Acrylic Resin Water Sorption Under Different Pressure, Temperature and Time Conditions

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The purpose of this work was to analyze water sorption by polymerized acrylic resins under different pressure, temperature and time treatments. A thermo-cured acrylic resin was used as the denture base (Classico Ltda.) and ethylene glycol di-methacrylate as a cross-linking agent, with processing carried out in a water bath at 73 °C for nine hours. Forty-five samples were prepared following the criteria and dimensions of specification # 12 of the American Dental Association (ADA), using a matrix in the shape of a stainless steel disc with 50 ± 1 mm diameter and 0.5 ± 0.05 mm thickness. The control group samples were stored in distilled water for 30 days, while groups GII to GIX were placed in a polymerization device with adjustable pressure, time and temperature. An analysis of the variance of the results revealed the influence of different factors on water sorption only, with significant factors being temperature, time, pressure and the interaction between time and temperature. Other interactions exerted no significant influence on water sorption. Neither additional treatments nor the control group (GI) showed any significant difference in comparison to the averages of other treatments.

1. Introduction

New materials and methods for denture resin processing are proposed from time to time with the main purpose of finding a technique to manufacture high quality dentures in less time than is spent using traditional processing techniques. The introduction of poly-methyl-methacrylate in 1937 opened up new prospects for the manufacture of totally and partially removable dentures.

Several studies have shown that resins are capable of absorbing water when immersed in liquid[6,10,16,21,31]. This absorption, which derives mainly from the polar properties of resin macromolecules through a diffusion process[3,24], increases the capacity of the denture resin base to adapt to and be retained on the edentulous ridge tissue[2,7,20,22,25]. The time required for sample saturation or drying is predictable[5] and may vary according to the resin processing method employed[5,9,10,11,19,22,24,29] and the composition of the resin storage fluid[1]. Resins stored in water increase in weight, but when placed in a dryer, their weight decreases and their dimensions become altered[11]. Specification # 12 of the

American Dental Association[8] recommends that the increase in weight of the polymer shall not exceed 0.8 mg/cm^2 of the surface after immersion in water for seven days at 37 ± 1 °C. Cury[9] observed that the mean water sorption presented by resin samples stored for 7 days was $0,010$ mg/cm^2. An accelerated water sorption process may be highly favorable from the clinical standpoint since it could accelerate the process of denture adaptation[6,16,21,31].

Two parameters are necessary for water sorption: coefficient of water diffusion and inside-outside water concentration of the sample[5]. Intermolecular water is subject to the attractive force of solid particles[30]. Water molecules act according to mathematical laws of water diffusion[5] and the coefficient of diffusion depends on temperature and pressure: both can accelerate or retard water sorption[4]. Thermodynamic principles must be considered in the presence of compressive force[23].

All fluids have a certain degree of compressibility and are influenced by these parameters[4]. Diffusion presumably occurs among macromolecules that are slightly forced apart, and the diffusion coefficient determines the rate of

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water sorption and time to reach equilibrium[4,17,30]. It has been proven that the coefficient of a heat-cured resin is 1.08 x 10 mm/s at 37 °C, and this value is halved when the temperature drops to 23 °C[21,24].

Henry Darci's law, of 1856, confirms the speed of water percolation caused by hydraulic gradients through the expression $v = Ki$, where K is a constant of permeability inherent to each body and i is the coefficient that represents the difficulty involved in liquid percolation[30].

The main factors producing water movement through isotropic and homogeneous elements are determined by the following principles: a) under pressure, water migrates from a high to a low pressure location, while under a temperature gradient, water flows from a high to a low temperature environment; b) in an electrostatic field, the flow goes from the highest to the lowest potential, *i.e.*, to the negative pole; c) under the effect of a temperature gradient, water tends to flow from the highest temperature to the lowest environment; d) under the effect of a difference in concentration of salts, the percolation moves from the point of highest molar fraction to the lowest one[27]. This author still considers that pressure applied on the body's surface increases proportionally with depth, which depends on the intensity of the body's strength and its thickness, and on the distribution and geometrical disposition of molecules. These findings are also confirmed by another author[23], who considers that the viscosity of liquids decreases with increased temperature. However, these explanations are not yet totally clear[14].

Under environmental conditions, the diffusion phenomenon requires a period of 30 days to occur totally in acrylic resins[21]. Thus, associating pressure, temperature and time may lead to the definition of an adequate level of water sorption in polymerized resin in a shorter timespan.

However, the literature contains no confirmation of a similar correlation for acrylic resins. Thus, the purpose of this work was to verify the correlation between water sorption by polymerized acrylic resins under different conditions of pressure, temperature and time treatments.

2. Experimental Procedures

A thermo-cured acrylic resin for denture base (Classico Ltda.) with a cross-linking agent (ethylene glycol dimethacrylate) processed in a water bath at 73 °C for 9 h[21] was used in this study.

Forty-five samples were manufactured according to a 50 ± 1 mm diameter and 0.5 ± 0.05mm thick steel disc (specification # 12 of the American Dental Association). After processing, the excess material of the samples was removed using a sharp blade, followed by sanding with sandpaper (T223-Norton®) using successively finer grits of 120, 240, 400, and 600 until complete smoothness and the pre-established dimensions of 50 ± 1 mm diameter and

0.5 ± 0.05 mm thickness were achieved, measured with a digital caliper rule (Stainless Hardened®). The samples were then dried with absorbent paper and divided into nine groups of five samples each.

The samples were dried at 37 ± 2 °C for 24 h in a desiccator containing thoroughly dry anhydrous silica gel, removed to a similar desiccator at room temperature for one hour, and then weighed with a precision of 0.2 mg (Acatec® BMC 1100). This cycle was repeated until the weight loss of each disk was no more than 0.5 mg in any 24-h period[8]. The samples were immersed in distilled water according to the treatment described in Table 1.

The GI samples were immersed in distilled water at 37 ± 1 °C (Fanen Ltda®, model 002 CB) for 30 days, while the samples of groups GII to GIX were stored in a container under controlled pressure, time and temperature (PP 1000®, Termotron). After treatment, the samples were removed from the water using tweezers, wiped with a clean, dry hand towel until devoid of visible moisture, waved in the air for 15 s, and weighed one minute after removal from the water. Water sorption was calculated as follows[8]:

$$\text{Water sorption}\left(\frac{mg}{cm^2}\right) = \frac{\text{Final weight} - \text{Initial weight (mg)}}{\text{Superficial area (cm}^2)}$$

The resulting values were then statistically analyzed, using a totally random delineation with a factorial scheme of 2 x 2 x 2 (temperature, pressure and time) with 5 repetitions. Temperature levels were 70 °C and 90 °C, with pressure rates of 40 and 60 Lbs. and sample exposure times of 60 and 90 min. An additional control treatment was made (37 ± 2 °C, 30 days, immersion in distilled H_2O), thus totaling treatments, using a factorial scheme of 2 x 2 x 2, plus an additional treatment. In addition, the Tukey test was applied to make comparisons between the groups[26].

Table 1. Groups and treatments proposed for the samples.

Groups	Treatment	Pressure (Lbs/pol^2)	Temperature (°C)	Time
I	1	Environmental	37 ± 2	30 days
II	2	40	70 ± 2	60 min
III	3	60	70 ± 2	60 min
IV	4	40	70 ± 2	90 min
V	5	60	70 ± 2	90 min
VI	6	40	90 ± 2	60 min
VII	7	60	90 ± 2	60 min
VIII	8	40	90 ± 2	90 min
IX	9	60	90 ± 2	90 min

3. Results

Table 2 shows average water cured levels using different treatments and compared to the level found in the Tukey test. A variance analysis showed the influence of different factors on water sorption only, as shown in Table 3, which demonstrates significant temperature, time, and pressure variations and interactions between time and temperature. Other interactions presented no significant influence. The additional treatment, or control group (GI), showed a significant difference in relation to the averages of other treatments, presenting better results. The treated samples

Table 2. Comparison of mean water sorption levels using the Tukey test.

Group	Mean
I	0,01168359 a
II	0,00680439 b
III	0,00651918 b
IV	0,00849530 b
V	0,00853605 b
VI	0,01217253 a
VII	0,01075664 a
VIII	0,01171415 a
IX	0,01054273 a

The values followed by the same letter are the same at a level of 1%.

Table 3. Analysis of variance of water sorption of acrylic resin samples subjected to alterations of pressure, temperature and exposure time.

Variation	Degree of freedom	Mean Square
Temperature	1	0,0001375**
Time	1	0,0000058*
Pressure	1	0,0000050*
Temperature x Time	1	0,0000120**
(Temper./ Time 60')	(1)	(0,0000341**)
(Temper./ Time 90')	(1)	(0,0001153**)
(Time./Temper. 70 °C)	(1)	(0,0000172**)
(Time./Temper. 90 °C)	(1)	(0,0000001ns)
Time x Pressure	1	0,0000002ns
Temperature x Pressure	1	0,0000034ns
Temperature x Time x Pressure	1	0,0000001ns
Control	1	0,0000223**
Error	36	0,0000011
C.V. (%)		10,61

* Significant at a probability level of $P < 0.05$.
** Significant at a probability level of $P < 0.01$.

(GVI and VIII) presented a sorption level similar to that of the control group (GI).

Temperature and time interactions revealed that, at a temperature of 90 °C, the exposure time was not an influencing factor (G VI, G VII, G VIII, and G IX) (Table 4).

Table 6 demonstrates that the temperature of 90 °C provided the highest water sorption rate under 60 Lbs of pressure. Treatment 6 (GVI) presented higher water sorption results than the control group (GI), although these data are insignificant at 1% or 5%. From Table 3 one can see that the water sorption levels were close to the control group (GI) when the temperature was 90 °C (G VI, G VII, G VIII, and G IX). Treatments 7, 8, and 9 (G VII, G VIII, and G IX) showed values close to the control group (GI), although no statistical differences among them were found. In these last four treatments, 6, 7, 8, and 9 (G VI, G VII, G VIII, and G IX), the water sorption levels were higher under 40 Lbs of pressure (Groups VI and VIII) than in the groups subjected to 60 Lbs of pressure (Groups VII and IX), with no statistical differences among them. In the groups treated at 90 °C (G VI, G VII, G VIII and G IX), the water sorption values were higher than in those for which the applied temperature was 70 °C (G I, G II, G III, and G IV). The latter treatments showed significantly lower water sorption values than the control group (GI).

At 70 °C, it was observed that the water sorption values were higher for treatments 4 and 5 (G IV, and G V) at 90 min than they were for treatments 2 and 3 (GII, and G III), also at 90 min. Pressure values were found to exert no influence on water sorption values in these treatments.

4. Discussion

The macromolecules of Poly (Methyl-methacrylate) are gigantic and highly complex molecules with a heterogeneous conformation, having discontinuous empty spaces and unequal interstices, which also varying according to their composition[21]. One of the main properties of acrylic resins is related to the polar properties of polymers and to the physical presence of these spaces, or their capacity to absorb water when immersed in liquid environments. The mechanism of liquid absorption originates from the diffusion of water molecules among polymeric macromolecules,

Table 4. Estimated averages of water cure as a function of time and temperature.

Time (min)	Temperature (°C)		Mean
	70	90	
60	0,0067 bB	0,0115 a A	0,0091 a
90	0,0085 aB	0,0111 a A	0,0098 a
Means	0,0076 B	0,0113 A	

Values followed by the same small letter in the columns and capital letter in the lines are the same at a level of 1% of significance by the F test.

Table 5. Forty Lbs. of pressure (G VI and G VIII) provide the highest possible rate of water sorption, confirming the statement made earlier herein.

Pressure	Time (min)		Mean
	60	90	
40	0,0095	0,0101	0,0098 a
60	0,0086	0,0095	0,0091 a
Means	0,0091 B	0,00121 A	

The values followed by the same letter are the same at a level of 5% of significance using the F test.

as set forth by the laws of diffusion[16,18,24]. Braden[4] introduced the theory of resin diffusion to assess the quantitative aspects of the kinetics of water sorption. The diffusion coefficient determines the rate of water sorption and the time to reach equilibrium, which are proportional to the sample's thickness. The diffusion coefficient is temperature-dependent. It is well-known fact that the coefficient of a heat-cured resin is 1.08 x 10 mm/sec at 37 °C and that this value is reduced by one half when the temperature drops to 23 °C[21].

Water sorption presumably occurs among macromolecules, which are forced slightly apart. This separation causes molecular mobility. Inherent stress created during heat curing of the acrylic resin can be relieved, with resulting intermolecular relaxation and possible changes in the shape of the denture. These properties are favorable for resin used in the elaboration of dentures because, after absorbing water, they provide more retention to the denture base in contact with the edentulous ridge. The time period required for water sorption varies according to different experimental conditions (24 h[19], 7 days[9,29], 17 days[21], 21 days[24], 25 days[10], 30 days[5,22,25], 60 days[16], 224 days[2], and even a year[31]). Accelerating the water sorption time through alterations in the pressure and temperature of the storage fluid decreases the time required for denture adaptation. From the clinical point of view, this is very interesting since it enables patients to adapt to their dentures more easily[21].

The theories of fluid dynamics confirm that the time rate for water absorption by solids establishes a correlation between the pressure rate and the temperature of liquids to

Table 6. Estimated average water sorption as a function of pressure and temperature.

Pressure	Temperature (°C)		Mean
	70	90	
40	0,0076	0,0119	0,098 a
60	0,0075	0,0106	0,0091 b
Means	0,0075 b	0,0135 a	

The values followed by the same letter are the same at a level of 1% of significance using the F test.

which bodies are subjected[17]. In this experiment, the samples immersed in water at 90 °C for 60 and 90 min showed a level of water sorption compatible with that of the control group, regardless of the level of pressure employed. Slightly higher sorption values were found in samples subjected to a liquid environment of less than 60 Lbs. of pressure. These values, however, were not statistically significant. Periods of 60 or 90 min did not influence sorption in either case. The samples subjected to a temperature of 70 °C showed significantly low water sorption values compared to those of the control group. However, no significant differences in sorption rates occurred in the samples from these groups (GII, G III, G IV, and G V). Water sorption by solids is directly influenced by alterations in temperature, *i.e.*, increases in temperature are inversely proportional to the viscosity of liquids[23]. This is probably due to the fact that, at 90 °C, the polymeric macromolecules that are formed possess a higher degree of changeability, causing the release of intermolecular tensions and augmenting the spaces between them[21], thereby facilitating the process of water diffusion[6,30]. The interference of temperature in the process of sorption by resins is also discussed by Phillips[21].

According to the literature, however, alterations in pressure would not change the amount of water absorbed by the groups whose temperature was kept at a constant level of 70 and 90 °C. Vargas[30] believes that the permanence of interstitial water inside a body is subject to the attractive force of molecules, and that this force tends to diminish as the distance between the molecules increases. We believe that, after a certain level of pressure, water sorption increases no further owing to the fact that the intermolecular distance remains constant. We also believe that increments in the external pressure mean compatibility of the body's internal pressure to equal values, in the opposite sense, as attested by the laws of physics. Conditions of relatively high compressibility, total saturation and violent (or rapid) application of external pressures of the liquid on a solid body may lead to momentary absorption of the liquid phase by the solid one, until compatibility between the two gradients is reached[6]. This fact contradicts Kutle's[14] statement that the viscosity of water decreases under abrupt increases (or oscillations) in pressure, since the pressure remained constant in our experiment[14]. Our results agree with Souto Silveira[27], who stated that the distribution of molecules and their geometric disposition tend to influence the curing of fluids by solid bodies.

Different chemical components such as copolymers[28], fluorine[13], glass fibers[18], and cross-linking agents[3,12] have been added to resin formulas in an attempt to improve the physical properties of cured resin. The resin used in this study contains ethylene-glycol di-methacrylate as the cross-linking agent in its liquid component, a fact that may influence its level of water sorption. The samples contain-

ing cross-linking agents showed higher levels of water sorption[12]. The control group showed results that were in agreement with those found in the literature[5,18]. However, after the stabilization of polymerization reactions caused by increases in temperature, macromolecules may lose their stability and become degraded[21]. This was not observed macroscopically in our experiment when our cured samples were subjected to temperature levels of 70 and 90 °C. However, we consider that the occurrence of this type of phenomenon can only be confirmed by evaluating other resin properties such as residual monomers and superficial microhardness. Like Arima *et al.*[3], we believe the cross-linking agents used in this study may have influenced the stability of the samples, even after the latter were subjected to higher temperature levels.

Although it has was observed that alterations in temperature may exert an influence on water sorption in resins, independently of the time and pressure level employed, we believe that further experiments with such combinations would be highly relevant.

5. Conclusion

Based on the results and experimental conditions of this experiment, we conclude that alterations in temperature influenced the index of water sorption when the pressure exceeded that of the environment, and that alterations in pressure did not affect water sorption levels when the pressure was higher than the ambient one.

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