

Thermal and Dynamic Mechanical Properties of γ -Ray-Cured Poly(methyl methacrylate) Used as a Dental-Base Material

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ABSTRACT: In this study, γ rays were used for the first time to cure dental-base material. The effect of the radiation dose on the thermal and rheological properties of poly(methyl methacrylate) (PMMA) used as a dental-base material was investigated. The commercial powder and liquid material (heat-curing-grade) were mixed and polymerized at 60 and 70°C in a constant-temperature water bath for 30 min and then were cured by γ rays, with total doses of 7.5, 15, 22.5, 30, 45, 52.5, 360, and 2160 krad. For each sample, the viscosity-average molecular weights were measured, and no significant differences were observed of total dose on molecular weights. A thermal investigation with differential scanning calorimetry showed an exothermic peak in the thermograms of samples that were not completely polymerized and crosslinked. The rheological nature of the samples was studied with dynamic mechanical analysis. A comparison of properties of γ -ray-cured samples and those cured by other methods revealed γ curing to be a superior method for producing high-molecular-weight homogeneous polymers with low porosity and crosslinking. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1291–1296, 2001

Key words: dental material; polymer for dental use; rheological behavior; thermal behavior

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is one of the plastics commonly used as dental-base materials.¹ In commercial applications,^{1–3} powdered PMMA, which has a viscosity-average molecular weight of about 1×10^6 , and liquid monomer are mixed in a volume-to-volume ratio of 3:1 to make dough. The powder contains benzoyl peroxide as an initiator; pigments (e.g., mercuric sulfide, cadmium sulfide, ferric oxide, and zinc oxide) to give

tissue-like shades; dyed synthetic fibers (nylon or acrylic fibers) to simulate the minute blood vessels underlying the oral mucosa; and plasticizers (dibutylphthalate or triphenylphosphate) to produce a softer, more resilient final polymer. The monomer contains an inhibitor (hydroquinone) to prevent premature polymerization and a crosslinking agent (glycol dimethylacrylate). The mixed dough is placed in a mold and pressed under high pressure. The monomer is then polymerized in a water bath at 60–70°C for 30–180 min. Compressed mold material is then cured to obtain the final crosslinked polymer. In dental applications,^{4–8} curing is done by one of the following techniques:

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1. Heating in boiling water.
2. Self-curing (at room temperature) if the monomer contains an activator such as a triamine to dissociate peroxide, which is present in the powder, after mixing.
3. Microwave irradiation in a microwave oven.
4. Exposure to light of a wavelength of about 400 nm.

In all these processes, the main purpose is to get a material that contains a minimum amount of residual monomer and has dimensional stability, high surface hardness, low specific gravity, adequate strength, and durability. However, in most applied curing techniques, the local elevated temperature causes vaporization of the monomer (normal boiling point = 100.8°C) and formation of pores in the material. In the self-curing technique, there are no high-temperature problems, but the residual monomer level is high. The partial crosslinking starts in the early stages of the curing process, and the material is not homogenous in terms of molecular-weight distribution.

To obtain a material with the desired properties, the use of γ radiation for curing may be more useful. Because γ rays can penetrate a material, the exposure to radiation would be homogenous and independent of the thickness of the sample, and local overheating would not be observed. Thus, minimum residual monomer and pores should remain in the material after the completion of radiation curing. Premature crosslinking would be avoided, and homogenous, high-average molecular-weight polymer chains could be obtained. This technique has not been reported before, and we hope it will be applied to the commercial processing of PMMA used as a dental-base material.

In this study, the thermal properties and dynamic mechanical analysis (DMA) of γ -ray-cured commercial PMMA used as a dental-base material were investigated. The results were compared to those of samples cured by heat and microwaves in our previous findings.⁴⁻⁶

EXPERIMENTAL

Materials and Methods

The powdered PMMA and liquid monomer were QC 20 (De Trey, Dentsply, England). The powder was prepared for a heat-activated process. Both powder and liquid were used directly without fur-

ther purification. Chloroform was Merck-quality and was distilled before use. Other materials used for the preparation of acrylic denture bases were plaster, molding wax, cellulose lacquers (used as separating agents), and polyethylene thin foils (used as insulators). They were used without further purification. A commercial denture flask was used for sample preparation in compression molding.

The samples were cured in a 220 model γ cell Co-60 irradiation source, a product of Atomic Energy of Canada Ltd. Co. (Ottawa, Canada). The dose rate of the source was 15 krad/h.

Dynamic mechanical tests were carried out on a TA-DMA model 983 (USA). The heating rate was 5°C/min from -75 to 250°C under a fixed frequency of 0.3 Hz. The differential scanning calorimetry (DSC) thermograms were taken on a TA Instrument DSC 910 S.

The viscosity-average molecular weights of samples were measured in a Ubbelohde-type glass viscometer with chloroform as a solvent at 25°C.

Procedure

The test samples (dimensions = 4.0 × 3.0 × 0.5 cm) were prepared with heat-activated polymerization followed by curing in the γ -radiation source. The procedure was as follows:

1. The plaster that was previously prepared in another cup was poured into the bottom of the flask.
2. The wax samples were placed in plaster. The cellulose lacquer used as a separating agent was used to insulate the surface of the plaster.
3. The flask was filled with plaster and then sealed.
4. The flask was kept under high pressure for 5 min.
5. The flask was then placed in hot water to soften the wax. The top and bottom parts of the flask were separated. Any residual wax was flushed out with hot water.
6. The powdered PMMA and liquid methyl methacrylate monomer were mixed in a 3:1 ratio in a glass beaker at room temperature. They were thoroughly mixed for about 20 min to make a homogenous dough.
7. The acrylic dough in the beaker was placed in a dental flask and kept under pressure for 10 min.

Table I Molecular Weights of Samples at Different Curing Times

Curing Time (min)	Molecular Weight $\times 10^5$ (70°C Curing)	Molecular Weight $\times 10^5$ (60°C Curing)
30	9.7	10.1
60	8.9	8.2
90	8.9	12.8
120	10.5	8.2
150	11.6	7.6
180	10.3	8.5
210	9.8	8.1

8. The flask containing the sample was then placed in a water bath at (1) 60°C and (2) 70°C for 30 min to polymerize the monomer.
9. Samples removed from the water bath and molding flask were then placed in the γ -radiation source with curing doses of 7.5, 15, 22.5, 30, 37.5, 45, and 52.5 krad.
10. The prepared samples were used for molecular-weight determination and thermal and DMA measurements.

RESULTS AND DISCUSSION

Molecular Weights of the Samples

The viscosity-average molecular weight of the samples polymerized at 60 and 70°C and then cured by γ radiation are given in Table I. The molecular weights were 8×10^5 to 12×10^5 . The measured molecular weight of the untreated powder sample (QC 20) was 10.3×10^5 . If the measured average molecular weights of samples were much larger than those of the powder, we could say that the monomer molecules were added to polymer chains in the powder. However, the molecular weights of the samples were generally smaller, and the polymer samples were completely soluble in chloroform in the curing periods tested. When the radiation curing dose increased to 360 krad or more, the polymers were partially soluble. The results show that even at lower irradiation doses, the monomer polymerized to relatively high molecular weights without being crosslinked as happens in other curing methods.⁴⁻⁸ At higher doses, the crosslinking started, and the material was more homogenous in terms of polymer chain lengths. In our previous stud-

ies,^{5,6} QC 20 samples polymerized under the same conditions and heat-cured samples were partially soluble in chloroform in the early stages of curing. Thus, premature crosslinking started on the surface of the material, which was affected more by temperature. However, γ rays penetrated the material homogeneously, and all parts of the sample matrix were affected similarly.

Thermal Analysis

The DSC thermograms of all the samples were studied, but similar ones are not given here. The DSC thermograms taken for QC 20 samples first polymerized at 60°C and then cured by γ radiation with total doses of 22.5, 52.5, and 2160 krad are given in Figure 1. The thermograms for polymerization at 70°C and curing of 22.5- and 52.5-krad doses are given in Figure 2. At this temperature, the thermogram for 2160 krad (as an extreme dose) was the same as that for a 52.5-krad dose of irradiated sample. Therefore, this is not included in the figure. In thermogram curves of

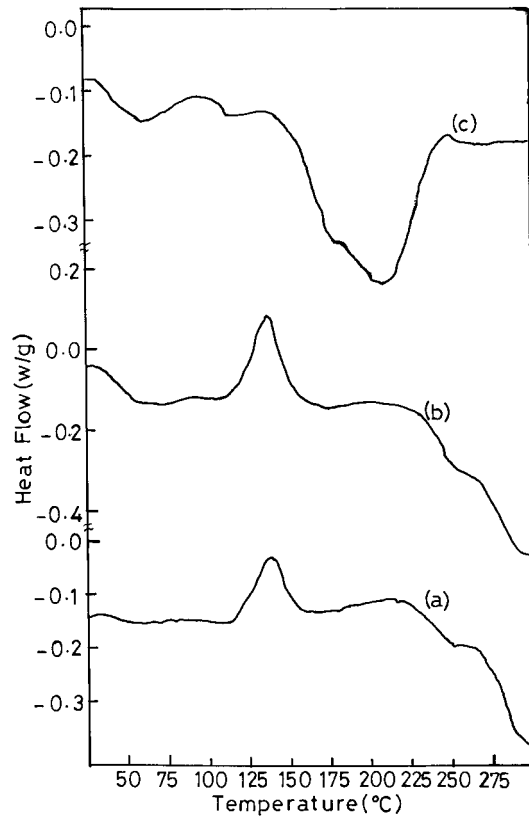


Figure 1 DSC thermograms of PMMA polymerized at 60°C and cured with (a) 22.5-krad, (b) 52.5-krad, and (c) 2160-krad doses of γ rays.

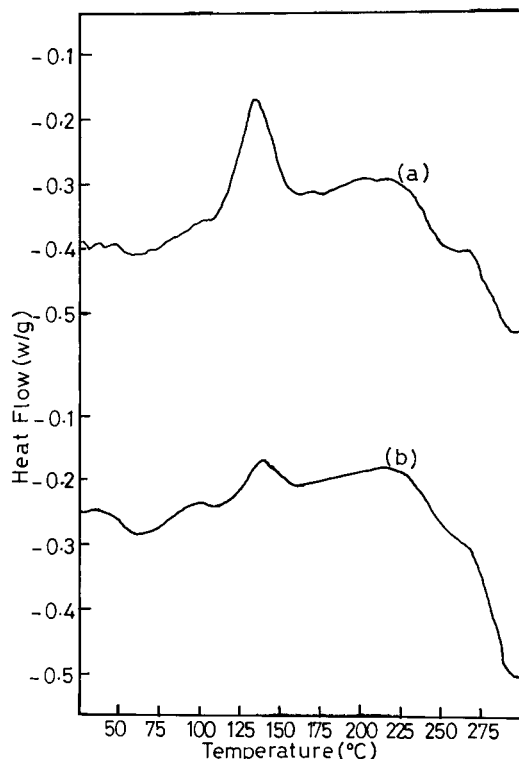


Figure 2 DSC thermograms of PMMA polymerized at 70°C and cured with (a) 22.5-krad and (b) 52.5-krad doses of γ rays.

samples cured with doses of 22.5 and 52.5 krad, an exothermic peak from about 105 to 165°C was observed. This was most probably caused by further thermal polymerization or crosslinking in this temperature range. The glass-transition temperature (T_g) of the samples was expected in this range and, therefore, was not observed. There was some indication for the secondary (β -relaxation) T_g related to an ester group at lower temperatures, but it was not very obvious. After 2160 krad of total irradiation, the exothermic peak [Fig. 1(c)] disappeared, and T_g was observed at 120°C. The endothermic peak at higher temperatures (175–230°C) showed the rheological flow and most probably the decomposition of crosslinks. As shown in Figure 2, the sample polymerized at 70°C and cured with 52.5 krad of radiation gave an exothermic peak of much-reduced peak area compared with the area of a sample cured with a dose of 22.5 krad. It can be concluded that the polymerization was almost complete under those conditions. Thus, if the initial polymerization is carried out at 70°C, instead of 60°C, the required total curing dose reduces to much lower values, which is an advantage.

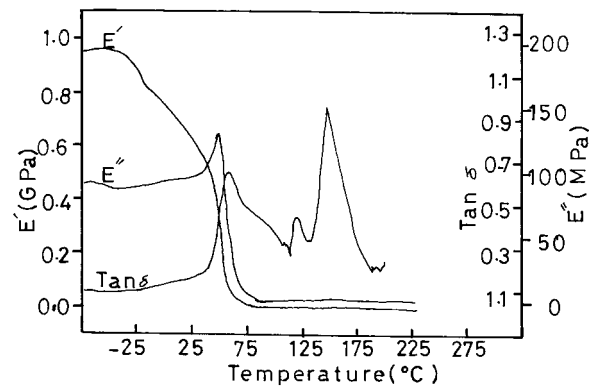


Figure 3 DMA scan of PMMA dental-base material polymerized at 60°C and cured with a 7.5-krad dose of γ rays.

DMA

The DMA scans of PMMA dental-base material that was first polymerized at 60 and 70°C and then cured by γ radiation with total doses of 7.5, 15, 30, 37.5, 45, and 52.5 krad were taken. Some of the spectra are shown in Figures 3–7. The spectra that are not given showed a similar trend of changes with small variations. In the region where the dynamic-modulus temperature curve has an inflection point, the $\tan \delta$ (lost factor) curve goes through a maximum. This dispersion occurs in the glass-transition region. A peak in $\tan \delta$ occurs when the impressed frequency matches the frequency of molecule relaxation through thermally activated processes.^{9,10} As a result, the $\tan \delta$ peak gives the T_g values. Figure 3 corresponds to polymerization at 60°C followed by irradiation of 7.5 krad. In this figure, the $\tan \delta$ curve gives peaks at 57 and 118°C, corresponding

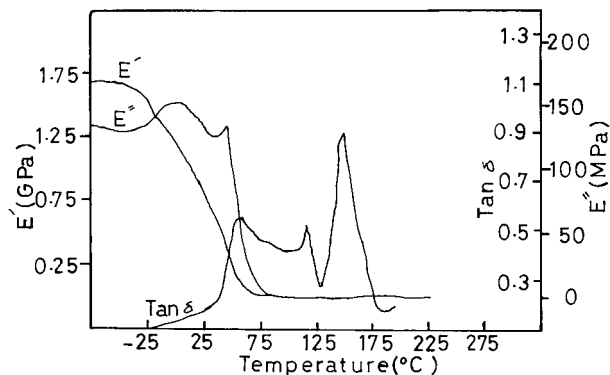


Figure 4 DMA scan of PMMA dental-base material polymerized at 60°C and cured with a 52.5-krad dose of γ rays.

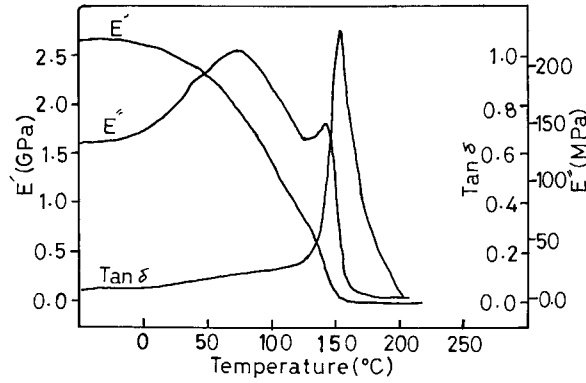


Figure 5 DMA scan of PMMA dental-base material polymerized at 60°C and cured with a 360-krad dose of γ rays.

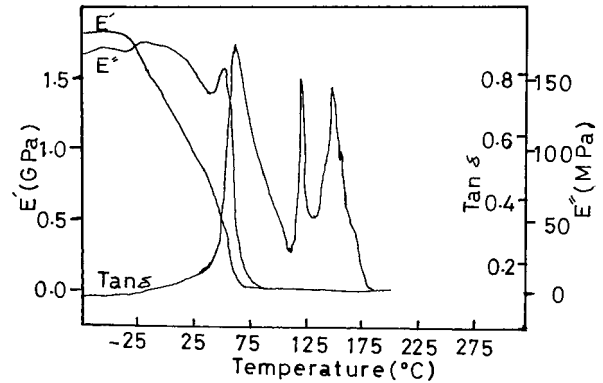


Figure 6 DMA scan of PMMA dental-base material polymerized at 70°C and cured with a 7.5-krad dose of γ rays.

to tertiary (δ) and secondary (β) relaxation caused by CH_3- and ester side groups, respectively, on the polymer chain. The peak at 149°C gives the α -relaxation, which corresponds to the T_g of the main chain. As shown in this figure, the storage modulus (E') decreased from an initial value of about 0.95 GPa rapidly with temperature, and the loss modulus (E'') exhibited a maxima. A similar trend was observed for the sample irradiated at 52.5 krad as seen in Figure 4. However, the initial storage modulus increased to about 1.74 GPa with the curing dose, and very small changes were observed in T_g values. For the polymerization at 70°C (Figs. 6 and 7), the initial E' was larger than that of the sample polymerized at 60°C and cured with the same radiation dose (Fig. 3). Another important change was in the $\tan \delta$ curve. The secondary and tertiary relaxation peaks combined into a peak at about 72°C. This shows that when the number of longer chains was increased, the mobility restriction was observed in the side groups more. This was even more obvious, as shown in Figure 5, when the polymer sample was cured with a 360-krad dose of radiation after polymerization at 60°C for 30 min. The observed number of peaks in the $\tan \delta$ curve decreased to one that was just the main-chain (α) relaxation. This can be considered the completion of the crosslinking of material.⁵

CONCLUSIONS

In this work, the application of γ rays for curing was used successfully in the preparation of dental-base material. The premature crosslinking in

heat-activated curing causes the formation of different defects in the material. In heat curing, the temperature increase starts on the surface and progresses slowly into the material, forming a temperature ingredient. At the same time, a high temperature makes the residual monomer vaporize and form bubbles in the sample. However, γ rays penetrate well into the material and do not cause the temperature to increase to high values. This makes the samples more homogenous and allows them to reach higher molecular weights before crosslinking. The optimum dose of irradiation to give the final desired material is less than 360 krad, and this is achieved by a 1-day irradiation. The irradiation time seems to be very long for this type of process. The main reason for the application of microwaves in dental-material curing is to decrease the operation time, which is desired by people working in this area.⁵ The γ

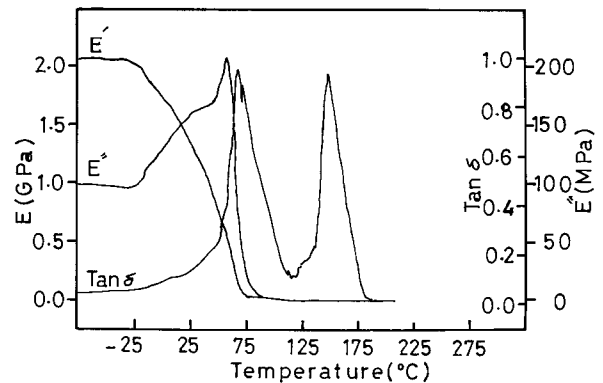


Figure 7 DMA scan of PMMA dental-base material polymerized at 70°C and cured with a 52.5-krad dose of γ rays.

source used in this work had a very small dose rate (15 krad/h), and when changed to total dose per day, the value (360 krad) is quite low. With a radiation source of a higher dose rate (as used in medical applications), the curing period will reduce to just a few minutes or even seconds. Therefore, the application of γ ray curing in dental curing will provide an advantage in both improved material quality and time saved.

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