

Mechanical Analysis of a Polyurethane for use in Dental Modeling

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Abstract

Background: Prosthetic rehabilitation is characterized by clinical and laboratorial phases, and the precision of dental models is an important and determining factor for the fit of dental restorations. Aim: Evaluate the high performance polyurethane resin 6470 and hardener Dt 082 (Huntsman Advanced Materials Química Brasil Ltda) loaded with 30% diatomite, for use in dental modeling. Methods and Material: Resin and hardener were manipulated in the ratio of 1:8 with the addition of a polyurethane accelerator in the proportion of 1 drop/200g of resin. The samples of pure polyurethane resin (PPR), modified with diatomite (DMPR) and gypsum type IV (Fuji Rock EP, GC) were analyzed for dimensional behavior, surface roughness Ra, and ability to copy details. Results: Tukey test ($\alpha = 0,05$) and variance showed that PPR or DMPR were superior to type IV gypsum for compressive strength, the diametral compression traction, abrasion wear resistance, impact and flexion three points. It could be verified that the PPR or DMPR is compatible with the silicone elastomers (condensation and addition); The 30% diatomite increased surface hardness, the compressive strength and the diametral compression traction, the impact fracture strength, the three point flexural strength, and the abrasion resistance of the polyurethane resin; The DMPR presents similar dimensional behavior to type IV gypsum. The diatomite reduced the copying capacity of the polyurethane resin and increased its surface roughness, but the loaded resin showed lower surface roughness and higher copy capacity than the type IV gypsum. Conclusion: In view of the results obtained there is the feasibility of using DMPR in dental modeling.

Key words: Polyurethanes. Diatomaceous Earth. Artificial Dental Stone.

INTRODUCTION

All the stages involved in the sequence of performing rehabilitative procedures are characterized by having a great potential for error (Dias, SC., *et al.*, 2007). In particular, the phase that involves molding and obtaining casts can be considered an extremely critical stage (Stober, T., *et al.*, 2010) since it constitutes exactly the time of transition from the clinical to the laboratory stage of the treatment. Success is dependent on the availability of a die material that meets certain clinical criteria (Duke, P., *et al.*, 2000). Therefore, the development of materials and techniques that increasingly improve both molding and the obtaining of models becomes essential, in order to achieve clinically successful treatment.

Obtaining dental casts is one of the most important steps in oral rehabilitation, since this stage determines the time when indirect restorations are made without the patient being present (Rudd, KD., *et al.*, 1970). Thus it is essential for these models to be capable of reproducing the real clinical situation with maximum precision (Stolf, DP., *et al.*, 2004). Plaster products are widely accepted in dental prosthesis, in spite of some limitations. These limitations are mainly the low resistance to fracture, dimensional instability, technique sensitivity and low resistance to wear by abrasion (Lindquist, TJ., *et al.*, 2003). Moreover, dental plasters do not have the same capacity for producing details observed in the elastomers (Campbell, S.D., *et al.*, 1985; Derrien and Sturtz 1995; Stober, T., *et al.*, 2010).

Although type IV gypsum has been used successfully for many years (Duke, P., *et al.*, 2000), several methods have been made to develop a die material with improved properties (Alsadi, S., *et al.*, 1996). Research for other dental modeling materials has resulted in a generation of polymer-based product alternatives to plasters, used in making precision models (Schwedhelm and Lepe 1997). Several studies (Nomura, GT., *et al.*, 1980; Stevens and Spratley 1987; Phillips 1991) have been conducted to analyze the behavior of epoxy resin when used in dental modeling. Duke *et al.* (2000) reported that the epoxy resin exhibited much better detail reproduction, abrasion resistance, and transverse strength than the gypsum materials. According to Derrien & Sturtz (1995) stone has limited transverse strength, and this may predispose working casts to fracture when they are removed from impressions.

Polyurethanes are tested as substitutes for gypsum-based arch models (Black, EM 2015). Due to the great industrial importance of polyurethanes, the chemistry of isocyanates has been studied extensively (Leterrier and G'sell 1988; Petrović and Ferguson 1991). The polyurethanes are high performance industrial polymers, normally produced by the reaction with an isocyanate (di or polyfunctional) with a polyol or other reagents (polymerizing agents or chain extenders) containing two or more reactive groups. The hydroxyl-containing composites may vary with regard to molecular weight, chemical nature and functionality. The chemical nature as well as functionality of reagents can be chosen according to the desired properties. This flexibility of choice of reagents enables an ample variety of composites with different physical and chemical properties to be obtained, which allows the polyurethanes to occupy an important place in the world

market of high performance synthetic polymers (Petrović and Ferguson, 1991). This material is considered an innovation in terms of materials for obtaining models and dies (Kim., S.Y., *et al.*, 2014b; Black, E.M., 2015) so that studies evaluating its properties are still scarce.

This study presents a mechanical evaluation of a polyurethane resin modified with diatomite for use in making dental models.

MATERIAL AND METHOD

The high performance polyurethane resin 6470 and hardener Dt 082 (Huntsman Advanced Materials Química Brasil Ltda., supplied by Maxepoxi, Santo Amaro, São Paulo, Brazil) was modified by the addition of diatomaceous earth (diatomite) a very light, powdery material, formed by the accumulation of siliceous frustules of dead diatomaceous algae, in the proportion of 30%. The resin was dosed in the proportion of 1/9 between resin and hardener, established by the manufacturer. The resin was manually manipulated for 30 seconds. A polyurethane accelerator was used (Huntsman Advanced Materials Química Brasil Ltda., supplied by Maxepoxi, Santo Amaro, São Paulo, Brazil) in the proportion of one drop to every 200 grams of resin. The accelerator reduces the material hardening time to ± 30 minutes, the working time being ± 3 minutes.

Ten test specimens were made with pure resin, 10 with the resin modified with diatomite, and 10 with type IV plaster (Fuji Rock EP), GC America Inc-USA to perform each of the following tests: resistance to compression ASTM D 695 2(a), traction resistance to diametral compression ASTM D 695 2(a), resistance to fracture by impact ISO 179-1: 2000., resistance to three point bending flexure (ISO 1567:1999), resistance to wear by abrasion ASTM D 4060 standard. For the surface hardness test (Rockwell) 9 test specimens were made for each material being analyzed.

The resistance to compression test and diametral compression test for tensile strength were performed in a Universal Test Machine EMIC DL2000, (EMIC, São José dos Pinhais, PR, Brazil), with a 2000 Kgf load cell and constant displacement speed of 1.3 mm/min.

The resistance to fracture by impact was tested in a CEAST Impact Machine model Resil 25 (CEAST – Pianezza, TO, Italy), using the Charpy type test. The test specimens were placed in the Ceaste test machine, in accordance with the specifications for the test. A formula was used to obtain the resistance to impact value (RI) in joules per meter, where:

$$RI = \frac{\text{value obtained} - \text{standard calibration value}}{\text{Test specimen thickness}}$$

The bending test was performed in an EMIC DL 2000 universal test machine (Emic - São José dos Pinhais, PR, Brazil), with the distance of 52 mm between the supports, with a 2000 Kgf load cell and speed of 5 mm/min. The rupture values were used to calculate the flexural strength by the following formula:

$$S = \frac{3wi}{2bd^2}$$

In which S = flexural strength (MPa)/i = distance between the points of support /b = test specimen width/d = test specimen thickness/w = maximum load for fracture.

The test for resistance to wear by abrasion was performed in a TABER abrasion meter, which determines mass loss per 1000 cycles, using the standard CS-17 abrasive wheel with a 1.000g load. The greatest mass loss identified signifies the least resistance to wear by abrasion, ASTM D 4060 Standard.

For the surface hardness test 27 metal matrixes with dimensions specifically for the surface hardness test were used. The matrixes were filled with the materials being analyzed. When seven days had elapsed after the test specimens were made, the test was performed using a Sussen Wolpert, type Testor – HT1 durometer. The Rockwell Hardness method was based on the penetration depth of a tempered steel ball measuring 12.7 mm into the part being tested, under a determined load. The process was performed in three stages, a) each test specimen was submitted to a pre-load (P1) of 10Kg and the meter was set to “zero”; b) a 60kg load was applied which, added to the pre-load, resulted in a nominal load of the test (P1+P2) until the pointer of the indicator stopped. The application time of this load was 15 seconds; c) the supplementary load was removed, and the surface hardness readout was taken. The hardness result was given in HRR, in which H represents the test, (Hardness), R represents the technique (Rockwell) and R which represents the method used, which was the use of the 10 Kg pre-load, with the ball penetrator.

Results:

With the object of comparing three modeling materials in the variation of the mean resistance to compression (Table 1), traction resistance to diametral compression (Table 2), resistance to fracture by impact (Table 3), resistance to three point bending flexure (Table 4), and resistance to wear by abrasion (Table 5), an analysis of variance based on a model of one factor (material) was used. The object of this parametric test was to compare more than two groups with regard to the mean of a variable of interest. When the analysis presented significant difference among the materials, the Tukey test was used with a level of significance of 5% ($\alpha = 0.05$) to establish the conclusions. It is pointed out that the presuppositions for the use of this analysis; that is, normality of residues and constant variance, were verified. All the results obtained by means of the mechanical tests performed were considered significant among the sample groups evaluated ($p < 0.001$), being $G3 > G2 > G1$.

Table 1: Resistance to Compression, values in kgf.

Fuji Rock Plaster G1	PU Resin G2	PU Resin+Diatomite G3
240.02	394.25	493.62
254.78	319.31	517.89
274.23	343.57	467.15
228.78	335.11	542.09
273.42	376.98	527.28
261.67	320.08	487.47
262.64	355.34	512.12
265.78	363.76	503.44
234.89	345.54	522.17
262.64	351.22	533.33

After the incorporation of 30% diatomite (G3) into the pure polyurethane resin (G2), an increase in compressive strength was observed. In addition, statistically significant differences were found among the groups ($P < 0.001$), so that $G3 > G2 > G1$.

Table 2: Resistance to traction by diametral compression, values in kgf.

Fuji Rock Plaster G1	PU Resin G2	PU Resin+Diatomite G3
158.25	363.77	572.89
140.5	397.05	561.46
151.13	390.12	564.95
141.2	399.49	571.67
155.95	373.14	561.36
158.05	383.76	537.16
155.74	377.78	549.59
135.89	367.75	543.27
136.03	378.75	554.57
142.31	377.07	547.88

In the analysis of Traction Resistance to Diametral Compression the results were similar to those found in the Compression Resistance analysis. After the incorporation of 30% diatomite (G3) into the pure polyurethane resin (G2), an increase in Traction Resistance to Diametral Compression was observed. In addition, statistically significant differences were found among the groups ($P < 0.001$), so that $G3 > G2 > G1$.

In the analysis of Resistance to Fracture by Impact, the results after the incorporation of 30% diatomite (G3) into the pure polyurethane resin (G2), demonstrated an increase in the resistance to wear by abrasion. In addition, statistically significant differences were found among the groups ($P < 0.001$), so that $G3 > G2 > G1$.

In the analysis of Resistance to 3 Point Bending Flexure, the results after the incorporation of 30% diatomite (G3) into the pure polyurethane resin (G2), demonstrated an increase in Flexural Strength. In addition, statistically significant differences were found among the groups ($P < 0.001$), so that $G3 > G2 > G1$.

In the analysis of Resistance to Wear by Abrasion, the results after the incorporation of 30% diatomite (G3) into the pure polyurethane resin (G2), demonstrated an increase Resistance to Wear by Abrasion. In addition, statistically significant differences were found among the groups ($P < 0.001$), so that $G3 > G2 > G1$.

Discussion:

The option was to load the resin with diatomite, a very light, powdery material formed by the accumulation of siliceous frustules of dead diatomaceous algae (Losic, D., *et al.*, 2009). Apart from being made of fossil skeletons, diatomite is essentially opaline hydrous silicasilica (Erdem, E., *et al.*, 2005). Diatomite has high permeability and high particles porosity (Erdem, E., *et al.*, 2005), which allow resins to penetrate, forming a network that reinforces the material. The diatomite used in this study for addition to the polyurethane polymer resin under the conditions that were used is considered as load. The load was used to seek mechanical gains for the resin. In some cases, loads are able to improve the properties of the polymeric matrix (Trotignon, JP., 1991). In the present study, diatomite in the proportion of 30% was used according to Dias *et al.*, (2007).

The values expressed by the modeling materials with regard to the criterion resistance to abrasion, table 5 demonstrate that the plaster presents lower resistance to wear by abrasion than the polyurethane resins. Considering this result, the benefits of the use of this material in modeling extensive and complex rehabilitations are pointed out. In rehabilitations, one expects that the models will not suffer wear by abrasion (Aiach, D., *et al.*, 1984). Therefore, transverse strength and dimensional accuracy of die materials are among the critical properties (Derrien and Stutz., 1995). They have low resistance to abrasion (Fan, PL., *et al.*, 1981), therefore, models obtained with these materials are susceptible to edge fractures and wear resulting from manipulation in the laboratory stages of the process for obtaining indirect restorations.

Peyton *et al.*, (1952) verified that plasters present their maximum hardness value within an interval of three days. The materials analyzed for resistance to wear by abrasion were analyzed after seven days had elapsed from the time of obtaining the samples.

Various attempts have been made to increase the hardness and resistance to wear by abrasion of plaster models: surface treatment with resinous substances (Lindquist, TJ., *et al.*, 2003), use of hardeners (Toreskog, S., *et al.*, 1966); addition of calcium and sodium lignosulphonates (Combe and Smith 1971), or impregnation of plaster dies with epoxy resin (Campagni, WV., *et al.*, 1986). The use of substances on the die surface compromises the juxtaposition of cast restorations, covers retentive details of preparations; the application of more than two layers of resinous material on the plaster die surface produces dimensional alterations of over 8µm (Ghahremannezhad, HH., *et al.*, 1983).

Some studies (Nomura, GT., *et al.*, 1980; Fan, PL., *et al.*, 1981) have shown that plasters present greater surface hardness when compared with epoxy resins and also verified that the surface hardness expressed by epoxy resins are lower than those presented by the improved plaster. This in turn, presents surface hardness four to five times higher than that presented by epoxy resin. When observing table 6, one verifies that the type IV plaster analyzed presents higher surface hardness than the polyurethane resin, but one also notes that the presence of the diatomite increases the surface hardness of the polymer. The high surface hardness expressed by the improved plasters does not confer good surface stability on the models obtained with these materials, as the plaster models do not resist wear by abrasion (Sanad, MEE., *et al.*, 1980), a condition that can be verified in table 5.

The loads generally used are very much more rigid than the plastics, and therefore, it is a well-known fact that such loads increase the composite hardness in comparison with that of virgin resin (Nielsen and Landel 1974; Kats and Milewski, 1984). Hardness is a function of the relative volume of load and the modulus load. Other factors that may influence the harness of loaded systems are: degree of load dispersion in the polymeric matrix; load distribution; interfacial connection; crossed links in additives; and probably many other factors; when observing table 6 one verifies that the presence of diatomite increased the surface hardness of the polyurethane resin.

Dental plasters are intensely manipulated during the laboratory stages of prosthetic procedures, and already begin the moment they are separated from the impression. Therefore, in order not to lose their fidelity, they need to be resistant to traction and compression. Dental plaster is widely used for obtaining models, but due to its low tensile strength, the models obtained with this material frequently suffer fractures (Aiach, D., *et al.*, 1984; Dias, S.C., *et al.*, 2007). Models that present teeth that have been prepared long and straight in shape, if made of plaster, easily fracture during removal from the impression (Bailey, J.H., *et al.*, 1988). Therefore, one expects the material used in dental modeling to resist the forces of traction. Considering the results for resistance to compression and traction by diametral compression in this study, expressed in tables 1 and 2, one verifies that the polyurethane resin - pure or modified with diatomite - presents higher resistance when compared with type IV plaster.

Comparing the accuracy of the polyurethane model with plaster model, Kim *et al.*, (2014a) observed a tendency for a reduced size in the margin of the polyurethane model, and a greater discrepancy in the occlusal surface, when compared to the gypsum models.

The incorporation of a rigid particulate load into a polymeric matrix increases the modulus of elasticity of the composite, and the effect of this on the resistance to impact is complex. Generally, the presence of mineral load in a polymer diminishes the resistance to impact of the system in comparison with that of

virgin resin. This can be explained by the fact that the inclusions present in a polymeric matrix act as stress concentrators, reducing the energy required for the induction and propagation of cracks. Furthermore, inclusions differ substantially from the matrix as regards ductility, having a high modulus, and therefore, weaken the composite. Nevertheless, rigid loads can serve to divert cracks and dissipate the energy associated with their growth, increasing the resistance to impact of the composite (Kats and Milewski 1987; Nielsen, LE., 1980).

It should also be pointed out that the packaging fraction of the load is a very important factor. Poorly packaged loads occupy larger volumes, and therefore, contribute to higher numbers of stress concentrators; or analyzing the composite as a whole, they reduce the matrix continuity more effectively. Since it is the matrix that absorbs most of the shock of impact, those loads that have high packaging fractions will tend to reduce the resistance to impact much less for the same relative volume of load; when observing Table (3) one verifies the effect of the diatomite load when incorporated into the polyurethane polymer. It was observed that the load increased the resin resistance to fracture by impact, a condition that can be attributed to the load distribution in the resin mass provided by its high permeability.

Table 3: Resistance to fracture by impact, values in Joules/m.

Fuji Rock Plaster G1	PU Resin G2	PU+Diatomite G3
14.8	56.2	65.6
14.1	57.3	66.8
15.3	55.5	64.5
16.4	56.3	67.3
13.4	57.7	63.5
14	53.6	68.3
14.8	54.6	65.7
14.1	52.4	66.8
13.9	56.5	65.6
15.2	56.6	67.1

Table 4: Resistance to three-point bending flexure, values in kgf.

Fuji Rock Plaster G1	PU Resin G2	PU Resin+Diatomite G3
12.1	71.49	99.09
15.52	70.31	95.33
10.54	77.31	94.08
13.66	63	96.29
13.52	57.49	101.42
12.67	70.13	97.74
12.26	68.42	102.87
12.82	72.77	104.81
10.82	77.64	96.53
13.24	65.59	100.92

Table 5: Resistance to wear by abrasion, loss of mass in grams.

Fuji Rock Plaster G1	PU G2	PU+Diatomite G3
0.143	0.043	0.038
0.146	0.038	0.036
0.137	0.037	0.035
0.140	0.040	0.038
0.140	0.042	0.030
0.142	0.045	0.036
0.137	0.036	0.037
0.139	0.040	0.037
0.143	0.043	0.036

0.143	0.046	0.037
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Table 6: Surface Hardness (Rockwell), values expressed in HRR.

PU Resin G2	PU Resin+Diatomite G3	Fuji Rock Plaster G1
74	103	96
76	90	101
75	103	106
78	78	98
84	97	101
83	77	93
80	95	93
82	93	77
78	104	88

Various further studies are still required to make polyurethane resin loaded with diatomite feasible for clinical use in making models, but when the results expressed in the study are analyzed, one verifies a high potential for this material.

Conclusion:

Conducting this study enabled the following conclusions to be drawn:

- 1- The diatomite load in the percentage of 30% increases the surface hardness, resistance to compression, traction resistance to diametral compression, resistance to fracture by impact, resistance to 3 point bending flexure and the resistance to wear by abrasion of the polyurethane resin.
- 2- In the comparison between the polyurethane resin modified with 30% diatomite and Type IV Plaster, the resin was superior in the tests of resistance to compression, traction resistance to diametral compression, resistance to fracture by impact, resistance to 3 point bending flexure and the resistance to wear by abrasion.
- 3- In view of the results found with the modification of polyurethane resin with 30% diatomite, it is feasible to use this material in dental modeling.

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