

Thermal and Mechanical Properties of Microwave- and Heat-Cured Poly(methyl methacrylate) Used as Dental Base Material

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ABSTRACT: The thermal and mechanical properties of dental base materials cured by microwave and conventional heat methods were studied. The commercial dental base poly(methyl methacrylate) (PMMA) powder and liquid were mixed in a 3/1 ratio. They were polymerized by a peroxy catalyst at 65°C, then cured with a boiling water temperature and microwave radiation for periods of 5, 10, 15, 20, 25, 30, and 35 min for heat curing and 1, 2, 3, 5, and 7 min for microwave radiation. The microwave radiation outputs used were 500 and 700 W. The products of 5-min heat curing and 1-, 2-, and 7-min microwave curing were soluble in chloroform. All the others were partially soluble. The viscosity-average molecular weights of the soluble samples were about 1×10^6 . The thermal properties of the polymer samples were studied by differential scanning calorimetry

(DSC). For the samples that were not cured completely, broad exothermic peaks at around 125°C were obtained in the DSC thermograms. The glass-transition temperatures for completely cured samples were 110–120°C. The mechanical properties of the samples were determined from tensile and three-point bending tests. The elastic modulus was highest for samples obtained by the conventional method with a 30-min curing period. However, the bending modulus was highest for 7-min cured samples in a 700-W microwave. The mechanical strengths of the 700-W output were higher than those at 500 W. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 251–256, 2003

Key words: mechanical properties; thermal properties; resins; dental polymers; glass transition

INTRODUCTION

Acrylic resins based on poly(methyl methacrylate) (PMMA) are estimated to represent 95% of the plastics used in prosthetics. They are used in the manufacture of artificial teeth and denture base materials and for restorative and repair purposes.^{1–4} However, there are many problems to be considered when using PMMA. For example, the resin should be properly crosslinked and contain a limited amount of residual monomer.^{5–7} MMA has a boiling point of 100.8°C at atmospheric pressure. Therefore, during curing the monomer can evaporate and make bubbles in the matrix of the resin, causing the formation of pores. These pores weaken the mechanical strength of the material. The monomer is also quite toxic and an irritant. It should not be present over a certain limit in the final product. In order to avoid this, radical initiated polymerization is first carried out at 60°C to consume all of the free monomer, then the temperature is raised to about 100°C to crosslink the polymer. The commercial material is packaged as powder and liquid. The powder generally contains resin (PMMA), initiator (0.5–1.5%

benzoyl peroxide), pigments (red HgS, yellow CdS, and/or brown Fe₂O₃), dyes, opacifier (TiO₂), and plasticizer (8–10% dibutyl phthalate or triphenylphosphate). The liquid contains monomer (MMA), inhibitor (0.003–0.1% hydroquinone), accelerator (for autopolymerized type, tertiary amines such as *N,N*-dimethyl-*p*-toluidine), plasticizer (butyl or acetyl methacrylate), and crosslinking agent (2–14% glycol dimethacrylate). All these additives affect the thermal and mechanical properties of the final product. Because PMMA cannot be directly molded into a desired dental form by thermal treatment, it is mixed with monomer to make a processable material. After polymerization of the liquid added to the powder polymer is completed, the pressure molded material is cured to obtain the final product.

The processing of materials in prosthetics is very important. Some of the expected properties, which are related to the type of material used and/or process conditions, are as follows:

1. adequate strength and durability;
2. dimensional stability;
3. good chemical stability;
4. absence of taste, odor, oral tissue irritation, and toxicity;
5. reasonable adhesion;

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TABLE I
Viscosity-Average Molecular Weight
of Cured PMMA Samples

Curing Method	Curing Period (min)	Average $[\eta]$	Molecular Weight
Heat	5	3.110	9.49×10^5
Heat	10	3.721	1.17×10^6
Heat	15	3.102	1.59×10^5
Heat	20	3.163	9.68×10^5
Heat	25	3.403	1.06×10^6
Heat	30	4.261	1.39×10^6
Heat	35	3.654	1.14×10^6
Microwave			
500 W	1	2.734	8.16×10^5
500 W	2	2.872	8.62×10^5
500 W	3	3.453	1.07×10^6
500 W	5	3.941	1.26×10^6
500 W	7	3.419	1.06×10^6
500 W	10	2.774	8.27×10^5
Microwave			
700 W	1	2.872	8.16×10^5
700 W	2	2.728	8.11×10^5
700 W	3	3.403	1.06×10^6
700 W	5	3.841	1.22×10^6
700 W	7	6.253	2.20×10^6
700 W	10	3.493	1.09×10^6

6. insolubility in oral fluids in the mouth;
7. satisfactory thermal properties; and
8. good mechanical properties.

These properties and many others can be achieved by the proper choice of resin materials and additives, in addition to suitable handling of the processes. In some applications the resin is reinforced with different reinforcement agents⁸⁻¹⁰ to improve the thermal and mechanical properties. The curing is carried out by heat, chemical activators, or light or microwave energy. Radiation such as γ -ray has been suggested for curing, which has certain advantages.^{10,11} Heat curing is the most commonly applied method and thus known as the conventional method.^{12,13} In this case, after polymerization at 60–70°C for about 30 min, the temperature is raised to 100°C for final curing.

Chemical activation or autopolymerization is done by tertiary amines added to the monomer (liquid part). A 400–500 nm visible light is used to cure the denture base resin.^{1,2} This method has quite limited applications. The research for microwave curing has received more attention¹⁴⁻¹⁷ in recent years. However, there are still many problems to be explained for an effective application. In this work, the denture resin is cured by microwave at two different power outputs. The effect of the microwave output power and length of curing period on the thermal and mechanical properties is investigated and the results compared with those of heat-cured material.

EXPERIMENTAL

Material and methods

The heat activated QC 20 (De Trey, Dentsply) acrylic resins in powder-liquid forms were used as received. All the solvents used were spectroscopic grade Merck products and used without further purification.

The heat-cured denture flask was homemade, but the microwave flask was fiber reinforced Acron MC (GC America Inc.) plastic. The constant temperature water bath was a closed Kotterman Laborotechnick model made of stainless steel, and the temperature was controlled within $\pm 0.01^\circ\text{C}$ accuracy. The viscosity measurements were done in an Ubbelohde type glass viscometer using chloroform as a solvent at 25°C. Differential scanning calorimetry (DSC) analysis was carried out by using a TA-DSC 910 S apparatus. The tensile and bending properties were determined using a computer controlled Lloyd LR 50 testing machine.

Procedure

The samples prepared for tensile measurements were standard dumbbell-shaped test specimens according to ASTM D 638M. The dimensions of the test specimens were measured with a micrometer. The dimen-

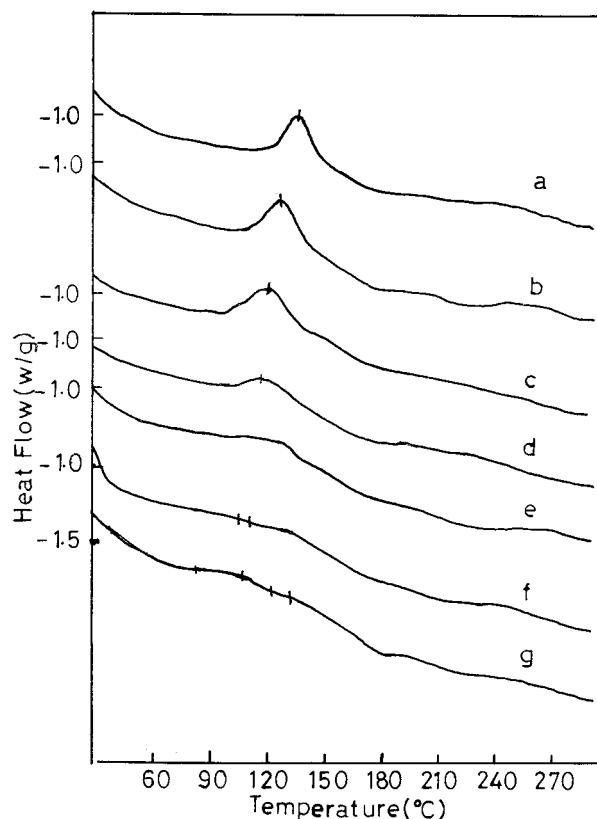


Figure 1 DSC thermograms of dental material samples cured by heat for 5 (curve a), 10 (curve b), 15 (curve c), 20 (curve d), 25 (curve e), 30 (curve f), and (curve g) 35 min.

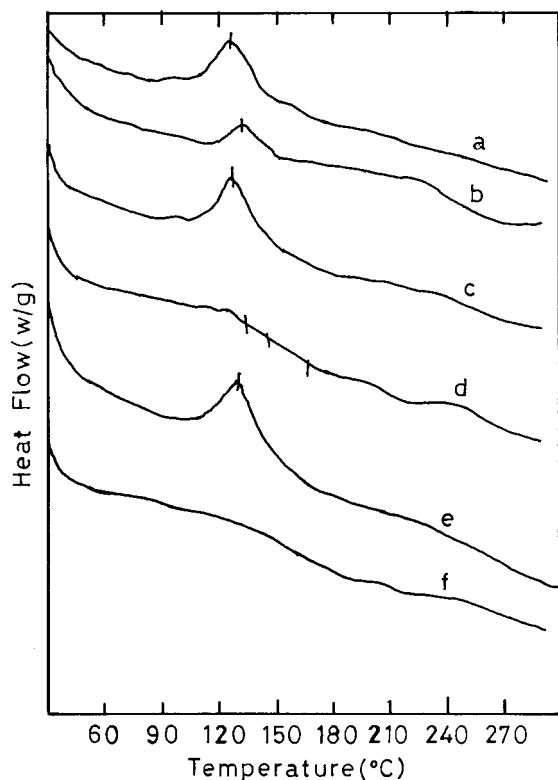


Figure 2 DSC thermograms of dental material samples cured by 500-W microwaves for 1 (curve a), 2 (curve b), 3 (curve c), 5 (curve d), 7 (curve e), and 10 min (curve f).

sions of the samples used for three-point bending measurements were 80 × 10 × 3 mm. These values were chosen for easy handling on the instrument and to give a better reading for the resin used.

The general procedure for the sample preparation was completed in five steps. In the first, the plaster was prepared in a cup and then poured into the bottom of the molding flask. The wax samples were placed in the plaster and the surface of the plaster was insulated with cellulose lacquer. In the second step, the top of the plaster was seated, the flask was filled with the plaster, and the lid was placed on it. Then it was kept under pressure for 5 min. In the third step, the flask was placed in hot water to soften the wax and to separate the top and bottom parts of the flask. Any residual wax was flushed out with hot water. The powder (PMMA) and liquid (MMA) parts of the denture material were mixed in a glass cup in a 3/1 ratio and the cup was sealed in the fourth step. Then the mixture was allowed to stand until a dough stage formed, which was then packed into the flask and kept under pressure for 10 min. All these steps were the same for both heat-cured and microwave-cured samples using their special flasks. In the fifth step, the flask used for heat activated polymerization was placed in a constant water bath at 65°C and kept there for 30 min. The temperature was then raised to boiling

water temperature (96°C) and the test samples were cured for periods of 5, 10, 15, 20, 30, and 35 min. After initial polymerization, the flask used for microwave curing was placed in the microwave oven without bolting. Test samples were cured in the microwave with outputs of 500 and 700 W for 1, 2, 3, 5, 7, and 10 min.

For the tensile tests, 500- and 2500-N load cells were used and the speed of testing was at 3 mm/min. The load versus extension curves of the specimens were recorded. The stress and strain values were determined for each test specimen. Three-point bending measurements were carried out using the same testing machine. The force versus the deflection curves were obtained. Stress, strain, and resilience values were calculated from the experimental results.¹⁰

RESULTS AND DISCUSSION

Molecular weight of samples

The viscosity-average molecular weights of the soluble fractions of the samples obtained by heat and microwave for different curing periods are tabulated in Table I. They were in the range of about 10⁶. There is no regular trend in the molecular weight with the increase of curing period. Because the measured molecular weights are for the soluble fraction of polymers, the crosslinking becomes predominant when the molecular weight exceeds these values. The increase

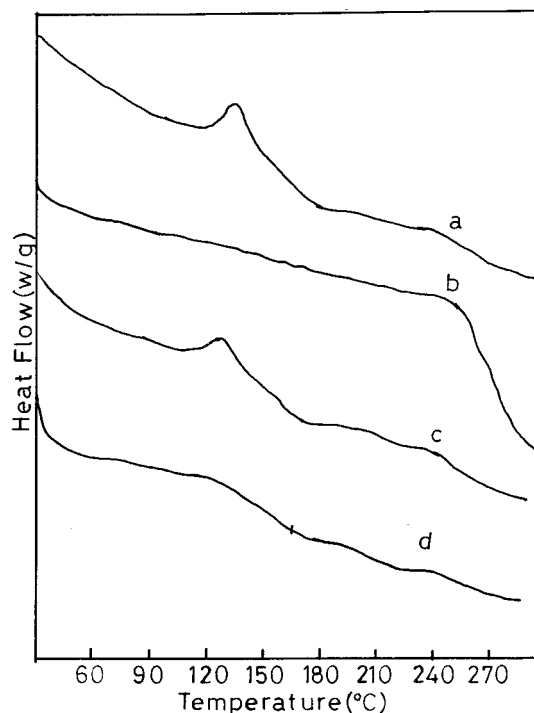


Figure 3 DSC thermograms of dental material samples cured by 700-W microwaves for 1 (curve a), 3 (curve b), 7 (curve c), and 10 min (curve d).

TABLE II
Tensile Test Results of QC 20 Samples Cured by Heat

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Elastic Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
5	23.727	2.382	0.252	0.014	100.469	8.734	2.827	0.381
10	24.967	2.240	0.224	0.017	117.663	9.716	2.703	0.316
15	25.496	5.179	0.263	0.035	114.513	6.727	3.507	1.131
20	56.285	1.747	0.407	0.024	145.643	7.437	10.943	0.348
25	52.830	3.618	0.373	0.025	148.790	17.021	9.766	0.865
30	54.762	3.676	0.354	0.039	161.207	14.672	9.728	1.515
35	57.490	4.638	0.420	0.032	143.600	13.716	12.032	1.567

of the insoluble fraction percentage with the curing period is an indication of increasing actual molecular weight. One of the most important results of this work is that the difference between the molecular weight of samples cured by 500- and 700-W microwave power is not significant. However, the samples obtained with a 5-min curing period at both 500 and 700 W are partially soluble in chloroform, but those at 7-min curing are totally soluble. This shows that depolymerization and/or degradation of the polymer chain becomes important at higher curing periods and the optimum curing period for microwaving should not exceed 5 min.

Thermal properties of samples

The DSC thermograms of heat-cured samples are given in Figure 1. Each of the thermograms (Fig. 1, curves a–d) for 5-, 10-, 15-, and 20-min curing periods gives an exothermic peak. The peak temperature for each of 5-, 10-, 15-, and 20-min curing period are 133.3, 125.5, 121.4, and 119.5°C, respectively. This is not a shift in the peak position but is instead a total peak area decrease with an increase in the curing period. These peaks correspond to the further crosslinking of the polymer samples. The peak area gives the total polymer fraction crosslinked at this stage. Because the amount of polymer fraction that is not crosslinked decreases with the curing period, the peak area also decreases. After a 25-min curing period, the exothermic peak partially disappeared and after a 30-min

curing period it completely disappeared. Therefore, in the heat-cured process, the optimum curing period should be longer than 30 min. However, if the residual monomer concentration is also considered, the curing period has to be much longer (about 3 h).⁷ The glass-transition temperature (T_g) is 118°C (Fig. 1, curves e and f). In other thermograms the T_g cannot be observed because of the exothermic peak corresponding to crosslinking at the same area of the thermogram. The T_g value is more distinct in curve f in Figure 1 (35-min curing period).

The DSC thermograms of the 500-W energy level microwave-cured samples are given in Figure 2. The thermograms are quite similar to those of heat-cured samples with some small differences. The exothermic peaks were observed for 1-, 2-, and 3-min curing at around 125°C. After 5-min curing, the exothermic peak almost disappears and looks very similar to the 25-min heat-cured sample. However, the interesting result is for the 7-min curing in which the exothermic peak exists. This supports the hypothesis that crosslinking is almost complete after the 5-min curing, but after the 7-min curing the exothermic peak reappears because of depolymerization and/or degradation. The crosslinking is completed after the 10-min curing, giving a T_g at 118°C (Fig. 2, curve f). For 700-W microwave curing, the DSC thermograms are shown in Figure 3. The thermograms are similar to that at 500 W with some differences. Crosslinking is completed after a 3-min curing period, and the polymer is soluble after a 7-min curing and is partially crosslinked.

TABLE III
Tensile Test Results of QC 20 Samples Cured by Microwave at 500 W

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Elastic Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	18.268	1.353	0.262	0.049	78.934	9.043	2.383	0.263
2	27.696	2.529	0.342	0.124	84.498	8.934	5.265	0.419
3	22.065	3.926	0.315	0.052	77.462	6.332	3.649	0.848
5	29.383	6.203	0.250	0.051	122.770	1.362	3.782	0.602
7	29.475	2.873	0.370	0.023	82.839	5.472	6.317	0.813
10	36.549	3.957	0.441	0.035	84.949	7.069	8.064	1.551

TABLE IV
Tensile Test Results of QC 20 Samples Cured by Microwave at 700 W

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Elastic Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	14.747	0.368	0.262	0.023	62.575	6.721	1.899	0.135
2	27.593	0.815	0.337	0.084	94.138	2.679	4.863	2.571
3	44.040	0.005	0.303	0.046	146.700	4.495	6.678	1.019
5	34.765	0.967	0.335	0.110	107.937	8.466	6.177	0.739
7	30.846	1.826	0.327	0.106	97.460	5.826	5.372	0.579
10	28.691	1.754	0.293	0.025	100.175	4.365	4.169	0102

Mechanical measurements of samples

The stress values were calculated by dividing the load in Newtons by the original minimum cross-sectional area of the specimen in square meters whereas the strain values were calculated by dividing the deflection data obtained at the end of the test by the gauge length for each sample. Then, the stress versus strain curve for each sample was plotted. These curves were typical for hard and brittle types of polymers. The slope of the curves gives the elastic modulus. Polymers can therefore be characterized as having high modulus, no yield stress, moderate ultimate strength, and low elongation at break. The resilience values were calculated by the area of the triangle under the elastic portion of the stress-strain curve. The tensile test data for heat-cured samples are tabulated in Table II. The ultimate stress shows two distinct stages with the increase in curing time. For a 5–15 min curing

period, the ultimate stress changes slowly from 23.7 to 25.5 MPa; then, a sharp increase (56.3 MPa) is observed at 20-min curing. It remains almost the same with an increase of curing time. The change in the values of strain, elastic modulus, and resilience with curing time show similar trends to that of the ultimate stress.

Tensile test results for microwave curing are given in Table III (500 W) and Table IV (700 W). All the test results for 700 W are slightly higher than those for 500 W. However, the values for both are much smaller than the heat-cured tensile test values. Ultimate stress and elastic modulus showed a relatively high increase with curing time up to the 5-min curing period, and then the elastic modulus showed an appreciable decrease for a 7-min curing period.

The transverse strength and flexural modulus are also important properties for the resins used in dental

TABLE V
Three-Point Bending Test Results of QC 20 Samples Cured by Heat

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Flexural Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
5	37.276	1.208	0.085	0.01	485.570	10.799	1.589	0.227
10	43.026	2.961	0.081	0.003	565.125	38.771	1.749	0.170
15	73.369	8.138	0.085	0.008	902.727	62.176	3.117	0.343
20	80.636	14.238	0.080	0.026	1075.180	36.593	3.370	1.648
25	82.653	10.858	0.076	0.009	1125.760	30.384	3.168	0.775
30	82.703	5.866	0.080	0.005	1053.720	43.721	3.328	0.444
35	72.745	11.565	0.070	0.009	1070.830	49.173	2.604	0.736

TABLE VI
Three-Point Bending Test Results of QC 20 Samples Cured by Microwave at 500 W

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Flexural Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	22.316	2.962	0.073	0.011	317.55	4.31	0.819	0.226
2	22.123	2.472	0.083	0.006	272.46	40.05	0.922	0.132
3	24.443	3.538	0.085	0.010	288.66	19.96	1.058	0.264
5	69.952	6.162	0.073	0.006	965.68	60.74	2.570	0.794
7	52.985	2.870	0.060	0.015	922.57	67.46	1.572	0.289
10	54.514	1.792	0.054	0.005	1028.86	97.96	1.469	0.144

TABLE VII
Three-Point Bending Test Results of QC 20 Samples Cured by Microwave at 700 W

Curing Time (min)	Ultimate Stress (MPa)		Ultimate Strain		Flexural Modulus (MPa)		Resilience (mM N/m ³)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	21.464	4.175	0.068	0.009	329.68	25.86	0.749	0.232
2	46.475	2.873	0.117	0.009	397.89	57.30	2.756	0.771
3	50.917	10.885	0.047	0.011	1082.86	30.07	1.249	0.0574
5	57.171	4.813	0.055	0.006	1035.19	41.90	1.420	0.575
7	54.299	8.631	0.050	0.011	1054.17	41.01	1.404	0.532
10	53.971	2.605	0.046	0.004	1189.43	63.56	1.241	0.156

applications. The results of the three-point bending tests are given in Tables V, VI, and VII. Similar to the tensile tests, the measurements for heat-cured samples (Table V) are generally higher than those of microwave curing at 500 (Table VI) and 700 W (Table VII). When comparing the microwave energies, higher values are attained for 700 W than for those of 500 W at early stages of curing.

CONCLUSION

In the preparation of dental base materials, the most important requirements are appropriate thermal and mechanical properties and minimum levels of residual monomer. The introduction of the microwave in the processing of dental base materials is a time saving and cleaner process. However, one of the main problems is local heating in the material, which prevents a homogenous matrix of the final product. When the microwave heating is used, the mechanical properties obtained are not superior to the standard heat-cured method. The best material is obtained when the polymer reaches its highest molecular weight before crosslinking. This is possible with radiation curing¹¹ but not with other methods, including the microwave. The chemical activation method eliminates the local heat problem in the sample, but in that case the residual monomer level is higher, as is the number of pores, which weaken the mechanical strength.

The molecular weights of the soluble fractions of samples showed that before crosslinking there is not much difference between the molecular weights of samples obtained by heat or microwave curing. The DSC results showed that the crosslinking is completed after a specific curing period for both heat and micro-

wave curing. However, when using microwave curing at longer curing periods (e.g., 7 min in this work), degradation of crosslinked segments may also take place. The mechanical strengths are generally better for heat curing compared to microwave curing. The results for microwaving are improved at higher (700 W) output power.

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