

Effect of Heating Rate on Glass Transition of a Cross-linked Denture Base Resin

Učinak stope zagrijavanja na temperaturi staklastog prijelaza umreženih smola za baze proteza

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Summary

The purpose of the study was to investigate the effect of different heating rates in the evaluation of the transition glass temperature of a dough-moulded poly(methylmethacrylate) denture base material. Cross-linking agent ethylene glycol dimethacrylate (EGDMA) was added to the MMA monomer component: in concentration of 10% by volume. The polymer component was an unpigmented PMMA homopolymer. A comparison group of specimens was made by use of monomer liquid without any cross-linking agent. Specimens were produced in moulds according to conventional dental flasking and curing procedures. Measurements of T_g were determined by thermomechanical analysis using a Stanton Redcroft TMA, Model 790 (PL Thermal Science Ltd., Epsom, UK). Heating rates of 5 °C/min, 10 °C/min and 15 °C/min were selected for this investigation. It was concluded that the addition of cross-linking agent would affect T_g denture base resins. T_g values were highly dependent on the heating rates used in thermomechanical analysis, being very significantly increased with a heating rate increase.

Key words: denture base acrylic resins, cross linking, glass transition temperature, heating rate

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Introduction

At room temperature, acrylic resins are hard and glass-like. When the temperature is increased, a critical temperature is reached at which a transition occurs to a softer, more flexible material. Such a transition occurs over a finite temperature interval, but is still realized abruptly enough to merit the term

glass transition temperature (T_g). This change is reversible and is a function of the molecular motion of the polymer chains.

Knowledge of the glass transition temperature (T_g) is important since it can add considerably to the understanding of a material's behaviour pattern, both in respect of the working properties and in service performance. As well as the considerable vari-

ations in temperature, found in the oral cavity during normal in-service functions, there is also the laboratory grinding and polishing procedures and patient cleaning regimes which may expose denture base polymers to high temperatures resulting in thermal distortions. In addition, the glass transition temperature can influence the dimensional stability and internal stresses that are present as a consequence of polymerization and thermal contractions (1).

Cross-linking of high polymers such as poly(methylmethacrylate) (PMMA) should increase resistance to temperature. Replacement of Van der Waals forces between polymer chains by the stronger carbon to carbon (C-C) primary bonds reduces the mobility of polymer segment by holding chains more rigidly together (2).

The effect of the addition of divinyl cross-linking agents with different cross-link chain lengths on the Tg of cast PMMA has been studied. For all cross-linking agents Tg increased initially as the mole fraction of cross-linking agent increased. Shorter chain length cross-link agents provided greater increase in Tg. As the mole fraction of dimethacrylate was increased further, the value of Tg continued to increase at a reduced rate to a limiting value or, in the case of the longer chains of methacrylates, reached a maximum and then decreased (3-5).

Ethylene glycol dimethacrylate (EGDMA), a divinyl cross-linking agent, is commonly added to denture base resins in concentrations of up to 15% of monomer value in order to provide craze resistance (6). However, this EGDMA percentage of monomer value, added to denture base material, produced an increase in Tg of approximately 3 °C and should be of no clinical significance (5).

It was found that different curing cycles produced variations in glass transition temperature of up to 20 °C, and the prolonged curing cycle of 7h at 70 °C plus 3h at 100 °C can be recommended to produce specimens with high Tg as well as optimum mechanical properties. A higher glass transition temperature is related to a higher molecular weight. Also the presence of unpolymerised monomer, depending on the type of curing cycle used, has a plasticizing effect and lowers the glass transition temperature (7).

Measurements of glass transition temperatures using differential scanning calorimetry have shown dependency upon the heating rates (1).

The glass transition temperature of the range of acrylic resins used in prosthodontics was determined by thermal mechanical analysis, dynamic mechanical thermal analysis and differential scanning calorimetry and it was found that the measuring technique yielded similar results. Due to familiarity and easy availability the thermal mechanical analysis has been recommended to be employed as a standard glass-transition evaluation technique for denture-base acrylic resins (8).

The purpose of the present study was to investigate the effect of three heating rates on the glass transition temperature of two types of dough-moulded PMMA resins using thermomechanical analysis.

Materials and methods

TS 1195 unpigmented PMMA homopolymer powder (Bonar Polymers Ltd. Co., Durham, UK) with 0.26% benzoyl peroxide and methylmethacrylate monomer liquid stabilized with 0.01% quinol (British Drug House Ltd., Bristol, UK) were used to produce 15 control specimens. The cross-linking agent was ethylene glycol dimethacrylate (EGDMA) (Ploy-Science Ltd., Northampton, UK), (Figure 1), added to the monomer in concentration of 10% by volume (V/V) to be mixed with homopolymer powder in order to produce 15 cross-linked specimens.

Cylindrical test specimens 5 mm diameter x 7 mm in length (Figure 2) were produced in moulds

MONOMER	ABBREVIATION	CHEMICAL STRUCTURE
METHYL-METHACRYLATE	MMA	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_3 \\ \\ \text{O} \end{array}$
ETHYLENE GLYCOL DIMETHACRYLATE	EGDMA	$\begin{array}{c} \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \\ \qquad \qquad \qquad \qquad \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-\text{C}=\text{CH}_2 \\ \qquad \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \qquad \text{O} \end{array}$

Figure 1. Molecular structure of methylmethacrylate monomer and ethylene glycol dimethacrylate cross-linking agent

Slika 1. Molekularna struktura metilmetakrilata monomera i etilen glikol dimetakrilatnog umreživača

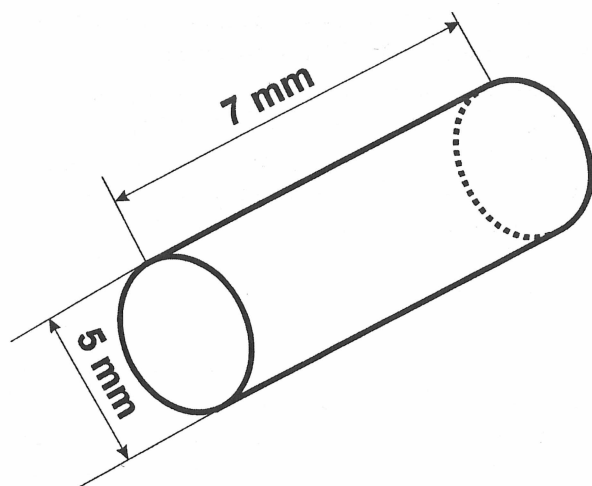


Figure 2. Specimen used in the study
Slika 2. Pripravak korišten u istraživanju

prepared by investigating master pattern blanks of the appropriate size in gypsum using conventional denture flasking techniques. The PMMA dough was prepared by adding the polymer powder to the monomer liquid in a ratio of 3,2:1 by volume. Addition of cross-linking agent extended the dough time. The specimens were cured in a thermostatically controlled water bath at a prolonged curing cycle (70 °C for 7 hours followed by three hours at 100 °C). The flasks were then allowed to bench-cool prior to deflasking.

After deflasking, the specimens were trimmed using progressively finer grades of silicon carbide grid paper, finishing with grade 600. All specimens were saturated in water for 28 days at 37 °C prior to testing. Measurement of T_g was carried out by use of a Stanton Redcroft Thermomechanical Analyser, Model 790 (PL Thermal Sciences Ltd., Epson, UK) linked to a conventional X-Y recorder (Figure 3).

The measuring procedure entailed in a probe of 5 mm diameter surface area at rest on the cylindrical specimen. The probe was connected to a transducer which allowed vertical movement of the probe be monitored on the X-Y recorder. A thermocouple is located close to the specimen and the temperature variation displayed on the X axis of the recorder. The system is regulated from the control unit. A nominal load of 10 g was used throughout the investigation. This produced sufficient probe sensitivity.

Heating rates of 5 °C/min, 10 °C/min and 15 °C/min were selected for this investigation as this allowed reasonable time for the evaluation of T_g.

T_g is measured from the trace plotted on the X-Y recorder (Figure 4). The thermocouple response is measured in millivolts. In order to convert this value to degrees centigrade, a calibration graph of temperature in °C against millivolts is supplied by the manufacturer.

Five specimens were tested for each of three curing cycles, i.e. 15 specimens per material produced without and 15 with the cross-linking agent. Statistical testing of differences between the groups was performed by Student's test.

Thermomechanical Analysis (TMA)

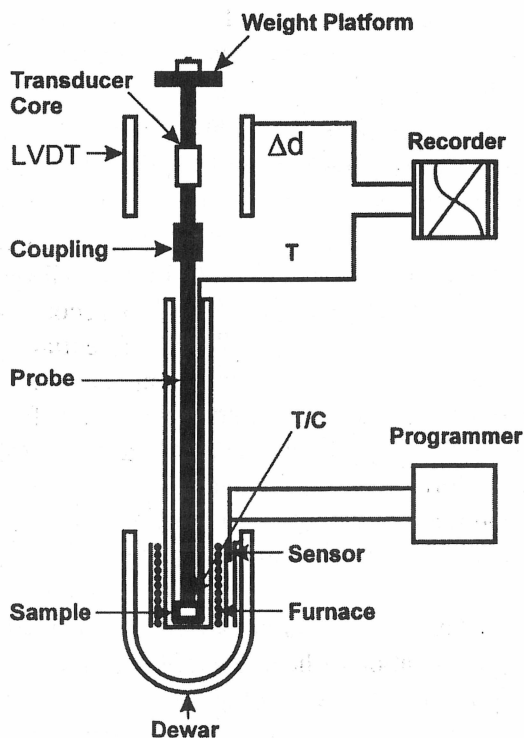


Figure 3. Schematic feature of the Stanton Redcroft Thermomechanical Analyser, Model 790

Slika 3. Shematske karakteristike Station Redcroft termomehaničkog analizatora, model 790

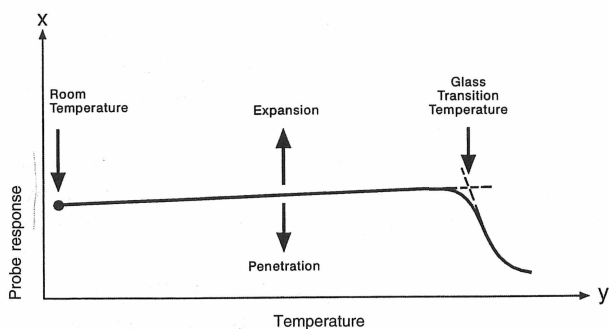


Figure 4. Determination of the transition glass temperature (T_g) from the recorder trace

Slika 4. Određivanje temperature staklastoga prijelaza (T_g) iz snimke registracijskog uređaja

Results

The effect of variation of the heating rate on the T_g the resultant specimens is shown in Table 1 and Figure 5. Results show that increased T_g values were

Table 1. The transition glass temperature ($^{\circ}\text{C}$) of the materials investigated, subjected in there different heating rates (% - percentage of cross - linking agent)

Tablica 1. Temperature staklastoga prijelaza ($^{\circ}\text{C}$) istraživanih materijala, podvrgnutih trima različitim brzinama zagrijavanja (%-postotak umreživača)

	%	5 $^{\circ}\text{C}/\text{min}$		10 $^{\circ}\text{C}/\text{min}$		15 $^{\circ}\text{C}/\text{min}$	
		X	SD	X	SD	X	SD
CONTROL	0	118.7	0.45	125.5	1.77	129.4	1.85
EGDMA	10	122.3	0.45	127.7	1.15	133.1	1.67

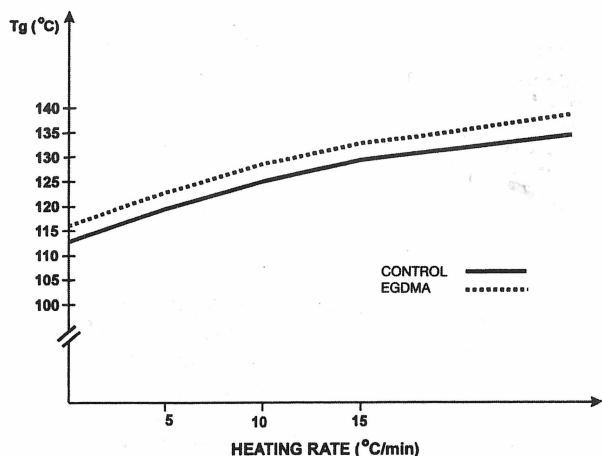


Figure 5. Graph of the results

Slika 5. Grafikon rezultata

re obtained when elevated heating rates were used. This finding was very significant ($p < 0.01$).

The addition of EGDMA produced an increase in T_g of approximately 3 $^{\circ}\text{C}$ at all heating rates: at 5 $^{\circ}\text{C}$ highly significant ($p < 0.001$), at 10 $^{\circ}\text{C}$ not significant ($p > 0.05$), at 15 $^{\circ}\text{C}$ significant ($p < 0.05$).

Discussion

Glass transition temperature (T_g) is an important property of denture base material since it reflects ability of the material to withstand elevated temperatures and is also related to the dimensional stability and internal stresses which are present as a consequence of polymerization contractions (1).

T_g values are not absolute but are dependent on the method of determination. A wide variety of methods are available and the T_g of denture base materials has been investigated by several workers (8-11). Huggett et al. (8) reviewed methods of T_g determination and concluded that thermomechanical analysis is a convenient and reliable method to be employed as an evaluation technique of denture base materials.

The heating rates of 5 $^{\circ}\text{C}$, 10 $^{\circ}\text{C}$ and 15 $^{\circ}\text{C}$ were selected for the present study in order to provide variety of probe sensitivity and yield elevated values of T_g when increasing the heating rate. This in agreement with the findings of McCabe and Wilson (1) who also obtained elevated T_g values according to increased heating rate, but using differential scanning calorimetry method. Glass transition measurements are related to the time scale chosen for the experimental evaluation. The glass transition approaches a limiting equilibrium value as the experimental time scale is increased. In other words, material tested at a very fast heating rate will provide higher value of T_g than the same material tested at lower rates of heating. This is due to the time lag between the application of heat material and the onset of molecular motions within the specimen.

The addition of cross-linking agent EGDMA produced an increase in T_g value unlikely to be of any clinical importance. The investigation of Huggett et al. (11) demonstrated a lowering effect of the EGDMA on the T_g , although the polymerization of spe-

cimens investigated did not include 100 °C in the curing cycle. The polymerization reaction proceeds by both copolymerization and cross-linking. Loshak (3) described the cross-linking and copolymer effects on Tg as being separate and additive. Whereas the cross-linking effect will always increase intermolecular rigidity and thus increase Tg, the copolymerization effect is dependent on the nature and amount of the divinyl monomer, and may produce a consequent reduction in Tg (5-11).

Increases in molecular weight raise Tg considerably as has been seen with prolonged curing cycles, compared with short or curing cycles which did not include polymerization at 100 °C (5,11), i.e., the presence of monomer, acting as a plasticizer, results in lowering of the glass transition temperature (1).

The specimens used in the present study had been stored in water. The plasticizing effect of the absorbed water on Tg will be investigated in future work.

Conclusions

1. Measurements of glass transition temperatures (Tg) are dependent upon the heating rate used for the evaluation. By increasing the heating rate increased Tg value will be obtained. This is important for theoretical and practical considerations and comparisons.

2. The increase in Tg of approximately 3 °C, produced by the addition of 10% EGDMA of monomer volume to denture base materials, should be of no clinical significance.

3. The relationship between Tg, cross-linking chain length, cross-linking agent concentration and curing cycles is complex, and thus future research is required.

Acknowledgements

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UČINAK STOPE ZAGRIJAVANJA NA TEMPERATURI STAKLASTOG PRIJELAZA UMREŽENIH SMOLA ZA BAZE PROTEZA

Sažetak

Svrha istraživanja bila je ispitati učinak različitih brzina zagrijavanja kod procjene temperature staklastoga prijelaza toplopolimerizirajućih poli (metilmetakrilnih) smola za baze proteza. Umreživač etilen glikol dimetakrilat dodan je monomer-komponenti MMA u koncentraciji od 10% po volumenu. Polimerna komponenta bila je nepigmentirani PMMA homopolimer. Napravljena je poredbena skupina uzoraka uporabom monomerne tekućine bez umreživača. Pripravci su napravljeni u kalupima, u skladu s uobičajenom kivetnom tehnikom. Mjerenja Tg određena su termomehaničkom raščlambom uporabom Stanton Redcroft TMA Model 790 (PL Thermal Sciences Ltd., Epsom, UK). Za to istraživanje odabrane su brzine zagrijavanja od 5 °C/min, 10 °C/min i 15 °C/min. Zaključeno je da dodavanje umreživača utječe na Tg smola za baze proteza. Tg vrijednosti jako su ovisne o brzinama zagrijavanja upotrijebljenih tijekom termomehaničke raščlambe s tim da se uvelike povisuju povećavanja brzine zagrijavanja.

Ključne riječi: akrilatne smole za protezne baze, umreživač, temperatura staklastoga prijelaza, stopa zagrijavanja.

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