

Processing Behavior and Mechanical Properties of Autopolymerizing Hypoallergenic Denture Base Polymers

Jürgen Schellenberg, Tobias Otto, Anke Schadewald

Institut für Kunststofftechnologie und -recycling, Industriestrasse 12, D-06369 Weißandt-Görlau, Germany

Correspondence to: J. Schellenberg (E-mail: juergen.schellenberg@ktr-online.de)

ABSTRACT: Driven by the phenomenon of increasing irritations and allergic reactions of dental prosthesis carriers preferably due to residual methyl methacrylate monomer in conventional dental materials, autopolymerizing hypoallergenic denture base polymers were prepared as two-component materials in the shape of paste/paste- or powder/liquid systems. The processing behavior of these materials was investigated regarding the processing and solidification times also in dependence on the polymerization catalyst concentration, whereas the whole processing and curing characteristics and the final polymer properties were evaluated by dynamic mechanical analysis in shear mode in the temperature range from -145°C to 200°C . The mechanical properties of the hypoallergenic denture base polymers were validated regarding stiffness (flexural modulus E') and fracture toughness (maximum factor of loading intensity K_{max} , total work of fracture W_f) and the effects of monomer composition, kind of resin powder, impact modification by the liquid component, and water immersion on these properties were investigated. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41378.

KEYWORDS: biomedical applications; mechanical properties; properties and characterization; structure-property relations

Received 25 June 2014; accepted 6 August 2014

DOI: 10.1002/app.41378

INTRODUCTION

After its introduction into the market for dental prostheses, polymethyl methacrylate has been the widely used denture base polymer for more than 70 years. This success was due to the advantageous properties of this material such as an excellent esthetics, a simple processing behavior and the ability to be repaired easily.^{1–3}

However, these properties were accompanied by some disadvantages which became apparent over time. It turned out that denture materials based on polymethyl methacrylate caused irritations and allergic reactions to the oral mucosa of the prosthesis carriers preferably due to residual methyl methacrylate remaining in the material after polymerization. But also dental lab technicians manufacturing the dental prostheses were significantly affected by handling the methyl methacrylate monomer especially causing contact dermatitis. In clinical studies, 12.5% of the dental technicians examined showed a positive reaction in the epicutane test, whereas only 1.2% of the patients tested displayed a positive result.^{4,5} Thus, the development and investigation of hypoallergenic denture base polymers is highly desirable.

Despite various alternative polymers used for the manufacture of hypoallergenic dental prostheses instead of polymethyl methacrylate like polyacetals (Dental D), polyamides (Sunflex), vinyl

plastics (Luxene 1180), polyether ether ketones (Bio XS), polycarbonates (Andoran), rubber, and thermoplastic polymethyl methacrylates (Polyan) often requiring a complex and expensive processing, e.g., by an injection molding process, these polymers do not fulfill all the desired properties provided by conventional dental materials based on polymethyl methacrylate.^{6,7} Therefore, especially hypoallergenic denture base polymers with characteristics according to polymethyl methacrylates are preferred. Here, particularly autopolymerizing materials allow an easy and expeditious processing of the components, in comparison to other polymerization methods used in heat-polymerizable materials, requiring the application of temperatures above 65°C to achieve complete polymerization.

An autopolymerizing (cold-curing, self-curing) hypoallergenic denture base polymer to manufacture complete dental prostheses commercially available is Sinomer Kalt N (equivalent to Puran CC). Occasionally, the corresponding heat-polymerized material was investigated regarding mechanical properties, water sorption and water solubility, residual methyl methacrylate monomer, and repair strength in comparison to other hypoallergenic and conventional polymethyl methacrylate materials.^{8–12}

By the generally accepted definition in prosthetic dentistry, hypoallergenic denture base materials show no residual methyl methacrylate monomer or a significantly lower residual methyl

methacrylate content in comparison to polymethyl methacrylate-based heat-polymerizing resins.^{8,13} In this publication hypoallergenic denture base polymers comprise polymers manufactured without methyl methacrylate in the monomeric liquid component, whereas the powdery resin component might contain small residual amounts of methyl methacrylate, accordingly.

Since there are no examinations of the processing behavior and no correlations on the mechanical properties of autopolymerizing hypoallergenic denture base polymers in the literature, such desirable materials were prepared and the processing behavior as well as the effects of monomer composition, kind of resin powder (bead polymers), impact modification and immersion in water on selected mechanical properties were investigated in detail.

EXPERIMENTAL

Materials

The monomers bisphenol A-glycidyl dimethacrylate (BisGMA, Aldrich), diurethane dimethacrylate (UDMA, Evonik), 1,6-hexanediol dimethacrylate (HDDMA, Sartomer), and iso-tridecyl methacrylate (ITMA, Degussa) were used without further purification.

The components of the initiator systems dibenzoyl peroxide (BPO, Pergan), *N,N*-bis(2-hydroxyethyl)-*p*-toluidine (Esschem Europe), 2,6-di-*tert*-butyl-4-methyl phenol (BHT, Merck) and, alternatively, 1-benzyl-5-phenylbarbituric acid, 5-*n*-butylbarbituric acid (both Chemische Fabrik Berg), trioctylmethylammonium chloride (Aliquat 336, BASF), and copper(II) chloride dihydrate (Roth) were used as received.

As the standard resin powder, a partially crosslinked polymethyl methacrylate (Degacryl 6690F, Evonik) was used. In addition, impact modified polymethyl methacrylates (MV Plastics: Adicryl DA 441, Adicryl DA 442; Esschem Europe: Impact Poly Clear F 154), a MBS impact modifier (RK-56P, Shandong Rike Chemical) as well as the reactive liquid rubber Hypro 1300X33 VTBNX (CVC Thermoset Specialties) were applied.

Preparation and Processing of the Denture Base Polymers

The denture base polymers can be prepared as an unpolymerized two-component material in the shape of a paste/paste-system or of a powder/liquid system. The paste/paste-system comprises a basic paste containing a part of the monomer mixture (BisGMA/UDMA/HDDMA/ITMA), a part of the resin powder, a part of the inhibitor (BHT), and the initiator (BPO), whereas the catalyst paste includes the other equal parts of monomer mixture, resin powder, inhibitor, and the cocatalyst (amine). In the powder/liquid system, the powder contains the whole amount of the resin powder and the barbituric acids, whereas the liquid consists of the entire monomer mixture and the cocatalysts (both chlorides). The components of both systems were prepared by an intensive dissolving and stirring, in the case of the pastes with an Unguator system. In addition, the pastes were devolatilized in vacuum at 40°C to avoid the formation of bubbles during processing.

The processing (polymerization) of the unpolymerized materials was started by the combination of the two components by intensive mixing at room temperature for 1 min, in the case of the paste system with a Mixpac equipment (Sulzer), followed after 20 min

by heating in a waterbath at a constant temperature of 50°C for 30 min when specimens for mechanical testing were prepared. Processing time and solidification time of the autopolymerizing denture base materials were determined after the combination of the components during manual stirring until appearing of the first inhomogeneities in the mixture or until solidification of the whole mixture by polymerization, respectively.

Dynamic Mechanical Analysis and Differential Scanning Calorimetry

The dynamic mechanical analysis (DMA) was performed on a DMA/SDTA 861 (Mettler-Toledo) with a temperature scan over a range of -20°C to 200°C and a heating/cooling rate of 3 K/min in flexural mode (sinusoidal stress at 1 Hz), recording the loss and storage moduli as well as the loss tangent $\tan \delta$ as the ratio of loss to storage modulus as a function of the temperature. In case of the investigation of the processing behavior of the hypoallergenic denture base materials, the investigations were performed in shear mode in a temperature range from -145°C to 200°C. Unnotched specimens of the determination of the fracture toughness were used for the DMA.

For the determination of glass transition temperatures by differential scanning calorimetry (DSC) measurements, the thermoanalytical system DSC 1 (Mettler-Toledo) was used at a heating rate of 10 K/min under nitrogen.

Fracture Toughness

The fracture toughness of the hypoallergenic denture base polymers was determined with a modified three-point bending test using a Zmart.Pro universal testing machine (Zwick GmbH & Co. KG) according to Ref. 14 at 23°C without immersion to water. The span distance between the two supports was 32 mm (l_t) and the constant testing speed was 1 mm/min.

Fracture toughness was characterized by two parameters, the maximum factor of loading intensity K_{\max} , and the total work of fracture W_f . The maximum factor of loading intensity was determined according to the equation

$$K_{\max} = \frac{f(x)P_{\max}l_t}{(b_t h_t^{3/2})} \sqrt{10^{-3}} \quad [\text{MPa m}^{1/2}]$$

with P_{\max} as the maximum load onto the test specimen in Newton, and $f(x)$ as a geometrical function of x :

$$f(x) = 3x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{[2(1+2x)(1-x)^{3/2}]}$$

$$x = \frac{a}{h_t},$$

where a is the crack length after testing determined by averaging the measurements.

The total work of fracture was calculated with the equation

$$W_f = \frac{U}{[2b_t(h_t - a)]} 1000 \quad [\text{J/m}^2],$$

where U is the recorded area below the load-/deflection curve in Nmm represented by the equation

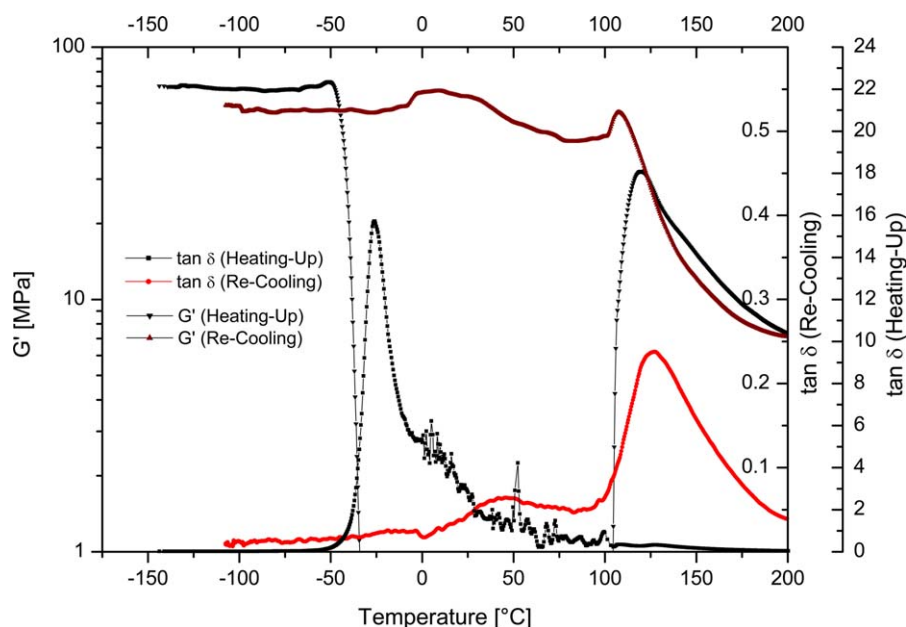


Figure 1. DMA-Investigation of processing behavior, curing characteristics and final properties of the hypoallergenic denture base polymer (BisGMA/UDMA/HDDMA = 40/25/35, resin powder: 53 wt %, catalyst: BPO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$U = \int PdU.$$

The test specimens were prepared with the size of $39 \times 8 \times 4$ mm [length \times high (h_t) \times width (b_t)] and initially notched in the middle of the specimens by a 0.5 mm saw blade with a deep of 3 mm, further sharpened by a scalpel to an additional deep of 100 μ m to 400 μ m.

RESULTS AND DISCUSSION

Processing Behavior

Conventional autopolymerizing denture base polymers on the basis of polymethyl methacrylate and formulated as a two-component material in the shape of the widespread powder/liquid system are processed by pouring the resin powder into the liquid monomer followed by an intensive mixing of both components. This induces a swelling and dissolution process because of the at least partial solubility of the polymethyl methacrylate in the methyl methacrylate monomer forming a dough-like kneadable substance getting more rigidity with time. After losing tackiness and adhesion to walls of the mixing vessel, the dough stage is reached and the material can be further processed by shaping into the dental mold, where it becomes tough and rubbery finally resulting in a hard dental polymer.^{15,16} This polymerization process can be considered as the formation of a semi-interpenetrating network of the denture base polymers, where one polymer is crosslinked (based on methyl methacrylate monomer and a small amount of a dimethacrylate), the other polymer is linear or branched (the polymethyl methacrylate resin powder), and both polymers are not covalently bonded to each other.¹⁷

In contradiction to conventional polymers autopolymerizing hypoallergenic denture base polymers do not contain methyl

methacrylate monomer and show a completely different processing behavior. Independently of the formulation as a powder/liquid or a paste/paste system, a flowable liquid or paste is formed after an intensive mixing of both components. Within the time until appearing of the first inhomogeneities in the mixture, the processing time, the composition stays visually homogeneous and flowable at roughly the same viscosity and can be poured into the dental mold. However, within a short period after the occurrence of first inhomogeneities, the mixture solidifies (solidification time). This behavior should also be the result of the partial or general insolubility of the resin powder in the selected monomers.

DMA Investigations

To investigate the processing behavior and the total curing characteristics of the hypoallergenic denture base polymers in detail, a DMA analysis was performed in shear mode using a paste formulation of a hypoallergenic denture base material without a cocatalyst. At first, the unpolymerized sample of the material was cooled to -145°C , followed by a scan in heating-up mode to 200°C demonstrating the polymerization and crosslinking behavior of the dental material, and at the last a recooling to -110°C characterizing the final properties of the denture base polymer. The temperature dependence of the storage shear modulus (G') and the loss tangent ($\tan \delta$) is demonstrated in Figure 1.

In the heatig-up mode, the unpolymerized dental paste consisting of the polymethyl methacrylate (PMMA) resin powder, the dimethacrylate monomer mixture, and the initiator system shows a high storage modulus at the beginning in the frozen state. Attaining the glass transition temperatures of the monomers and thus the softening of the dental paste, the storage modulus drops off by over six orders of magnitude resulting in a mostly viscous-liquid system. At temperatures of about 90°C ,

the initiator decomposes and starts polymerization and cross-linking of the monomers of the dental paste forming a solid denture base polymer leading to a significant increase of the storage modulus by over six orders of magnitude. A further enhancement of the temperature partially counteracts this increase by a softening of the dental polymer as a result of exceeding the glass transition temperatures of the partially crosslinked PMMA resin powder within the network structure of the polymerized dimethacrylate monomers. This behavior is confirmed by the trend of the loss tangent with a dominating peak at -26°C reflecting the glass transition temperatures of UDMA and BisGMA of -36°C and -12°C (determined independently by DSC), the melting point of HDDMA of about 10°C ,¹⁸ as well as by the smaller peaks of glass transitions of the crosslinked PMMA resin powder of 123°C , crosslinked dimethacrylate mixtures at about 130°C (both also determined independently by DSC), and the glass transition of PMMA at 100°C including β relaxation in the broader area at 30°C – 60°C .^{19–21}

The behavior and the properties of the cured denture base polymers are visible in the recooling mode of the DMA. Here, the storage modulus of the crosslinked dental material is on a high level in general. Starting at a temperature of 200°C , the modulus remarkably rises with decreasing temperature because of freezing of relaxations of the partially crosslinked PMMA resin in the network of the polymerized dimethacrylate monomers and stabilizes at high values with small variations at temperatures below about 110°C . This dependence is accompanied by the loss tangent $\tan \delta$ with the dominating peak at a maximum of 127°C in the range of the glass transition temperatures of the partially crosslinked PMMA resin of 123°C and the crosslinked polydimethacrylates of about 130°C , and the smaller broad relaxation area with a maximum at about 45°C . In this area, the β relaxation of the PMMA obviously is superimposed by relaxations of the dimethacrylate network formed in the cured denture base material. Here, glass transition temperatures of the cured homopolymers of UDMA and BisGMA of 68°C and 67°C were described, respectively.^{22,23}

For a detailed characterization of the viscous-liquid paste system and thus the processing behavior of the dental material, the DMA investigations allow the determination of the viscosity of the denture base polymers formulated either as a paste or a powder/liquid system in a temperature range until the crosslinking to the final polymer. This viscosity (η') can be calculated from the loss shear modulus (G'') according to the equation

$$\eta' = \frac{G''}{\omega} = \frac{G''}{2\pi \cdot f}$$

with ω as the circular frequency, and f as the frequency.²⁴

The dependences of loss and storage moduli over the whole order of magnitude range and the resulting viscosity shown in Figure 2 in the heating-up mode indicate a liquefying of the not yet crosslinked dental paste after exceeding the glass transition temperatures of the monomers by a significant drop of the viscosity to a minimum of 0.69 Pa s at 64°C .

With the start-up of the polymerization and the following crosslinking of the dimethacrylate monomers, the viscosity rapidly jumps up by over five orders of magnitude and the

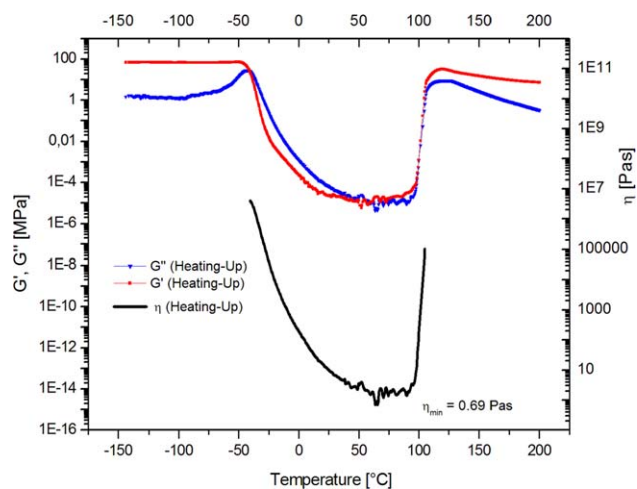


Figure 2. Determination of the viscosity-temperature dependence of the hypoallergenic denture base polymer of Figure 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cured denture base polymer is formed. It is remarkable, that the viscosity of the dental material is below 20 Pa s in a temperature region of about 20°C to 99°C . Usually, formulated dental materials have viscosities of the paste or the powder/liquid mixture below this value to be processed easily. Furthermore, the viscosity of the hypoallergenic denture base material is relatively low and about constant until 97°C and does not indicate any increase because of a kind of dough formation by swelling and dissolution processes as in the case of conventional denture materials based on polymethyl methacrylate.

Processing and Solidification Times

The most important properties to characterize the component mixture of the hypoallergenic autopolymerizing material at the preparation of the denture base are processing time and solidification time. A detailed investigation of both properties is shown in Figure 3 in dependence on the catalyst concentration (barbituric acids) of a powder/liquid system.

Processing and solidification times decrease significantly with increasing catalyst concentration and can be used to adjust both times according to the requirements at the manufacturing of the dental prosthesis by the dental technician. Furthermore, it can be observed, that both times proceed very closely to each other, but with a difference increasing with lower barbituric acid concentration. Since the component mixture shows about the same viscosity within the processing time, especially the polymerization and crosslinking behavior of the dental material in the remaining time until the solidification can be explained in accordance to the behavior of dimethacrylate-based dental composites. Here, the transition from a viscous liquid to an elastic gel, the gelation, is followed by an autoacceleration owing to an enhanced free radical concentration because of a significantly reduced bimolecular termination at a still sufficient diffusivity of small monomer molecules. Subsequently, by limiting the diffusion even of the monomer molecules based on the high viscosity of the mixture, the reaction rate declines substantially, called autodeceleration, and causes the transition from the rubbery state to a glass, the vitrification.²⁵ In addition, this process

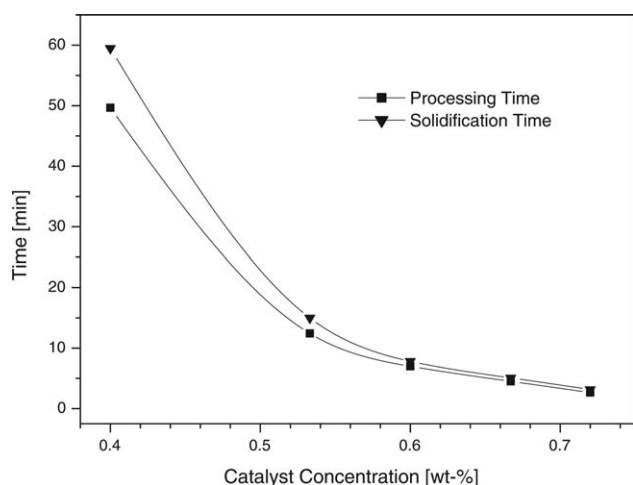


Figure 3. Dependence of processing and solidification times of a powder/liquid system on catalyst concentration (BisGMA/UDMA/HDDMA = 40/25/35, resin powder: 45 wt %, catalyst: 1-benzyl-5-phenylbarbituric acid/5-n-butylbarbituric acid = 3/1).

can be considered as a polymerization-induced macrophase separation because of the presence of the polymethyl methacrylate resin powder²⁶ and can explain the increasing difference of processing and solidification times as a result of lower reaction rates.

Mechanical Properties

Influence of Monomer Composition. An opportunity to attain hypoallergenic denture base polymers is the substitution of the methyl methacrylate monomer of conventional materials by other monomers, mono- and dimethacrylates. Since monomethacrylates of a moderately higher chain length like butyl, hexyl, or benzyl methacrylate are not desirable because of their olfactory properties, and monomethacrylates of much higher molecular weight like stearyl methacrylate are not suitable since they are solid materials, iso-tridecyl methacrylate is a monomer to be investigated together with HDDMA as a dimethacrylate. After formulation of the corresponding paste/paste systems of such autopolymerizing hypoallergenic denture base materials and the preparation of the solid polymers, the flexural moduli E' of these polymers were measured by DMA as shown in Figure 4, at different temperatures the dental prosthesis is potentially exposed to.

At a temperature of 0°C, Figure 4 indicates an increase of the flexural modulus with an enhanced content of the dimethacrylate in the monomer mixture. This dependence is much more pronounced at higher temperatures and is a result of the increased network density of the dental materials received at a higher dimethacrylate incorporation based on a higher dimethacrylate content in the monomer mixture. In comparison to the requirements of DIN EN ISO 20795-1¹⁴ with a flexural modulus of the denture base polymers of at least 1500 MPa (autopolymerizable materials) and of at least 2000 MPa (heat-polymerizable materials) at a temperature of 37°C, even a content of 60 wt % dimethacrylate in the monomer mixture is not sufficient to provide this property safely. Therefore, monomer mixtures with only a small or no amount of monomethacrylates in the

mixture with dimethacrylates are preferred for autopolymerizing hypoallergenic denture base polymers because of their mechanical properties, in contradiction to conventional materials based on methyl methacrylate, where only minor amounts of dimethacrylates can be used for the control of a slight crosslinking of the polymers.

Effect of Resin Powder. The mechanical properties of the autopolymerized hypoallergenic denture base polymers were significantly affected by the resin powders used, independently of the formulation as a paste/paste or powder/liquid system. To receive dental materials with an improved toughness, the conventional resin powders based on polymethyl methacrylate can be used together with special impact modifiers. On the other hand, resin powders already impact modified can be utilized. Both opportunities were applied in the formulation of paste/paste systems and the corresponding polymerization to hypoallergenic denture base polymers. The mechanical properties of these dental materials received with different resin powders are shown in Figure 5 with regard to stiffness represented by the flexural modulus E' and toughness reflected by the maximum factor of loading intensity K_{max} and the total work of fracture W_f .

All dental polymers exhibit a high flexural modulus with values above 3000 MPa, also at application temperatures of the dental prostheses of 37°C. This is much higher than the flexural moduli measured for the comparable, but heat-polymerized hypoallergenic denture base material Sinomer (Alldent) with values in the range of 1720 MPa to 2200 MPa.^{8–10} Whereas the combination of a conventional polymethyl methacrylate with an impact modifier based on MBS (binary copolymer of methyl methacrylate and 1,3-butadiene) (Degacryl 6690F/MBS RK-56P) at an usual concentration indicates only a low toughness regarding K_{max} and W_f , the formulations with resin powders already impact modified are more preferred regarding a high toughness of the dental materials (Adicryl DA 441, Adicryl DA 442, Impact Poly Clear F 154). The correlation of a higher toughness

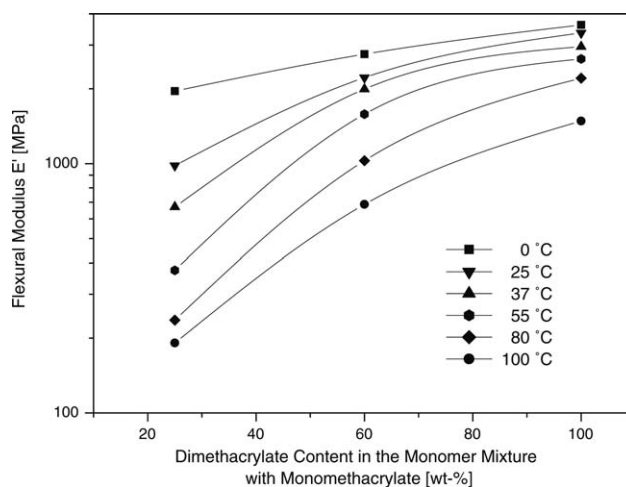


Figure 4. Correlation between flexural modulus (E' ; DMA) and dimethacrylate content in the monomer mixture with monomethacrylate of autopolymerized hypoallergenic denture base materials at different temperatures (dimethacrylate: HDDMA, monomethacrylate: ITMA, resin powder: 53 wt % Adicryl DA 441, catalyst: BPO).

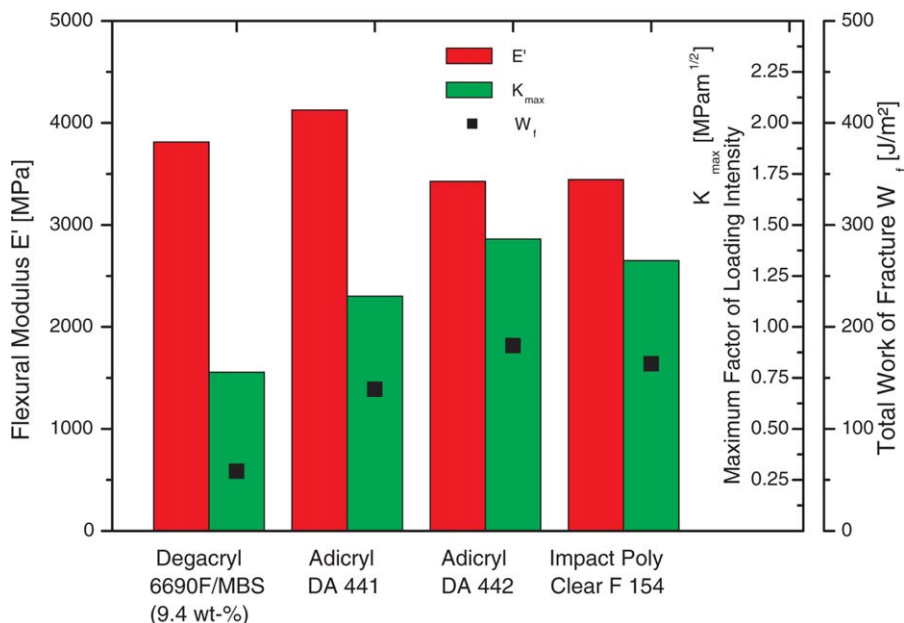


Figure 5. Mechanical properties of autopolymerized hypoallergenic denture base materials in dependence on resin powder (BisGMA/UDMA/HDDMA = 40/25/35, resin powder: 53 wt %, catalyst: BPO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at a lower stiffness of the dental materials can also be observed at the resin powders already impact modified. This behavior is accompanied by a decrease of the glass transition temperature ($\tan \delta$) from 130.3°C (Degacryl 6690F/MBS) to 124.6°C (Adicryl DA 441), 121.2°C (Adicryl DA 442), and 123.7°C (Impact Poly Clear F 154) too.

Impact Modification by the Liquid Component. Besides the resin powder, the liquid component of the dental material can contribute to an additional impact modification of the

autopolymerized hypoallergenic denture base polymer, independently of the system formulation as a paste/paste or powder/liquid.²⁷ Therefore, a reactive methacrylate terminated liquid butadiene polymer was used for impact modification in an autopolymerizing hypoallergenic denture base material formulated as a paste/paste composition. The dependence of the mechanical properties of the polymerized dental polymers regarding bending stiffness and toughness on the concentration of the impact modifier up to 6 wt % is demonstrated in Figure 6.

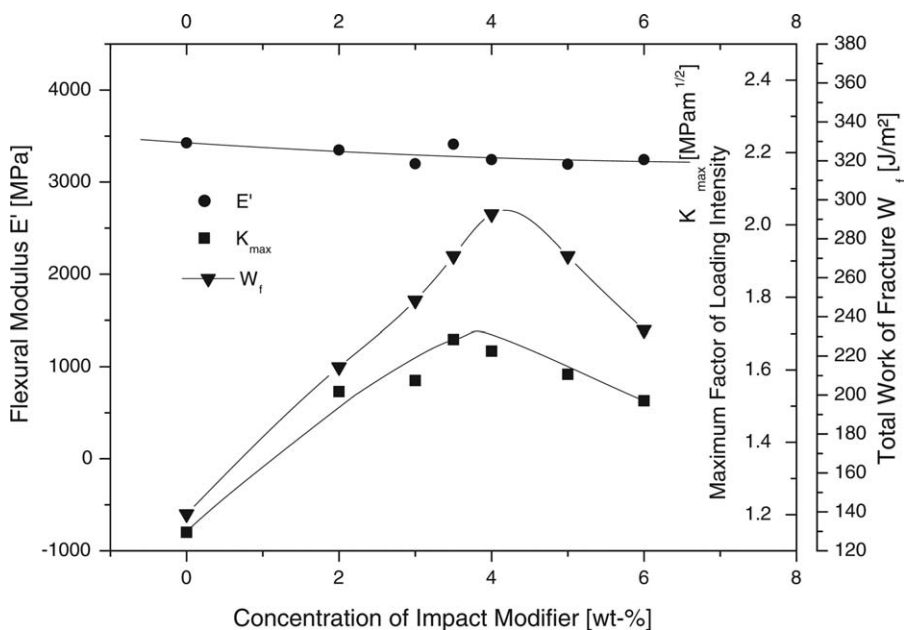


Figure 6. Dependence of mechanical properties of autopolymerized hypoallergenic denture base materials on the concentration of the impact modifier in the liquid component (BisGMA/UDMA/HDDMA = 40/25/35, resin powder: 53 wt % Adicryl DA 442 including the impact modifier Hypro 1300X33 VTBNX, catalyst: BPO).

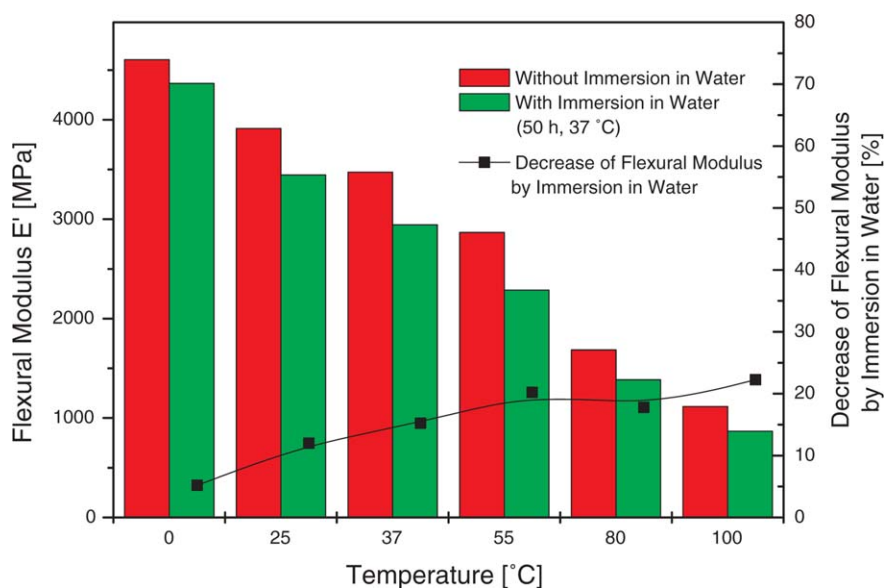


Figure 7. Influence of water immersion on the flexural modulus of autopolymerized hypoallergenic denture base polymers at different temperatures (BisGMA/UDMA/HDDMA = 40/25/35, resin powder: 53 wt % Adicryl DA 441, catalyst: BPO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Whereas the flexural modulus E' only slightly decreases within the whole concentration range of the modifier and reaches values above 3000 MPa, both mechanical parameters of the fracture toughness, K_{\max} and W_f , show a maximum at an impact modifier concentration of about 4 wt %. While the maximum factor of loading intensity K_{\max} characterizes the sensitivity of the dental polymer to crack initiation, the total work of fracture

W_f relates to the resistance of the material to a further propagation of the crack.²⁸ At first, the incorporation of the liquid butadiene within the monomer mixture of the dimethacrylates by polymerization leads to an enhancement of both toughness parameters of the crosslinked dental polymers with an increase of the modifier concentration, because of the flexibility of the butadiene segments. After the maximum however, the toughness of the dental materials drops off, probably caused by a too vigorous softening of the material due to an increased flexibility by the enhanced amount of butadiene segments incorporated. In comparison to the results in Figure 5 it is obvious, that the toughness of the autopolymerized hypoallergenic denture base polymers can significantly be increased by an impact modification of the liquid component, in addition to the impact modification of the resin powder.

Influence of Water Immersion. Since dental prostheses are exposed to water either in the oral environment or outside in case of e.g., cleaning processes, the investigation of the influence of water immersion on the stiffness of the dental material is desirable. Therefore, an autopolymerized hypoallergenic denture base polymer was prepared and the flexural modulus E' was measured by DMA at different temperatures from 0°C to 100°C with and without the immersion in water at 37°C for 50 h, according to Ref. 14 in case of testing the flexural modulus in an unmodified three-point bending examination (Figure 7).

Figure 7 shows a decrease of the flexural modulus from about 4600 MPa to 1100 MPa without immersion in water, and from

about 4400 MPa to 870 MPa in case of water immersion over the whole temperature range. The percentage decrease of the flexural modulus is slightly increasing with temperature at first, but leveling off at about 20% above 55°C. Furthermore, the decrease of the flexural modulus is accompanied by a decrease of the glass transition temperature ($\tan \delta$) from 122,1°C (without) to 119,8°C (with immersion in water), which has to be considered as an external plasticization of the dental material by the water immersion.^{29,30}

CONCLUSIONS

Autopolymerizing hypoallergenic denture base polymers without any methyl methacrylate in the monomer component can be prepared according to the processing requirements as two-component materials in the shape of paste/paste- or powder/liquid systems.

In contradiction to conventional dental polymers these materials show a completely different processing behavior. Within the processing time, the composition stays visually homogeneous and flowable at roughly the same viscosity, but solidifies within a short period after the occurrence of first inhomogeneities. Investigations by dynamic mechanical analysis in shear mode provide a useful overview on the whole processing and curing characteristics and the final polymer properties.

Monomer mixtures with only a small or no amount of higher monomethacrylates in the mixture with dimethacrylates are preferred for autopolymerizing hypoallergenic denture base polymers because they show improved mechanical properties in comparison to mixtures containing monomethacrylates above about 20 wt % (ITMA). Formulations with resin powders already impact modified are more favored regarding a high toughness of the hypoallergenic denture base materials. The toughness of the autopolymerizing hypoallergenic denture polymers can significantly be increased by an impact modification

of the liquid component, e.g., by about 4 wt % of a reactive methacrylate terminated liquid butadiene polymer, in addition to the impact modification of the resin powder. The influence of water immersion on the flexural modulus has to be considered and decreases the flexural modulus of the denture base material by about 20% at higher temperatures.

ACKNOWLEDGMENTS

The authors are grateful to the Central Innovation Program SME (AIF) for financial support (grant no. KA2888501SL1) and to the companies mentioned for the donation of the materials used in this study.

REFERENCES

- Schmidt, A. *Zahntechnik* **1978**, *19*, 436.
- Price, C. A. *Aust. Prosthodont. J.* **1994**, *8*, 47.
- Culbertson, B. M.; Kerby, R. E. Dental Applications. In *Encyclopedia of Polymer Science and Technology*; Wiley: New York, **2010**; Online Publication, p 1.
- Iron, R. Alles zur Allergologie. Bon-Med: Sankt Augustin 2004, 2. Ed., Methylmethacrylat (MMA).
- Azhar, D. A.; Syed, S.; Luqman, M.; Ali, A. A. *Dent. Mater. J.* **2013**, *32*, 519.
- Blankenstein, F. *Das internationale Zahntechnik Magazin* **2012**, *16*, 180.
- Jarkas, M. I. Werkstoffmechanischer Vergleich hypoallergener Prothesenbasiskunststoffe. Dissertation. Martin-Luther-Universität Halle-Wittenberg, **2007**, p 19, 50.
- Pfeiffer, P.; Rolleke, C.; Sherif, L. *J. Prosthet. Dent.* **2005**, *93*, 372.
- Mansour, S.; Jarkas, M. I.; Setz, J. M.; Boeckler, A. F.; Bierögel, C.; Grellmann, W. *Int. Poster J. Dent. Oral Med.* **2009**, *11*, 433.
- Jarkas, M. I. Werkstoffmechanischer Vergleich hypoallergener Prothesenbasiskunststoffe. Dissertation. Martin-Luther-Universität Halle-Wittenberg, **2007**.
- Pfeiffer, P. *J. Prosthet. Dent.* **2004**, *92*, 72.
- Pfeiffer, P.; An, N.; Schmage, P. *J. Prosthet. Dent.* **2008**, *100*, 292.
- Jarkas, M. I. Werkstoffmechanischer Vergleich hypoallergener Prothesenbasiskunststoffe. Dissertation. Martin-Luther-Universität Halle-Wittenberg, **2007**, p 19.
- DIN EN ISO 20795-1:2013-06. Dentistry - Base polymers - Part 1: Denture base polymers.
- Caesar, H. H. Die Ausbildung zum Zahntechniker; Verlag Neuer Merkur: München, **1996**; Part 1, p 300.
- Braden, M.; Clarke, R. L.; Nicholson, J.; Parker, S. *Polymeric Dental Materials*; Springer-Verlag: Berlin, Heidelberg, New York, **1997**; p 56.
- Vallittu, P. K. *J. Adhesion Sci. Technol.* **2009**, *23*, 961.
- SR239A - Technical Data Sheet; Sartomer: Paris **2005**; p 1.
- Kunststoff-Handbuch, Band IX: Polymethylmethacrylate; Vieweg, R.; Esser, F., Eds.; Carl-Hanser-Verlag: München, **1975**; p 254.
- D. W. van Krevelen. *Properties of Polymers*; Elsevier Science B. V.: Amsterdam, **1997**; p 173.
- Kreibich, U. T.; Schmid R. Glasübergang und Nebenrelaxationen. In *Polymere Werkstoffe, Band I: Chemie und Physik*; Batzer, H., Ed.; Georg Thieme Verlag: Stuttgart, New York, **1985**; p 309.
- Podgorski, M. *Dent. Mater.* **2010**, *26*, e188.
- Sideridou, I.; Tserki, V.; Papanastasiou, G. *Biomaterials* **2002**, *23*, 1819.
- Ni, J. Sample preparation for DMA shear measurements. In *Thermal Analysis of Polymers. Part 4: TGA, TMA and DMA of thermosets. Thermal Analysis UserCom 34*; Mettler Toledo, **2011**, p 15.
- Leprince, J. G.; Palin, W. M.; Hadis, M. A.; Devaux, J.; Leloup, G. *Dent. Mater.* **2013**, *29*, 139.
- Szczepanski, C. R.; Pfeifer, C. S.; Stansbury, J. W. *Polymers* **2012**, *53*, 4694.
- Schellenberg, J.; Schadewald, A. DE 10 2012 111 266 (to Institut für Kunststofftechnologie und -recycling, **2012**).
- Lee, H.-H.; Lee, C.-J.; Asaoka, K. *Dent. Mater. J.* **2012**, *31*, 157.
- Kunststoff-Handbuch, Band IX: Polymethylmethacrylate; Vieweg, R.; Esser, F., Eds.; Carl-Hanser-Verlag: München, **1975**; p 338, 425.
- Elias, H.-G. *Makromoleküle, Vol. 2 Physikalische Strukturen und Eigenschaften*; Wiley-VCH: Weinheim, **2001**; p 462.