

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

IFFET YAZICI MUHTAROĞULLARI,¹ ARIFE DOĞAN,¹ MUHAMET MUHTAROĞULLARI,² ALI USANMAZ³

¹ Department of Prosthodontic, Faculty of Dendistry, Gazi University, Ankara, Turkey

² Department of Prosthodontic, Faculty of Dendistry, Hacetepe University, Ankara, Turkey

³ Department of Chemistry, Middle East Technical University, Ankara, Turkey

Received 15 March 1999; accepted 28 June 1999

ABSTRACT: In this study, the particle size distribution, molecular weight, thermal analysis (TGA) differential scanning calorimetry (DSC) and thermogravimetric analysis, and dynamic mechanical analysis (DMA) of poly(methyl methacrylate) used as dental base material were investigated. The commercial raw material used were prepared for microwave curing, and they were cured by microwave and conventional heat methods. The average particle size of the powder studied (103.1 μm) were much larger than that of the commercial powders (50–78 μm) for conventional curing. The particle size distribution were almost symmetrical and narrow. The viscosity-average molecular weight were larger for microwave curing and increased with curing time. The glass transition temperature T_g measured (about 110°C) by DSC increased with curing period in microwave oven. The values of T_g were close to each other for both curing techniques. The degradation temperature range observed by TGA were 200–377°C. The movements of molecular chains in their conformations were studied by DMA in the form of changes in different mechanical properties with temperature. It was shown that crosslinking increased with increase of curing time. The changes were more noticeable in microwave curing compared to conventional heat curing. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2971–2978, 1999

Key words: poly(methyl methacrylate); dynamic mechanical analysis; thermal properties; dental use; particle size

INTRODUCTION

The most commonly used acrylic resin in preparation of dental base material is poly(methyl methacrylate) (PMMA). In a commercial application, powdered PMMA with a molecular weight^{1,2} of about 1×10^6 and an average particle size of 60 to 70 μm is mixed with liquid monomer in ratio of

about 3 to 1.^{3,4} The well-mixed dough is polymerized in a constant temperature water bath at about 60–70°C for a period of 30 to 60 min.⁵ The initiator (generally benzoyl peroxide that added to powder by manufacturer) decompose at this temperature and starts polymerization. The polymer is then placed in a desired mould and cured to final product.

In conventional processes, the curing is carried out by heat treatment or autopolymerization.^{6–9} In the first process, the material in the mould is placed in a water bath at boiling temperature for

Correspondence to: A. Usanmaz.

Journal of Applied Polymer Science, Vol. 74, 2971–2978 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/122971-08

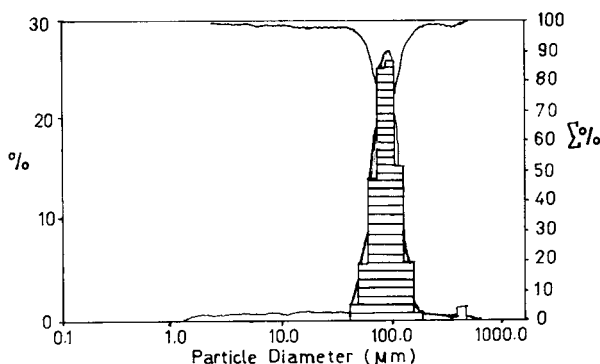


Figure 1 Distribution of particle size of PMMA powder.

several hours to complete the polymerization and crosslinking. A crosslinking agent (generally glycoldimethacrylate) in liquid enhances the process.^{1,2} In the second process, a small amount of tertiary amine initially added to the liquid (monomer) by the manufacturer chemically activates the polymerization at room temperature, but total polymerization takes a longer time.

The important properties that has to be considered and improved in either preparation techniques of the final material are as follows:

1. amount of residual monomer,
2. dimensional stability,
3. color stability,
4. water absorption,
5. mechanical properties.

Therefore, many modifications have been studied and reported for the preparation of better improved material. In this context, the curing by microwave was first introduced in 1968 by Nishii¹⁰ and investigated further by other workers.^{11–18} It is now a commercial method, and manufacturers have made modification in their products to be used by microwave curing. Several authors^{15–18} have reported that curing of PMMA by microwave showed more improved material properties for dental applications.

In this study, the thermal and mechanical properties of microwave and heat-cured commercial PMMA used as dental base material are investigated. The properties are compared, and the advantages of each curing technique are determined. In our previous publication,¹⁹ we had used conventional mechanical testing for heat-cured PMMA. In this work, we used dynamic mechanical analysis (DMA) to get more improved infor-

mation for microchanges related to curing conditions.

EXPERIMENTAL

Materials and Methods

Powder PMMA and liquid monomer were Acron MC microwave-curing denture base acrylic raw materials, and they were used without further purification. Chloroform and glycol were of Merck quality and distilled before use.

The particle size of powder material was determined by a Mastersizer/E (UK) Malvern Instrument using 1 : 1 ratio glycol : water mixture.

Microwave polymerization was carried in a 1000-W microwave made by Vestel (Turkey) using Acron MC microwavable Flask as container for irradiation.

Differential scanning calorimetric (DSC) thermograms were taken on a DSC 910 S, TA Instrument and thermogravimetric analysis (TGA) was done on a thermogravimetric analyzer 95 K1 TA Instrument (UK). The dynamic mechanical measurements were carried on DMA 983, TA Instrument (UK).

The viscosity-average molecular weight were measured in an Ubbelohde-type viscometer using chloroform as solvent at 25°C.

Procedure

For the heat-cured samples, the powder and liquid samples provided by manufacturer were mixed in 100 g to 43 mL ratio at 25°C and mixed throughly for 20 min to make a homogenous

Table I Viscosity-Average Molecular Weight of Cured PMMA Samples

Curing Method	Curing Period (Min)	Average $[\eta]$	Molecular Weight
Microwave	1	2.9174	8.8×10^5
Microwave	2	4.3253	1.4×10^6
Microwave	3	7.2927	2.7×10^6
Heat	5	4.3798	1.4×10^6
Heat	10	3.9662	1.2×10^6
Heat	15	3.0972	9.4×10^5
Heat	20	3.3594	1.0×10^6
Heat	25	3.5871	1.1×10^6
Heat	30	3.9808	1.2×10^6

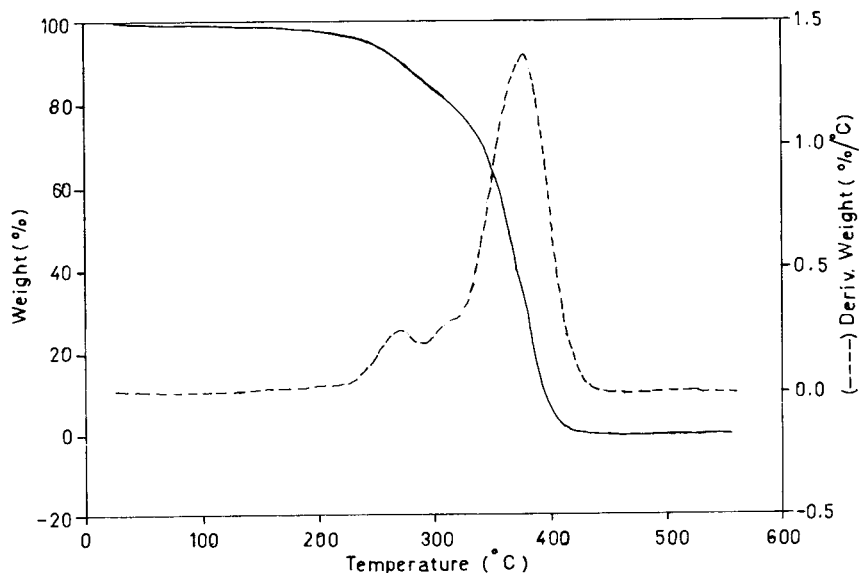


Figure 2 TG thermogram of PMMA.

dough. The dough was then placed in mould and pressed for 10 min under high pressure, then polymerized in a water bath at 70°C for 30 min. The curing was done at a boiling water temperature for the periods of 5, 10, 15, 20, 25, 30, and 35 min. Five samples prepared under the same conditions of polymerization and curing time were used for each measurements.

For microwave curing samples, the dough preparation and polymerization were the same as that of heat cured. However, in this case, further polymerization and curing were carried in a microwave oven. The curing periods were 1, 2, and 3 min.

The samples prepared were used for molecular weight determination and thermal and DMA measurements.

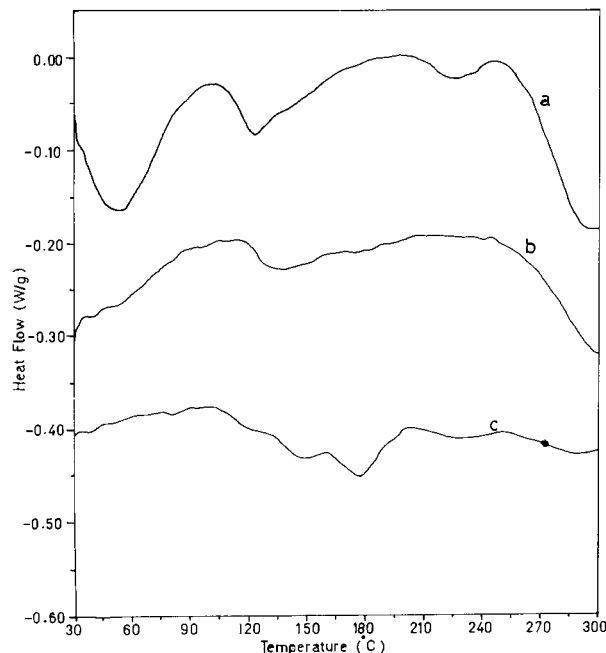


Figure 3 DSC thermogram of PMMA cured in microwave oven for (a) 1, (b) 2, and (c) 3 min.

RESULTS AND DISCUSSION

Particle Size Determination

The particle size distribution for powder as received is given in Figure 1. The average diameter of particles is 103.1 μm , and the distribution range 68.3–147.3 μm . Distribution is almost symmetrical and narrow. This can be considered as a good quality of sample. The reported values^{20,21} for the heat-cured powder samples are 50 to 78 μm . The larger particle size for microwave samples indicates that the larger surface area is not required as much as that for heat-cured resins because penetration of microwaves into particles is easy.

Molecular Weight of Samples

The viscosity-average molecular weights of PMMA samples prepared under different conditions are given in Table I. The molecular weight of

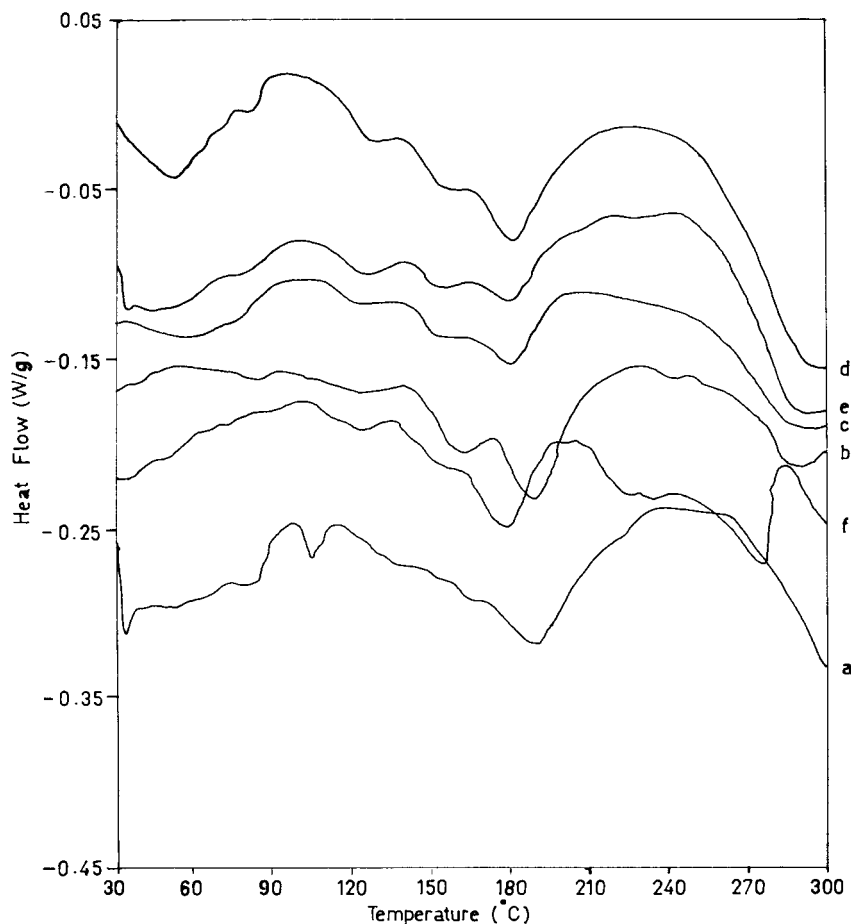


Figure 4 DSC thermogram of PMMA cured by heat for (a) 5, (b) 15, (c) 20, (d) 25, (e) 30, and (f) 35 min.

powder used is 1.03×10^6 . All the microwave-cured samples studied were soluble, but the heat-cured samples were partially soluble, and the insoluble fraction increased with curing time. The molecular weight increases with curing time in microwave, reaching 2.65×10^6 in a 3-min curing period. However, the molecular weights of soluble fraction of heat-cured samples do not show a regular trend of change with curing time. This shows that when the average molecular weight reaches a certain value, polymer crosslinking predominant and it becomes insoluble. In microwave curing, the molecular weight increase much higher values before the crosslinking of polymer chains can be observed. This is an important advantage of microwave curing in dental applications.

Thermal Analysis

The thermal gravimetric (TG) thermograms of all samples studied were similar with small shifts in

peak position. A TG thermogram of PMMA is given in Figure 2. The decomposition starts at about 200°C, shows a deflection at about 250°C, and ends up at 400°C. The differential thermogram has two peaks at 266 and 377°C. The first peak is a weak one, indicating that first-stage decomposition is small but that main decomposition reaches maximum at 377°C. This might be due to the high probability of thermal depolymerization of PMMA.

The DSC thermograms of microwave-cured polymer samples are given in Figure 3. For 1-min curing period [Fig. 3(a)], an observed broad exothermic peak centered at about 109°C disappears at 2 and 3 min of curing [Fig. 3(b) and (c)]. This peak corresponds most probably to further polymerization and crosslinking. The T_g of polymer (at about 110°C) becomes more distinct after a 3-min curing period [Fig. 3(c)]. At this stage, the molecular weight of polymer is highest, but it is

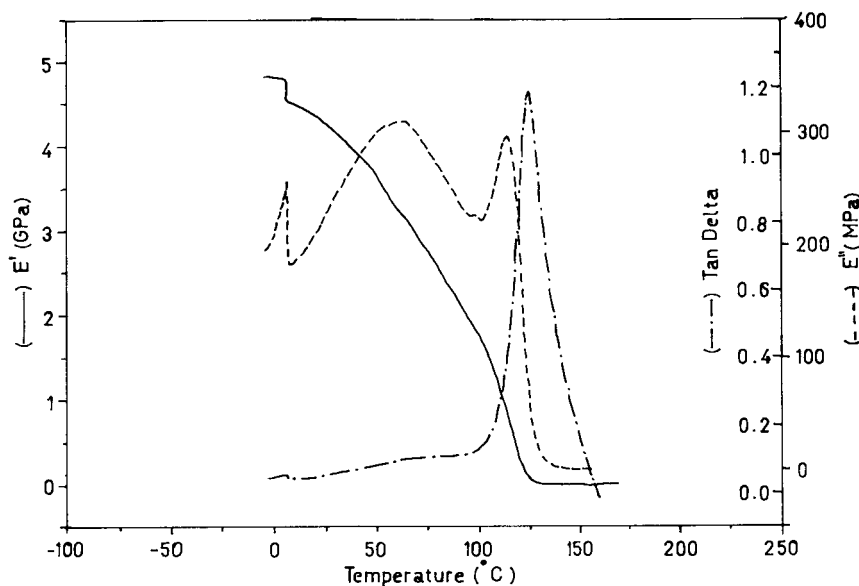


Figure 5 DMA spectrum of microwave-cured PMMA for 1 min.

still soluble in chloroform, indicating very limited or no crosslinking.

The DSC thermograms of heat-cured polymer samples are given in Figure 4. The curing period changes from 5 to 35 min. In 5 min of curing [Fig. 4(a)], a relatively sharp peak at 90–100°C indicates further polymerization and/or crosslinking. This peak becomes broader with an increase in curing time, then almost disappears at 35 min of curing [Fig. 4(f)]. This shows that curing is almost completed at this stage.¹⁹ The T_g at about 110°C can be observed more clearly at a higher curing period. The secondary and tertiary relaxation peaks for side groups $-\text{CH}_3$ and $-\text{COOCH}_3$ are observed at lower temperatures. At higher temperatures, polymer changes to a rubbery state and flow of the polymer takes place. The decomposition is predominant in the temperature range of about 200–300°C. This is also supported by a TG thermogram (Fig. 2).

Dynamic Mechanical Analysis (DMA)

Dynamical mechanical test is a powerful test method to study the polymeric materials.^{22–24} In this study, the detailed of structural changes of PMMA as dental base material, with a change in temperature and curing time, were investigated by using DMA. The DMA spectra showing storage modulus E' , loss modulus E'' , and loss tangent $\tan \delta$, for microwave-cured PMMA samples are shown in Figures 5 and 6. The storage modulus

E' in the glassy state is about 4.6 GPa and decreases with an increase of temperature, reaching zero at about 150°C. The loss modulus E'' shows three peaks at 6, 61, and 114°C for 1-min curing (Fig. 5) and at 17, 63, and 129°C for 3-min curing (Fig. 6), respectively. The increase in peak positions indicates the increase in the average molecular weight of polymer samples with curing time. The spectrum for $\tan \delta$ gives only one main peak at 125°C (Fig. 5) and at 141°C for 1- and 3-min curing times, respectively. These peaks correspond to the T_g of polymer samples. The values are higher than the T_g (about 110°C) observed from DSC spectrum. This is due to the fact that DMA measurements are sensitive to the structural changes on a microlevel, where DSC is not as much sensitive at these ranges. The main peak observed in spectra of loss modulus and loss tangent correspond to polymer main chain relaxation (α); the peaks at lower temperatures in loss modulus correspond to β, γ -relaxation for side groups and/or chain segments.²⁵

The DMA spectra of heat-cured PMMA samples are given in Figures 7–9 for curing periods of 5, 20, and 35 min. The general trend of spectra is similar to that observed for the microwave-cured samples. However, there are some detail differences. The difference in spectrum of storage modulus is not great, but the relaxation at lower temperatures are more complex. The main peak in $\tan \delta$ spectrum is almost the same

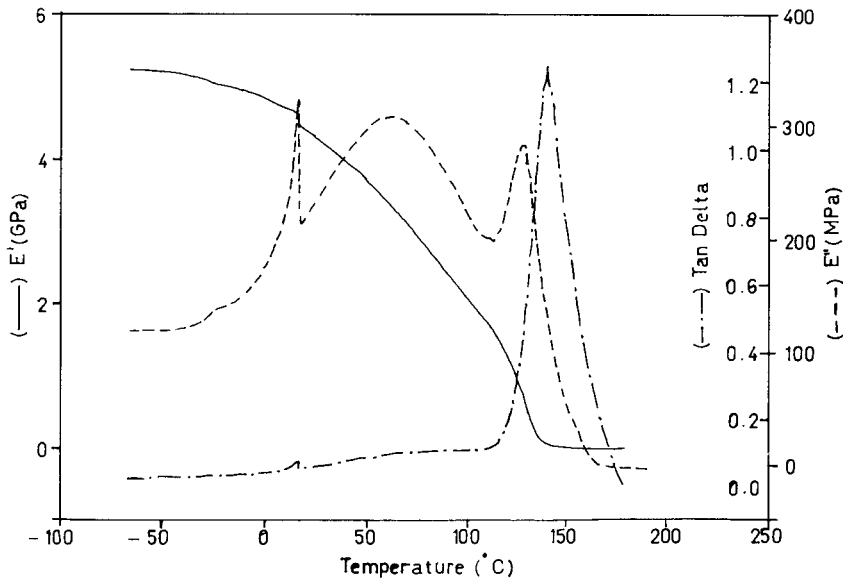


Figure 6 DMA spectrum of microwave-cured PMMA for 3 min.

for curing periods of 5 and 20 min, but it shifts from 137 to 148°C for 35 min of curing. This peak becomes tripled. It shows that the average molecular weight is high enough for 5–20 min-curing periods to give the T_g that is insensitive to further changes in molecular weight of polymer. The most important changes with curing period are observed for loss modulus E'' . A multisplitting peak in the temperature range of -50 to 30°C and two other peaks centered at 63

and 109°C in the spectrum for 5 min of curing (Fig. 7) correspond to γ, β, α transition of side groups and main chain relaxation.^{25–26} The peak shapes and positions changes with curing time. For 20 min of curing (Fig. 8), the γ -transition peak becomes narrower and tripled, the β -transition peak remained almost the same, and the α -transition peak shifted to 125°C. The γ -transition peak becomes more complex again in 35 min of curing (Fig. 9). Most probably, at

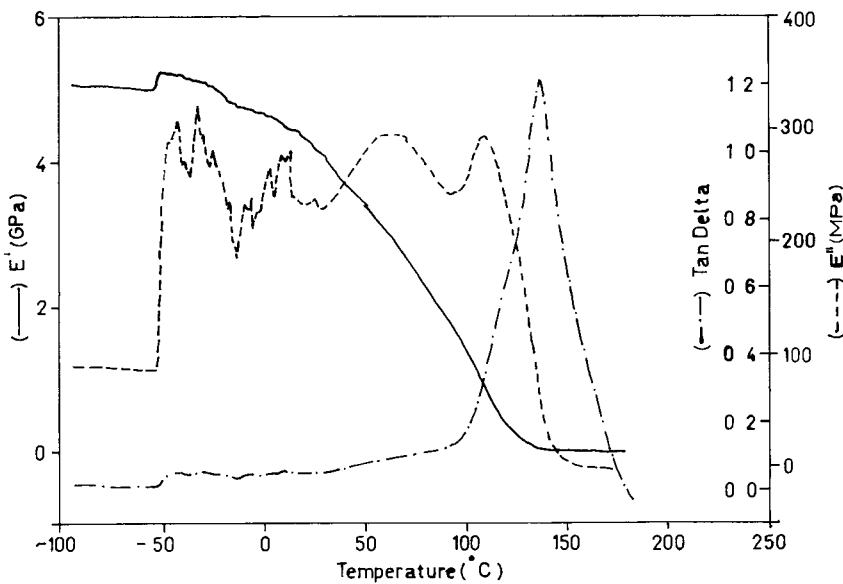


Figure 7 DMA spectrum of heat-cured PMMA for 5 min.

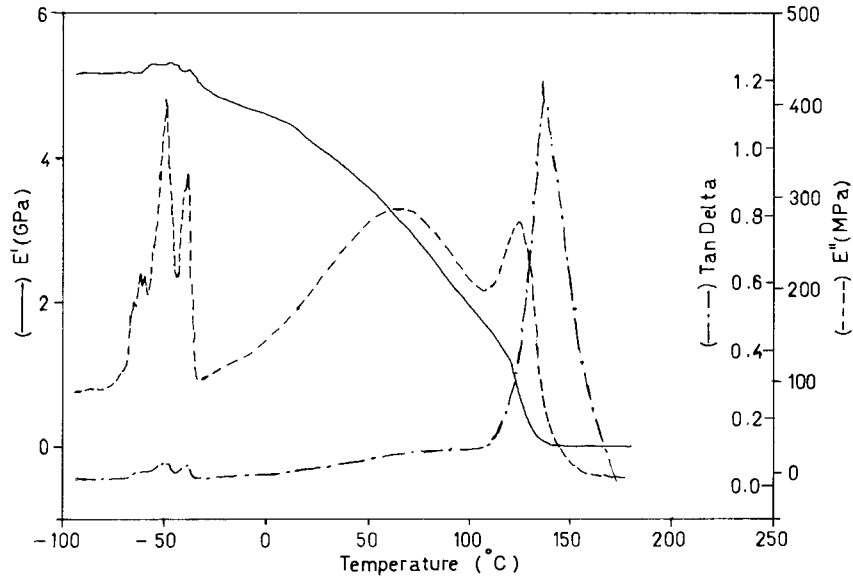


Figure 8 DMA spectrum of heat-cured PMMA for 20 min.

longer curing heat degradation, microstructural reorientation takes place.

CONCLUSION

In this study, the curing of PMMA, used as dental base material, has been done by conventional heat curing and by microwave curing. In heat-curing process, the heat penetration into matrix

of material is slower, and some of the monomer (bp = 100.8°C at 1 atm) may vaporize to form bubbles at curing temperature (boiling water). Therefore, the crosslinking will be more probable on the surface compared to inside; the monomer bubbles will weaken the mechanical strength of the material. In microwave curing, the penetration into matrix is much better, and a homogeneous treatment of material can be achieved. The observed higher molecular weight of soluble ma-

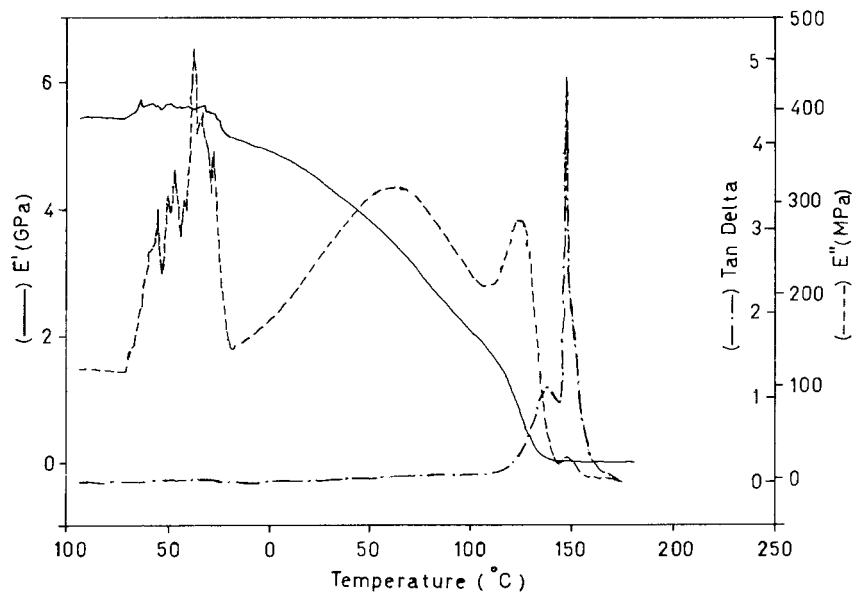


Figure 9 DMA spectrum of heat-cured PMMA for 35 min.

terial obtained for microwave treatment is an important advantage of the process. One of the important disadvantages of microwave curing is the expected higher local temperature in the material.

The use of DMA compared to conventional mechanical testing and thermal investigation¹⁹ gives much more information related to microstructural changes in material treatment.

REFERENCES

1. Craig, R. G.; Peyton, F. A. *Restoration Dental Materials*, 9th ed.; C. V. Mosby: St. Louis, MO, 1993.
2. Phillips, R. W. *Skinner's Science of Dental Materials*, 9th ed.; W. B. Saunders: Philadelphia, PA, 1991.
3. Jerolimov, V.; Huggett, R.; Brooks, S. C.; Bates, J. F. *Quint Dent Technol* 1985, 9, 431.
4. Jerolimov, V.; Brooks, S. C.; Huggett, R.; Stafford, G. D. *Int J Prosthodont* 1989, 2, 56.
5. Mutlu, G.; Huggett, R.; Harrison, A. *J Dent* 1992, 20, 2015.
6. Donovan, T. E.; Hurst, R. G.; Campagni, W. V. *J Prosthodont* 1989, 2, 56.
7. Davy, K. W. M.; Broden, M. *Biomaterials* 1991, 12, 540.
8. Honorez, L. S. D.; Catalan, A.; Angnes, U.; Grimonster, J. *J Prosthet Dent* 1989, 61, 510.
9. Wolfaardt, B. D. S.; Cleaton-Jones, P.; Fatti, P. *J Prosthet Dent* 1986, 55, 518.
10. Nishii, M. *J Osaka Dent Univ* 1968, 2, 23.
11. Reitz, P. V.; Sanders, L.; Levin, B. *Quint Int* 1985, 8, 547.
12. De Clerck, J. P. *J Prosthet Dent* 1987, 57, 650.
13. Shlosberg, S. R.; Goodacre, C. J.; Munoz, C. A.; Moone, K. B.; Schnell, R. C. *Int J Prosthodont* 1989, 2, 453.
14. Ilbay, S. G.; Güvener, S.; Alkumru, H. N. *J Oral Rehabil* 1994, 21, 103.
15. Wei, J. B.; Shideker, T.; Hawley, M. C. *Polym Sci* 1996, 4, 18.
16. Sadamari, S.; Ganefiyanti, T.; Hamada, T.; Arima, T. *J Prosthet Dent* 1994, 72, 19.
17. Dyer, R. A.; Howlett, J. A. *J Dent* 1994, 22, 236.
18. Turck, M. D.; Richards, M. W. *J Prosthet Dent* 1992, 69, 340.
19. Usanmaz, A.; Türker, F.; Doğan, A.; Akkaş, N. *J Appl Polym Sci* 1998, 69, 1409.
20. Mutlu, G.; Huggett, R.; Harrison, A. *J Prosthet Dent* 1994, 71, 186.
21. Mutlu, G.; Huggett, R.; Harrison, A. *Med Sci Res* 1991, 19, 425.
22. Clarke, R. L. *Biomaterials* 1989, 10, 494.
23. Clarke, R. L. *Biomaterials* 1989, 10, 549.
24. Clarke, R. L. *Biomaterials* 1989, 10, 630.
25. McCrum, N. G.; Buckley, C. P.; Bucknal, C. B. *Principle of Polymer Engineering*, 2nd ed.; Oxford University Press: Oxford, 1997, UK, pp. 136–137.
26. Ward, I. M.; Hadley, D. W. *An Introduction to Mechanical Properties of Solid Polymers*; John Wiley & Sons, New York, 1996; pp. 171–177.