

Influence of Microwave Heating on the Polymerization Kinetics and Application Properties of the PMMA Dental Materials

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ABSTRACT: The effects of heating mode (conventional isothermal heating (CIH) and microwave isothermal heating (MWIH)) on the kinetics of polymerization and the properties important for the application (residual monomer, hardness, and water absorption) of three commercial poly(methyl methacrylate) (PMMA) base dental materials were investigated. The degree of monomer conversion was determined by infrared spectrometry. The hardness of the polymerized samples was measured by shore D method, whereas the water absorption was measured gravimetrically. Kinetics models for polymerizations using different heating modes were determined by model fitting method. The rate of the MWIH polymerization was eight times

higher compared with the CIH polymerization. The CIH polymerization is found to be the phase-boundary controlled reaction for which the rate of contracting volume is the rate limiting step, whereas MWIH polymerization is found to be the first-order reaction and the monomer concentration in the polymerization mixture is the rate limiting step. The samples of PMMA base dental materials synthesized by MWIH polymerization exhibit better application properties (hardness and water absorption). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3598–3606, 2011

Key words: dental polymers; hardness; infrared spectroscopy; kinetics (polym)

INTRODUCTION

Microwave heating (MWH) is a widely accepted, nonconventional energy source for organic synthesis¹ and different physicochemical processes such as sintering,² nucleation and crystallization,³ combustion synthesis,⁴ calcinations,⁵ solvent-free reactions,⁶ heterogeneous catalysis,⁷ and combinatorial chemistry.⁸

Microwave synthesis represents a major breakthrough in synthetic chemistry methodology, a remarkable change in the way chemical synthesis is performed and in the way it is perceived in the scientific community.⁹ Microwave-assisted heating could accelerate the rates of polymerization reactions and improve properties of the products, which is the reason why microwave-assisted chemical synthesis has attracted wide attention.

In the field of dental materials, microwaves found their earliest applications as simple and effective methods for prosthetic disinfection.^{10,11} Apart from

that, microwaves have also been used in dentistry for methyl methacrylate (MMA) polymerizations.^{12–16}

One of the most important unmodified acrylic materials is poly(methyl methacrylate) (PMMA). Although it was first discovered and commercialized many years ago, PMMA is one of the most widely used industrial and commercial polymeric materials and still remains an active material for research. PMMA dental materials are widely used in dentistry because of their good mechanical properties, biocompatibility, reliability, dimensional stability, relative ease of manipulation, and good esthetic appearance.^{17,18} Polymerization of MMA under conventional conditions has been studied comprehensively.¹⁹ Conventional and microwave kinetics of MMA polymerization were compared with each other and discussed.²⁰ It was found that at all the investigated temperatures and powers, polymerization rates increased in the presence of microwave energy by up to 8.9 times compared with conventional polymerization.²⁰

Microwave processing of PMMA denture base materials has been shown to provide similar transverse strength, Knoop hardness, density, and residual monomer content as in conventional heat-polymerized materials.¹⁴ Wallace et al.²¹ compared dimensional accuracy of microwave- and heat-polymerized denture materials and found that microwave-polymerized samples had equal or better dimensional accuracy

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TABLE I
The Physical and Chemical Properties of Powder Component of Used Dental Materials

Material	M_n (g/mol·10 ⁻⁵)	M_w (g/mol·10 ⁻⁵)	PI	Monomer content (%)	Average particle size (μm)
Biocryl	1.27	3.82	3.01	4.3	55
Poli Hot	1.40	4.82	3.44	3.5	62
Futura Basic Hot	1.52	4.07	2.66	3.2	68

than the conventionally polymerized materials. Geerts and Jooste²² concluded that bond strength of microwave-polymerized PMMA to denture teeth was superior to that of conventional heat-polymerized PMMA. Baffle et al.²³ compared the porosity of denture resin cured by microwave energy with that of denture resin cured by the conventional heat method and found that microwave-processed dental materials made of MMA monomer and polymer showed significantly higher mean porosity because of vaporization of the monomer, which produced porosity in the final set material. Lai et al.²⁴ also found that microwave-cured materials have higher porosity than heat-cured materials and that the amount of porosity increased with an increase in microwave energy level. Thus, the water bath-cured specimens showed better flexural strength and flexural modulus than the microwave-cured specimens. Lai et al. also investigated surface hardness and rubber phase distribution and found no significant differences in the surface hardness and the domain size distribution of the effective rubber phase. Usanmaz et al.²⁵ investigated the thermal and mechanical properties of dental base materials cured by microwave and conventional methods. The mechanical properties of the samples were determined from tensile and three-point bending tests. The elastic modulus and ultimate stress were higher for samples obtained by the conventional polymerization when compared with microwave polymerization.

The aim of this work was to compare the properties of base dental materials (residual monomer, hardness, and water absorption) important for their application, synthesized by conventional isothermal heating (CIH) and isothermal microwave heating (MIH). Also, the kinetic models of polymerization were determined and compared.

MATERIALS AND METHODS

Materials

The PMMA base dental materials, Biocryl (Galenika, Serbia), Poli Hot (Polident, Slovenia), and Futura Basic Hot (Schutz, Germany), all in powder-liquid forms, were used as received. The liquid component consists of MMA as monomer and ethylene glycol dimethacrylate as a crosslinker. The powder compo-

nent consists of prepolymerized beads of PMMA coated with dibenzoyl peroxide as an initiator.

The values of basic physicochemical properties of powder component of used base dental materials (number average molar mass (M_n), weight average molar mass (M_w), polydispersity index (PI), monomer content, and average particle size) were kindly supplied by manufacturers and are shown in Table I.

Sample preparation

Denture base materials were prepared according to the respective manufacturer's instruction. The formulations were mixed in proportions recommended by the manufacturer's instructions (2.1 g of powder component and 1 mL of liquid). Specimens were prepared by conventional and isothermal microwave polymerization. The mixed resins were packed into teflon molds designed to produce disk measuring 25 mm in diameter and 3-mm thick samples, which were used for all measurements. The molds were then clamped tight and placed in a thermostatically controlled water bath (NE1B-8, Progen Scientific, London, UK), and the denture base dental materials were polymerized for 5, 10, 15, and 20 min at 90°C ($\pm 1^\circ\text{C}$). For isothermal microwave polymerization, samples and the dough preparation, as well as the polymerization, were same as in the case of conventional polymerization. Microwave polymerization was conducted in a focused microwave reactor (Discover, CEM Corp., Matthews, North Carolina, US) supplied with a programmed temperature control system. All the reactions were carried out in the microwave field of 2.45 GHz, maintaining the desired temperatures at 90°C ($\pm 1^\circ\text{C}$). The temperature in the microwave system was controlled by an IR sensor. At least three samples prepared under the same conditions were used for each measurement.

Determination of the degree of monomer conversion

Degree of monomer conversion (DMC) was determined by both high-performance liquid chromatography (HPLC)²⁶ and Fourier transform infrared spectrometer (FTIR)²⁷⁻³¹ methods.

HPLC method

Surveyor HPLC system (Thermo Fisher Scientific, Pittsburgh, United States) was used for the determination of the residual monomer on the reverse-phase Zorbax Eclipse® XDB-C18 column, 4.6 mm × 75 mm i.d. and 3.5 mm particle size (Agilent Technologies, Santa Clara, United States), and a UV detector at 220 nm. Before the separation column, precolumn was installed 4.6 mm × 12.5 mm i.d. and 5 mm particle size (Agilent Technologies). Peak heights were calculated by using Waters Baseline 810 Software Program. A four-point calibration curve was constructed by plotting peak areas against concentrations (external standard method) at a flow rate of 0.8 mL/min of mobile phase (67% methanol and 33% water) under isocratic conditions. Polymerized specimens were mechanically crushed (Cross Beater Mill SK 100, Retsch, Germany) under a rotation of 3420 rpm. One hundred milligrams of each specimen were taken and placed in glass container. In each container, 10 mL of methanol was added, and containers were sealed and kept in dark for 3 days. Twenty microliters of each solution was injected into the column. Triplicate measurements were made. On the chromatogram, the peak that possessed the same retention time with reference MMA was accepted as residual MMA. The residual MMA concentrations were determined by comparing the peak areas with that of reference standard via calibration curve. The residual MMA content was calculated and expressed as a wt% of the original weight of the crushed specimen.

FTIR method

DMC of polymerized samples was determined by infrared spectrometry. The spectra were recorded on Bomen MB 100 Fourier transform infrared spectrometer (FTIR), Hartmann and Braun, Canada. The 10 mg from each polymerized sample was finely ground with 100 mg of KBr. The mixture was transferred to pneumatic pellet-making press and left for 3 min under pressure. The KBr discs with the polymer sample were placed in the IR cell, and the spectrum was recorded. All spectra were obtained from 10 scans at resolution of 4 cm⁻¹. The height of the absorption peak of the C=C at 1638 cm⁻¹ and carbonyl peak at 1730 cm⁻¹ was determined by baseline technique. Measurements were repeated five times. The DMC was calculated according to eq. (1):

$$\text{DMC} = 100 - \frac{\frac{A_{1638}^p}{A_{1730}^p}}{\frac{A_{1638}^m}{A_{1730}^m}} \times 100 \quad (1)$$

where A_{1638}^p is the height of absorption peak of the C=C at 1638 cm⁻¹ for polymer, A_{1730}^p is the height

of absorption peak of the C=O at 1730 cm⁻¹ for polymer, A_{1638}^m is the height of absorption peak of the C=C at 1638 cm⁻¹ for monomer, and A_{1730}^m is the height of absorption peak of the C=O at 1730 cm⁻¹ for monomer.

Degree of conversion (α) was calculated by equation:

$$\alpha = \frac{\text{DMC}}{\text{DMC}_{\max}} \quad (2)$$

where DMC_{\max} is the maximal DMC.

Model fitting method

Kinetic models of the CIH and MWH polymerizations were examined by the so-called model fitting procedure. The model fitting procedure is widely used to determine the suitability of various kinetic reaction models for solid-state reaction.³² According to the model fitting method, the kinetic reaction models, for any solid phase reaction, generally occurring at a reaction interface are classified into five groups depending on the theoretical reaction mechanism: (1) power law reaction, (2) phase-boundary controlled reaction, (3) reaction order, (4) reaction described by the Avrami equation, and (5) diffusion controlled reactions.

The model fitting method is based on the following. The experimentally determined conversion curve $\alpha_{\text{exp}} = f(t)_T$ has to be transformed into the experimental normalized conversion curve $\alpha_{\text{exp}} = f(t_N)_T$, where t_N is the so-called normalized time. The normalized time, t_N , was introduced to normalize the time interval of the monitored process and was defined by the equation:

$$t_N = \frac{t}{t_{0.9}} \quad (3)$$

where $t_{0.9}$ is the moment in time at which $\alpha = 0.9$.³³ The kinetic model of the investigated process was determined by analytically comparing the experimentally normalized conversion curves with the normalized model's conversion curves. Based on that comparison, a theoretical kinetic model for which the sum of squares of the residual from the experimentally normalized conversion curves is minimal was then chosen.

A set of the reaction kinetics models used to determine the model, which best describes the kinetics of the polymerization of PMMA base dental materials, is shown in Table II, where $f(\alpha)$ is the analytical expression describing the kinetic model and $g(\alpha)$ is the integral form of the kinetic model.

Hardness measurements

Hardness was measured on Instron durometer D-XD (Instron, Norwood). The measurements were taken

TABLE II
The Set of the Kinetic Reaction Models Used to Determine the Model of Polymerization Kinetic

Kinetics models	$f(\alpha)$	$g(\alpha)$
Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
Zero order (Polanyi–Winger equation)	1	α
Phase–boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Phase–boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
First order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third order	$(1-\alpha)^3$	$0.5 [(1-\alpha)^{-2}-1]$
Avrami–Erofe'ev	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami–Erofe'ev	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami–Erofe'ev	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
One-dimensional diffusion	$1/2\alpha$	α^2
Two-dimensional diffusion (bidimensional particle shape)	$1/[- \ln(1-\alpha)]$	$(1-\alpha) \ln(1-\alpha)+\alpha$
Three-dimensional diffusion (tridimensional particle shape), Jander equation	$3(1-\alpha)^{2/3} / 2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (tridimensional particle shape), Ginstling–Brounshtein	$3/2 [(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

$f(\alpha)$ is the analytical expression describing the kinetic model and $g(\alpha)$ is the integral form of the kinetics model;
 $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt$

at 10 measuring points at each sample, and mean value and standard deviation were calculated.

Water absorption measurements

For water absorption measurements, prepared dental material samples (2.0 ± 0.2 g) were kept in distilled water at 37°C for 28 days. They were weighted (with ± 0.1 mg accuracy) on analytical balance Precisa XT220A (Precisa Gravimetrics AG, Dietikon, Switzerland) at interval of 3 h for the first 3 days and then every 24 h. The excess water on specimens was removed before weighing by blotting with a filter paper.

RESULTS AND DISCUSSION

The FTIR spectrums of liquid and powder component of used base dental materials were kindly supplied by manufacturers. Sample spectrum of Biocryl liquid and powder component are shown in Figure 1(a,b).

As shown in Figure 1(a,b), the characteristic bands appear at wavenumber 1730 cm^{-1} that corresponds to C=O stretching vibration of ester group and at 1638 cm^{-1} , which corresponds to C=C stretching vibration. The bands at wavenumbers 3000 cm^{-1} and 2950 cm^{-1} correspond to the C–H stretching of the methyl group (CH_3), whereas the bands at 1300 cm^{-1} and 1450 cm^{-1} are associated with C–H symmetric and asymmetric deformation vibration, respectively. The band at 1165 cm^{-1} corresponds to the stretching vibration of the ester group C–O, whereas C–H out of plane vibrations are at 990 cm^{-1} ,

800 cm^{-1} , and 750 cm^{-1} . FTIR spectra of liquid component (Fig. 1a) differ from powder component in intensity of peak height at 1638 cm^{-1} , which is 17 times higher than that for powder component (Fig. 1b).

Figure 2(a–c) shows FTIR spectra of dental material (Biocryl) conventionally polymerized with different polymerization time.

It could easily be seen that as the polymerization time increases, the peak height at 1638 cm^{-1} decreases, which indicates the advancement of polymerization through the disappearance of the carbon–carbon double bond.

The changes of the DMC with time (at 90°C) for the microwave and conventional polymerization, determined by FTIR and HPLC method, are shown in Table III.

On the basis of the results presented in Table III, it could be observed that the increasing polymerization time leads to the increase in the DMC for all the investigated base dental materials. Also, for the same polymerization time, the DMC is higher for MWIH-polymerized samples compared with the CIH-polymerized samples, but as the polymerization time increases this difference decreases. As shown in Table III, the results obtained by both HPLC and FTIR methods give similar results with a difference less than 2%.

Established changes in the DMC lead to the conclusion that the models of the kinetics of polymerization are different for MWIH and CIH polymerizations. To investigate these hypotheses, the kinetics of MWIH and CIH polymerization are examined by the model fitting method.

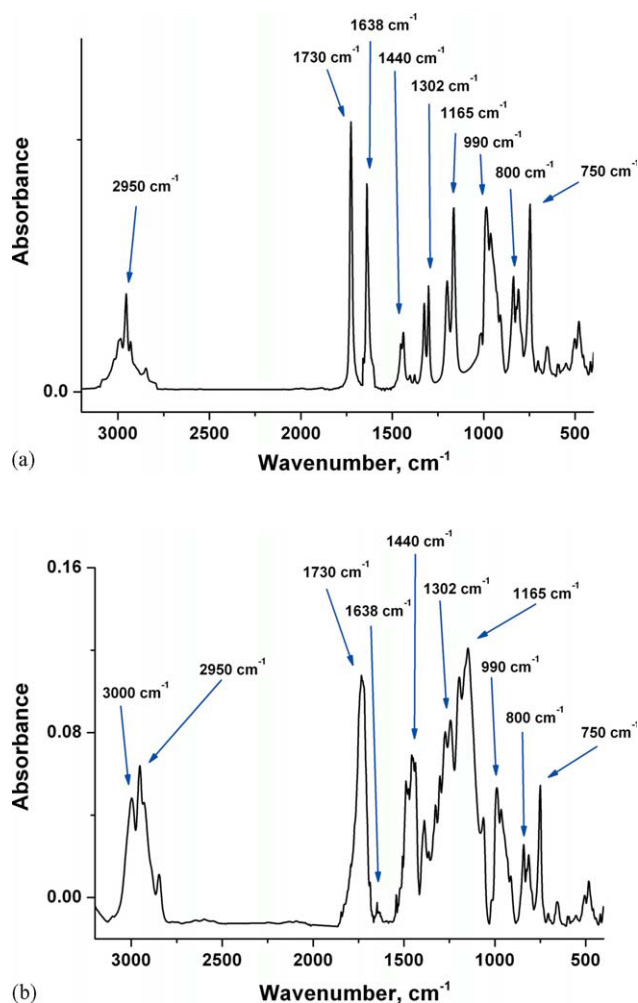


Figure 1 (a) The FTIR spectra of Biocryl liquid component. (b) The FTIR spectra of Biocryl powder component.

Figure 3 shows the normalized experimental conversion curves (in the form of experimental points) and the normalized theoretical conversion curves for kinetic models that best fit experimental data for conventional and microwave polymerization for Biocryl, as a representative sample.

From the results presented in Figure 3, it can be clearly observed that the conversion curves differ for conventional and microwave polymerization, which is a direct confirmation of the difference in the kinetics models of these polymerization modes.

By analytical comparing of the experimental normalized conversion curves with theoretical models of the normalized conversion curves, it was established that the CIH polymerization kinetics could be described by eq. (4):

$$1 - (1 - \alpha)^{1/3} = k_m t \quad (4)$$

and MWH polymerization kinetics could be described by eq. (5):

$$-\ln(1 - \alpha) = k_m t \quad (5)$$

In eqs. (4) and (5), the k_m is the polymerization rate coefficient.

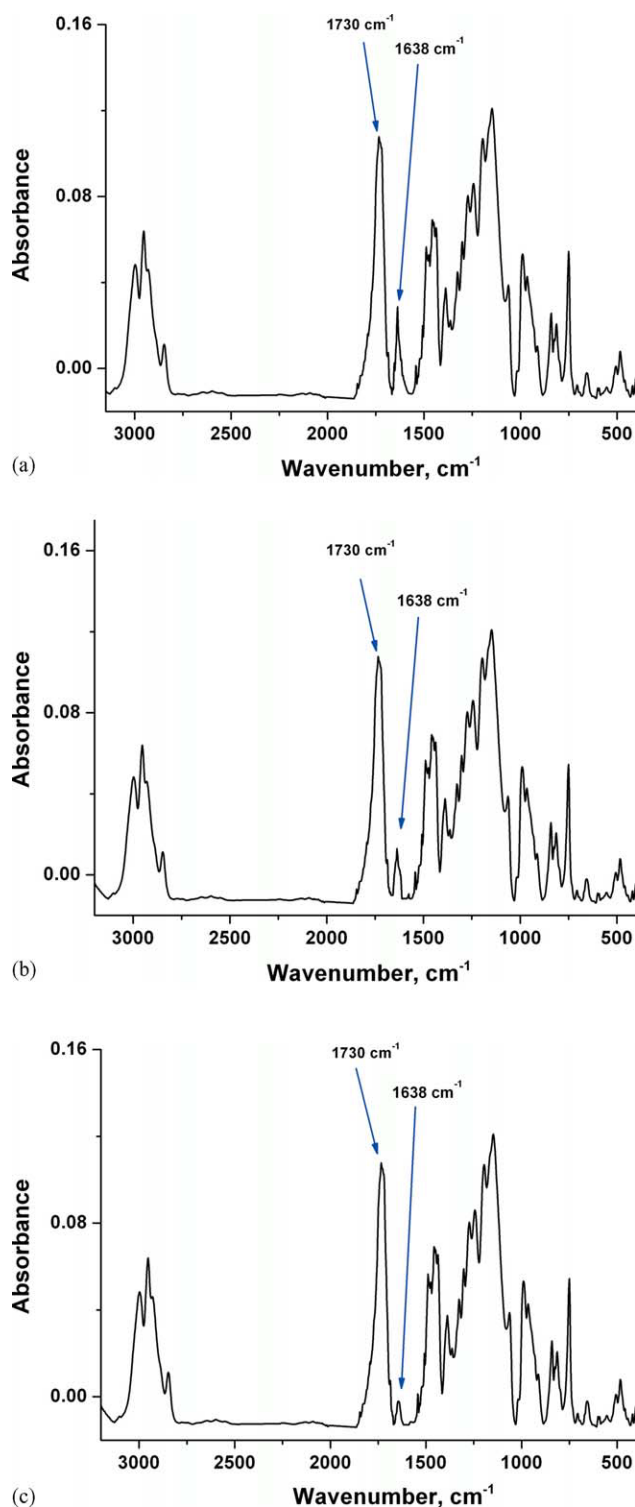


Figure 2 (a). The FTIR spectra of Biocryl sample CIH polymerized 0 min. (b) The FTIR spectra of Biocryl sample CIH polymerized for 5 min. (c) The FTIR spectra of Biocryl sample CIH polymerized for 10 min.

TABLE III
The Effect of Polymerization Time on the Degree of Monomer Conversion for the Used Base Dental Materials Determined by FTIR and HPLC methods ($\Delta_{\text{DMC}} = \text{DMC}_{\text{MWIH}} - \text{DMC}_{\text{CIH}}$)

Sample	Polymerization time (min)	FTIR method			HPLC method		
		Degree of monomer conversion (%)		Δ_{DMC} (%)	Degree of monomer conversion (%)		Δ_{DMC} (%)
		DMC_{CIH}	DMC_{MWIH}		DMC_{CIH}	DMC_{MWIH}	
Biocryl	5	81.3	90.9	9.6	81.5	90.4	8.9
	10	92.2	95.8	3.6	92.1	95.9	3.8
	15	96.5	98.5	2	96.5	98.7	2.2
	20	97.8	98.9	1.1	97.9	99	1.1
Poli Hot	5	81.5	90.2	8.7	81.3	90.4	9.1
	10	91.8	95.5	3.7	91.8	95.4	3.6
	15	96.3	98.4	2.1	96.6	98.6	2
	20	97.7	99	1.3	97.9	99.2	1.3
Futura Basic Hot	5	82.1	90.8	8.7	82.5	90.6	8.1
	10	91.7	95.7	4	91.8	95.5	3.7
	15	96.2	98.3	2.1	96.5	98.5	2
	20	97.6	98.9	1.3	97.7	98.9	1.2

The dependences of $[1-(1-\alpha)^{1/3}]$ and $-\ln(1-\alpha)$ versus time for Biocryl, as a representative sample, are shown in Figure 4.

As can be seen from the results presented in Figure 4, both of the examined dependencies give straight lines in the entire range of the investigated degree of conversion, which proves the correctness of the assumed kinetic models and allows calculation of the polymerization rate coefficients. Calculated values of the k_m for all of the used base dental materials are shown in Table IV.

The values of the rate coefficient for the MWIH polymerization for all of the investigated materials are significantly higher (~ 8 times) than for the CIH polymerization. The increase in the rate coefficient is most probably a consequence of a quick transfer of microwave energy in the reaction system, which

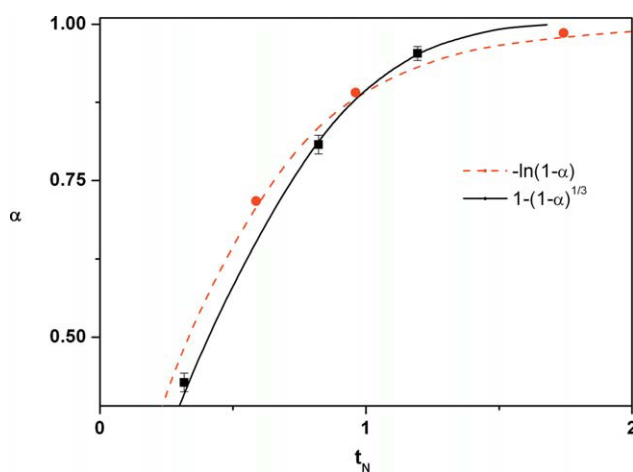


Figure 3 The normalized theoretical conversion curves and experimental points for (■) CIH polymerization and (●) in red MWIH, for Biocryl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

leads to the rearrangement of the energy of the reactive species and further leads to the different model of the kinetics of polymerization.²⁰

Established kinetics models of polymerization for investigated samples clearly indicate that the rate limiting step for the CIH polymerization is the rate of the decrease of the volume of interaction interface between monomer and polymer beads, whereas for MWIH polymerization the limiting step is the remaining concentration of the MMA in the reaction mixture.

The established different kinetics models of polymerization under the CIH and MWIH and calculated different values of the k_m are the cause of the decreasing differences in the degrees of monomer conversion (Δ_{DCM}) with increasing time of polymerization. Actually, for the degrees of monomer conversion greater than 95%, the rate of polymerization

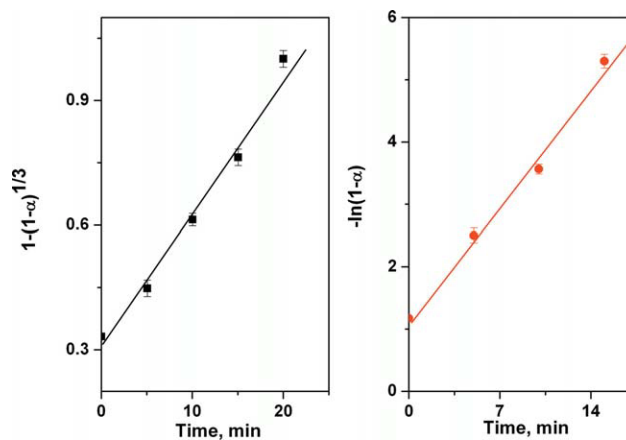


Figure 4 The plot of $[1-(1-\alpha)^{1/3}]$ versus time for (■) CIH polymerization and $-\ln(1-\alpha)$ for (●) in red MWIH polymerization, for Biocryl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
The Polymerization Rate Coefficients for Different Base Dental Materials and Polymerization Modes (R^2 —correlation coefficient)

Material	CIH		MWIH	
	k_m (min^{-1})	R^2	k_m (min^{-1})	R^2
Biocryl	0.0355	0.981	0.258	0.986
Poli Hot	0.0286	0.997	0.255	0.986
Futura Basic Hot	0.0268	0.999	0.252	0.995

for the CIH is greater than the polymerization rate for the MWIH and because of that the differences between monomer conversions with increasing time decrease.

The established kinetic model of polymerization under the CIH implies that the kinetic of polymerization depends on the average particle diameter of the polymer beads.

Dependence of polymerization rate coefficient of the average particle diameter for CIH and MWIH polymerization is examined and shown in Figure 5.

From Figure 5, it could be observed that the average particle diameter has insignificant effect on the k_m of MWIH, whereas the k_m of CIH significantly decreases with increasing average particle diameter of polymer beads, which further confirms the validity of determined kinetic models.

One of the most important properties for the application of dental materials is their hardness, and hence, the effect of polymerization mode on the hardness of the produced dental materials was investigated. The values of hardness for the samples obtained by MWIH and CIH polymerization are shown in Table V.

As can be seen from the results presented in Table V, as the polymerization time increases, the values of hardness increase also for all of the used base

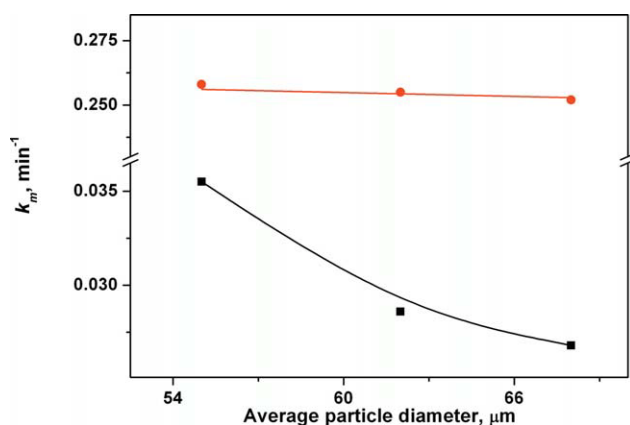


Figure 5 Dependence of the polymerization rate constant (k_m) on average particle diameter for (■) CIH polymerization and (●) in red MWIH polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
The Hardness of Investigated CIH and MWIH-polymerized Samples ($\Delta_H = H_{\text{MWIH}} - H_{\text{CIH}}$)

Sample	Polymerization time (min)	Hardness (Shore D)		Δ_H (Shore D)
		H_{MWIH}	H_{CIH}	
Biocryl	5	68 ± 2	54 ± 5	12
	10	74 ± 2	65 ± 4	9
	15	78 ± 2	74 ± 3	4
	20	80 ± 1	75 ± 4	5
Poli Hot	5	65 ± 2	51 ± 7	14
	10	73 ± 2	63 ± 2	10
	15	75 ± 2	70 ± 4	5
	20	77 ± 2	74 ± 3	3
Futura Basic Hot	5	67 ± 2	54 ± 3	13
	10	72 ± 2	64 ± 4	8
	15	76 ± 2	72 ± 3	4
	20	78 ± 2	75 ± 2	3

dental materials. The values of hardness are higher for the MWIH-polymerized samples than for the CIH-polymerized samples for the same polymerization time. There is no significant difference in hardness for the samples prepared from different base dental materials under the same conditions.

With increasing polymerization time, the difference in hardness for the MWIH- and CIH-polymerized samples decreases. If we compare the obtained values of hardness with the corresponding DMC, the hardness can be found to be the linear function of the DMC. As presented in Figure 6, the dependence of hardness on the DMC for the obtained samples by using Biocryl chosen as a representative series of samples gives straight lines both for CIH- and MWIH-polymerized samples.

Because the dependence of hardness on the DMC gives straight line for all of the examined base dental materials, the obtained equations for the linear

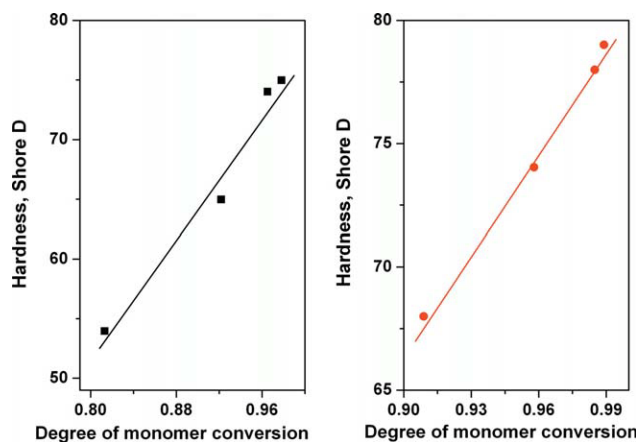


Figure 6 The dependence of hardness on the degree of monomer conversion for (■) CIH polymerization and (●) in red MWIH polymerization, for Biocryl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
The Equilibrium Water Absorption of Investigated
Samples for CIH and MWIH Polymerization for Three
Base Dental Materials ($\Delta W_A = W_{A_{CIH}} - W_{A_{MWIH}}$)

Sample	Polymerization time (min)	Water absorption (%)		ΔW_A (%)
		$W_{A_{CIH}}$	$W_{A_{MWIH}}$	
Biocryl	5	-13.09	-2.35	-10.74
	10	-3.75	1.89	-1.86
	15	1.71	1.42	0.29
	20	1.42	1.15	0.27
Poli Hot	5	-13.06	-2.57	-10.49
	10	-3.82	2.22	-1.60
	15	1.76	1.35	0.41
	20	1.51	1.20	0.31
Futura Basic Hot	5	-12.87	-2.48	-10.39
	10	-3.96	2.14	-1.82
	15	2.01	1.78	0.23
	20	1.87	1.47	0.40

correlations for the used base dental materials are shown in eq. (6)–(11).

$$H = 129DMC - 51 \quad R^2 = 0.961 \quad (6)$$

$$H = 136DMC - 61 \quad R^2 = 0.975 \quad (7)$$

$$H = 132DMC - 55 \quad R^2 = 0.984 \quad (8)$$

$$H = 135DMC - 55 \quad R^2 = 0.992 \quad (9)$$

$$H = 129DMC - 51 \quad R^2 = 0.927 \quad (10)$$

$$H = 130DMC - 51 \quad R^2 = 0.958 \quad (11)$$

where H is hardness, shore D.

The eq. (6)–(8) correspond to the CIH-polymerized samples of Biocryl, Poli Hot, and Futura Basic Hot respectively, and the eq. (9)–(11) correspond to MWIH-polymerized samples of Biocryl, Poli Hot, and Futura Basic Hot, respectively.

Higher values of hardness for microwave than for conventionally polymerized samples could be explained by the amount of residual monomer. As the amount of residual monomer gets higher, the hardness decreases.

Another important property of dental materials is water absorption. The results of equilibrium water absorption at 37°C for used base dental materials are presented in Table VI.

It has been found that the samples of each base dental materials prepared by the CIH polymerized for 5 and 10 min and MWIH polymerized for 5 min gave negative values for water absorption. Water absorption decreases with increasing polymerization time, and the values were smaller for the MWIH than the CIH-polymerized samples.

By comparing the values of water absorption versus the DMC for the MWIH- and the CIH-polymerized samples, it can be seen that for the DMC below

95%, the negative values for water absorption are obtained, whereas for the degrees of monomer conversion higher than 95% positive values for water absorption were obtained. The results can be explained in the following manner. Residual monomer leached in water,³⁴ and water absorption was the overall effect of monomer released and absorbed water. Also, the decreasing water absorption for MWIH-polymerized samples is the result of a smaller amount of residual monomer.

CONCLUSIONS

The heating modes significantly affect both the kinetic and the investigated properties of the PMMA base dental materials. Polymerization rate is approximately eight times higher for the MWIH than for the CIH polymerization. The MWIH polymerization is found to be the first-order reaction, which means that the monomer concentration in the polymerization mixture determines the polymerization rate. The CIH polymerization is found to be the phase-boundary controlled reaction for which the rate of contracting volume is the rate limiting step. The samples of PMMA base dental materials synthesized by MWIH polymerization exhibit better application properties. The hardness of material is increased while the content of residual monomer, and water absorption is decreased in the MWIH compared with the CIH-polymerized samples for the same polymerization temperature and time.

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References

- Lidstöm P.; Tierney, J. P. *Microwave-Assisted Organic Synthesis*; Blackwell Scientific: Oxford, 2004.
- Janney M. A.; Himrey H. D.; Schmidt M. A.; Kiggans J. O. *J Am Ceram Soc* 1991, 74, 1675.
- Cozi A. D.; Fathi Z.; Clark, D. E. *Ceram Trans* 1993, 36, 317.
- Yin T.; Barmatz M. *Ceram Trans* 1995, 59, 541.
- Kim H. Y.; Jeon J. Y. *MRS Symp Proc* 1994, 347, 507.
- Varma R. S. *Tetrahedron* 2002, 58, 1235.
- Will H.; Scholz P.; Ondruschka B. *Chem Ing Tech* 2002, 74, 1057.
- Bleckwell H. E. *Org Biomol Chem* 2003, 1, 1251.
- Collins M. J. In *Microwave Synthesis-Chemistry at the Speed of Light*; Hayes, B.L., Ed.; CEM Publishing, Matthews 2002, p 11.
- Pavarina, A. C.; Neppelenbroek K. H.; Guinesi, A. S.; Vergani C. E.; Machado A. L.; Giampaolo, E. T. *J Dent* 2005, 33, 741.
- Neppelenbroek, K. H.; Pavarina, A. C.; Spolidorio, D. M. P.; Vergani, C. E.; Machado, A. L.; Mima, E. G. O. *Int J Prosthodont* 2003, 16, 616.
- Lidstrom, P.; Tierney, J.; Wathey, B; Westman, J. *Tetrahedron* 2001, 57, 9225.
- Kimura, H.; Teraoka, F.; Saito, T. *J Osaka Univ Dent School* 1983, 23, 43.

14. Shlosberg, S. R.; Goodacre, C. J.; Monoz, C. A.; Moore, K. B.; Schnell, R. C. *Int J Prosthodont* 1989, 2, 453.
15. Sanders, J. L.; Levin, B.; Reitz, P. V. *J Prosthet Dent* 1991, 66, 299.
16. Yunus, N.; Harrison, A.; Huggett, R. *J Oral Rehab* 1994, 21, 641.
17. Skinner's Science of Dental Materials, 9th ed., Philips, R. W. Ed.; W. B. Saunders Company: Philadelphia, 1991.
18. Anderson, J. N. *Applied Dental Materials*, 7th ed., McCabe, J. F. Ed.; Blackwell Scientific: London, 1990.
19. Poly(Methyl Methacrylate) (PMMA). In *Encyclopedia of Polymer Science and Engineering*; Mark, H.; Bikales, Ch. G.; Overberger, G., Eds.; Wiley: New York, 1985; Vol. 1, p 211.
20. Jovanovic, J.; Adnadjevic, B. *J Appl Polym Sci* 2007, 104, 1775.
21. Wallace, P.; Graser, G.; Myers, M.; Proskin, H. *J Prosthet Dent* 1991, 66, 403.
22. Geerts, A. V. G.; Jooste, C. *J Prosthet Dent* 1990, 70, 406.
23. Baffle, M.; Graser, N. G.; Myers, M.; Li, K. H. E. *J Prosthet Dent* 1991, 66, 269.
24. Lai, C. P.; Tsai, M. H.; Chen, M.; Chang, H. S.; Tay, H. H. *Dent Mater* 2004, 20, 133.
25. Usanmaz, A.; Ateş, J.; Dogan, A. *J Appl Polym Sci* 2003, 90, 251.
26. Celebi, N.; Yuzugullu, B.; Canay, S.; Yucel, U. *Polym Adv Technol* 2008, 19, 201.
27. Ferracane, J. L.; Mitchem, J. R.; Todd, R. *J Dent Res* 1997, 76, 1508.
28. Brown, M. E.; Dollimore, D.; Galway, A. K. Reaction in the Solid State, in *Comprehensive Chemical Kinetics*, Bamford, C. H.; Tipper, C. F. H. Ed.; Elsevier: Amsterdam, 1980.
29. Vyazovkin, S.; Wight, C. A. *Thermochim Acta* 1999, 53, 340.
30. Oréfice, L. R.; Discacciati, A. C. J.; Neves, D. A.; Mansur, S. H.; Jansen, C. W. *Poly Testing* 2003, 22, 77.
31. Viljanen, K. E.; Skrifvars, M.; Vallittu, K. P. *Dent Mater* 2007, 23, 1420.
32. Chung, H. K.; Sharma, B.; Greener, H. E. *Dent Mater* 1986, 2, 275.
33. Viljanen, K. E.; Lassila, V. J. L.; Skrifvars, M.; Vallittu, K. P. *Dent Mater* 2005, 21, 172.
34. Bayraktar, G.; Guvener, B.; Bural, C.; Uresin, Y. *J Biomed Mater Res B: Appl Biomater* 2006, 76B, 340.