Effect of Cross-linking Chain Length on Glass Transition of a Dough-moulded Poly (methylmethacrylate) Resins

Učinak dužine molekularnog lanca umreživača na temperaturu staklastog prijelaza toplopolimerizirajućih smola za baze proteza

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Summary

The purpose of the study was to investigate the effect of the addition of various divinyl cross-linking agents on the glass transition temperature of a dough-moulded poly(methylmethacrylate) (PMMA) resin. Three different cross-linking agents, ethylene glycol dimethacrylate (EGDMA), tetra(ethylene glycol dimethacrylate) (TEGDMA) and poly(ethylene glycol dimethacrylate) (PEG 600 DMA), which form an homologous series of ethylene oxide adducts in which the cross-linking contains one, four and an average of 13 (C-C-O) units respectively, were added to the MMA monomer component in concentrations of 0–40% by volume of monomer liquid concentration. The polymer component was an unpigmented PMMA homopolymer. Specimens were produced in moulds according to conventional dental flasking and curing procedures and measurements of Tg were determined by thermomechanical analysis. The addition of EGDMA produced a highly significant increase in Tg at all concentrations. The addition of TEGDMA produced no significant change at 10% and 20% concentrations but significantly lowered Tg at 30% and 40%. PEG 600 DMA produced significant lowering at all concentrations. It was concluded that cross-linking of a dough-moulded PMMA resin by divinyl cross-linking agents can significantly affect Tg but that the relationship between Tg, cross-linking chain length and cross-linking agent concentration is complex.

Key words: *denture base acrylic resins, cross-linking, glass transition temperature.*

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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 (Tg). This change is reversible and is a function of the molecular motion of the polymer chains.

Cross-linking of high polymers such as poly-(methylmethacrylate) (PMMA) should increase resistance to temperature. Replacement of van der Waal's forces between polymer chains by the stronger carbon-carbon (C-C) primary bonds reduces the mobility of polymer segment by holding the chains more rigidly together (1).

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 yet (2, 3). 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 methacrylates, passed through a maximum then decreased. The maximum increase in Tg obtained by the addition of EGDMA was approximately 20°C at concentrations greater than 20% of MMA monomer volume.

Ethylene glycol dimethacrylate (EGDMA), a divinyl cross-linking agent, is commonly added to denture base resins in concentrations of up to 15% of monomer volume in order to provide craze resistance (4).

Unlike cast PMMA, studied by Loshaek as well as by Micko and Paszner (2, 3), dough--moulded PMMA denture base resins consist of the remains of original polymer powder beads which are not cross-linked, embedded in a matrix of newly-formed cross-linked interstitial material (5), (Fig. 1).

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 reccomended to produce specimens with high Tg as well as optimum mechanical properties (6).

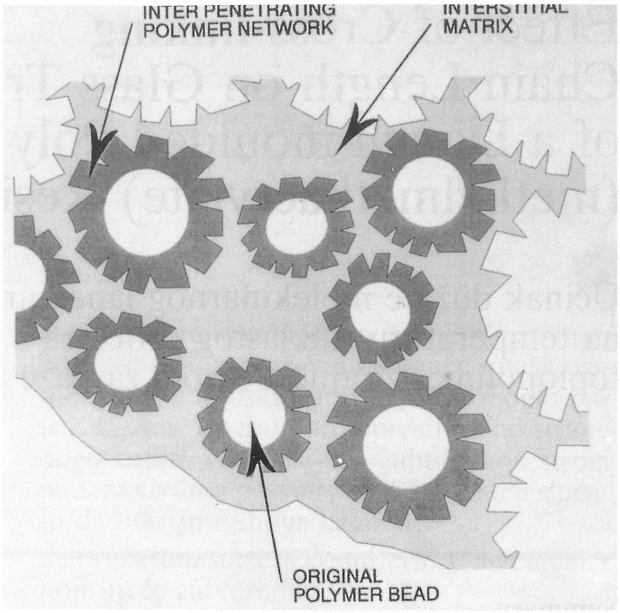

Figure 1. *Structure of polymerised (cross-linked) denture base acrylic resin.*

Slika 1. *Struktura polimerizirane i umrežene akrilatne smole za baze proteza*

It was also determined the effect of divinyl cross-linking agents having different chain lengths on the mechanical properties of a dough-moulded PMMA resin (7).

The purpose of the present study was to investigate the effect of prolonged curing cycle and cross-linking chain length of those cross-linking agents used by Caycik and Jagger (7).

Materials and Methods

TS 1195 unpigmented PMMA homopolymer powder (Bonar Polymers Ltd. Co., Durham, UK) with 0,26% benzoyl peroxide and methylmethacrylate monomer liquid stabilised with 0,01% quinol (British Drug House Ltd., Bristol, UK) were used to produce the specimens. The cross-linking agents chosen for this investigation ethylene glycol dimethacrylate (EGDMA), tetra(ethylene glycol dimethacrylate) (TEGDMA) and poly(ethylene glycol dimethacrylate) (PEG 600 DMA) (Polyscience Ltd., Northampton, UK) form an homologous series in which the cross-link contains 1, 4 and an

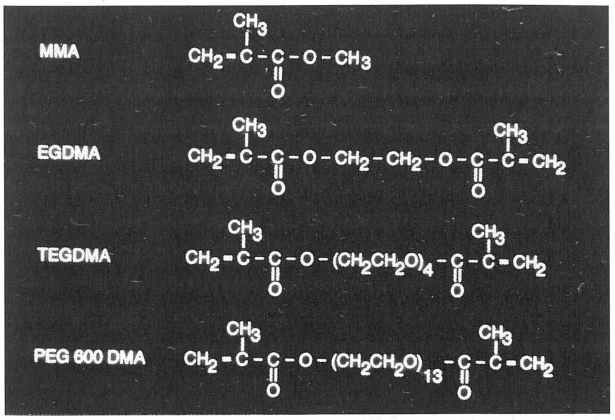

Figure 2. *Molecular structure of the cross-linking agents used in the study.*

Slika 2. *Molekularna struktura umreživača korištenih u istraživanju*

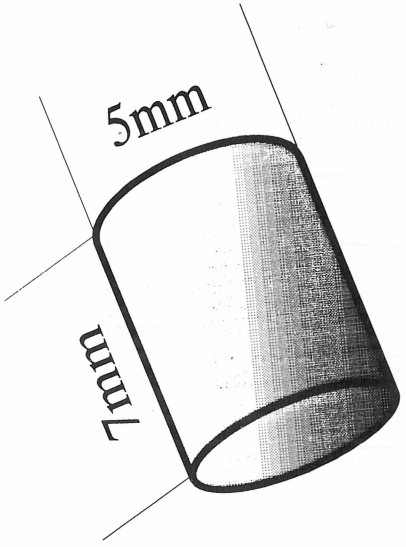

Figure 3. *Specimen used in the study, 5 mm in diameter and 7 mm in length.*

Slika 3. *Akrilatni pripravak korišten u istraživanju, promjera 5 mm i dužine 7 mm*

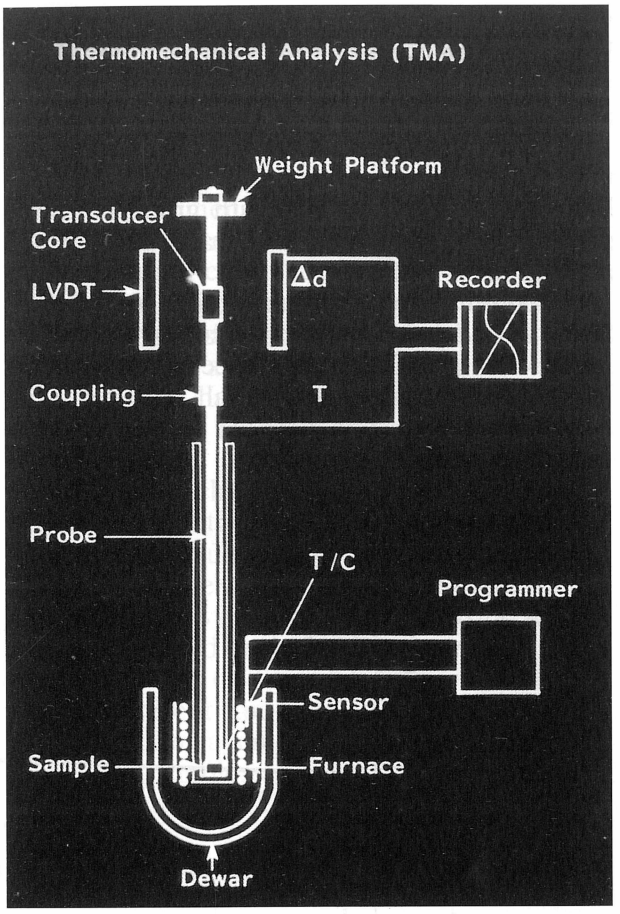

Figure 4. *Shematic feature of the Stanton Redcroft Thermomechanical Analyser, Model 790, linked to a conventional X–Y recorder.*

Slika 4. *Shematski prikaz aparata Stanton Redcroft Thermomechanical Analyser, Model 790, povezanog s pisačem (X–Y)*

average of 13 (C-C-O) units respectively (Fig. 2). The cross-linking agents were added to the monomer in concentrations of 0, 10, 20, 30 and 40% by volume (V/V).

Cylindrical test specimens 5 mm diameter x 7 mm length (Fig. 3) were produced in moulds prepared by investing 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 agents, particularly in high concentrations extended the dough times. The specimens were cured in a

thermostatically controlled water bath at a prolonged curing cycle (70° 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 grit paper, finishing with grade 600. All specimens were saturated in water for 28 days at 37°C prior to testing.

Measurement of Tg was carried out using a Stanton Redcroft Thermomechanical Analyser, Model 790 (PL Thermal Sciences Ltd., Epsom, UK) linked to a conventional X-Y recorder (Fig. 4).

The measuring procedure entailed 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 to be monitored on the X-Y recorder.

A thermocouple is located close to the specimen and the temperature variation is 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.

A rate of 5°C/min was selected for this investigation as this allowed a reasonable time for the evaluation of Tg.

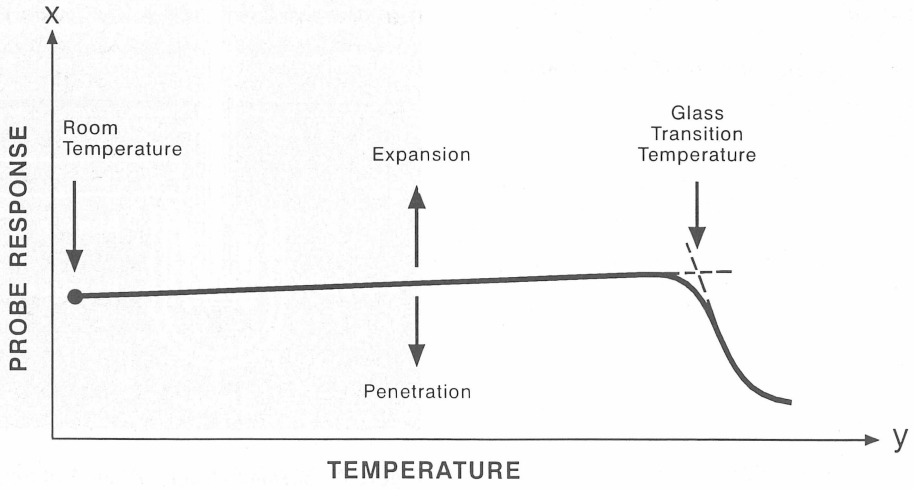

Figure 5. *Determination of the transition glass temperature (Tg) from the recorder trace.*
Slika 5. *Određivanje temperature staklastog prijelaza (Tg) s krivulje zapisa*

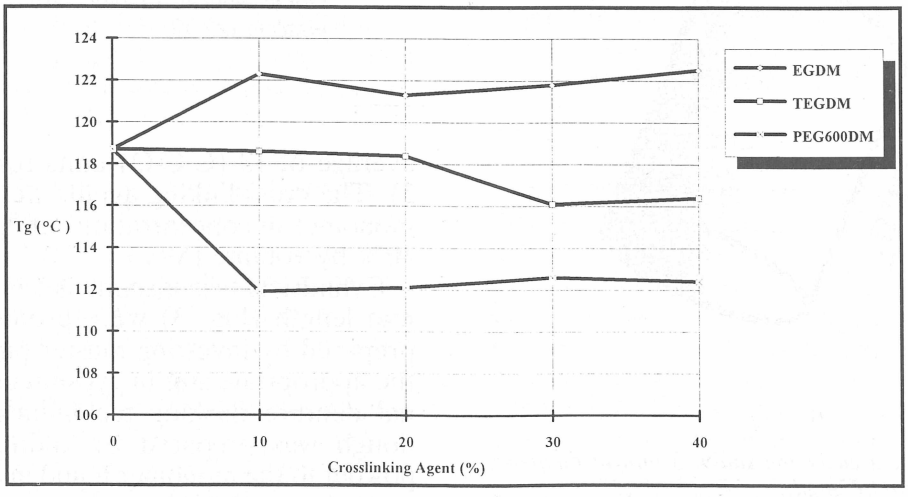

Figure 6. *Graph of the results from the study (O = control).*
Slika 6. *Grafički prikaz rezultata istraživanja (O = kontrolni uzorak)*

Tg is measured from the trace plotted on the X-Y recorder (Fig. 5). 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 material produced with different cross-linking agents at various percentages. Statistical testing of differences between groups was done by Student's t-test.

Results

The effect of the addition of the cross-linking agents on the Tg of the resultant specimens is shown in Table 1 and Figure 6. The addition of EGDMA produced a highly significant ($p < 0.001$) increase in Tg at all concentrations. The addition of TEGDMA produced no significant change ($p > 0.05$) at 10% and 20% concentrations but significantly lowered Tg at 30% and 40% concentrations ($p < 0.01$). PEG 600 DMA produced a highly significant ($p < 0.001$) lowering of Tg at all concentrations.

Table 1. *The transition glass temperatures (°C), together with their standard deviations (SD) and coeficients of variation (CV) of the materials investigated.*

Tablica 1. *Temperature staklastog prijelaza (°C) istraživanih materijala, uz pripadajuće standardne devijacije (SD) i koeficijente varijabilnosti (CV)*

CROSSLINKING AGENT IN MONOMER	%	Tg (°C) n = 5	SD	CV (%)
CONTROL	0	118.7	0.45	0.4
EGDMA	10	122.3	0.45	0.4
	20	121.3	0.45	0.4
	30	121.8	0.45	0.4
	40	122.5	0.79	0.6
TEGDMA	10	118.6	0.55	0.5
	20	118.4	0.42	0.4
	30	116.1	0.42	0.4
	40	116.4	0.42	0.4
PEG600DM	10	111.9	0.22	0.2
	20	112.1	0.42	0.4
	30	112.6	0.55	0.5
	40	112.4	0.55	0.5

Discussion

Glass transition temperature Tg is an important property of a denture base material since it reflects an ability of the material to withstand elevated temperatures and in addition it is related to the dimensional stability and internal stresses which are present as a consequence of polymerisation contractions (8).

Tg values are not absolute but are dependent on the method of determination. A wide variety of methods are available and the Tg of denture base materials has been investigated by several workers (9,10). Huggett and al. (11) reviewed methods of Tg 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 rate of 5°C/min was selected for the present study as it provided good probe sensitivity and avoided excessive heating which yields elevated values of Tg.

In the present study the effect of the addition of cross-linking agent on Tg of the resultant materials was complex and is in general agreement with the findings of Loshaek (2) and Micko and Paszner (3).

An understanding of the reaction of a divinyl monomer with MMA helps to explain the results.

The polymerisation reaction proceeds by both copolymerisation and cross-linking. Loshaek (2) 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 copolymerisation effect is dependent on the nature of the divinyl monomer and may produce a consequent reduction in Tg.

A further factor affecting the Tg is efficiency of the cross-linking reaction which is always less than 100%. Unreacted monomers and partially reacted pendant methacrylate groups will be present, and act as plasticisers which reduce Tg. At higher cross-linking agent concentrations the reaction is less efficient and hence a greater plasticising effect occurs. Further, the efficiency of the cross-linking reaction is inversely related to chain length. The dependence of the Tg on cross-link chain length may thus be explained by both reduced cross-link efficiency and by the copolymerisation effect.

That the cross-linking agents had relatively less effect on the Tg of the dough-moulded ma-

terials than of the cast polymerised materials of Loshaek (2) and Micko and Paszner (3) can be explained by the relatively smaller amount of cross-link material that is present only in the interstitial matrix of the dough-moulded material.

Due to samples saturation with water some plasticization effect could take place and will be investigated in the future work. Although dough-moulded polymerisation is generally used, the effect of postcuring at higher temperatures on the Tg of the resins investigated could be also considered.

Conclusions

1. Cross-linking of a dough-moulded PMMA resin by divinyl cross-linking agents can significantly affect Tg, but the relationship between Tg, cross-linking chain length and cross-linking agent concentration is complex.

2. The increase in Tg of approximately 3°C produced by the addition to denture base materials by manufacturers of up to 15% EGDMA of monomer volume should be of no clinical significance.

Aknowledgements

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UČINAK DUŽINE MOLEKULARNOG LANCA UMREŽIVAČA NA TEMPERATURU STAKLASTOG PRIJELAZA TOPLOPOLIMERIZIRAJUĆIH SMOLA ZA BAZE PROTEZA

Sažetak

Svrha istraživanja bila je utvrditi učinak dodavanja različitih divinilnih umreživača na temperaturu staklastog prijelaza toplopolimerizirajućih poli(metilmetakrilatnih) smola za baze proteza. Tri različita umreživača, etilen glikol dimetakrilat (EGDMA), tetra-(etilen glikol dimetakrilat) (TEGDMA) i poli(etilen glikol dimetakrilat) (PEG 600 DMA), koji čine homologni niz dodataka etilenskog oksida, te u kojima umreživači sadrže 1,4 odnosno prosječno 13 (C-C-O) jedinica, dodavani su monomer kapljevini (MMA) u koncentraciji od 0–40% volumena. U istraživanju je korišten, kao polimer-prašak komponenta, nepigmentirani PMMA-homo-polimer. Pripravci su napravljeni u kalupima, u skladu s uobičajenom kivetnom tehnikom toplopolimerizirajućeg postupka. Mjerenje temperature staklastog prijelaza (Tg) provedeno je termomehaničkim analitičkim postupkom. Dodatak EGDMA doveo je do porasta Tg-vrijednosti u svim koncentracijama, uz visoki stupanj značajnosti. Dodatak TEGDMA, u koncentracijama od 10% i 20%, nije doveo do značajnih promjena, dok je Tg značajno snižen u 30% i 40%-tnim koncentracijama. PEG 600 DMA utjecao je na značajno sniženje Tg-vrijednosti u svim istraživanim koncentracijama. Zaključeno je da umreživanje toplopolimerizirajućih akrilatnih smola za protezne baze pomoću divinil umreživača može značajno utjecati na temperaturu staklastog prijelaza (Tg-vrijed-

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nost), uz napomenu kako je međuovisnost između Tg-vrijednosti, dužine molekularnog lanca i koncentracije umreživača kompleksne naravi.

Ključne riječi: *akrilatne smole za protezne baze, umreživači, temperatura staklastog prijelaza.*

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