Synthesis and Characterization of Poly(methyl methacrylate) Polymerized by Microwave Energy or Conventional Water Bath

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ABSTRACT: In this work, the influence of three different suspension agents (agar, sodium alginate, and gelatin) in the synthesis of poly(methyl methacrylate) (PMMA) particles is reported. Sodium alginate was the best suspension agent, obtaining characteristics closer to commercial denture base resins. Synthesized particles and two commercial acrylic resins (Acron MC and Lucitone 199) were characterized by light microscopy, scanning electron microscopy, characteristic X-ray energy dispersive spectroscopy, thermogravimetric analysis, and molecular weight measurements. Mechanical tests (transverse deflection behavior) were done using two heat-polymerizing techniques. The results indicated that both the PMMA particles and the commercial acrylic resins have similar characteristics. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3953–3960, 2008

Key words: suspension polymerization; poly(methyl methacrylate); transverse deflection; molecular weight; particle size

INTRODUCTION

The term suspension polymerization describes a process in which monomer, relatively insoluble in water, is dispersed as liquid droplets with steric stabilizer and vigorous stirring (which is maintained during polymerization) to produce polymer particles as a dispersed solid phase.[1]

Initiators soluble in the liquid monomer phase are employed in this polymerization process. The major aim in suspension polymerization is the formation of an as uniform as possible dispersion of monomer droplets in the aqueous phase with controlled coalescence of these droplets during the polymerization process. If the process is carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and isolate by filtration.[2–8] A particle size between 10 and 500 μm is possible to have in suspension polymerization.[8]

The sodium alginate is the sodium salt of organic acid. Gelatin is a solid substance extracted from the collagen and it has been commonly used in pharmaceutical manufacturing. Agar is an unbranched polysaccharide obtained from the cell membranes of some species of red algae. These three products may be used as a stabilizers, thickeners, surfactants, or texturizer in several applications.[9]

The presence of suspending agents (e.g., stabilizers) hinders the coalescence of monomer droplets and the adhesion of partially polymerized particles during the course of polymerization, so that the solid beads may be produced in the same spherical form in which the monomer was dispersed in the aqueous phase.[1] However, contamination of the suspension agents by remnants of the elements used during the polymerization process, such as monomer, diluents, can introduce experimental limitations for certain guest compositions and polymer properties.[3] Other disadvantage is the particles' agglomeration that could occur during synthesis. Also, washing and drying are required.[2]

Poly(methyl methacrylate) (PMMA) is an important member in the family of polyacrylic and methacrylic esters. PMMA has several useful properties, including exceptional optical clarity, good weatherability, high strength, and excellent stability.[7] In the plastic industry, it has many important applications such as molding, electronics, automotive industry, decorative panels, pharmaceuticals, agriculture, paint production. In dentistry, PMMA prepared particles have great applications in prosthetic dentistry.[2,4,5]

Acrylic resins have been used for denture fabrication for over 60 years. The most popular denture

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base material is heat-cured PMMA.[10,11] Virtually all dentures are constructed from these materials using the conventional polymer/monomer dough molding process and cured using a water-bath system.[10] Nishii[12] first reported the use of microwave energy to polymerize denture base materials in 1968. Kimura et al.[13] reported that the curing of the acrylic resin in a very short time was possible using this technique. Other advantages of the microwave technique are the cleaning in the procedure, and the similar properties of this acrylic resin to the resin polymerized in water bath; because of these, many technicians process denture bases with conventional acrylic resins using microwave energy, but no satisfactory results are obtained in porosity and transverse deflection. Microwave polymerized acrylic resins are harsher, less flexible, and with less impact resistance than the acrylic resin polymerized in water bath.[14] However, the mechanical properties of these materials, such as impact strength and transverse deflection, are not ideal because recurrent fractures of denture base acrylic resins, polymerized either by hot water bath or microwave energy, are still a reported problem.[10,15,16]

The synthesis of PMMA prepared via free radical suspension polymerization using three different suspension agents (agar, sodium alginate, and gelatin) is reported in this work. These suspension agents were selected because they are used as stabilizers and surfactants in many chemical reactions. Thus, morphological analysis of experimental PMMA and two commercial acrylic resins for denture bases, as well as thermogravimetric analysis (TGA), molecular weight measurements, and transverse deflection are presented. The particle size and morphology were measured by light microscope (LM) and scanning electron microscopy (SEM). The chemical analysis used to know the element percentage composition in each of the samples, which could have an important role in the results obtained in this work, was carried out by characteristics X-ray energy dispersive spectroscopy (EDS).

EXPERIMENTAL

Materials, synthesis, and morphological characterization

Methyl methacrylate (MMA, 99%; Sigma-Aldrich, Mexico), benzoyl peroxide (BPO; Promotores y Catalizadores Orgànicos de México, Mexico), sodium hydroxide (JT Baker, México) were used as received. Agar (Medental S.A. Mexico), sodium alginate (Manufacturera Dental Continental, Mexico), and gelatin (Knox, Maizena, Mexico) were used as suspension agents. Commercial heat-cured acrylic resin PMMA (Lucitone 199, Dentsply/Trubyte, York, PA) and other commercial microwave energy (Acron MC, GC International Corp., Tokyo, Japan) used in dentistry were selected as control groups.

PMMA was synthesized as follows: 100 g of MMA, 8.1 g NaOH, 0.26 g BPO, 400 mL H_2O, and 2.5 g of suspension agent. The mixture was placed in a four-neck flask (1000 mL) fitted with a reflux condenser and nitrogen gas inlet tube. Then the mixture was stirred at 600 rpm and 70°C for 2 h. At the end of the reaction, the mixture was washed several times with pure water and dried at room temperature.

The particle size, morphology, and chemical analysis were performed to the obtained particles with the three different suspension agents.

The synthesized (Experimental PMMA) particles with closer chemical and morphological characteristic to the commercial acrylic resins for denture bases were compared physically and mechanically with two commercial acrylic resins Lucitone 199 and Acron MC.

The studied PMMA were observed with a LM to calculate the particle size, with a SEM JEOL JSL-5600LV attached to a NORAN-EDS equipment for the study of morphology and chemical analysis. An Ernst Leitz Wetzlar LM (100×) was used for size measurement. Fifty particles of each PMMA were randomly selected and measured. The particle size was determined using the microscope scale. For SEM observation, each PMMA sample was dropped on a carbon-coated tape.

Weight loss profiles of the test materials were examined for loss of mass at a heated rate of 10°C/min in nitrogen atmosphere from room temperature to 600°C. The weight percent filler in each cured product was determined by ashing of each material in a TGA unit (2950TGA, TA Instruments, Twin Lakes, WI).

Dilute PMMA solutions were made in pure acetone. The viscosities were measured using an Ubbelohde capillary viscometer. The test was performed at 25°C. The viscosity average molecular weight (M_v) was calculated using the Mark–Houwink–Sakurada equation (13): $[\eta] = 0.0075M_v^{0.7}$ at 25°C.

Mechanical behavior

Ten specimens with a size of 65 × 10 × 2.5 mm^3 were made of each material. PMMA was mixed with MMA and BPO to prepare the specimens. Group 1 was made by mixing the Experimental PMMA with MMA and BPO and processed according to Lucitone 199 manufacturer instructions (90 min at 73°C then boiling water for 30 min). Group 2 was made by mixing the Experimental PMMA with MMA and BPO and processed according to Acron MC manufacturer instructions (microwave-polymerized at 500 W for 3 min). Group 3 (Lucitone 199) and Group 4 (Acron MC) were processed according to the man-

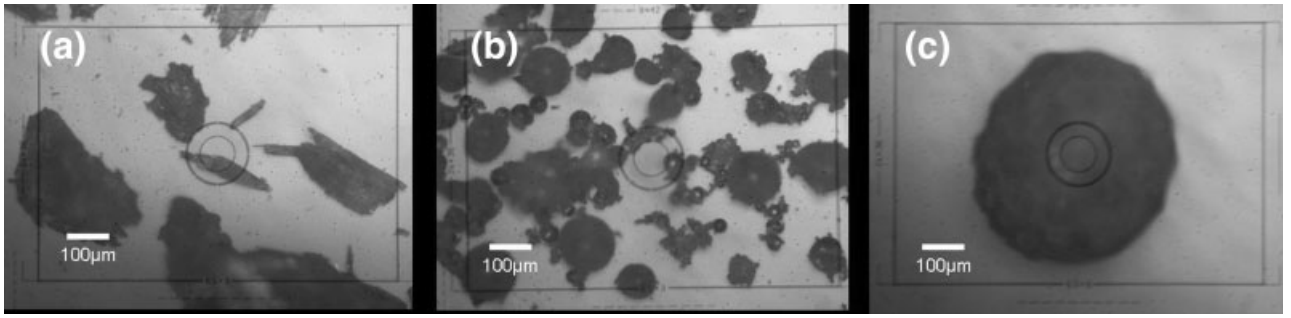

Figure 1 LM images of the PMMA prepared via free radical suspension polymerization with different surfactants: (a) agar, (b) sodium alginate, and (c) gelatin.

ufacturer instructions. Group 5 (Lucitone 199) was processed according to Acron MC manufacturer instructions and Group 6 (Acron MC) was processed according to Lucitone 199 manufacturer instructions.

The transverse deflection was evaluated on the specimens subjected to flexural loading conditions and was determined by centrally loading the surface specimen on a 3.2-mm-diameter knife-edge support with a cylindrical knife-edge (3.2 mm diameter) at a cross-head speed of 0.5 kg/min until fracture using a tension-compression cell (Mecmesin, Horsham, England). The load-deflection curve was registered, and the fracture load, flexural strength, and elasticity modulus were determined. The transverse deflection test was performed according to the ADA (American Dental Association) 12th.[17] The flexural modulus was calculated using the equation: $E = FL^3/4\partial bh^3$, where ∂ is the deflection corresponding to load F at a point in the straight-line portion of the load-deflection curve, L is the length between the knife-edge support, b is the width, and h is the thickness of the specimen. The flexural stress (S) was calculated using the equation: $S = 3PL/2bh,^2$ where P is the load at 34 and 49 N according to ADA 12th.[17]

RESULTS AND DISCUSSION

PMMA suspension polymerization particles

In PMMA suspension polymerization, organic monomer phase in small droplets dispersed by stirring in aqueous phase is polymerized into hard solid particles.[18]

In this investigation, three kinds of suspension agents (agar, sodium alginate, and gelatin) were used to synthesize PMMA. Particles with different characteristics were obtained, even though the same synthesis conditions were used, but just varying the suspension agents.

Figure 1 shows the particle size distribution. As it can be seen in this figure, all samples had different morphology, depending on the suspension agent. Sodium alginate and gelatin produced similar morphology, spherical but with different size. Agar produced a laminar shape. Comparing the particle sizes between gelatin and sodium alginate, it is clear that PMMA particles prepared with gelatin were about seven times larger than the ones with sodium alginate.

Particle size, morphology observations, and chemical analysis

SEM images of the obtained particles are shown in Figure 2. PMMA spherical forms were obtained with sodium alginate [Fig. 2(b)] and gelatin [Fig. 2(c)]. The PMMA particles obtained with agar [Fig. 2(a)] were flat and irregularly shaped. The particles synthesized using sodium alginate were spherical but with regular borders, whereas polymer obtained through gelatin showed larger spherical size (diameter < 100 μm) but with irregularities in their surfa-

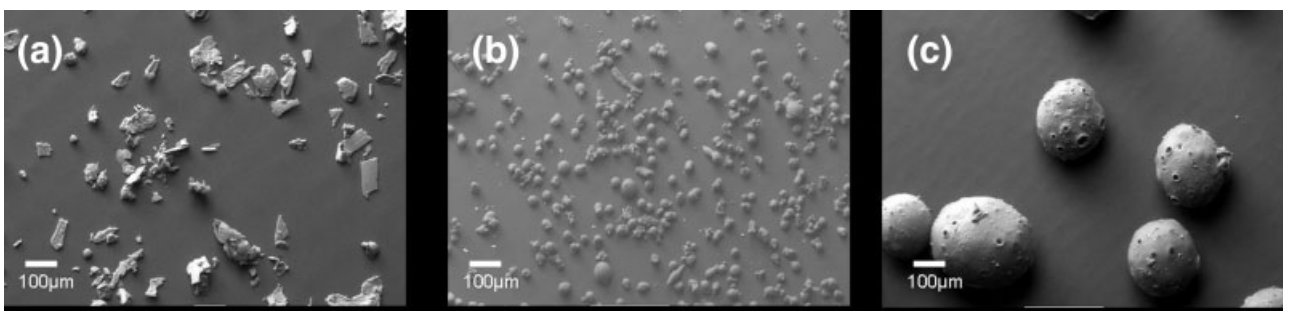

Figure 2 SEM images of the PMMA particles obtained using different suspension agents: (a) agar, (b) sodium alginate, and (c) gelatin.

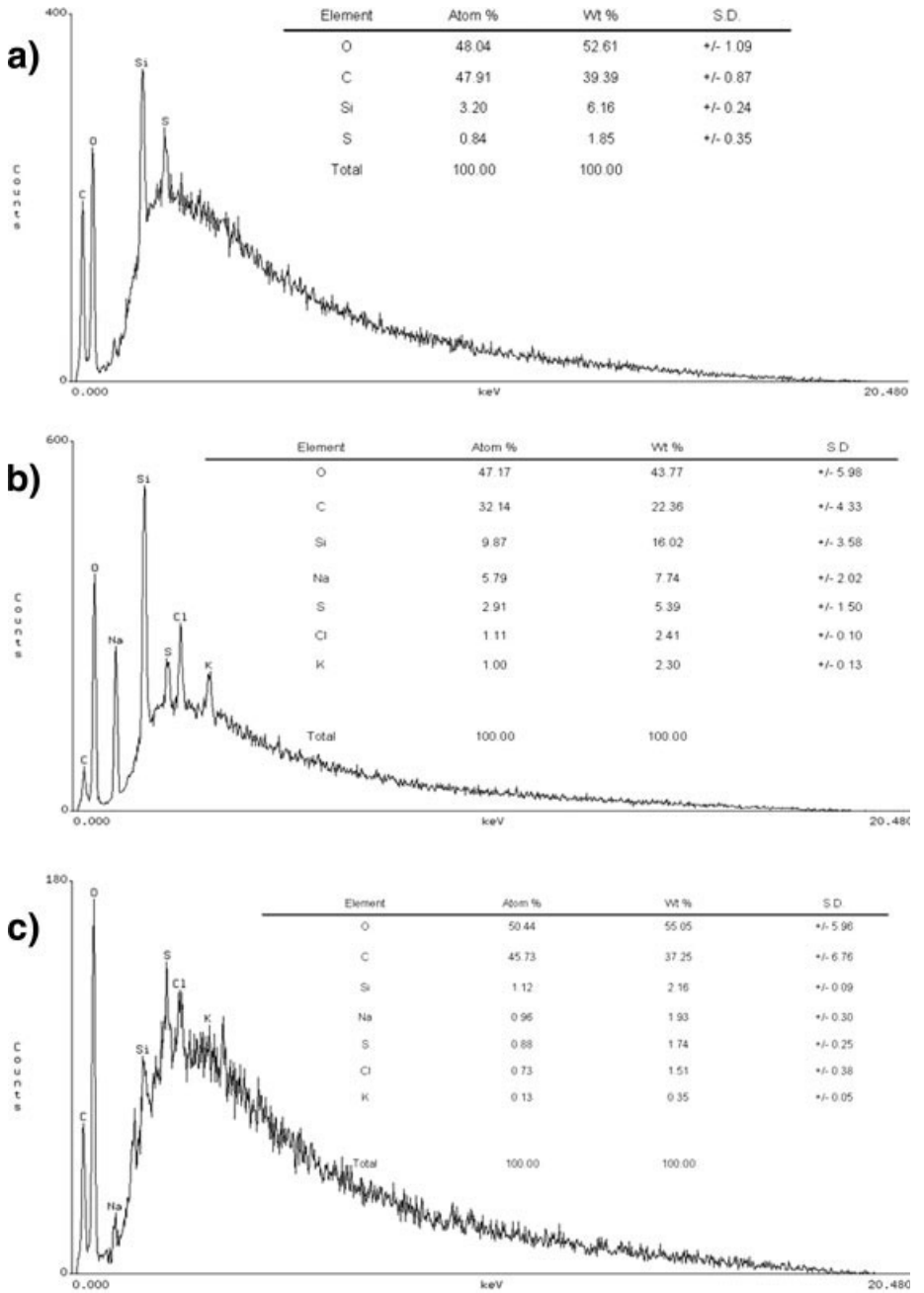

Figure 3 EDS spectra of the PMMA particles obtained with the three suspension agents: (a) agar, (b) sodium alginate, and (c) gelatin. Note the presence of Na, Cl, and K in (b) and (c), although in minor percentage in (c).

ces. This difference in morphology depends mostly on the suspension agent used to produce the particles. The particles prepared using agar as a suspension agent were not spherical, as reported by Rios,[4] who obtained spherical particles using agar and polyvinyl alcohol as suspension agents.

Figure 3 shows the EDS spectra analysis of the particles from the different suspension agents: agar [Fig. 3(a)], sodium alginate [Fig. 3(b)], and gelatin [Fig. 3(c)]. All of them exhibit peaks that correspond to C and O atoms mainly. In fact, these elements were seen in all types of PMMA particles because they are the principal components. However, note also the existence of peaks corresponding to Na, Cl, and K atoms in the spectra shown in Figure 3(b,c) additionally to the C, O, Si, and S atoms observed in the spectrum in Figure 3(a). Surely these differences in composition will have a heavy influence in the results obtained in each case.

Experimental and commercials PMMA

The particles prepared with sodium alginate (Experimental PMMA) showed characteristics similar to

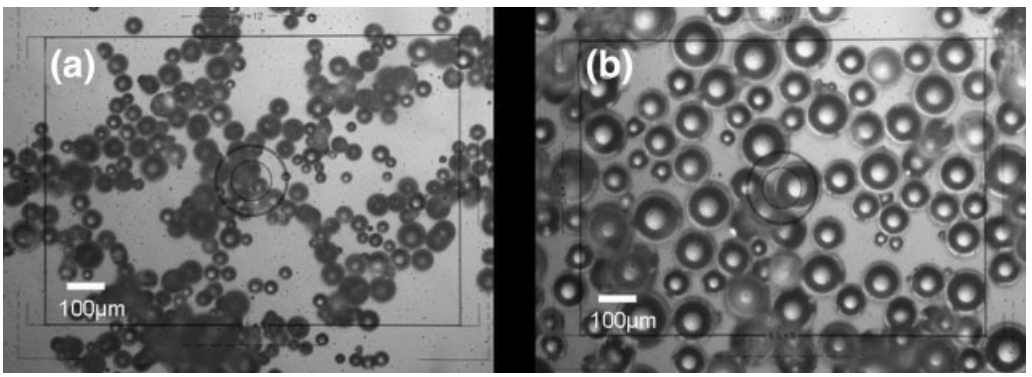

Figure 4 LM images of the commercial acrylic resins: (a) Lucitone 199 and (b) Acron MC.

those of commercial denture base resins. Thus, it was morphological and physically compared with the particles of two commercial acrylic resins: Lucitone 199 and Acron MC. Both commercial acrylic resins are used in dentistry for denture bases and polymerized with different techniques. Lucitone 199 polymerizes in water bath and Acron MC with microwave energy.

Characterization

Particle size

Figure 4 shows the LM images of the commercial acrylic resins: Lucitone 199 [Fig. 4(a)] and Acron MC [Fig. 4(b)]. Both materials have spherical particles with regular borders. Lucitone 199 shows shorter diameter particles. The average particle size of Acron MC was about 54% larger than Lucitone 199 particles. The Experimental PMMA had the smallest average particle size (Table I).

Morphological observations and chemical analysis

SEM images of the commercial acrylic resins are shown in Figure 5. Experimental PMMA [Fig. 2(b)] showed almost spherical particles and a few of them presented irregular forms. Lucitone 199 and Acron MC [Fig. 5(a,b)] exhibit spherical particles with regular borders. Figure 6 shows the EDS spectra analysis of the particles from the two commercial acrylic resins. Both exhibit peaks that correspond to C, O, and Si atoms as well as in the Experimental PMMA [Fig. 3(b)]. However, note also the existence of Ti and S atoms in the spectrum of Acron MC [Fig. 6(a)].

Thermogravimetric analysis

Figure 7 shows the TGA plots of the Experimental PMMA and the two commercial acrylic resins. The three polymers decomposed initially around 145°C. The decomposition of all polymers occurs in three steps: the first step at the temperature range 142–148°C with a weight loss lower than 4%; the second step at 332–339°C with a weight loss lower than 14%; and the third step at 369–380°C with a weight loss lower than 50%. The three PMMA decompose completely between 400 and 420°C. The curves to the Experimental PMMA, Acron MC, and the Lucitone 199 acrylic resins are similar. The curves obtained with the Experimental PMMA are similar to the curves obtained in previous studies[11,19,20] where the PMMA decomposition starts at about 200°C, shows a deflection at about 250°C, and ends at 400°C.

Molecular weight

Measurements of dilute solution viscosity provide the simplest and most widely used technique for routinely determining molecular weights.[2] Viscometry is usually employed to complement the results obtained from another techniques, generally in the determination of molecular mass of samples, provided the constants K and a are available in literature.[21] The average molecular weight viscosity of the Experimental PMMA and the two commercial acrylic resins were determined by viscometry and the results are given in Table I. The molecular weight of the Experimental PMMA was higher than those of Lucitone 199 and Acron MC.

Mechanical behavior

The transverse strength of a material is obtained when one loads a simple beam supported at each

TABLE I
Average Particle Size and Standard Deviations of Two Commercial Acrylic Resins and the Experimental PMMA, and the Viscosity Molecular Weight of Each PMMA Tested

Acrylic resin	Particle size (µm)	M_v ($\times 10^{-5}$ g/gmol)
Experimental PMMA	48 ± 8	36
Lucitone 199	55 = 18	19
Acron MC	85 = 32	14

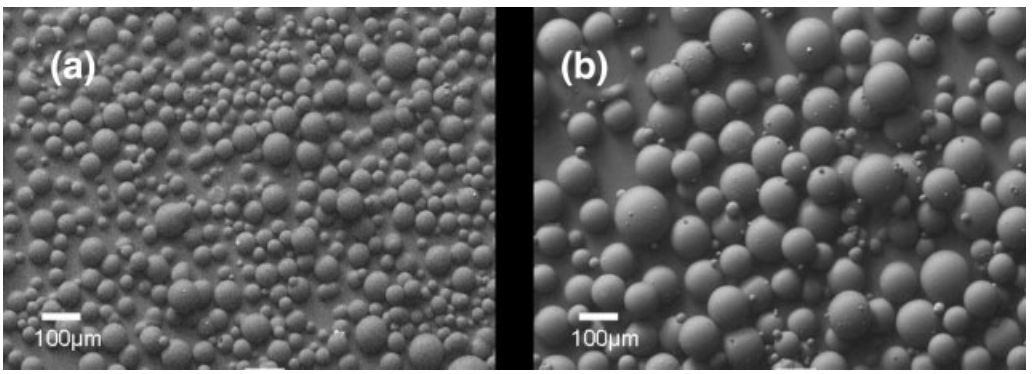

Figure 5 SEM images of two commercial denture base resins: (a) Lucitone 199 and (b) Acron MC.

end, with a load applied in the middle. Such a test is called a three-point bending test, and transverse strength is often described in dental and engineering literature as the modulus of rupture or flexural strength. The transverse deflection test is especially useful in comparing denture base materials in which a stress of this type is applied to the denture during mastication. This test determines not only the strength of the material indicated but also the amount of distortion expected. The transverse stress and accompanying deformation are also important in long bridge spans in which the biting stress may be severe.[15]

Table II shows the mean values of the transverse deflection at 34 and 49 N and the flexural modulus (E). At 34 N, all groups showed value less to 2.5 mm; ADA 12th[17] states a maximum of 2.5 mm of transverse deflection at 34 N. At 49 N all groups pre-

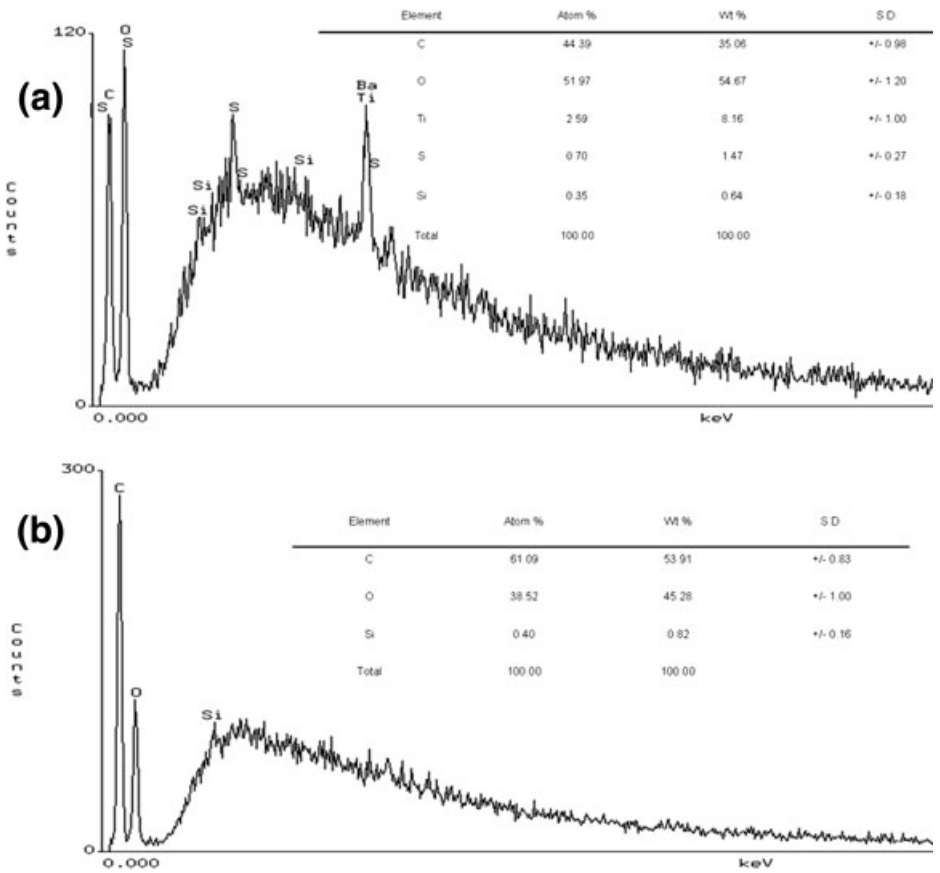

Figure 6 EDS analysis of the commercial PMMA spheres for denture bases: (a) Acron MC and (b) Lucitone 199. Note the presence of Ti and S in (a), and that the percentage of Si is similar in both spectra.

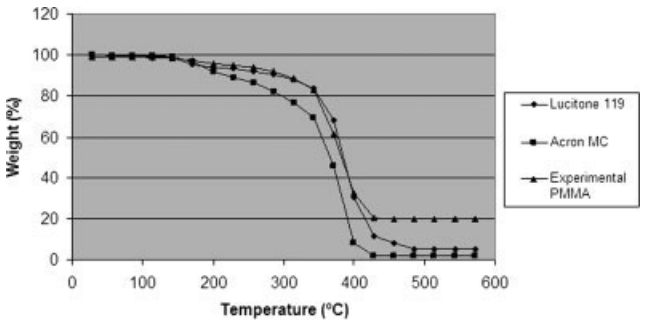

Figure 7 TGA curves of the experimental PMMA and two commercial acrylic resins.

sented values between 2.0 and 5.5 mm; except Group 5 that shows less value. ADA 12th states a range from 2 to 5.5 mm of transverse deflection at 49 N.

The elastic modulus denoted by *E*, also called modulus of stiffness in flexural test, represents the stiffness of a material within the elastic range. Table II exhibits the values of flexural modulus of four groups. Groups 1, 2, and 6 obtained values less at 2.5 GPa. The lowest flexural modulus belonged to the Experimental PMMA polymerized with microwave energy (1.6 GPa) and the highest values were for the Group 5 (2.8 GPa). It shows that water bath process produce denture bases more flexible than that process with microwave energy. Experimental PMMA processed with both techniques is on the values of transverse deflection at 34 and 49 N, but Lucitone 199 processed with microwave energy had less value in transverse deflection at 49 N and did not fulfill with the ADA 12th. Acron MC when processed in water bath fulfills with the transverse deflection values.

The flexural stress (*S*) to the six groups at the load of 34 N was 41.16 MPa and 58.80 MPa at 49 N. The *E* and *S* results obtained in this study for the commercial acrylic resins matched the results reported by Williamson et al.[22]

Takamata et al.,[23] Shlosberg et al.,[24] Reitz et al.,[25] and Sanders et al.[26] compared some mechanical properties, and included the transverse strength of different denture base acrylic resins by both microwave irradiation and heat activation. These investigators concluded that two polymerization methods did not cause differences in the properties of the acrylic resins. This study also indicates that the Experimental PMMA and the commercial acrylic resins are similar in mechanical behavior even when the experimental polymer was polymerized with microwave energy or with the conventional water bath.

To overcome the less flexural modulus, experimental PMMA could be reinforced by adding materials such as aramid fiber, ultra-high molecular weight polyethylene fiber, glass fiber,[27] or mineral fillers, for example, silicon dioxide or calcium carbonate.

CONCLUSIONS

Using sodium alginate in suspension polymerization, PMMA particles were produced with similar characteristics than commercial acrylic resins in the form of granular beads, particle size, transverse deflection, and elastic modulus.

Commercial acrylic resins processed according to the manufacturers' instructions had good mechanical behavior, but it did not happen if the techniques are inverted. When water bath acrylic resin was processed using microwave energy, the samples do not fulfill with the required values in transverse deflection and obtained a higher elastic modulus.

The experimental acrylic resin can be processed with both techniques, water bath or with microwave energy, and it fulfills with the required values in transverse deflection. Therefore, it can be used to prepare denture base polymer.

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TABLE II
Average Transverse Deflection at 34 and 49 N, Flexural Modulus (*E*), and Standard Deviations

	Load					
	34 N		49 N		Elastic modulus	
Groups	Mean (mm)	DS	Mean (mm)	DS	Mean (GPa)	DS
1. PMMA Experimental (water bath)	1.7	0.52	3.5	0.99	2.0	0.47
2. PMMA Experimental (microwave energy)	1.8	0.34	3.1	0.33	1.6	0.37
3. Lucitone 199	1.6	0.20	3.1	0.36	2.5	0.25
4. Acron MC	1.5	0.28	2.9	0.31	2.5	0.21
5. Lucitone 199 (microwave energy)	1.5	0.22	1.8	0.23	2.8	0.25
6. Acron MC (water bath)	1.4	0.13	3.0	0.26	2.3	0.18

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