

ORIGINAL ARTICLE

Effect of thermal shock on mechanical properties of injection-molded thermoplastic denture base resins

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Abstract

Objective. This study investigated the effect of thermal shock on the mechanical properties of injection-molded thermoplastic denture base resins. **Materials and methods.** Four thermoplastic resins (two polyamides, one polyethylene terephthalate, one polycarbonate) and, as a control, a conventional heat-polymerized polymethyl methacrylate (PMMA), were tested. Specimens of each denture base material were fabricated according to ISO 1567 and were either thermocycled or not thermocycled ($n = 10$). The flexural strength at the proportional limit (FS-PL), the elastic modulus and the Charpy impact strength of the denture base materials were estimated. **Results.** Thermocycling significantly decreased the FS-PL of one of the polyamides and the PMMA and it significantly increased the FS-PL of one of the polyamides. In addition, thermocycling significantly decreased the elastic modulus of one of the polyamides and significantly increased the elastic moduli of one of the polyamides, the polyethylene terephthalate, polycarbonate and PMMA. Thermocycling significantly decreased the impact strength of one of the polyamides and the polycarbonate. **Conclusions.** The mechanical properties of injection-molded thermoplastic denture base resins changed after thermocycling.

Key Words: *thermal shock, mechanical properties, thermoplastic denture base resin, thermocycling*

Introduction

Removable partial dentures (RPD) are retained at the undercuts of the abutment teeth using metal clasps. The retentive arm of the metal clasp is deflected during the insertion and removal of an RPD, but it is preferable for the denture base to remain stiff and undergo little deflection during chewing as the denture base is placed on the soft tissue. However, the metal clasps of anterior RPDs are not esthetic, nor can they be used for patients with allergies to metal. Recently, an RPD without metal clasps has been used in dental practice [1,2]; this type of RPD is retained at the undercuts of the abutment teeth using denture base resin. Injection-molded thermoplastic resins (polyamide, polyethylene terephthalate and polycarbonate) are used for RPD denture bases without metal clasps because these thermoplastic resins have a higher elasticity than heat-polymerizing base resin (PMMA). The flexibility of the injection-molded thermoplastic resin is important because it affects the ease of insertion and removal of the RPD,

as well as its retention and the stress to the abutment teeth.

Although injection-molded thermoplastic resins for denture base material have been investigated [3–11], the mechanical properties of polyamide, polyethylene terephthalate and polycarbonate for denture base material have not been compared. In a previous study [12], the mechanical properties of injection-molded thermoplastic denture base resins (polyamides, polyethylene terephthalate and polycarbonate) were estimated. It was found that (1) all of the injection-molded thermoplastic resins had significantly lower flexural strength at the proportional limit (FS-PL), lower elastic modulus and higher or similar impact strength than the conventional heat-polymerized acrylic resin, (2) the polyamide thermoplastic resins had low FS-PL and low elastic modulus; one of them possessed very high impact strength and the other one had low impact strength, (3) the thermoplastic resin composed of polyethylene terephthalate had moderately high FS-PL, moderate elastic modulus and low impact strength and (4) the thermoplastic resin

composed of polycarbonate had moderately high FS-PL and elastic modulus and moderate impact strength.

The oral environment is subject to constant temperature changes from the vastly different temperatures of food that we ingest. It is preferable for the thermoplastic resins of RPDs without metal clasps at the retentive area to maintain long-term flexibility in the mouth. Therefore, evaluating 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.

The purpose of the present study was to investigate the effect of thermal shock on the mechanical properties of injection-molded thermoplastic denture base resins. The null hypothesis was that the mechanical properties of thermocycled injection-molded thermoplastic denture base resins were not different from the mechanical properties of non-thermocycled injection-molded thermoplastic denture base resins.

Materials and methods

Four injection-molded thermoplastic resins were selected for this study and a conventional heat-polymerized polymethyl methacrylate (PMMA) was used as a control (Table I).

The flexural properties and Charpy impact strength of the denture base materials were measured

according to ISO 1567 [13] and ISO 1567:1999/Amd 1:2003 [14].

Specimens

The specimens of each denture base material tested for flexural properties were fabricated according to the manufacturers' instructions in gypsum molds with cavities (65 mm long \times 10 mm wide \times 3.3 mm high). Each specimen was polished with 600-grit SiC paper. The accuracy of the dimensions was verified with a micrometer at three locations for each dimension to within a 0.05-mm tolerance for width and height.

Specimens of each denture base material for Charpy impact testing were fabricated according to the manufacturers' instructions in gypsum molds with cavities (50 mm long \times 6 mm wide \times 4 mm high). Each specimen was polished with 600-grit SiC paper, and the accuracy of each dimension was verified with a micrometer to within a 0.2-mm tolerance for width and height at three locations. A notch (type A) was cut in the middle of each specimen, as described in ISO 179 [15]. An edgewise notch was cut 1.2 mm deep, leaving a residual depth of 4.8 mm beneath the notch.

The specimens for flexural properties were held at 37°C for 50 h in distilled water and the Charpy impact test specimens were stored at 37°C for 7 days in distilled water. Half of the specimens were then thermocycled between 5°C water and 55°C water for 50 000 1-min cycles. Ten specimens were fabricated

Table I. Denture base materials tested in this study.

Constituent	Material	Manufacturer	Processing method	Lot number
Polyamide (Nylon 12)	Valplast	Valplast International Corp., NY	Injection molding technique; heat processed at 215°C for 20 min, injected at 1 MPa pressure and bench cooled for 30 min	080632
Polyamide (Nylon PACM12)	Lucitone FRS	DENTSPLY International Inc., PA	Injection molding technique; heat processed at 300°C for 17 min, injected at 1 MPa pressure and bench cooled for 30 min	090417A
Polyethylene terephthalate	EstheShot	i-Cast Co. Ltd., Kyoto, Japan	Injection molding technique; heat processed at 230°C for 20 min, injected at 1 MPa pressure and bench cooled for 30 min	JBB
Polycarbonate	Reigning	Toushinyoukou Co. Ltd., Niigata, Japan	Injection molding technique; heat processed at 320°C for 30 min, injected at 1 MPa pressure and bench cooled for 30 min	COC28T
PMMA	Acron	GC Corp., Tokyo, Japan	Heat-polymerized, compression molding technique; heat-processed at 70°C for 90 min, then at 100°C for 30 min and bench cooled for 30 min	Powder: 0910232, Liquid: 0910051

per group in each denture base material-thermocycling combination.

Flexural properties

The flexural strength at the proportional limit (FS-PL) [16–20] and flexural modulus of the specimens were tested. Each specimen was placed on a 50 mm-long support for three-point flexural testing. A vertical load was applied at the mid-point of the specimen at a crosshead speed of 5 mm/min on a load testing machine (ASG-J, Shimadzu Co. Ltd., Tokyo, Japan). The FS-PL (MPa) was calculated according to the following formula:

$$\text{FS-PL} = 3PL / 2bd^2$$

where P = load at the proportional limit, L = span distance (50 mm), b = width of the specimen and d = thickness of the specimen. The load at the proportional limit was determined from each load-deflection graph.

The elastic modulus (GPa) was calculated using the following formula:

$$\text{Elastic modulus} = FL^3 / 4bd^3D$$

where F = the load at a convenient point in the straight line portion of the load/deflection graph and D = the deflection at load F.

Charpy impact test

The Charpy notched impact strength test was carried out on a pendulum impact tester (DC-C; Toyo Seiki, Tokyo, Japan). The test span was 40 mm.

The specimens were conditioned in the container at 23°C for 60 min prior to testing. After conditioning, each specimen was removed from the water and placed on the specimen supports of the testing apparatus with the notch facing away from the point of impact from the pendulum; then the pendulum was released in order to fracture the specimen. The Charpy impact strength (kJ/m²) of the notched specimen was calculated using the formula:

$$\text{Impact strength} = (J1 - J2) \times 10^3 / bh$$

where J1 = the value of energy absorbed by the specimen, J2 = the friction energy of the system, b = the depth behind the notch and h = the height of the specimen.

All the tests were performed under uniform atmospheric conditions of 23.0 ± 1°C and 50 ± 1% relative humidity.

A two-way analysis of variance (ANOVA) (STATISTICA, StatSoft Inc., Tulsa, OK) was applied to study the differences among the denture base materials and the effect of thermocycling. A one-way ANOVA (STATISTICA) was applied if there was a significant difference resulting from an interaction between these two variables ($p = 0.05$). The Newman-Keuls post-hoc comparison ($p = 0.05$) (STATISTICA) was applied when appropriate.

The data on non-thermocycled denture base materials were reported in a previous study comparing the mechanical properties of the thermoplastic denture base resins [12].

Results

The two-way ANOVA revealed that there were significant differences in FS-PL because of the denture base material variable and the interaction between the denture base material and the effect of thermocycling ($p < 0.05$). A one-way ANOVA and the Newman-Keuls post-hoc comparison were applied to the denture base material/thermocycling combination. The results are depicted in Table II and Figure 1. The thermocycled specimens of Valplast and Acron possessed significantly lower FS-PL than the non-thermocycled specimens. The FS-PL of the thermocycled LucitoneFRS was significantly higher than of the non-thermocycled specimens.

The two-way ANOVA revealed that there were significant differences in the elastic modulus caused by the variables of denture base material and the effect of thermocycling and their interaction ($p < 0.05$). The one-way ANOVA and the Newman-Keuls post-hoc comparison were applied to the denture base material/thermocycling combination. The results are depicted in Table II and Figure 2. The thermocycled Valplast specimen showed a significantly lower elastic modulus compared to the non-thermocycled specimen. The thermocycled specimens of the other denture base materials tested for elastic modulus were significantly higher than the non-thermocycled specimens.

The two-way ANOVA revealed significant differences in impact strength because of the denture base material, the effect of thermocycling and their interaction ($p < 0.05$). The one-way ANOVA and Newman-Keuls post-hoc comparison were applied to the denture base material/thermocycling combination. The results are depicted in Table II and Figure 3. The impact strength of the thermocycled LucitoneFRS and Reinging specimens was significantly lower than of the non-thermocycled specimens.

Discussion

The null hypothesis of this study was rejected and the mechanical properties of the thermocycled injection-molded thermoplastic denture base resins

Table II. Mean and standard deviation (SD) of the mechanical properties of the denture base material/thermocycling groups ($n = 10$).

Denture base material	Thermocycling	Flexural strength at proportional limit (MPa)	Elastic modulus (GPa)	Charpy impact strength (kJ/m^2)
Polyamide (Valplast)	No	13.7 (0.8)	1.04 (0.11)	6.86 (0.48) ^{a,b}
Polyamide (Valplast)	Yes	8.3 (0.5)	0.73 (0.07)	9.68 (0.86) ^a
Polyamide (Lucitone FRS)	No	22.3 (0.9)	1.45 (0.05)	30.24 (9.82)
Polyamide (Lucitone FRS)	Yes	32.8 (1.6) ^a	1.55 (0.07)	8.03 (4.44) ^{a,b}
Polyethylene terephthalate (EstheShot)	No	30.4 (2.1) ^{a,b}	1.98 (0.08)	4.09 (0.59) ^{b,c}
Polyethylene terephthalate (EstheShot)	Yes	31.9 (3.7) ^{a,b}	2.18 (0.11) ^a	1.27 (0.41) ^c
Polycarbonate (Reigning)	No	29.6 (1.0) ^b	2.19 (0.11) ^a	21.32 (5.50)
Polycarbonate (Reigning)	Yes	32.3 (2.6) ^{a,b}	2.44 (0.11)	13.29 (0.86)
PMMA (Acron)	No	38.2 (4.0)	2.77 (0.12)	1.06 (0.12) ^c
PMMA (Acron)	Yes	29.3 (3.1) ^b	2.89 (0.12)	1.61 (0.09) ^c

The same letter denotes groups that were not significantly different from each other ($p > 0.05$).

were different from those of the non-thermocycled injection-molded thermoplastic denture base resins.

In this study, the specimens were tested by thermocycling 50 000 times between 5°C and 55°C water in 1-min cycles. Thermocycling involves two phenomena: thermal stress and water sorption. With regard to conventional heat-polymerized polymethyl methacrylate, water is adsorbed into poly(methyl methacrylate) by the process of diffusion. The water molecules ingress into the vacancies between the poly(methyl methacrylate) polymeric chains and push them further apart, causing the material to expand [21]. These water molecules also act as plasticizers to facilitate the movement of the polymeric chains. One of their plasticizing effects is to facilitate the relaxation that could cause a shape change [22]. Thermal stress is created as a result of the varying amount of thermal expansion and shrinkage that the unlike materials experience during thermocycling. Furthermore, an

increase in temperature accelerates the water sorption rate for denture polymers without changing the equilibrium sorption value [22]. Some studies have focused on the relationship between the flexural properties of a heat-polymerized denture polymer and water immersion. One of these studies reported that the flexural strength of a heat-polymerized denture polymer significantly decreased when the duration of water immersion increased from 1 to 30 days [17]. After 4 months' water immersion, the flexural strength of a heat-polymerized denture polymer had significantly decreased [19]. Water immersion for a period of 90 days also decreased the flexural strength of three denture polymers [23]. Another study showed a similar decrease in ultimate flexural strength and flexural modulus for denture polymers immersed in water for 48 weeks [24]. In the present study, thermocycling significantly decreased the FS-PL of the PMMA (Acron) and increased the elastic modulus of the PMMA (Acron). The FS-PL results were

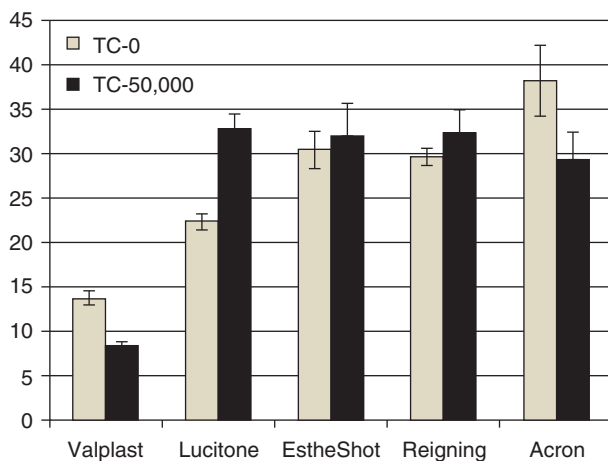


Figure 1. Mean flexural strength at proportional limit (MPa) and standard deviation of the denture base materials before and after thermocycling ($n = 10$). TC-0: 0 thermocycle, TC-50,000: 50 000 thermocycles.

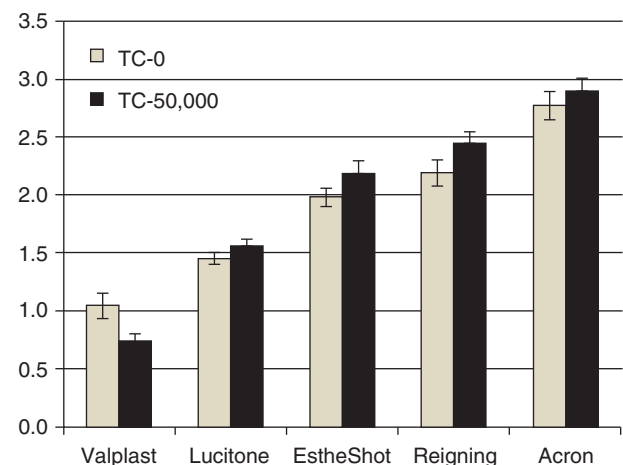


Figure 2. Mean elastic modulus (GPa) and standard deviation of the denture base materials before and after thermocycling ($n = 10$). TC-0: 0 thermocycle, TC-50,000: 50 000 thermocycles.

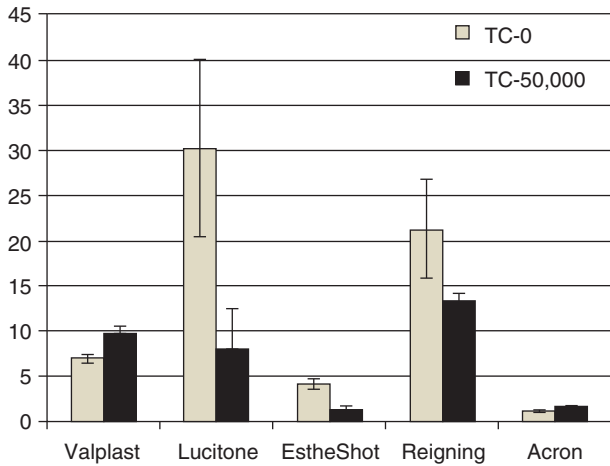


Figure 3. Mean Charpy impact strength (kJ/m^2) and standard deviation of the denture base materials before and after thermocycling ($n = 10$). TC-0: 0 thermocycle, TC-50,000: 50 000 thermocycles.

congruent with the previous studies, but the increased elastic modulus values were different from these studies. It seems that not only water sorption but also static fatigue caused by thermal stress affected the present results. The static fatigue affected the flexural properties of the PMMA (Acron) and, therefore, the PMMA (Acron) became stiff and weak after thermocycling.

There are few articles on the physical properties of injection-molded thermoplastic denture base resins. It is reported [25] that the water sorption values of the injection-molded thermoplastic denture base resins and PMMA were as follows: a polyamide (Lucitone FRS) > PMMA (Acron) > a polyamide (Valplast) > a polyethylene terephthalate (EstheShot) > a polycarbonate (Reigning). However, there is little information about the relationship between the flexural properties of injection-molded thermoplastic denture base resins and water immersion or thermal stress. In this study, the elastic moduli of one of the polyamides (Lucitone FRS), the polyethylene terephthalate (EstheShot) and the polycarbonate (Reigning) significantly increased after thermocycling. The reason for these increases was likely because static fatigue caused by thermal stress affected the elastic moduli of these resins as with PMMA (Acron). Likewise, the impact strength of one of the polyamides (Lucitone FRS) and the polycarbonate (Reigning), which was tougher in the four non-thermocycled injection-molded thermoplastic resins, significantly decreased and caused brittleness after thermocycling. The reason is also most likely due to static fatigue caused by thermal stress. Moreover, the polyethylene terephthalate (EstheShot) remained brittle after thermocycling. From these reasons, it seems that the three injection-molded thermoplastic resins stiffened after thermocycling. However, the FS-PL of these resins did not weaken. The non-thermocycled injection-molded thermoplastic denture

base resins were weaker than the non-thermocycled PMMA (Acron). Therefore, these weaker resins are most likely to strengthen after becoming stiff.

The first dental use of polyamide was not successful because of excessive water absorption [26]. Since then, however, polyamide has been improved, and there are now many kinds of polyamides employed in industry. In this study, thermocycling significantly reduced the FS-PL and the elastic modulus of the one of polyamides (Valplast) and the flexural properties were different from those of the other polyamide (Lucitone FRS). There are now many kinds of polyamides used in industry, perhaps due to differences in composition and physical properties.

In the present study, the static thermal shock test was also applied because it is necessary to estimate the effect of dynamic fatigue or long-term water immersion on the mechanical properties of injection-molded thermoplastic denture base resins.

This study indicated that thermal shock affected the mechanical properties of the injection-molded thermoplastic denture base resins. As mentioned earlier, the flexibility of the injection-molded thermoplastic resin for RPDs without metal clasps affects the ease of insertion and removal of the RPD, retention of the RPD and the stress to the abutment teeth; hence, changes in the flexibility after thermocycling is clinically very important. The findings of this study suggest that the flexibility of the thermoplastic resin in an RPD without metal clasps at the retention area will change as the patient uses the denture over time. Therefore, RPDs without metal clasps fabricated from injection-molded thermoplastic denture base resins require a level of maintenance far exceeding that of conventional removable partial dentures.

Conclusions

Under the present experimental conditions, the following conclusions can be drawn:

- (1) Thermocycling significantly decreased the FS-PL of one of the polyamides tested and significantly increased the FS-PL of the other polyamide.
- (2) Thermocycling significantly decreased the elastic modulus of one of polyamides and significantly increased the elastic moduli of the other polyamide, the polyethylene terephthalate and the polycarbonate.
- (3) Thermocycling significantly decreased the impact strength of one of the polyamides and the polycarbonate.

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