

Effect of thermocycling on some mechanical properties of polyamide hypoallergenic denture base material (comparative study)

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ABSTRACT

Background: Hypoallergenic denture base material became recently the most attractive option due to their use as alternative to poly methyl methacrylate in hypersensitive patients. The study of the effects of thermocycling on the mechanical properties is very important, as it is beneficial for clinical purposes.

Materials and methods: One hundred and sixty specimens were prepared according to manufacturer's instructions and they were divided into two groups: Valplast and Vertex as a control group (eighty specimens for each), twenty specimens from each material were used to test each of property. They were either thermocycled or not thermocycled (n = 10).

Results: There was significant difference between polyamide and conventional heat cured acrylic in the four tested properties. Furthermore, thermocycling significantly decreased the flexural strength of both polyamide and the heat cured acrylic and it significantly increased the tensile strength and hardness of both tested materials. Thermocycling did not significantly affect the impact strength of both materials.

Conclusions: Vertex showed higher values of flexural strength than Valplast, flexural strength of both materials decreased post-thermocycling. Although the flexural strength of valplast was relatively low, it demonstrated greater impact strength than Vertex, impact strength of both tested materials was not affected by thermocycling. The tensile strength of Vertex was more than Valplast, for both materials tensile strength increased after thermocycling. The hardness of Vertex was higher than that of Valplast, both materials' hardness increased after thermocycling.

Keywords: polyamide, thermocycling, flexural, impact, tensile strength, and hardness. (J Bagh Coll Dentistry 2012; 24(Sp. Issue 2):25-30).

INTRODUCTION

Poly methyl methacrylate (PMMA) resin has been widely used as a denture base material due to its desirable properties of excellent esthetics, ability to repair and simple processing technique ^(1,2)

Poly methyl methacrylate denture base has dominated the market for more than 50 years ⁽³⁾. Conversely some disadvantages have also been described, hypersensitivity to methyl methacrylate and allergic reaction to residual monomer have been reported ^(4,5). Due to the general increase in patients with allergy, dentists are confronted with more patients with allergic reaction to the classic PMMA denture base material ^(6,7). To overcome the allergy problem, other denture base materials, including methyl methacrylate (MMA) free materials, have been introduced. The PMMA has presumably been replaced by hypoallergenic denture base materials ⁽⁸⁾.

The recent developments in the field of science of dental materials and polymer technology enabled us to overcome some of the drawbacks of PMMA by improvement and development of newer and more novel forms of denture base resins. Hypoallergenic denture resin is one such invention ⁽⁹⁾.

Some new types of hypoallergenic denture base resin, such as polyamide (Pa) which is composed of monomers of higher molecular weight than methyl methacrylate or oligomers ⁽¹⁰⁾. These monomers are trapped into the polymer structure and their release should be minimal ⁽¹¹⁾.

Since the Pa is still at an experimental stage it was felt that an evaluation of its mechanical properties may facilitate its further refinement. With regard to PA denture base resins, previous researchers such as ^(2,10-15) studied some physical and mechanical properties (like flexural strength, modulus of elasticity, colour stability, solubility, sorption, surface roughness and impact strength). Despite these studies, little is known about the mechanical properties of Pa after thermocycling as one of artificial ageing process. The effect of thermal shock on the mechanical properties of injection molded thermoplastic denture base resins is beneficial for clinical purposes, but presently, there is insufficient information about it.

During mastication, the oral cavity gets in contact with food at different temperatures. The most critical effect of temperature is due to chewing of hot food and drinking of cold fluid, this temperature changes may affect the mechanical properties of denture base, so Dootz et al ⁽¹⁶⁾ and Hekimoglu and Anil ⁽¹⁷⁾ have shown

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that material ageing can dramatically affect the physical and mechanical properties.

Mechanical properties are very important to be measured after ageing process because acrylic resin removable dentures are susceptible to fracture after periods of clinical use. In a survey prevalence of fractured dentures found that 68% of dentures were broken within 3 years of their fabrication⁽¹⁸⁾. Information about the mechanical properties of acrylic materials could help in the understanding and improvement of denture fractures⁽¹⁹⁾.

MATERIALS AND METHODS

One hundred and sixty specimens (eighty specimens for each material) were prepared. Forty specimens from each material were subjected to thermocycling as an artificial ageing process, and forty specimens from each material were not subjected to thermocycling as control group. Forty specimens used for the following tests (flexural strength, impact strength, tensile strength and surface hardness) ten specimens for Pa and ten specimens for heat cured acrylic resin (Hca) were evaluated for differences in means for each test with and without thermocycling.

Plastic patterns were prepared with the following dimensions:

A- Specimens for flexural strength test: Rectangular shape, (65x10x2.5mm), the flexural strength test is a part of ANSI/ADA specification no.12 (ISO 1567) for denture base resin.

B- Specimens for impact strength test: Rectangular shape, (80x10x4mm), for charpy impact strength, ISO standard 179-1:2000 were followed.

C- Specimens for tensile strength test: Flat dumbbell shape, (16±1mm length, 3±0.2mm width, and 2±0.2mm thickness at the parallel segments). The tensile strength test was conducted according to ISO 527:1993.

D- Specimens for surface hardness: Disc shape, 25mm in diameter and 2mm in thickness according to ANSI/ADA specification no.17.

Preparation for Hca Specimens

The plastic patterns were inserted in the lower half of flask, care was taken that only one half of the pattern thickness was embedded in the stone, where the plastic patterns were placed, sufficient distance between them and also from the walls of the flask was kept, after setting of the stone the patterns and the stone were painted with separating medium and the counter part of the flask was then assembled and another mix of dental stone was poured to complete flasking, the flask was opened and the plastic patterns were

removed carefully, and the stone molds were ready for packing. The polymer/monomer in ratio of 2.3g/1ml according to manufacturer's recommendation was thoroughly mixed. Once the mixture reached the dough stage, it was kneaded thoroughly to make homogeneous dough.

The dough was then packed into the mold with slow pressure, final closure was done under a hydraulic press at (100 KPs/cm²) to ensure even flow of the material within the mold. After the final closure, the flask was left in the clamp for 30 minutes at room temperature to allow proper penetration of the monomer into the polymer beads, even flow of the material, and outward flow of excess material⁽²⁰⁾.

Curing was carried out by placing the clamped flask in the water bath and processed by short curing cycle (90 minutes at 74°C followed by 30 minutes at 100°C) according to (ADA specification No.12: 1999) for curing acrylic denture base material. Then the flask was left on bench to cool slowly before deflasking, and then the specimens were removed from the mold. Any specimens had faults or defects should be discarded, then finishing and polishing of HCA specimens as usual manner.

Preparation for Pa Specimens

The lower half of flask was prepared as for heat cured acrylic specimens, but a wax sprues were fabricated onto the plastic patterns before filling the upper half with stone. After setting of stone of upper half, wax elimination was done in the boiling water bath for 5 minutes, according to manufacturer's recommendations for Pa specimens. The flask was opened for removing the plastic patterns and let the stone mold to dry to get rid of moisture.

Capsule was placed in cylindrical metal sleeve and this sleeve was placed in the metal ring heater of the injection machine for 12 min., and when the temperature reached 288°C the ring alarmed that the Pa was ready to be injected under pressure 1.0 MPa.⁽¹⁴⁾ Meanwhile, the Pa flask was closed and screwed tightly in its specially designed clamp and placed in hot oven at 75°C for 12 min. All these steps carried out according to manufacturer's recommendations. Once the ring was heard, screwing of the press arm quickly till the spring was completely compressed, the Pa flowed into the mold, the pressure was kept for 15 seconds, then relieved and clamped flask was taken out of the machine and left to cool at the bench before deflasking, then the samples finished and polished as manufacturer recommended.

Thermocycling of the Specimens

Thermocycling was carried out by soaking the specimens alternatively into (5°C and 55°C) ±2°C water bath chambers with 14 sec. dwelling time at each temperature and 1 sec. transition time.

The specimens were submitted to thermocycling for continuous 30 hrs, in 1hr the specimens were submitted to 120 cycles and this effectively ensured that each specimen was exposed to 3600 cycles.

Mechanical Tests

The specimens were tested for transverse strength with a three point bending test using the universal testing machine at 50mm span length.

Charpy impact tester machine (pendulum) was used. The bar of the material was supported as a beam and struck in the middle with weighted swinging pendulum.

An instron testing machine was used to measure the tensile strength of the specimens. All specimens were placed under tension until failure in a unilateral testing machine at a cross-head speed of 1mm/min. for acrylic and 25 mm/min. for polyamide until fracture⁽¹⁴⁾.

Surface hardness testing was conducted by using stainless steel cone indenter of (5 mm in diameter) which attached to universal testing machine and subjected to 123 N, the indenter was remained in contact with each specimen tested for a fixed time of 30 seconds that made indentation⁽²¹⁾, after that it was removed and the indentation diameter was immediately measured after each indentation by travelling microscope.

RESULTS

Flexural Strength Test

The results indicated very clear and highly significant difference between mean of the flexural strength for Hca and Pa both with and without thermocycling; the higher mean values were for Hca; both with and without thermocycling. The highest mean value was for Hca without thermocycling (**129.48 MPa.**). The lowest mean value was for Pa with thermocycling (**45.84 MPa.**). The flexural strength of Hca and Pa decreased after thermocycling. The t-test between different experimental groups indicated a highly significant difference between with and without thermocycling groups for both tested materials; table 1 and 2.

Table 1: t-test of flexural strength between with and without thermocycling groups for the same material

Mat	Thermo-cycling	Group difference		
		t-test	P-value	Sig.
Hca	without	11.49	P<0.01	HS
	with			
PA	without	4.71	P<0.01	HS
	with			

Table 2: t-test of flexural strength between Hca and Pa with and without thermocycling

Thermo-cycling	Mat	Group difference		
		t-test	P-value	Sig.
without	Hca	32.62	P<0.01	HS
	Pa			
with	Hca	24.98	P<0.01	HS
	Pa			

Impact Strength Test

The results indicated very clear and highly significant differences between means of the impact strength for Hca and Pa both with and without thermocycling; the higher mean value was for Pa; both with and without thermocycling. The highest mean value was for Pa with thermocycling (**41.00 KJ/m²**). The lowest mean value was for Hca without thermocycling (**9.33 KJ/m²**). In both materials the impact strength was not significantly influenced by thermocycling. The t-test between different experimental groups indicated no significant difference between with and without thermocycling groups for both tested materials; table 3 and 4.

Table 3: t-test of impact strength between with and without thermocycling groups for the same material

Mat	Thermo-cycling	Group difference		
		t-test	P-value	Sig.
Hca	Without	-1.52	P>0.05	NS
	with			
Pa	without	-0.69	P>0.05	NS
	with			

Table 4: t-test of impact strength between Hca and Pa with and without thermocycling.

Thermo-cycling	Mat	Group difference		
		t-test	P-value	Sig.
Without	Hca	-17.20	P<0.01	HS
	Pa			
With	Hca	-22.73	P<0.01	HS
	Pa			

Tensile Strength Test

The results indicated very clear and highly significant differences between means of the tensile strength for Hca and Pa both with and without thermocycling; the higher mean value was for Hca; both with and without thermocycling. The highest mean value was for Hca with thermocycling (**67.06 MPa.**). The lowest mean value was for Pa without thermocycling (**33.44 MPa.**). In both materials the tensile strength increased after thermocycling.

The t-test between different experimental groups indicated a highly significant difference between with and without thermocycling group for both tested materials; table (5) and (6).

Table 5: t-test of tensile strength between with and without thermocycling groups for the same material

Mat	Thermo-cycling	Group difference		
		t-test	P-value	Sig.
Hca	without	-21.79	P<0.01	HS
	with			
Pa	without	-5.25	P<0.01	HS
	with			

Table 6: t-test of tensile strength between Hca and Pa with and without thermocycling.

Thermo-cycling	Mat	Group difference		
		t-test	P-value	Sig.
without	Hca	25.99	P<0.01	HS
	Pa			
with	Hca	36.31	P<0.01	HS
	Pa			

Brinell Hardness Test

The results indicated very clear and highly significant differences between means of the hardness for Hca and Pa both with and without thermocycling; the higher mean value was for Hca; both with and without thermocycling. The highest mean value was for Hca with thermocycling (**7.92 kg/mm²**). The lowest mean value was for Pa without thermocycling (**3.35 kg/mm²**). In both materials the hardness increased after thermocycling.

Table 7: t-test of Brinell hardness between with and without thermocycling groups for the same material

Mat	Thermo-cycling	Group difference		
		t-test	P-value	Sig.
Hca	Without	-8.79	P<0.01	HS
	With			
Pa	Without	-8.59	P<0.01	HS
	With			

The t-test between different experimental groups indicated a highly significant difference between with and without thermocycling groups for both tested materials (table 7, 8).

Table 8: t-test of Brinell hardness between Hca and Pa with and without thermocycling.

Thermo-cycling	Mat	Group difference		
		t-test	P-value	Sig.
without	Hca	20.79	P<0.01	HS
	Pa			
with	Hca	15.80	P<0.01	HS
	Pa			

DISCUSSION

Flexural Strength

The Hca flexural strength was significantly higher than that of Pa. The difference is related to the strength and numbers of primary and secondary bonds⁽²²⁾. Furthermore, the low flexural strength of Pa might be related to its polymerization process during synthesis⁽²²⁾, which is condensation polymerization, while it is addition polymerization for heat cured acrylic^(23,24). O'Brien⁽²²⁾ explained the high flexural strength of Hca as it is cross linked, while Pa is not cross linked polymer, so the difference is related to the presence of cross linking agent in the polymer structure, although Powers and Sakaguchi⁽²³⁾ stated the cross linking agent has little effect on the transverse and hardness properties of polymers.

After thermocycling the flexural strength decreased in Hca, thermocycling and water immersion lead to leach out of plasticizers and acrylic material became brittle⁽²⁵⁻²⁷⁾ this brittleness was clearly demonstrated in the fracture behavior of the specimens, all the specimens were broken with a sharp line fracture, exhibiting typical brittle fracture behavior that is characterized by lack of distortion of the broken parts⁽²⁸⁾.

Flexural strength of Pa was decreased after thermocycling. Thermal stress is created as a result of the varying amount of thermal expansions and contractions during thermocycling, this caused static fatigue which affected the Pa flexural properties⁽²⁹⁾.

Impact Strength

Pa showed significantly higher impact strength than Hca. Pa structure is based primarily on aliphatic chains⁽³⁰⁾. The backbone of Pa is regular and symmetrical, so forms very good resistance to shock and repeating stress⁽³¹⁾. Porosities of Hca more than that of Pa denture base material, this comes from presence of residual monomer and its evaporation leads to formation of these porosities,

also the compression packing of Hca leads to more porosities than injection molding processing of Pa⁽³²⁾. Pa contains flexible agents in its composition, so it absorbs more energy to fracture⁽¹⁰⁾.

The impact strength of Hca was not significantly changed by thermocycling. Although thermocycling may lead to further polymerization, because the surface of specimens affected by this continuous polymerization more than the deep bulk of them, so this might explain why the hardness of Hca was increased but the impact strength was not affected⁽³³⁾.

The impact strength of Pa was not significantly affected by thermocycling; because the monomer of Pa is oligomer so it is trapped into the polymer structure, so its release into water would be minimal⁽¹⁰⁾.

Tensile strength

The Hca tensile strength was significantly higher than that of Pa. This difference might be due to the difference between these two polymers in the process of polymerization^(14,15). The difference is also related to the strength and numbers of primary bonds⁽²²⁾. the higher tensile strength of Hca could be attributed to its high molecular weight linear polymer molecules⁽³⁴⁾.

After thermocycling the tensile strength of Hca was significantly increased. The leaching out of the residual monomer, plasticizer could result in increasing tensile strength⁽³⁵⁻³⁸⁾. Further polymerization may occur in the acrylic specimens submitted to thermocycling⁽³³⁾.

After thermocycling the tensile strength of Pa was increased. The complete polymerization of Pa specimens submitted to heat energy during the experiment is probably the reason⁽¹⁰⁾.

Indentation Hardness

The Hca hardness was significantly higher than that of Pa, Goiato et al⁽¹⁰⁾ explained that as the conventional resin based on poly methyl methacrylate does not have flexible agents in its composition, so it has more resistance to penetration of the indenter.

Hardness was increased in Hca after thermocycling. This might be due to further polymerization, by thermocycling^(33,34,38). Leach out of monomer and other soluble components by diffusion from the polymer^(33,38,39). Leach out of external plasticizers that resulting in the hardening of the Hca⁽⁴⁰⁾.

After thermocycling the hardness of Pa was significantly increased, this might be related to further polymerization and their submission to heat energy during the experiment⁽¹⁰⁾.

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