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Effect of deep-freezing on some properties of acrylic resin

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Abstract
The objective of this study was to evaluate the effect of freezing the acrylic resin polymer/monomer dough mix on a range of properties of the polymerized denture base material. Powder and liquid of acrylic resin were mixed and at the dough stage transferred to a deep freezer and frozen for periods of 24 h, 1 week, 1 month, 3 months, and 6 months. At the end of the storage time, sufficient dough was removed, thawed, packed, and polymerized, and specimens were prepared from the polymerized plates. A control series was prepared from dough which had followed conventional mixing and packing procedures without freezing. The strength properties, hardness, and flash thickness were examined. Statistical analysis was carried out using ANOVA (one-way and two-way) with multiple range tests. The flexural strength was significantly ($p = 0.03$) increased and the impact strength, hardness, and flash thickness were not affected by freezing the material during the dough stage. The flexural modulus was significantly ($p = 0.0001$) reduced when the storage time in the freezer was increased to 3 months. Six months' frozen material proved to be unpackable. It was concluded that the acrylic resin polymer/monomer dough mix can be stored in the freezer for up to 1 month without any statistically significant effect on the properties of the polymerized denture base material.

Key Words: *Denture base, heat polymerizable, physical properties, polymer*

Introduction

Poly(methyl methacrylate) has been employed as a denture base material since the 1930s because of its unique combination of properties. Despite its popularity, not all its characteristics are ideal. Today, most dentures are constructed by the dough-molding press/pack technique, in which a poly(methyl methacrylate) powder and methyl methacrylate liquid mix is forced to flow into, fill and conform to the shape of the mold. When the powder and liquid are mixed, the mass passes through a series of stages: sandy, stringy, doughy, and rubbery. The material is ready for manipulation at the doughy stage. Therefore the material should be packed during the doughy stage, since manipulating a material too early, or beyond this time, results in either breakdown of the material structure or damage to the mold, and consequently influences the accuracy and quality of the molded denture. Ideally, the doughy stage should be as long as possible, and the dough should exhibit good flow characteristics so that optimum packing plasticity is achieved [1].

The flow properties of the acrylic resin depend on factors such as the type and structure of the polymer, concentration of the polymer/monomer mix, and technique [2]. Another factor which may influence the flow of the material is variation in temperature [3] during dough-forming and storage of the mix.

The viscosity-limited working time can pose problems when making a packing involving multiple denture preparations. It may therefore be desirable to extend the working time of poly(methyl methacrylate) denture base resin when making a multiple packing. Freezing the mixed dough prior to packing can extend the working time. This allows the laboratory to use portions as and when necessary for economy of both material and time – supposedly without adversely affecting properties of the polymerized material – and it is hypothesized that it may also increase the interpenetrating polymer network and hence improve the properties of the polymerized resin.

The aim of this study was to evaluate the effect of deep-freezing and storage time of the polymer/monomer dough mix on some properties of the polymerized

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Table I. Characterization of denture base material used

Powder	
Polymer type	Heat-polymerizable poly(methyl methacrylate)
Number average molecular weight (Mn)	441,500
Weight average molecular weight (Mw)	1,506,911
Polydispersity ratio Mw/Mn	3.41
Powder particle size (μm)	54
Glass transition temperature (Tg) °C	121.41
Liquid	
Monomer	Methyl methacylate
Inhibitor	0.006 hydroquinone

acrylic resin denture base material. The properties investigated were flexural strength, flexural modulus, impact strength, hardness, and flash thickness.

Material and methods

A heat-polymerizable poly(methyl methacrylate) denture base resin (Lucite International Ltd, Newton Aycliffe, UK) was used. The characterization of the material is listed in Table I.

Polymer powder (32 ml) was mixed with monomer liquid (10 ml). The mixture was left to stand in a plastic mixing vessel until it reached the dough stage. For evaluation of the dough stage of the powder/liquid mixtures, a packing plasticity test was performed using a needle penetrometer (Sonner and Runge, KB, Berlin, Germany). The needle penetrometer method of measuring doughing and manipulation times was described in detail in a previous study [3]. The point where the penetration into the dough decreased sharply (penetration <10 mm) indicated the beginning of the dough stage (doughing time/initial packing time) and penetration of <3 mm indicated the end of the manipulation stage (final packing time). At a penetration of <3 mm the material is not workable. The setting time is defined as the time from mixing until the material becomes rubbery and unworkable (at the completion of the manipulation time). When the mix reached the initial dough stage, it was transferred to deep freeze storage at $-18°C$ and after periods of 1 day, 1 week, 1 month, 3 months, and 6 months a portion of the mix was removed, allowed to thaw, assessed using a needle penetrometer, and then tested. Thawing of the mix was assessed using the needle penetrometer. The mix was allowed to thaw until a penetration of 10 mm–3 mm was achieved before the dough was packed into a gypsum mold in a dental flask. The 6 months' stored mix was not workable when it was thawed. Molds were prepared by investing master pattern blanks in gypsum. Room temperature was $22\pm1°C$. The poly(methyl methacrylate) blanks were cured for 14 h at 70°C and 3 h at 100°C. The flasks were allowed to bench cool before opening and the cured plates were carefully removed from the mold. The excess flash was removed (and retained for flash thickness measurement) and the specimens finished with wet, self-adhesive, waterproof, silicon carbide paper disks of 203 mm diameter, 320 A and 600 A grit size, respectively.

Each block was cut into appropriate size specimens with a band saw. The specimens were then returned to the polishing machine and carefully finished to the dimensions $50\times6\times4$ mm for the impact tests, i.e. $64\times10\times2.5$ mm for the flexural test and $38\times38\times2.5$ mm for the hardness test. A tolerance of ±0.03 mm was accepted. The specimens were water-saturated prior to testing.

Impact test

The impact strength was determined using a Charpy type test. In order to ensure more consistent results, specimens were notched. The material fractures at the notch, since this is the weakest part. For the impact test on each specimen, a V notch was cut to a depth of 0.8 mm, leaving an effective depth under the notch of 3.2 mm. This was done with a Zwick notch cutter (Model 5000) and a notch broach 69 D. Each specimen was fractured in air at $22\pm1°C$ using the Zwick Pendulum Impact Tester Model 5102 (Zwick Instruments, Leominster, UK) with a pendulum of testing capacity 0.5J.

Flexural test

The flexural test was carried out using a Lloyd's Instrument Material Testing machine (Model L2000R; Lloyds Instruments plc, Southhampton, UK) using the three-point method. The test rig consisted of a loading wedge and a pair of supporting wedges placed 50 mm apart, which is the average intermolar distance of a denture. The specimen thickness of 2.5 mm is the average thickness of an upper denture base. Each test specimen was centered on the testing rig so that the loading wedge, set to travel at a speed of 5 mm/min, engaged the center of the upper surface of the specimen until the specimen broke. The specimens were tested in a water-bath at $37+1°C$ to simulate mouth conditions. Flexural strength and flexural modulus were recorded.

Surface hardness test

Surface hardness was investigated using the Wallace semi-automatic microindentation tester (H. W. Wallace & Co Ltd, Croydon, Surrey, UK) fitted with a servo-assisted loading mechanism. Surface hardness tests were undertaken in air at $22+1°C$. The Wallace microhardness instrument measures the depth of indentation produced on the specimen surface when a 300 g load is applied by a diamond indentor for 15 s.

Table II. Statistical analysis of the data on the effect of freezing on the impact strength (kj/m^2) of the acrylic resin

a. Analysis of variance

Source	Sum of squares	d.f.	Mean square	F-ratio	*p*-value
Between groups	0.087748	4	0.021937	1.73	0.1605
Within groups	0.57127	45	0.0126949		
Total	0.659018	49			

b. Multiple range tests

Time	95% LSD count	Impact strength (KJ/m^2)	Homogeneous groups
Control	10	1.53 ± 0.08	X
24 h	10	1.56 ± 0.01	X
1 week	10	1.53 ± 0.01	X
1 month	10	1.63 ± 0.01	X
3 months	10	1.60 ± 0.02	X

In the right-hand column, Xs in the same vertical line demonstrate a group of means within which there are no significant differences.

Table III. Statistical analysis of the data on the effect of freezing on the flexural strength (mpa) of the acrylic resin

a. Analysis of variance

Source	Sum of squares	d.f.	Mean square	F-ratio	*p*-value
Between groups	22.5901	4	5.64753	2.93	0.0307
Within groups	86.5892	45	1.92421		
Total	109.179	49			

b. Multiple range tests

Time	95% LSD count	Flexural strength (MPa)	Homogeneous groups
Control	10	72.87 ± 1.65	X
24 h	10	73.43 ± 1.17	X X
1 week	10	73.16 ± 0.93	X X
1 month	10	74.15 ± 1.61	X X
3 months	10	74.7 ± 1.42	X

In the right-hand column, Xs in the same vertical line demonstrate a group of means within which there are no significant differences.

Table IV. Statistical analysis of the data on the effect of freezing on the flexural modulus (mpa) of the acrylic resin

a. Analysis of variance

Source	Sum of squares	d.f.	Mean square	F-ratio	*p*-value
Between groups	302016.0	4	75504.1	7.42	0.0001
Within groups	457811.0	45	10173.6		
Total	759827.0	49			

b. Multiple range tests

Time	95% LSD count	Flexural modulus (MPa)	Homogeneous groups
Control	10	2079.2 ± 64.5	X X
24 h	10	2084.2 ± 62.9	X X
1 week	10	2107.6 ± 72.6	X
1 month	10	2008.1 ± 64.1	X
3 months	10	1894.2 ± 182.7	X

In the right-hand column, Xs in the same vertical line demonstrate a group of means within which there are no significant differences.

Table V. Statistical analysis of the data on the effect of freezing on the hardness indentation values (μm) of the acrylic resin

a. Analysis of variance

Source	Sum of squares	d.f.	Mean square	F-ratio	*p*-value
Between groups	20.958	4	5.23951	4.84	0.0025
Within groups	48.7515	45	1.08337		
Total	69.7095	49			

b. Multiple range tests

Time	95% LSD count	Hardness (μm)	Homogeneous groups
Control	10	27.22 ± 0.77	X
24 h	10	27.53 ± 0.80	X
1 week	10	28.57 ± 1.39	X
1 month	10	27.59 ± 0.96	X
3 months	10	28.89 ± 1.14	X

In the right hand column, Xs in the same vertical line demonstrate a group of means within which there are no significant differences.

Table VI. Statistical analysis of the data on the effect of freezing on the flash thickness (mm) of the acrylic resin

a. Analysis of variance

Source	Sum of squares	d.f.	Mean square	F-ratio	*p*-value
Between groups	0.15773	4	0.0394326	6.73	0.0013
Within groups	0.117156	45	0.0058578		
Total	0.274886	49			

b. Multiple range tests

Time	95% LSD count	Flash thickness (mm)	Homogeneous groups
Control	10	0.41 ± 0.04	X X
24 h	10	0.48 ± 0.11	X X
1 week	10	0.34 ± 0.03	X
1 month	10	0.45 ± 0.10	X
3 months	10	0.57 ± 0.03	X

In the right-hand column, Xs in the same vertical line demonstrate a group of means within which there are no significant differences.

Flash thickness

After the cured plates were carefully removed from the mold, the thickness of the excess flash was measured using a Mitutoyo's Absolute Precision Digimatic Caliper (Mitutoyo Ltd, UK).

Results

The results, presented in Tables II–VI, were subjected to statistical analysis using ANOVA (one-way and two-way) with multiple range tests (Statgraphics Plus V5.0; Manugistics Inc., Rockville, Md., USA).

The ANOVA Tables IIa, IIIa, IVa, Va, and VIa decompose the variance of impact strength, flexural strength, flexural modulus, hardness and flash thickness into two components: a between-group component and a within-group component. If the *p*-value of the F-tests is less than 0.05 there is a statistically significant difference; if greater than or equal to 0.05, there is not a significant difference between the groups.

Tables IIb, IIIb, IVb, Vb, and VIb apply a multiple comparison procedure to determine which means are significantly different from which others. Homogeneous groups are identified using columns of Xs. Within each column, the levels containing Xs form a group of means within which there are no statistically significant differences. The method currently being used to discriminate among means is Fisher's least significant difference (LSD) procedure. With this method there is a 5.0% risk of calling each pair of means significantly different when the actual difference equals 0.

Discussion

Freezing the acrylic resin polymer/monomer mix during the dough stage may extend the working time without adversely affecting the properties of the finished material. The present study investigates the effect of freezing of the acrylic resin polymer/monomer mix on the flexural strength, flexural modulus, impact strength, hardness, and flash thickness of heat-polymerizable acrylic resin denture base material.

The fracture of acrylic resin dentures as a result of being dropped is a common occurrence. In this study for all the impact tests, the specimens broke with a sharp fracture, exhibiting a typical brittle fracture behavior. Analysis of the results using a one-way analysis showed no significant difference between the groups (Table IIa).

The flexural test was undertaken as this is considered relevant to the loading characteristics of a denture base in a clinical situation. The machine chosen for the tests, the Lloyd's Instruments material testing machine, is routinely used and widely accepted as a recognized method. The flexural modulus and flexural strength of a material is a measure of stiffness and resistance to fracture. The International Standard ISO 1567 [4] regulations for denture base polymers specify that flexural strength must not be less than 65 MPa and flexural modulus at least 2000 MPa.

For flexural strength, a one-way analysis of variance demonstrated a significant difference between groups (Table IIIa). The 3 months' frozen specimens demonstrated the highest strength value followed by specimens frozen for 1 month, 24 h, and 1 week. The control specimens demonstrated the lowest value. Although the difference in actual values was very small (difference between largest and smallest mean modulus of rupture 1.83 MPa), there was a significant difference between the control specimens and the specimens frozen for 3 months (Table IIIb). All the results satisfied the criteria laid down in the standard.

The flexural modulus is a measure of stiffness of a material and is equal to the ratio of the stress to strain in the linear portion of the stress–strain curve. A one-way analysis of variance for the flexural modulus showed a significant difference between the groups (Table IVa). The 3 months' frozen specimens demonstrated the lowest value, which is significantly different from the control, 24 h frozen, 1 week frozen, and 1 month frozen specimens (Table IVb). All the tested groups except 3 months' frozen specimens satisfied the standard.

In the hardness test, the higher the indentation values, the softer the material (Table V). A one-way analysis of variance for hardness reflected a significant difference between the groups (Table Va). There was no significant difference between the control specimens and the specimens frozen for 24 h and those for 1 month. Nor was there any significant difference between the specimens frozen for 1 week and those frozen for 3 months (Table Vb). Although there was a significant difference between the first group (control, 24 h, 1 month) and the second group (1 week, 3 months), in actual values, these differences were very small (difference between largest and smallest mean hardness 1.60 μm). These small differences could be attributed to differences in surface finish.

The flow properties of the polymer/monomer mix used to pack the mold in denture base construction is of importance, since flow characteristics of the dough mix can influence the thickness of flash and consequently the accuracy and quality of the molded denture. A one-way analysis of variance for the flash thickness showed a significant difference between the groups (Table VIa). There was no significant difference between the control specimens and the specimens frozen for 24 h, 1 week, 1 month. Nor was there any significant difference between the specimens frozen for 24 h and those frozen for 3 months (Table VIb). In this case it can be said that freezing the mixed dough does not affect the flash thickness of the material.

From the results of this study it was concluded that:

- There is economic advantage of freezer storage of acrylic resin polymer/monomer mix.
- Freezing acrylic resin polymer/monomer mix during the dough stage increases the working time of the acrylic resin denture base material.
- The impact strength of heat-polymerizable acrylic resin denture base material was not altered by freezing.
- The flexural strength of heat-polymerizable acrylic resin denture base material was increased by freezing.
- The flexural modulus of heat-polymerizable acrylic resin denture base material was not altered by freezing up to 1 month.
- A small difference in hardness and flash thickness between the groups was observed, but this is unlikely to be of clinical relevance.

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