as non-wetting ($>90^\circ$), wetting ($<90^\circ$), and spreading ($\sim 0^\circ$).

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The objective of this study was to investigate the wettability of impression materials during their working time, as a good wettability is desired to obtain a high fidelity impression. We established the hydrophilicity of 18 commercially available impression materials.

The paper is structured as follows: After a short presentation of the basic notions of wettability in “Introduction”, in the chapter “Materials and Methods” are presented some product sheet information of the 18 investigation impression materials, sample preparation for measurements and sessile drop method for measuring the contact angle. The chapters “Results” and “Discussions” present the values of contact angle obtained and the discussions about the time evolutions of contact angle, the origin of hydrophilicity of the impression materials, respectively. In the last chapter the conclusions are presented grouped on the material types.

2. Materials and Methods

Hydrophilicity of a material is defined and quantitatively described by the shape of a water droplet placed on a flat surface of this material and the angle between the baseline of the drop and the tangent at the three-phase-line (solid/liquid/vapour) (see the fig. 1). At thermodynamic equilibrium, there is a balance of forces in the plane of the surface, expressed by the Young equation (see eq.1).

The investigated dental impression materials were: addition silicones (A-Silicone), condensation silicones (C-Silicone), polyether based materials and an alginate one (see table 1). These materials were provided by several manufacturers as follows: 3M Espe, Bayer, Coltène Whaledent, GC, Heraeus, Ivoclar, Kerr, Spofa Dental, Zhermack.

To obtain the sample of impression materials the components were mixed and a small quantity was placed on a glass clean plate; another glass plate covered the mixture by gently pressing against the 1mm width spacers. After about 60s, one of these glass plates was removed yielding a layer with constant thickness and a smooth surface. The resulted sample has a disk shape, with thickness of 1mm and a diameter of about 25mm.

The contact angles of water (double distilled) made against these thin horizontal sample films of the different materials were determined from analysis of profile images of symmetrical sessile drops of water placed on them. The measurements were made using the Drop Shape Analysis System model DSA100 (Kruss GmbH, Hamburg). The sample was placed on its stage, under the tip of a water-dispensing disposable blunt-end stainless steel needle with an outer diameter of 0.5mm. The needle was attached to a syringe pump controlled by computer for delivery of the water drop on the tested surface. The volume of water drops was of about 2 μ l.

Table 1: Impression materials and their main features

Type	Item	Sample label	Consistence	Working time (min)	Total set time (min)
<i>Addition silicone</i>	1	AS1	Low Viscosity	2	5
	2	AS2	High Viscosity	0:45	2:15
	3	AS3	High Viscosity	2	5:30
	4	AS4	Low Viscosity	2	5:30
	5	AS5	Low Viscosity	1:30	2:30
	6	AS6	High Viscosity	1:05	3:05
	7	AS7	Low Viscosity	2:15	3:30
	8	AS8	High Viscosity	2:00	4:00
<i>Condensation silicone</i>	9	CS9	High Viscosity	1:30	3:30
	10	CS10	Low Viscosity	1:30	3:30

	11	CS11	High Viscosity	1:30	5:00
	12	CS12	Low Viscosity	1:15	4:30
	13	CS13	Low Viscosity	1:30	5:00
	14	CS14	High Viscosity	1:00	4:00
	15	CS15	High Viscosity	1:00	4:00
<i>Polyether</i>	16	P16	Low Viscosity	2:30	6:00
	17	P17	Low Viscosity	2:30	5:30
<i>Alginate</i>	18	A18	Mixture of 0.6 g alginate and 1.4 ml water	1:45-2:00	2:15-2:30

Drop images were acquired as function of time also using the DSA100 system. The dispensing of the drop, the time schedule of video capture (25 frames/s for the duration of 30 s), and the subsequent analysis of the contact angles (and of other drop parameters) were performed using the DSA3 software supplied with the instrument.

Contact angles were measured by fitting the shape of the sessile drop with the circle equation and then calculating the slope of the tangent to the drop at the liquid-solid-vapour interface line. The camera was positioned thus to observe the drop under an angle of about 4° with respect to the plane of sample surface supporting the droplet. For each sample there were possible 3-5 trials according to the specific total set time of each material. The tests were performed at room temperature.

3. Results

In figure 2 are given some representative images of the evolution of the drop before and after the contact with the surface of one of the studied impression materials (A1) using the video capture. We can observe that the contact angle decreases in time.



Figure 2: Sequential steps in contact angle determination for AS1 material.

In order to discuss the time evolution of contact angle we introduce: the curing time of the impression material, τ , the water contact time with the substrate, Δt , and the total age, t of the impression material since mixing. The total age can be written as a sum between curing time, τ and water drop contact time, Δt .

$$t = \tau + \Delta t \quad (2)$$

In figures 3 are presented the contact angles vs. total age, t for investigated impression materials grouped as follows: a) and b) for A-Silicone, c) and d) for C-Silicone, e) and f) for Polyether materials.

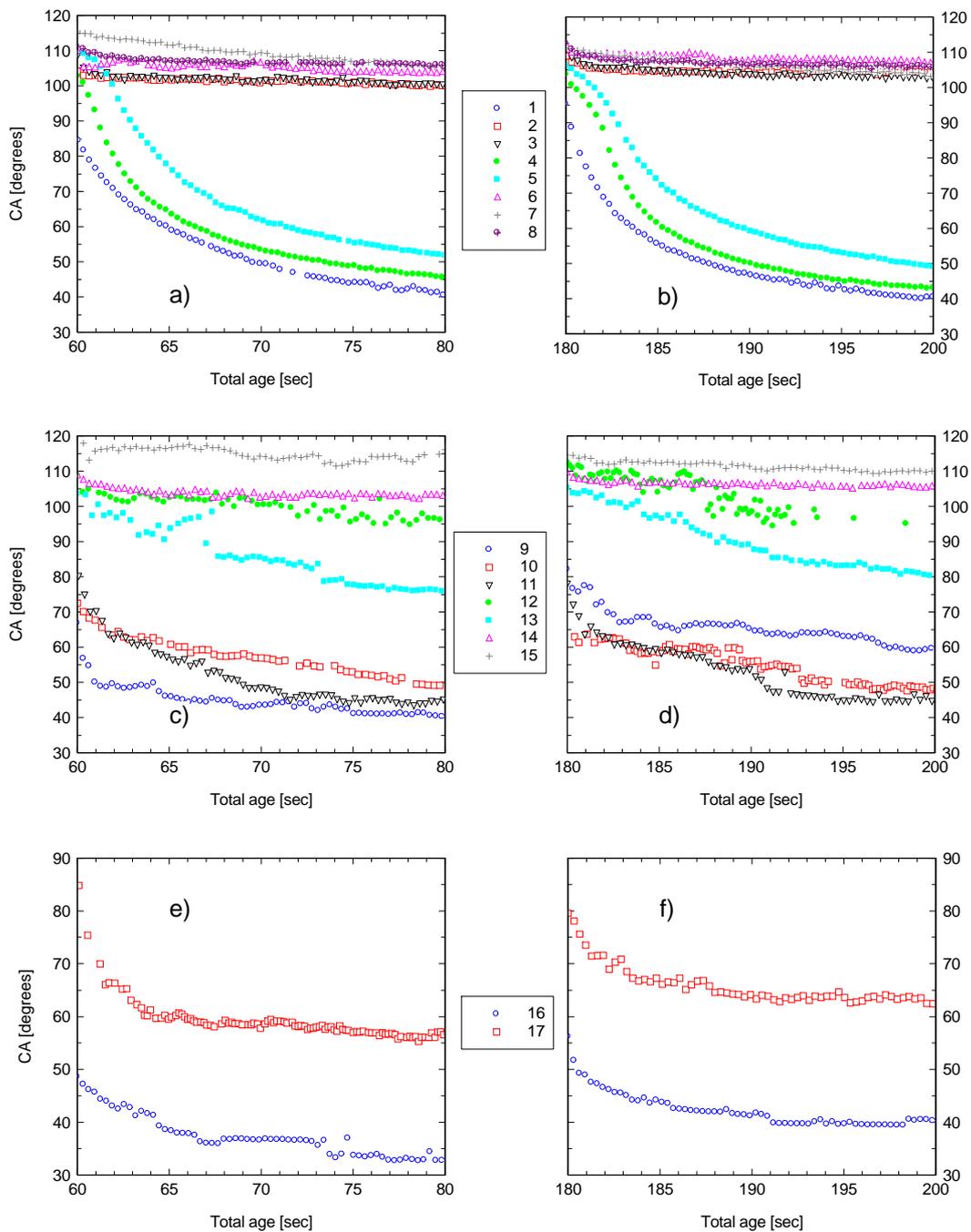


Figure 3: Evolution of the contact angle, CA of the impression materials as a function of total age t . a) A-Silicone materials (curing age, $\tau = 60s$). b) A-Silicone materials (curing age, $\tau = 180s$). c) C-Silicone materials (curing age, $\tau = 60s$). d) C-Silicone materials (curing age, $\tau = 180s$). e) Polyether materials (curing age, $\tau = 60s$). f) Polyether materials (curing age, $\tau = 180s$). The item number corresponding to table 1 appears in the figure legend.

A strong variation of the contact angle on the curing time was obtained for Alginate (sample 18), as shown in Figure 4. For this material, the contact angle increases with the increasing of the curing time, as it results for the three water drops placed on the surface at $\tau = 60s$, $\tau = 120s$ and $\tau = 180s$.

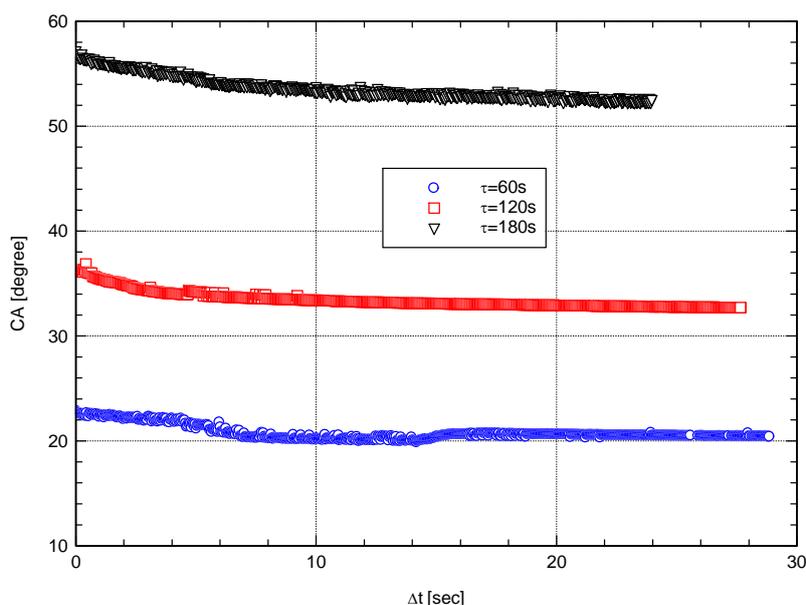


Figure 4: Evolution of the contact angle, CA of three water drops on Alginate material (item 18) vs. water contact time with the substrate, Δt .

4. Discussion

The results for A- Silicones can be divided in two groups namely: the first group of materials (items 2, 3, 6 – 8) is the group whose contact angle remains constant over the whole observation domain and whose average value is about 105° , showing that the material is hydrophobic. The second group (items 1, 4, 5) shows an evolution from hydrophobic character ($>90^\circ$) to the hydrophilic one ($\sim 45^\circ$). The wetting properties of this second group of A-silicones were improved by addition of a surfactant by the manufacturers (the corresponding Material Safety Data Sheets). Longer curing time does not influence this behaviour as is resulted by comparing Figure 3a with 3b.

For the second group (items 1, 4, 5) the time evolution of the contact angle may be explained by the variation of surface tension of water drop in eq. 1, assuming that the solid surface tensions are constant. The decreasing of the water surface tension (due to dissolution in water of some substrate constituents) would decrease the contact angle. Hosseinpour and Berg [16] have measured the surface tension of a water drop placed on an A-Silicone (Take 1) and on Polyether (Impregum) substrates at 5 minute intervals of contact with different pre-aged material. Their measurements show a decrease of surface tension of water in contact with the substrate, indicating the surfactant leaching from investigated materials. In this way, the behaviour of our materials under investigation (whose contact angle values decrease) can be explained.

We observed that the studied C-silicones, whose results are shown in Figure 3c and d, can be grouped into three categories, first group represents the hydrophobic materials which do not evolve in time (items 12, 14, 15), the second group, initial hydrophobic materials which are evolves to hydrophilic (item 13) and the third group of hydrophilic materials whose contact angle decreases in time (items 9-11).

Comparison of the results for a curing time of 60s (Figure 3c) with those for a curing time of 180s (Figure 3d) shows that the curing time does not influence the behaviour of the sample (12-15).

The results obtained for Polyether materials (items 16, 17) show that they are quite hydrophilic, in good agreement with results from literature [16]. The trend of the time evolution of contact angle shows a rapid decrease at the beginning, followed by the saturation, independent of curing time. By comparing Figure 3e with Figure 3f, we observe that there is a weak dependence of the contact angle values on the curing time.

It is seen from Figure 4 that the value of contact angle for Alginate has the smallest value in comparison with other investigated materials, which could be due to the water existing in the material (see Consistence in Table 1). On account of the mode of substrate preparation this material contains a quantity of water (initial 70% wt.), which probably leads to a substrate with surface tension higher than usually have the polymers [17]. Kwok and Neumann [17] evaluated the interfacial tension at the interface of solid - liquid

(water) using the solid surface tension, γ_{SV} and liquid surface tension, γ_{LV} and obtained for the contact angle the formula:

$$\cos \theta_{\gamma} = -1 + 2\sqrt{\gamma_{SV} / \gamma_{LV}} \left[\frac{4(\gamma_{SV} / \gamma_{LV})^{1/3}}{(1 + (\gamma_{SV} / \gamma_{LV})^{1/3})^2} \right]^{(\alpha \gamma_{SV})^{2/3}} \quad (3)$$

with $\alpha = 1.17\text{m}^2/\text{mJ}$, an essentially independent constant for the polymeric substrates studied in [17]. Using eq.3 one obtains that higher values of solid surface tension γ_{SV} as the Alginate has, give lower contact angle values.

The increasing contact angle with the curing time, obtained by us for Alginate is also well explained using eq. 3, as it gives $\gamma_{SV} = 52\text{mJ}/\text{m}^2$ for $\theta = 51.4^\circ$; $\gamma_{SV} = 62\text{mJ}/\text{m}^2$ for $\theta = 33.3^\circ$; $\gamma_{SV} = 68\text{mJ}/\text{m}^2$ for $\theta = 20^\circ$ and it is expected that the surface tension of the solid decreases by water evaporation from substrate; therefore contact angle increases. The same type of behaviour but less evident was obtained for the items 9-11, C-silicones, explained by the same equation describing the γ_{SV} modification.

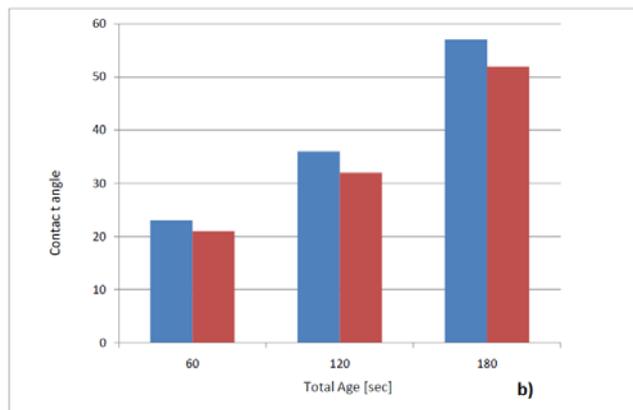
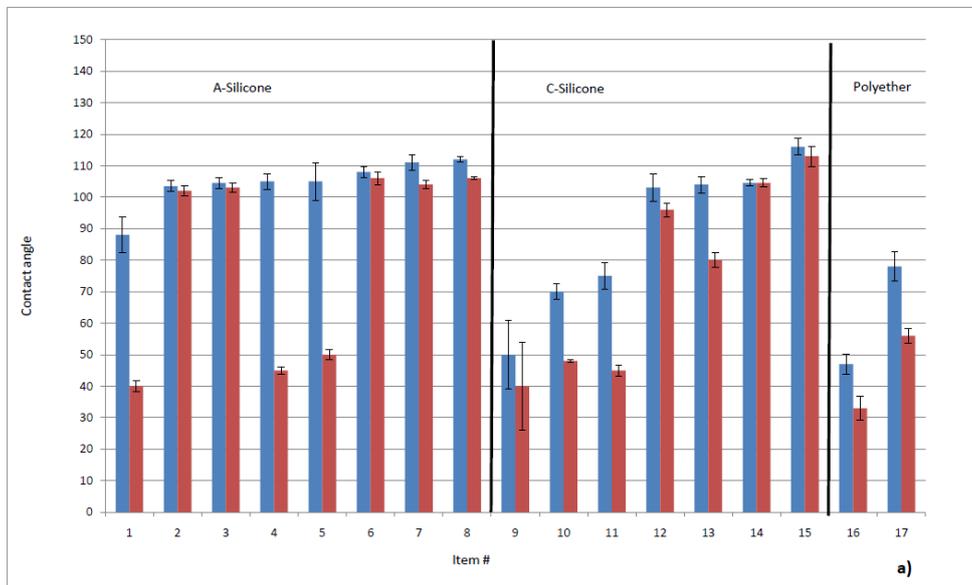


Figure 5: a) Average contact angle values at (■) $\Delta t = 0\text{s}$ and (■) $\Delta t = 20\text{s}$ for the first 17 impression materials. b) Contact angles for Alginate (18) at different curing times (1) – $\tau = 0\text{s}$, (2) – $\tau = 60\text{s}$, (3) – $\tau = 120\text{s}$. At (■) $\Delta t = 0\text{s}$, (■) values for $\Delta t = 20\text{s}$

Figure 5 presents the results obtained for the average values of contact angles for two water contact time $\Delta t = 0s$ and $\Delta t = 20s$. 17 of the studied impression materials like A-silicones, C-Silicones and Polyether materials were presented in figure 5a. The 18th material appears in figure 5b due to its special behaviour (the important dependence on curing time). To obtain this average value, we made the average of all results of the experimental curves (3-5, depending on material) in the time interval of 1s (for example for $\Delta t = 0s$, from $\Delta t = 0s$ to $\Delta t = 1s$) and we assigned this average value to the considered point (to $\Delta t = 0s$). We note that each curve contains about 25 points (it was recorded). As it can be seen from figure 5 the value of the contact angle decreases in time (the value from $\Delta t = 20s$ is lower than the value from $\Delta t = 0s$). On the graph the standard deviation (SD) value from the average value it is marked by error bars (figure 5a).

5. Conclusions

Studying the water contact angle values it was obtained that some A-Silicones and C-Silicones have angles greater than 90° . For other A-silicones, supplied by the manufacturer with added surfactant, the water contact angle decreases in time. Some C-silicones are hydrophilic, just from the initial moment. Polyether impression materials showed significantly lower initial contact angles than C-Silicone and A-Silicone based materials, and proved to be hydrophilic. By comparing the values of contact angles of water on these materials it is obvious that Alginate is the most hydrophilic, but this property decreases rapidly in time.

The decreasing of the contact angle in time can be well explained by a decrease of water surface tension by diffusion of the surfactant probably present in the substrate.

The increasing of the contact angle for Alginate in function of the curing time may be explained by the increasing of surface tension of the substrate caused by evaporating of the water contained in this material through its preparation.

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