Thermal and Mechanical Properties of Poly(methyl methacrylate) Used as Dental Base Material

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ABSTRACT: The thermal and mechanical properties of poly(methyl methacrylate) prepared at different curing times were studied using DSC, TGA, tensile, and three-point bending test methods. The molecular weights of the polymer samples were determined from the viscosity measurements. The curing time applied for two different commercial materials, manufactured for dental use, ranged from 15 to 180 min. The samples cured for 15 and 20 min were soluble in chloroform completely, but the others were partially soluble. The insoluble fraction increased with curing time but the molecular weight of the soluble fraction remained constant. DSC thermograms showed further curing of the samples cured for 15 and 20 min. After curing for 180 min and/or annealing at room temperature for about 13 months, the samples were completely crosslinked. The characteristic values obtained from the tensile and the three-point bending tests were similar for samples cured at different times. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1409–1417, 1998

Key words: poly(methyl metacrylate); thermal properties; mechanical properties; dental use; molecular weight

INTRODUCTION

Information about thermal properties of plastics used in dentistry is important because, in their applications, they are subjected to temperature changes which may cause deformation and dimensional distortions. The two important thermal variables are the glass transition temperature, T_g, and the thermal conductivity. Some thermal and thermomechanical methods[1–13] have been used to determine the T_g of poly(methyl methacrylate) (PMMA). The T_g values reported are close to 105°C but the T_g changes with molecular weight[8] and curing cycles.[5] Jerolimov et al.[5] reported variations in the T_g up to 20°C with curing cycles. They reported high T_g as well as optimal mechanical properties for a curing period of 3 h at 100°C following 7 h polymerization time at 70°C of an acrylic denture basis. The chain degradation of PMMA has been studied extensively over the last 45 years; however, there are still many points that need to be explained. Early studies[13] on PMMA showed the chain-end-initiated unzipping-type degradation. It is now generally accepted that the degradation site of the chain depends on the mode of the monomer addition. The head-to-head linkage is reported[7] to be easy to break at temperatures ranging between 245 and 270°C for different oligomers. The peaks of the DTG curves reported by Inaba et al.[8] for

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the degradation of high molecular weight PMMA are in the range of 370–390°C, being smaller for higher molecular weights.

The mechanical properties are important for dental materials because they are subjected to the forces of different types in service. These properties depend on the sample preparation conditions such as the pressure applied during curing, the curing cycle used, and the rate of cooling after processing.[14–19] They are also closely related to voids in the polymer matrix that cause high water absorption and a dimensional change of the material in the applications.[16,17,20] If the polymerization time at 60–70°C applied for commercial dental base material is cut short and the temperature is increased to 100°C before complete monomer consumption, the unpolymerized monomer (bp = 100.8°C) will vaporize and cause porosity in the polymer matrix. This type of porosity is not desired in dental base material since it deteriorates its mechanical strength and the excess residual monomer[17,21,22] gives a toxic effect in service. In most of the dental applications, the acrylic resins are reinforced by other polymers or metal wires to improve the mechanical properties.[23–25]

In this study, the thermal and mechanical properties of PMMA cured at different times were investigated to obtain the optimum curing time for some commercial products and to characterize the PMMA used as a dental base material. The molecular weights of PMMA were determined by the viscosity measurements to understand the network formation of the material and to determine the relation between the molecular weight and the thermal–mechanical characteristics.

EXPERIMENTAL

The two types of unveiled heat-activated acrylic resins used in this study were QC 20 (De Trey, Dentsply, UK) and Paladon 65 (Kulzer, Wehrheim, Germany), both in powdered PMMA with a relatively low molecular weight and a liquid monomer. The solvents used were of spectroscopic grade and they were used without further purification.

The powder–liquid mixtures were prepared according to the respective manufacturer's instruction. They were mixed in proportions recommended by the manufacturer. The dough prepared from the powder–liquid (in a ratio of 3 to 1) was first polymerized for 30 min at 60°C by peroxide initiation present in the powder fraction; then, the temperature was increased to the boiling temperature of water to carry out further polymerization and curing was done for 15, 20, 25, 30, 35, 90, 120, and 180 min. The samples were removed from the polymerization bath, placed in a mold of the desired dimension for the mechanical test, and cooled to room temperature.

The samples used for the viscosity and thermal measurements were prepared by cutting from the molded samples using a 2.5-mm engineering twist drill with a 250 rpm drilling velocity.[17] The intrinsic viscosities of the PMMA samples having different curing cycles were measured in an Ubbelohde-type viscometer using chloroform as the solvent at 25°C. The samples cured at 15 and 20 min were soluble in the solvent but those with higher curing cycles were only partially soluble. Accordingly, for these samples, viscosity measurements of only the soluble fractions were carried out.

The DSC measurements for the QC 20 heat-cured resins were performed on a Perkin–Elmer Model 4 DSC. The sample sizes used were 5–15 mg and the run rate was 10°C/min. The TG analyses of the samples were carried on a DuPont 951 Model TGA with a rate of 10°C/min under a nitrogen atmosphere. The tensile and the three-point

Table I Molecular Weights of QC 20 Samples

Curing Time (min)	$[\eta]$	$k_{red} - k_{inh}$	Molecular Weight
15	2.951	0.453	8.91×10^5
20	3.249	0.422	1.00×10^6
25	3.235	0.532	9.95×10^5
30	3.955	0.400	1.26×10^6
35	3.511	0.535	1.09×10^6
90	4.029	0.470	1.29×10^6
120	3.420	0.586	1.06×10^6
180	3.282	0.530	1.01×10^6

Table II Molecular Weights of Paladon 65 Samples

Curing Time (min)	$[\eta]$	$k_{red} - k_{inh}$	Molecular Weight
15	1.809	0.619	4.94×10^5
20	2.265	0.605	7.84×10^5
25	2.050	0.465	5.74×10^5
30	2.291	0.479	6.50×10^5
35	2.122	0.534	6.00×10^5
90	1.712	0.513	4.62×10^5
120	2.178	0.668	6.20×10^5
180	1.848	0.573	5.00×10^5

bending tests were performed on a Lloyd LR 50K material testing machine (Southampton, UK) using standard dumbbell-shaped test specimens for the tensile strength measurements and test specimens with dimensions of $80 \times 10 \times 3$ mm for the three-point bending measurements. At least five specimens for each different curing cycle were tested. All the machine controls and data acquisition were done by a personal computer with DAPMAT-1.4 software. The load cells used were 5 and 30 kN and the test speed was kept constant at 2.5 mm/min. The span length was 40 mm throughout the bending experiments. After placing the specimens on the supports, load was applied at the midspan. Load versus deflection data were collected at a rate of 3.3 data points per second. Stress–strain data were obtained from the load-deflection data using the strength of materials formulas given below. The use of such stress–strain diagrams for comparative evaluation puts the analysis on a more uniform basis.

The stress, σ, in terms of the modulus of elasticity, E, and the strain, ε, is

$$\sigma = E\varepsilon$$

If the force applied at the midspan is P; the span length, L, and the moment of inertia of the beam cross section, I, the maximum (midspan) deflection, δ_{max}, will be

$$\delta_{max} = PL^3/48EI$$

For a beam with a rectangular cross section of width w and of depth t,

$$I = (1/12)wt^3$$

For the three-point bending case, the maximum bending moment, M_{max}, is

$$M_{max} = PL/4$$

In this case, the maximum stress will be

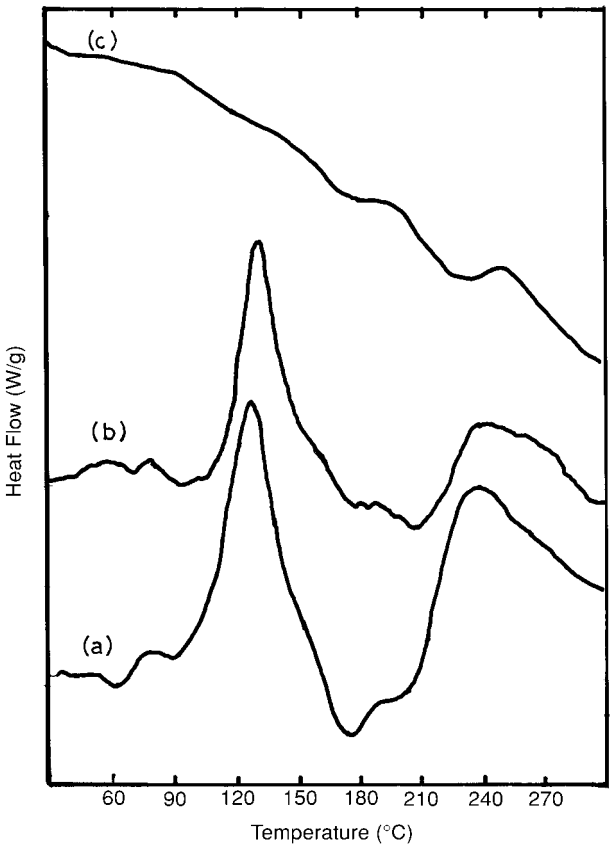

Figure 1 DSC thermograms of QC 20 samples cured for 20 min (a) without annealing, (b) 7 months annealing, and (c) 13 months annealing at room temperature.

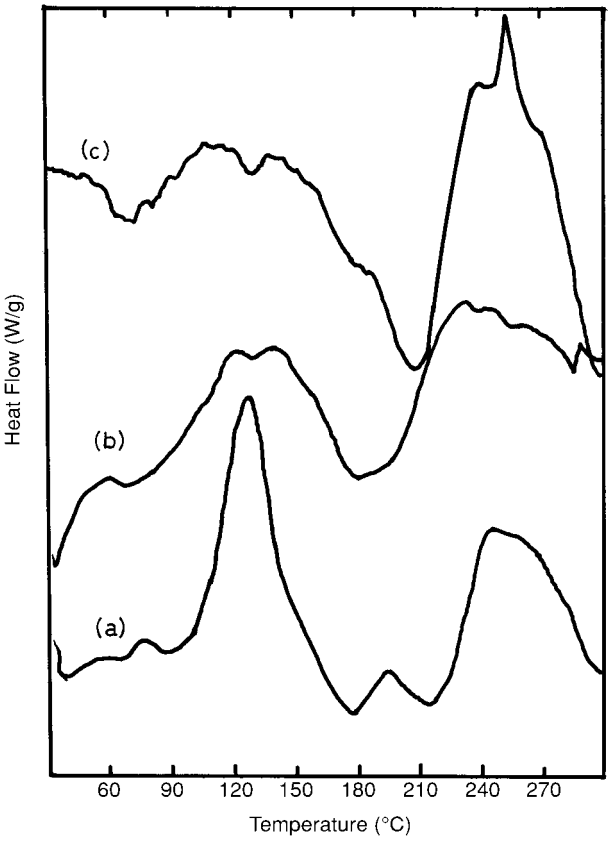

Figure 2 DSC thermograms of QC 20 samples cured for (a) 30 min, (b) 90 min, and (c) 120 min.

$$\sigma_{max} = M_{max}c/I$$

where c is the distance to the extreme fiber from the neutral axis ($c = t/2$). Finally, the modulus of elasticity is

$$E = PL^3/48I\delta_{max}$$

RESULTS AND DISCUSSION

Molecular Weight Determination

Molecular weight measurements were carried in a glass capillary Ubbelohde-type viscometer using chloroform as the solvent at 25°C. The results were plotted according to

$$\eta_{red} = \eta_{sp}/c = [\eta] + k_{red}[\eta]^2c \quad \text{Huggins' equation}$$

$$\eta_{inh} = \ln \eta_r/c = [\eta] + k_{inh}[\eta]^2c \quad \text{Kraemer's equation}$$

The intercepts were intrinsic viscosities, $[\eta]$, and slopes $k_{red}[\eta]^2$ and $k_{inh}[\eta]^2$, respectively. k_{red} and k_{inh} were calculated for each measurement. All the drawings and related calculations were carried out by a computer program written for this purpose.[26] The correlation coefficients for a straight line obtained for all samples were 0.98 or higher. The results are tabulated in Tables I and II for QC 20 and Paladon 65 samples, respectively. The $[\eta]$ values estimated by the Huggins and Kraemer plots of the samples coincide with each other within an accuracy of 1%. The $k_{red} - k_{inh}$ values, also tabulated in Tables I and II, are very close to 0.5. Therefore, we can assume that chloroform is a good solvent for PMMA. The molecular weights were calculated from the following relation[27]:

$$[\eta] = 3.4 \times 10^{-5}M^{0.83}$$

The molecular weights of the soluble samples (for

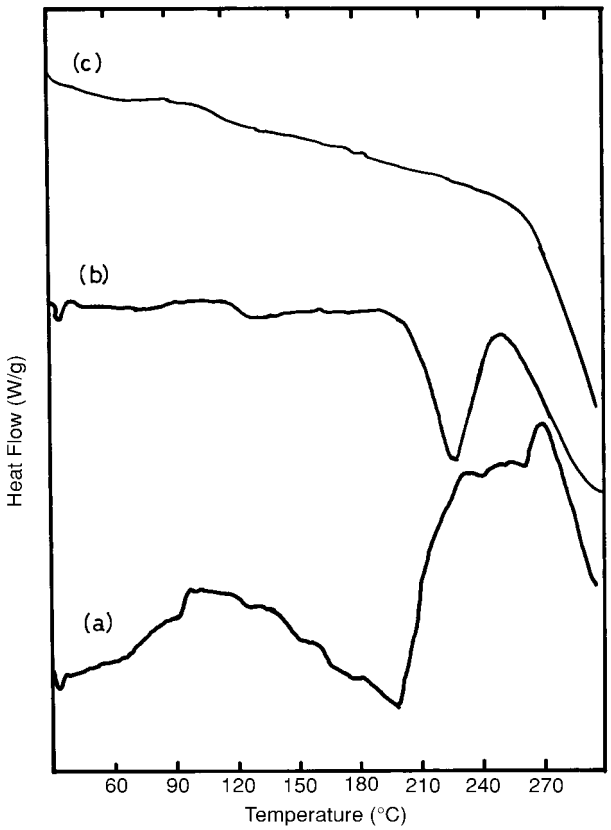

Figure 3 DSC thermograms of QC 20 samples cured for 180 min (a) without annealing, (b) 7 months annealing, and (c) 13 months annealing at room temperature.

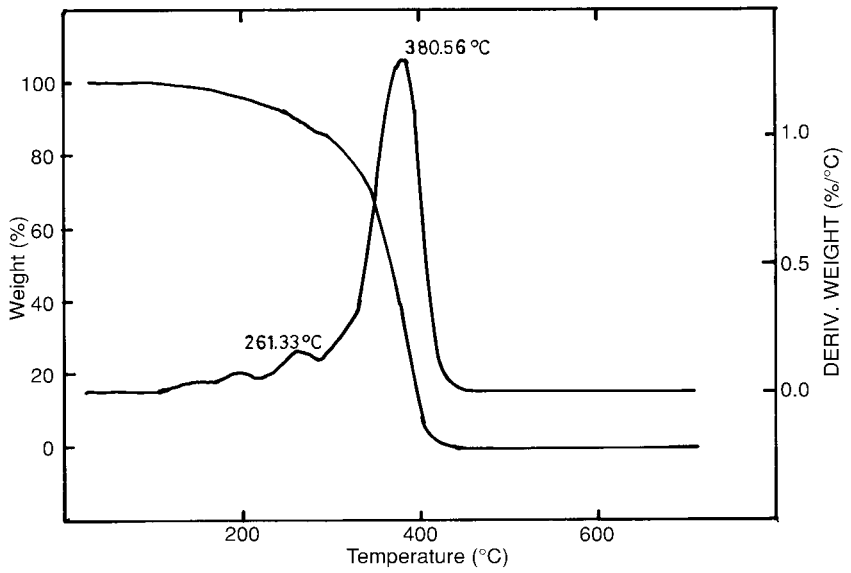

Figure 4 TGA thermogram of QC 20 samples cured for 20 min.

curing times of 15 and 20 min) and of the soluble fractions of all the other samples are almost the same with a value of 10^6. The values for the QC 20 samples are a little higher than those for the Paladon 65 samples. This shows that the crosslinking (or network-structure formation) becomes significant after reaching a limited molecular weight. The increase of curing time causes formation of more network, insoluble fraction, but it does not change the limiting molecular weight of the soluble fraction which decreases in amount with curing time. The amount of the insoluble fraction was less than 10% in a 25-min curing cycle but increased to more than 90% after a 180-min curing cycle. This shows that the crosslinking agent added to the liquid fraction by the manufacturer [usually ethylene glycol dimethacrylate (EGDM)[28]] became effective at curing times greater than 20 min. The linear polymer reached a molecular weight of about 10^6 at the initial polymerization temperature of 60°C followed by a curing cycle period of about 20 min. Afterward, the main reaction was the crosslinking by the added crosslinking agent.

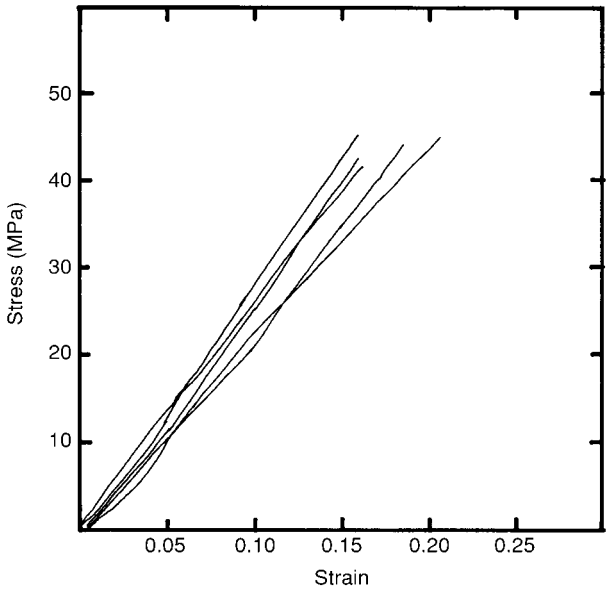

Figure 5 Stress–strain curves obtained from tensile tests of QC 20 sample cured for 30 min.

Thermal Properties of PMMA

The DSC and TG methods were used to investigate the thermal behavior of the QC 20 PMMA samples obtained at different curing periods. The DSC thermograms of the QC 20 samples cured for 20 min (a) without annealing, (b) annealed for 7 months at room temperature, and (c) annealed for 13 months at room temperature are given in Figure 1. The T_g values observed in Figure 1(a) at 64 and 78°C most probably correspond to the side groups of $-CH_3$ and $-COOCH_3$, respectively. The exothermic peak at 128–130°C indicates further polymerization and crosslinking. The T_g of the main chain and/or the rubber flow temperature for the crosslinked samples are observed at 182 and 207°C, respectively. This is a

Table III Results of Tensile Tests for QC 20 Samples

Curing Time (min)	Ultimate Stress, σ_u (MPa) Mean Value (SD)	Ultimate Strain, ε_u Mean Value (SD)	Elastic Modulus (MPa) Mean Value (SD)
15	47.86 (8.68)	0.223 (0.040)	214.24 (3.67)
20	38.73 (7.80)	0.130 (0.014)	245.86 (40.46)
25	54.58 (2.30)	0.242 (0.031)	257.52 (28.73)
30	43.60 (1.55)	0.175 (0.021)	258.34 (30.61)
35	50.01 (6.02)	0.207 (0.028)	244.02 (29.81)
90	49.19 (3.20)	0.209 (0.020)	239.86 (12.05)
120	36.12 (3.98)	0.175 (0.017)	206.41 (10.90)
180	50.00 (4.17)	0.130 (0.030)	245.66 (32.87)

very high T_g value and, therefore, most probably both are rubber-flow temperatures. The exothermic peak retains its position even after 7 months of annealing at room temperature [Fig. 1(b)], but it disappears after 13 months of annealing [Fig. 1(c)]. The decomposition starts at about 240°C for all samples. The T_g values assigned to the side groups are not observed after 13 months annealing at room temperature, but several T_g values at higher temperatures are observed for the main chain. The rubber-flow temperature is not well defined now and the material is more homogeneous.

The results are in agreement with those obtained for molecular weight determination. After 20 min of the curing cycle, the amount of crosslinking obtained is very limited. Thus, the linear polymer is now cured further at a temperature centered at 120°C. However, the curing at room temperature also takes place, but at longer periods. This is, in this case, observed after about 13 months of annealing time.

The DSC thermograms of the samples cured for 30, 90, and 120 min are given in Figure 2. The thermogram of the 30-min cured sample is similar to that cured for 20 min [Fig. 1(a)] with some shifts in the peak positions. However, significant and gradual changes take place for samples cured for 90 and 120 min. The T_g's for side groups are now shifted to higher values and the exothermic peak showing further polymerization/crosslinking becomes broader and disappears gradually.

The DSC thermograms of the 180-min cured samples (a) without annealing, (b) 7 months annealing, and (c) 13 months annealing are shown in Figure 3. In this case, the T_g's for the side groups at lower temperatures do not exist in the spectra. The T_g's for the main chain appear at 120°C and the rubber-flow temperature at 199°C [Fig. 3(a)]. The T_g value is close to the values reported[5,8] in the literature. The rubber-flow temperature shifted to 226°C after 7 months of annealing at room temperature [Fig. 3(b)] and it disappeared after 13 months of annealing [Fig. 3(c)], but the T_g temperature did not change much with annealing. Thus, the crosslinking is most probably completed after 13 months of annealing following a 180-min curing cycle.

The thermal gravimetric analysis (TGA) showed the same behavior for all samples cured

Table IV Results of Tensile Tests for Paladon 65 Samples

Curing Time (min)	Ultimate Stress, σ_u (MPa) Mean Value (SD)	Ultimate Strain, ε_u Mean Value (SD)	Elastic Modulus (MPa) Mean Value (SD)
15	45.70 (2.81)	0.200 (0.034)	230.15 (48.91)
20	44.00 (9.89)	0.166 (0.016)	284.94 (50.91)
25	43.63 (4.88)	0.210 (0.050)	215.80 (53.59)
30	44.82 (6.03)	0.243 (0.015)	187.95 (1.14)
35	45.26 (3.27)	0.247 (0.021)	215.34 (15.55)
90	47.56 (4.91)	0.243 (0.005)	213.27 (15.07)
120	40.91 (8.29)	0.186 (0.043)	232.00 (7.33)
180	46.03 (4.31)	0.185 (0.023)	236.16 (22.59)

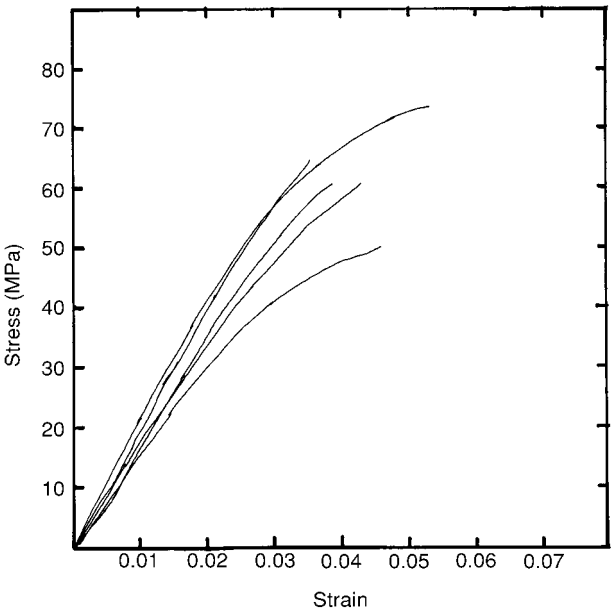

Figure 6 Stress–strain curves obtained from three-point bending test of QC 20 sample cured for 30 min.

at different times. The thermograms (TG and DTG) of the 20-min cured samples are shown in Figure 4. The decomposition trend shows a typical depolymerization trend in that a smooth decrease in the weight of the sample with temperature is observed. The DTG curve gives two peaks ranging at 254–266 and 377–386°C for the samples cured for different times. There is no regular change in the peak positions with curing time; the peak position for the main decomposition peak is at 381°C for 20-min curing and increases to 386°C for 30-min curing, then decreases to a constant value of 377°C for 90-, 120-, and 180-min curing times. The lower-temperature peaks are more dispersed for lower curing times (20 and 30 min) but they change into almost a single peak at further curing. The small peak most probably corresponds to the decomposition of the oligomers with mostly head-to-head linking. These results agree well with the reported values by Meisters et al.[7] The main-chain decomposition peak temperature is similar to that of Inaba et al.[8] When the curing time is increased, the mode of chain addition is not very selective and, therefore, more head-to-head addition may take place, which lowers the decomposition temperature.

Mechanical Properties of PMMA

In the tensile test, the stress–strain curves were obtained for at least five specimens of each sample cured at different periods for QC 20 and Paladon 65. As an example, the stress–strain curves of the QC specimens cured for 30 min are given in Figure 5. The curves are typical for hard and brittle types of polymers that can be characterized as having a high modulus, no yield stress, moderate ultimate strength, and low elongation at break. The stress–strain data and the elastic moduli for QC 20 are given in Table III and those for Paladon 65 in Table IV, respectively. The applied nonparametric *t*-test showed that there is no significant difference among the characteristic values of stress, strain, and elastic moduli within a confidence limit of 95%. The standard deviations, with the exception of a few measurements, are in the range of reasonable values for this type of measurement. The values of stress, strain, and elastic moduli do not change significantly with curing time. This is probably because the rheological and mechanical properties are sensitive to molecular weight only up to a critical molecular weight.[29] In our case, the molecular weight of the samples

Table V Results of Three-point Bending Tests for QC 20 Samples

Curing Time (min)	Ultimate Stress, σ_u (MPa) Mean Value (SD)	Ultimate Strain, ε_u Mean Value (SD)	Flexural Modulus (MPa) Mean Value (SD)
15	61.89 (8.07)	0.021 (0.007)	1825.7 (547.2)
20	61.29 (15.48)	0.034 (0.005)	1657.3 (523.8)
25	68.91 (10.80)	0.048 (0.008)	1729.0 (207.5)
30	44.76 (9.29)	0.032 (0.004)	1637.6 (178.1)
35	66.68 (12.98)	0.038 (0.007)	2043.2 (238.9)
90	62.78 (12.13)	0.038 (0.009)	2233.5 (349.1)
120	57.99 (10.63)	0.034 (0.004)	2546.6 (326.4)
180	54.62 (13.43)	0.031 (0.007)	2834.4 (348.9)

Table VI Results of Three-point Bending Tests for Paladon 65 Samples

Curing Time (min)	Ultimate Stress, σ_u (MPa) Mean Value (SD)	Ultimate Strain, ε_u Mean Value (SD)	Flexural Modulus (MPa) Mean Value (SD)
15	57.95 (12.16)	0.031 (0.007)	1910.0 (791.8)
20	64.88 (15.73)	0.037 (0.008)	2005.0 (531.4)
25	61.23 (10.25)	0.036 (0.002)	1876.0 (369.2)
30	51.75 (6.48)	0.030 (0.007)	2037.0 (643.4)
35	64.34 (7.78)	0.037 (0.006)	1823.0 (427.6)
90	68.10 (9.00)	0.032 (0.003)	2425.0 (496.5)
120	68.55 (11.88)	0.035 (0.008)	1782.0 (283.5)
180	65.94 (5.15)	0.040 (0.007)	1861.0 (165.6)

(about 10^6) cured for even the least duration should be much larger than the critical values for PMMA. The effect of sample thickness on the elastic moduli has been noted.[19]

The stiffness of the plastics subjected to bending is of great importance in dental applications. For this reason, the flexural properties of the samples cured for different times were measured. Typical stress–strain curves obtained from the three-point bending test of the QC 20 samples cured for 15 min are shown in Figure 6. Other curves are similar. The curves indicate a hard and brittle material.

The results obtained from the three-point bending tests of QC 20 and Paladon 65 are given in Tables V and VI, respectively. The application of the nonparametric *t*-test showed no significant difference within a 95% confidence limit. There is not any significant change in the flexural modulus with increase in the curing time. These values are in satisfactory agreement with the reported data.[30–32] The curing time affects the croslinking and network structure but this type of change is apparently not easy to identify by mechanical testing. Other studies[28] have also shown that the crosslinking of denture-base materials with EGDM has a limited effect on the mechanical properties of the material considered.

CONCLUSIONS

The molecular weight determination of PMMA showed that the polymerization at shorter curing cycles gives a soluble polymer chain with molecular weights in the order of 10^6. Longer curing cycles produce a more network (insoluble) polymer structure but do not increase the molecular weight of the soluble fractions. The mechanical properties, obtained by tensile tests and three-point bending tests, did not show significant variation at these molecular weights, which should be higher than that of the critical values for PMMA. The low elastic moduli obtained from the tensile measurements are probably related to the "structural behavior" of the specimens rather than to their "material behavior" during the tests. The DSC method is more sensitive in studying the structural changes in PMMA when compared to mechanical tests. To obtain more information related to changes in the structural behavior with the curing cycles, investigation with dynamical mechanical testing, which is more sensitive in this respect, is in progress and will be reported later.

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