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PHYSICAL PROPERTIES OF A RADIOPAQUE DENTURE BASE MATERIAL

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NATIONAL BUREAU OF STANDARDS

PHYSICAL PROPERTIES OF A RADIOPAQUE DENTURE BASE MATERIAL

ABSTRACT

Physical properties were determined for radiopaque composite denture base materials consisting of poly(methyl methacrylate) as the matrix and 30, 40, and 50% by weight of a silane-treated barium fluoride-containing glass powder as the reinforcing filler. Specimens without glass were included for comparison.

All of the materials met the requirements of American Dental Association Specification No. 12 for Denture Base Polymer except that the material containing 50% glass had less deflection than the minimum required at the 5000 Gm load in transverse testing.

There was little or no difference among the materials with respect to hardness, indentation resistance, water sorption, color stability, and resistance to drop impact.

Addition of glass to the 30% level decreased the transverse strength while 50% glass specimens had slightly greater transverse strengths as compared to specimens with no glass. In general, the addition of glass increased the time to reach the packing stage, densities, and Young's, bulk, shear, and flexural moduli, had only slight effect on solubility and

decreased the cold-cure repairability and the coefficient of linear thermal expansion.

The solubility of the glass powder was about four times that of powdered porcelain teeth after 24 hours, and totaled 0.55% after five days.

PHYSICAL PROPERTIES OF A RADIOPAQUE DENTURE BASE MATERIAL

Introduction

Evidence of need for radiopaque denture base materials was presented in a previous report.[1] A review of 123 cases of denture foreign bodies indicated that radiographic localization would be facilitated if the base material was radiopaque.

Another report described the characteristics of a series of trial specimens made to determine what combinations of polymers and radiopaque glass yielded specimens having optical translucency, radiopacity, and handling and molding properties that would make them suitable for further research and development.[2] Although several combinations of polymers and glasses had promise, the material selected for further investigation was one composed essentially of poly(methyl methacrylate) (PMMA) and a silane-treated radiopaque glass. Mixes containing these materials could be compression molded using methods and equipment in common use and they could be pigmented and opacified to

yield specimens that had optical translucency and color that simulated oral soft tissues. Also, radiographic diagnosis was facilitated by the radiopacity gained in specimens containing from 29 to 57% of the glass filler.

In the present investigation, some pertinent physical properties were determined on radiopaque, composite, denture base materials containing 30, 40, and 50 weight percent glass as the filler and PMMA as the matrix. The properties of the same denture base material without glass were also determined for comparison and control.

Properties investigated included: packing facility, water sorption, solubility of the composites and of the glass filler, color stability, transverse deflection and strength, repairability, indentation and recovery, hardness, density, resistance to impact fracture, Young's modulus, flexural modulus, shear modulus, bulk modulus, and thermal expansion.

A subsequent paper[3] will describe the use of these materials in the construction of twenty technic dentures to

determine the dimensional changes occurring as a result of processing and water storage, the effects of silane treatment of porcelain teeth, and the mixing, molding, and finishing characteristics during actual conditions of denture fabrication.

Materials*

The following materials were used in making the specimens:

1.) Liquid. The liquid was composed of methyl methacrylate (MMA) (Rohm and Haas Co.) 98.5% by weight and ethylene dimethacrylate (Borden, Inc.) 1.5% by weight. The MMA contained 35 ppm of 2,6-di-t-butyl-4-methyl phenol (BHT) as a stabilizer. The liquid was prepared and allowed to stand for 24 hours before use.

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* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure.

In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the material or equipment identified is necessarily the best available for the purpose.

2.) Powder. The powder was a homopolymer of MMA containing 5% by weight of dibutyl phthalate as a plasticizer (Esschem Co., Division of Sartomer Resins, Inc. Type #P5-69-203). The polymer was composed of beads with diameters from 5 to 120 μm with most of the material consisting of beads greater than 40 μm in diameter. The refractive index n_D^{25} was 1.493.

3.) Filler. The radiopaque glass (Corning Glass Works Code X816JL) had the following batch formulation: SiO_2, 44; BaF_2, 28; B_2O_3, 16; and Al_2O_3, 12 in mole percent.[4] The formulation given in weight percent is: BaF_2, 50; SiO_2, 27; Al_2O_3, 12; and B_2O_3, 11. The powder was elutriated by mixing, settling, and decanting in an attempt to remove very small particles and then treated with 3-methacryloxypropyltrimethoxysilane (Union Carbide A-174). Both the elutriation procedure and silane treatment were described

previously.[3] After silane treatment, the powder was passed through a U. S. Standard Sieve No. 100 (maximum opening 149 μm) to remove any lumps of caked or agglomerated material. The particle sizes of the powder were about 1 to 50 μm and the refractive index n_D^{25} was 1.535. Some testing was done using the glass powder as received (without silane treatment). The powder was tumbled before use to ensure thorough mixing.

4.) Pigment and opacifier. Most of the specimens were pigmented with cadmium red (United Color and Pigment Co.) and opacified with anhydrous titanium oxide (Fisher Scientific Co.).

5.) Repair material. NuWeld (The L. D. Caulk Co., Division of Dentsply International, Inc.). This is a cold-curing powder-liquid system.

Methods

Testing was carried out on specimens containing 0, 30, 40, and 50% by weight of the radiopaque glass. In this report, mixes and specimens will be referred to on the basis of their glass content in weight

percent. A glass content of 30% yielded specimens having the approximate minimum necessary radiopacity with good working properties in the mix; a glass content of 50% represented the approximate upper level of glass which could be used and still maintain acceptable working properties; the 40% content represented a compromise between radiopacity and working properties.

Table 1 lists the compositions of the various mixes with the four different glass contents. To each mix was added 0.029% of cadmium red pigment and 0.029% of titanium oxide opacifier. To gain uniform distribution of the pigment and opacifier, they were first mixed thoroughly with a small amount of the polymer. The remainder of the polymer and the glass was then added with additional thorough mixing. Attempts to mix all of the dry ingredients at one time resulted in a non-uniform color.

Unless otherwise specified, all specimens were cured in flasks immersed in water at 73 ± 2°C for 1-1/2 hours and then in boiling water for 1/2 hour. The flasks in the

Table 1 · Composition of mixes

Ingredients	Composition of Mixes			
	wt %	wt %	wt %	wt %
Liquid	20.4	23.0	21.0	20.0
Powder	79.6	47.0	39.0	30.0
Filler	00.0	30.0	40.0	50.0

clamps were then air cooled at 23 ± 5°C for 1/2 hour and immersed in water at 23 ± 10°C for 15 minutes. In some cases, the flasks were allowed to cool to room temperature in the curing bath.

Packing, water sorption, water solubility, transverse deflection and strength, and color stability: The tests for packing, water sorption, water solubility, transverse deflection, and color stability were run according to the methods outlined in American Dental Association Specification No. 12 for Denture Base Polymer[5] with the following exceptions: (1) number of specimens used, (2) the mold for the transverse specimens was lined with an alginate separating medium instead of tinfoil, and (3) the mold for the sorption and solubility specimens was lined with polyethylene trial pack separating sheets as there was a tendency for the cured 40 and 50% glass specimens to stick to the stainless steel mold.

After the original 24-hour sorption and solubility tests had been completed, the disc-shaped specimens were resurfaced with #240 silicon carbide paper in order to remove the resin-rich outer surface. Another 24-hour test was then completed followed by a ten-day test during which the immersion water

was changed seven times. Four specimens for each material were used.

Additional specimens for transverse deflection and strength testing were made using 30 and 40% levels of the glass which had not been silane treated. Four specimens of each were made.

Repairability: Repairability of the materials containing 0, 30, and 40% glass were determined by transverse deflection and strength tests using a method described previously.[6] A 6.4 mm section was removed from the middle of each of the plates from which the transverse bend specimens were to be machined. The two ends of the plates were then repositioned in the flask and repair material was added and cured. Four transverse bend specimens were then machined from each of the repaired plates and tested according to the method outlined in American Dental Association Specification No. 12. The following repairs were made: 30% glass specimens were repaired with material containing 30% glass, heat cured and with NuWeld; 40% glass specimens were repaired with material containing 40% glass, heat cured and with NuWeld; 0% glass specimens were repaired with NuWeld.

Indentation and recovery: Specimens for indentation and recovery and for hardness were made in upper denture flasks in dental stone molds 2.8 x 27 x 29 mm lined with an alginate mold lining material. Two specimens of each material were made and finished so that the top and bottom were parallel. The test sides were hand finished with silicon carbide paper ending with number 600.

Indentation and recovery testing was done with a Rockwell Superficial Hardness Tester using the 30Y scale as outlined in American Dental Association Specification No. 15 for Acrylic Resin Teeth.[7] Three tests were made on each of the two specimens both dry and after 14 days storage in water at 37°C.

Hardness: Hardness values were obtained using the Rockwell Superficial Hardness Tester and the 15W scale. A 3.17 mm steel ball was applied at a minor load of 3 kg and the dial gauge was set at zero. A major load of 15 kg was then applied for 15 ± 1 second and the dial reading was recorded. Five tests were made on each specimen both dry and after 14 days storage in water at 37°C.

Density: The densities of the four different materials were found by determining the weight and volume of specimens that had been machined for ultrasonic modulus testing.

Drop impact resistance: Resistance to drop impact was measured with an instrument similar to one described by Cornell et al.[8] The test used in this investigation involved the determination of the mean height at which specimens fractured when subjected to a falling steel ball. The instrument used is seen in Figure 1. A close-up picture of the specimen holder is seen in Figure 2.

Specimens for the drop impact test were made in denture flasks (3 specimens in each flask). The molds were disc shaped, 3.4 mm deep and 38.1 mm in diameter with a slight taper so that the specimens could be easily removed. After deflasking, the flash was removed from the specimens with a carborundum stone and surface blemishes were removed by hand sanding. The hand sanding also served to flatten the specimens so that they were stable when placed in the holder. The thickness of each specimen was measured and those that were significantly thicker than the others were further sanded to bring

them within the range of 3.25 to 3.45 mm. Each specimen was placed in the holder (Fig. 2) to insure that it did not bind and was adjusted so that there was slight lateral movement. Thirty-six specimens of each material were made and stored in water at 37°C for at least one week prior to testing.

Testing was done basically as described in ASTM designation D-2463-65T[9] for determining the drop impact resistance of polyethylene containers. A specimen was placed in the holder and a steel ball 20.64 mm in diameter and weighing 35.77 Gm was dropped onto the middle of the specimen from a height estimated to be just great enough to cause failure. If failure occurred the ball was dropped on another specimen from a height of 3 cm less than the initial drop height. If failure did not occur on the initial drop, the ball was dropped from a height 3 cm greater than the initial drop height. All of the specimens were tested in this manner. The height of each drop was either increased or decreased by 3 cm according to the results of the previous drop. No specimen was used more than once. Failure was considered to be any crack or fracture visible to the naked eye.

The mean failure heights and standard deviations were computed using either failures or non-failures according to which was less frequent.[10] The results of the first 10 drops were used only to establish the approximate mean failure height as a starting point for the succeeding drops and were not used in the computations.

Thermal expansion: The coefficient of linear thermal expansion of the materials was determined by the use of a fused quartz tube apparatus.[11] The apparatus consisted of a glass water jacket surrounding a quartz tube within which was placed the specimen with a quartz plunger on its top. Expansion was measured by means of a dial gauge in contact with the top of the quartz plunger. Temperatures from 5 to 70°C were obtained by circulating water in the jacket from a temperature controlled water bath.

For the thermal expansion measurement, two specimens (203.0 x 11.1 x 11.1 mm) of each material were formed in a brass mold. After packing, the mold was covered with brass platens under pressure from "C" clamps. Curing was carried out at 73°C for nine hours after which

the mold was allowed to cool to room temperature in the curing bath. This curing cycle was selected because of the increased likelihood of porosity in specimens of this size if curing cycles involving higher temperatures had been used. Specimens were removed from the mold, the flash removed, and the lengths measured. They were stored in water at 23 ± 2°C for at least 7 days before testing. In order to determine the effects of longer water conditioning, one 30% glass-containing specimen was tested again after 23 days.

The testing was begun on each specimen by first raising the temperature in the jacket to 70°C and retaining it at that temperature until no movement of the dial gauge indicator was noted. The initial reading was recorded after which the temperature was lowered about 10°C and again allowed to remain until no movement in the gauge was observed. This was repeated at each 10°C interval to 5°C (the last interval being only 5°C) after which the temperature was raised in 10°C intervals to 70°C. The entire cycle from 70°C to 5°C and back to 70°C was repeated giving a total of 4 determinations for

each specimen and 8 for each material. The coefficients of thermal expansion were determined for the ranges of 5 - 37°C and 37 - 70°C, in order to compare the results with a previous study.[11]

Resistance to deformation: The flexural modulus was calculated using the data obtained in the transverse bend tests. A tangent was drawn to the initial straight line portion of the load deflection curves and the slope of the tangent determined. The modulus was calculated from the equation:

$$E_B = \frac{L^3 m}{4bd^3}$$

where E_B = modulus in bending; L = beam span; m = slope of the tangent; b = beam width, and d = beam depth.

Young's, shear, and bulk moduli were determined by an ultrasonic pulse-echo technic described elsewhere.[12] The technic involves the determination of the transit-times of ultrasonic pulses through specimens of the test materials. Velocities for both transverse and longitudinal impulses were obtained. These velocities and the densities were used in the following equations to compute the various moduli for each material.[12]

$$\text{Young's modulus } E = \rho V_T^2 \left(\frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \right)$$

$$\text{Shear modulus } G = \rho V_T^2$$

$$\text{Bulk modulus } K = \frac{\rho(3V_L^2 - 4V_T^2)}{3}$$

Where ρ = density

V_T = transverse wave velocity

V_L = longitudinal wave velocity

Specimens for the ultrasonic test were made by turning rods of each material on a jeweler's lathe to a uniform diameter of 8 - 9 mm. The rods were sectioned to form four cylindrical specimens with lengths of about 6, 12, 19, and 25 mm for each material. The specimens were stored in air at 23 ± 2°C for 7 to 14 days before testing.

Young's modulus was also obtained by the use of a dynamic modulus tester (H. M. Morgan Co., Inc. Model PPM-SR) with a planar mount. It is similar in principle to the ultrasonic method in that it measures the transit time of a sonic pulse through the test material. Specimens for the dynamic modulus tester were formed in dental stone molds in

denture flasks. Specimen size was 2.2 x 12 x 75 mm. They were tested dry and after 21 days storage in water. Young's modulus was calculated from the following equation:

$$E = \rho C^2$$

where E = Young's modulus; ρ = density of the material, and C = velocity of the impulse.

Glass solubility: The water solubility of the silane treated glass powder was determined each day for 5 days. The 1 day water solubilities of the glass powder as received and of powdered porcelain denture teeth were also determined for comparison. All tests were run in duplicate. The porcelain teeth (Trubyte-Nue Hue, Dentsply International, Inc.) were cleaned in boiling detergent solution, washed with chloroform and rinsed with boiling water. They were crushed in a steel mortar to reduce them to particle sizes of about 2 mm. The particles were placed in a porcelain jar mill with Burundum grinding cylinders (The United States Stoneware Co.) and milled dry for 16 hours. The resulting powder was passed through a U. S. Standard Sieve No. 100.

One part by weight of each test powder was added to 9 parts by weight of water and the mixtures were stirred for 24 hours with a suspended Teflon® stirrer. The mixtures were then filtered through a Millipore® filter (maximum opening 0.22 μm, Millipore Filter Co.) and the filtrates were placed in tared weighing bottles. The water was evaporated and the bottles dried to constant weight in a vacuum oven at 95°C and about 33.7 kN/m^2 (250 mm Hg). A stream of air was passed through the oven during the drying procedure. Solubility was determined on a percent basis.

A spectrochemical analysis was made on the 24-hour residue of each material.

Results and discussion

Mixing and packing: All four materials complied with the packing test in American Dental Association Specification No. 12. Each material entered all of the 0.75 mm holes in the brass die at least 0.5 mm and in most cases 1.0 mm or more. There was little difference among the

materials except that those mixes containing 40 and 50% glass tended to adhere to the brass die. The addition of glass did not reduce the consistency enough to cause difficulty in completely filling a denture mold.

However, differences did exist among the mixes in that it required more time to reach the packing stage as the percentage of glass was increased. The approximate times to reach the packing stage varied from 16 minutes for a mix containing no glass to 22 minutes for a mix containing 50% glass. This reflects an increasing ratio of monomer to polymer.

Water sorption and solubility: The results of the tests for water sorption and solubility are listed in Table 2. The data for sorption indicate that the addition of glass had little effect and the values for all glass levels fell well within the requirement of American Dental Association Specification No. 12. There was an indication that the glass-resin interface was not serving as a point of entry for water

Table 2 · Water sorption and solubility

eight Glass	Sorption*			Solubility†		
	24 hr	24 hr‡ resurfaced	10 days resurfaced	24 hr	24 hr‡ resurfaced	10 days resurfaced
%	mg/cm^a	mg/cm^a	mg/cm^a	mg/cm^a	mg/cm^2	mg/cm^2
0	0.4	0.4	0.4	0.00	0.00	0.01
30	0.4	0.4	0.4	0.00	0.00	0.02
40	0.4	0.4	0.4	0.00	0.01	0.02
50	0.4	0.3	0.3	0.01	0.01	0.03
ADA spec	0.7 max.	---	---	0.04 max.	---	---

* Average increase in weight per surface area of four discs 50 mm in diameter and 0.5 mm thick after immersion in H_2O at 37°C for the time specified.

† Average loss in weight per surface area of four discs, 50 mm in diameter and 0.5 mm thick after immersion in H_2O at 37°C for the time specified and dried to constant weight.

‡ Hand sanded on #240 silicon carbide paper to remove the resin-rich surface.

since the sorption values did not change appreciably after the specimens were resurfaced even after 10 days water immersion.

The water solubility values also fell well within the range allowed by American Dental Association Specification No. 12. Resurfacing and longer storage in water caused some increase in solubility, especially of the glass containing specimens. It appeared, therefore, that the slight increased solubility was perhaps due to glass dissolution.

Color stability: All of the materials complied with the color stability test in American Dental Association Specification No. 12. There was still no perceptible color change in the specimens after 72 hours under the sun lamp.

Transverse deflection and strength: The results of the transverse bend tests are listed in Table 3. This test simulated one type of stress introduced into a denture base material during function. It can be seen that the materials containing glass were much stiffer in transverse bending than the material containing no glass and the

Table 3 · Transverse deflection* and strength; repairability

Weight of glass	No. of specimens	Deflection†		Load at failure	S.D.‡	Repair material	No. of repair specimens	Load at failure of repair	Percent of original strength
		3500 Gm	5000 Gm						
%		mm	mm	Gm	Gm			Gm	
0	8	1.8	3.5	6000	0§	NuWeld	4	3300	55
30 - silane treated	8	1.3	2.6	5600	140	NuWeld	4	2900	52
						30% glass heat-cured	4	5000	89
40 - silane treated	8	1.1	2.2	6000	25	NuWeld	4	2300	39
						40% glass heat-cured	4	4500	75
50 - silane treated	8	0.9	1.7	6300	220	Not tested	-	----	--
30 - untreated	4	1.7		4500	0	Not tested	-	----	--
40 - untreated	4	1.8		4000	0	Not tested	-	----	--
ADA Spec #12		2.5 max	2.0 min 5.5 max						

* Tested according to method outlined in ADA Specification No. 12

† Deflection measured from an initial load of 1500 Gm to the load indicated

‡ Standard deviation $= \sqrt{\frac{n \cdot \Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$ where n = number of values; x = any individual value

§ Values of zero occurred because all specimens fractured in the 30 second interval between loadings during which the indicated load was maintained.

stiffness increased as the weight percent of glass was increased. The deflection of the 50% glass specimens was only 50% of the deflection occurring in 0% glass specimens at the same load and did not meet the minimum requirement of 2.0 mm at a load of 5000 Gm in American Dental Association Specification No. 12. However, it does not seem that this reduced deflection would detract from the material's suitability as a denture base.

The transverse strengths of the materials (Table 3) varied from a low of 5600 Gm for the 30% glass specimens to 6300 Gm for the 50% glass specimens.

The significance of silane treatment of the glass powder on transverse bending and strength may be seen by comparing data in Table 3. The deflection of the specimens containing glass which was not silane treated was about the same as that of specimens containing no glass. The transverse strengths of specimens containing 30% untreated glass were 80% of the

values of those made with treated glass; at the 40% glass level, they were only 67% as strong. This points out that the simple addition of fillers to the matrix may cause a deterioration of these properties. Without silane treatment, the glass particles weaken the material instead of reinforcing it.

Repairability: Dentures are often subjected to forces which cause fracture of the base material. The most common repair materials are cold-curing resins because they are quicker, easier and more economical to use, cause less warpage of the base, and do not require the patient to be without his denture for an extended period. Heat-cure repairs are less common, more difficult to use, and may cause a warpage of the base material but do yield stronger repairs. A cold-curing resin (without glass) and the heat-cured resins containing glass were evaluated on the 30 and 40% glass-containing materials by means of transverse strength tests.

As can be seen in Table 3, the heat-cure repairs, using identical materials to that from which the specimens themselves were made, had transverse strengths from 75 to 89%

of the strength of the original specimens. Those repaired with the cold-cure resin had from 39 to 52% of their original strengths. The denture base material containing no glass when repaired with the cold-cure resin, had 55% of its original strength. Therefore, when using a cold-cure repair resin there was a greater reduction in the strength of the repaired 30 and 40% glass materials as compared to repaired denture base materials containing no glass. All failures in the repair tests occurred at the interface between the base and the repair material.

Indentation: The data in Table 4 summarize the results of the indentation testing. The addition of glass resulted in a greater resistance to indentation. The indentation of 50% glass specimens was about 80% as great as that on specimens containing no glass. However, the ability to recover from the indentation was greater in the unfilled specimens (88.2%) when compared to the glass-containing specimens (80.6 to 84.2%). The net result is that the residual indentation is only slightly greater in the glass-containing specimens. Therefore, the indentation left on a denture by a piece of hard food would be about the same with all

Table 4 · Indentation tests*

Weight of glass	Dry specimens†				Wet specimens‡			
	Depth of indentation	Depth of residual indentation	Recovery after flow	S.D.§	Depth of indentation	Depth of residual indentation	Recovery after flow	S.D.§
%	mm	mm	%	%	mm	mm	%	%
0	0.085	0.010	88.2	0.7	0.090	0.011	87.7	0.5
30	0.076	0.012	84.2	0.5	0.080	0.014	82.5	1.0
40	0.072	0.013	81.9	1.3	0.075	0.014	81.3	0.3
50	0.067	0.013	80.6	0.8	0.070	0.014	80.0	0.1

* Two specimens of each material were used with 3 tests made on each specimen with a Rockwell Superficial Hardness Tester (30Y scale)

† Specimens stored 7 days at 23 ± 2°C and 50 ± 10% relative humidity

‡ Specimens stored 14 days in water at 37°C

§ Standard deviation $= \sqrt{\frac{n \cdot \Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$; where n = number of values, x = any individual value

of the materials. The 14 day storage in water had little effect on the indentation and percent recovery.

Hardness: There was no significant difference in the hardness values as determined from the Rockwell Superficial Hardness Tester using the 15W scale (Table 5). Water storage for 2 weeks at 37°C lowered the hardness values only slightly.

Density: The density of the four materials increased as the relative percentage of glass was increased. The values in Gm/cc were 1.19 for 0% specimens; 1.47 for 30% specimens; 1.58 for 40% specimens, and 1.72 for 50% specimens. Thus, a denture made from the glass-containing materials would be considerably heavier than one made from a base containing no glass and could be objectionable from a clinical standpoint.

Drop impact resistance: Fractures of denture base materials commonly occur because the dentures are dropped, thus subjecting them to impact forces. Therefore, the measurement of the resistance of denture base materials to this type of fracture is an important one. Drop impact testing was selected in this study instead of the more commonly used Izod impact test because the specimens are easier and more

Table 5 · Rockwell Superficial Hardness*

Weight of glass	Dry specimens†		Wet specimens‡	
	Hardness number	S.D.§	Hardness number	S.D.§
%				
0	78.9	1.1	76.4	0.7
30	78.3	0.6	75.6	0.5
40	78.6	0.6	76.5	0.5
50	79.1	0.3	77.9	0.6

* 15W scale; a minor load of 3 kg was applied and the dial gauge was set at 0. The major load of 15 kg was applied for 15 ± 1 second and the dial reading recorded. Two specimens of each material were used and 5 tests were made on each specimen

† Stored 7 days at 23 ± 2°C and 50 ± 10% relative humidity

‡ Stored 14 days in water at 37°C

§ Standard deviation = $\sqrt{\frac{n \cdot \Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$; where n = number of values, x = any individual value

economical to make, they do not require machining, and the specimen thickness is more representative of that which actually exists in a denture.

The results of the drop impact testing are listed in Table 6. When one considers the rather large deviations in the results, it would appear that there is little difference among the four materials as measured by this test. The reasons for the large deviations in the results are not known, but it could not be accounted for on the basis of the differences in thickness of the specimens.

Thermal expansion: The linear coefficients of thermal expansion are listed in Table 7 and represent the average of eight runs for each material. The coefficient decreases as the amount of glass in the specimens is increased. This could be expected since the coefficient of the glass is about $7.0 \times 10^{-6}/°C$ (28 to 62°C) and that of the resin is 76.0×10^{-6} (5 to 37°C). However, the decrease is not linearly proportional to the volume percent of the glass powder added to each material (calculated on an additive basis) and is greater in each case. Evidently, the glass powder acts to restrain the expansion of the resin matrix.

Table 6 · Drop impact tests

Weight of glass	Mean failure height*	Standard deviation†
%	cm	cm
0	57	11
30	57	16
40	52	14
50	50	10

* Mean height at which specimens failed when subjected to a falling steel ball 20.64 mm in diameter, weighing 35.77 Gm

mean failure height[10] $= C + \frac{d\Sigma in_i}{N} \pm \frac{1}{2}d$

† Standard deviation[10] $= 1.62\ d\left[\frac{\Sigma i^2 n_i}{N} - \left(\frac{\Sigma in_i}{N}\right)^2 + 0.029\right]$

Where C = normalized height of lowest line on which a test is recorded

d = interval between drop heights

i = interval starting at 0 for the lowest drop height at which a test is recorded and increasing by one unit

n_i = number failing or not failing at any given interval

N = number failing or not failing

Table 7 · Coefficients of linear thermal expansion

Weight of glass	Coefficient of thermal expansion*			
	5 - 37°C		37 - 70°C	
	x 10^{-6}	S.D.†	x 10^{-6}	S.D.†
%				
0	76.0	0.5	89.2	1.2
30	62.2	0.6	71.7	0.8
40	57.2	0.4	68.6	0.8
50	49.9	0.5	57.8	0.7

* Determined by 4 tests on each of 2 specimens for each material. Specimens 203 x 11.1 x 11.1 mm (8 x 7/16 x 7/16 inch)

† Standard deviation = $\sqrt{\frac{n \cdot \Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$; where n = number of values, x = any individual value

The coefficients were higher in the 37 to 70°C range for all four materials. In a previous study it was found that resin denture base materials containing 14 and 21% by weight of glass fibers had lower coefficients at the higher temperature ranges presumably because the fibers restrained the expansion more at higher ranges than at the lower ranges.[11] This was not the case with the silane-treated glass powders (Table 7). One of the specimens, tested again after storage in water for 23 days, had a coefficient equal to those obtained after seven days storage in water.

The importance of the differences in thermal expansion on the fit of clinical dentures would not be significant. In a previous study, neither the patient nor the dentist could detect disparities in the fit of dentures having such small magnitudes of differences as would be caused by the differences in thermal expansions of these materials.[13]

The importance of the lower coefficients of thermal expansion may be significant in attempting to bond porcelain denture teeth to the resin-glass composite denture base by means of appropriate silane coupling agents. Results will be presented in a subsequent report.[3]

Resistance to deformation: The resistance to deformation from different types of applied forces is seen in Table 8 which lists the values for various moduli for each material. The modulus with each type of loading can be seen to increase twith increasing amounts of glass. The effect of storage in water for 21 days appears to be negligible in the case of Young's modulus as determined by the sonic method.

Whether such added resistance to deformation is an advantage or is, in fact, desirable is not known. It is believed by some dentists that denture bases should be somewhat flexible since they might cause less injury to the underlying oral structures. Added stiffness might be a factor in attempts to bond silane treated porcelain teeth to the denture base.

Table 8 · Summary of modulus values

Method	Modulus	Conditioning	Weight percent of glass in resin			
			0	30	40	50
			MN/m^2*	MN/m^2*	MN/m^2*	MN/m^2*
Sonic†	E_s-Young's	Dry‡	5310	7520	8830	10,900
		Wet§	5100	7240	8690	9580
Transverse bending‖	E_b-flexural	Dry‡	2280	3030	3450	4270
Ultrasonic#	E-Young's	Dry‡	5580	7650	8960	10,200
Ultrasonic#	G-shear	Dry‡	2070	2960	3450	3920
Ultrasonic#	K-bulk	Dry‡	5580	6690	7520	8140

* To convert Newtons per square meter to pounds per square inch, divide by 6.894×10^3
† Average of 6 specimens of each material
‡ Stored 7 - 14 days at 23 ± 2°C and 50 ± 10% relative humidity
§ Stored 21 days in water at 23 ± 2°C
‖ Obtained from data on transverse bend tests
Average of 4 specimens of each material

Glass solubility: The 24-hour water solubilities of the glass powders both silane treated and as received were 0.24% and 0.30% respectively and that of the powdered porcelain teeth was 0.06%. The relative inertness of porcelain teeth in the oral environment has been well established by long periods of clinical usage and points out the severe nature of this solubility test. The solubility of the silane treated glass powders for periods up to five days as shown in Figure 3 was 0.55%.

The results of the spectrochemical analysis of the 24 hour residues are listed in Table 9. The major constituents found in the residue from the reinforcing glass powder were aluminum, calcium, silicon, and barium. The origin of the calcium is uncertain since it was not in the nominal batch composition. It may be from impurities present in the original glass or from the method of sampling the residues that remained in the glass weighing bottles. The discrepancies in the amounts of certain elements such as boron and aluminum in columns 1 and 2 in Table 9 is probably attributable to experimental error.

Table 9 · Results of the spectrochemical analysis of the residues obtained from the glass and porcelain 24 hr solubility tests

Element	Materials Tested		
	Silane Treated Glass	Untreated Glass	Porcelain Teeth
	Composition by Weight		
	%	%	
Ag	-	-	t
Al	1-10	.1-1	m
As	-	-	-
Au	-	-	-
B	.1-1	1-10	M
Ba	>10	>10	?
Be	-	-	-
Bi	-	-	-
Ca	1-10	1-10	m
Cd	-	-	-
Ce	-	-	-
Co	?	?	-
Cr	.001-.01	?	?
Cu	.01-.1	.01-.1	m
Fe	.01-.1	.001-.01	m
Ga	-	-	-
Ge	-	-	-
Hf	-	-	-
Hg	-	-	-
In	-	-	-
Ir	-	-	-
K			M
La	-	-	
Mg	.1-1	.1-1	m
Mn	.001-.01	.001-.01	-
Mo	-	-	-
Na	.1-1	.1-1	M
Nb	-	-	-
Ni	.01-.1	?	-
Os	-	-	-
P	-	-	-
Pb	-	-	-
Pd	-	-	-
Pt	-	-	-
Rh	-	-	-
Ru	-	-	-
Sb	-	-	-
Sc	-	-	-
Si	1-10	1-10	M
Sn	-	-	-
Sr	.1-1	.1-1	-
Ta	-	-	-
Te	-	-	-
Th	-	-	-
Ti	?	?	-
Tl	-	-	-
U	-	-	-
V	-	-	-
W	-	-	-
Y	-	-	-
Zn	.1-1	.1-1	-
Zr	-	-	-

- Not detected

t Trace noted

m Minor constituent

M Major constituent

? Detection uncertain

Aluminum, calcium, and silicon are relatively innocuous elements and would present no problem of toxicity. However, water soluble salts of barium, notably $BaCl_2$ and $BaNO_3$ are extremely toxic. The lethal dose of the chloride is not known but has been reported to be as low as 0.8 to 0.9 Gm. The toxicity of BaF_2 may be about the same as that of NaF in man.[14,15] Whether enough soluble barium salts could be absorbed from the denture materials to present a toxicity hazard is not known. However, the water solubility of the radiopaque composite denture base material is very low (Table 2).

Summary and conclusions

Physical properties were determined for radiopaque composite denture base materials composed essentially of poly(methyl methacrylate) as the matrix and 30, 40, and 50% by weight of a silane-treated glass powder as the reinforcing filler. The poly(methyl methacrylate) without glass was included for comparison.

All of the materials complied with the requirements of American Dental Association Specification No. 12 for Denture Base Polymer except that the transverse bend specimens containing 50% glass were too stiff for the minimum deflection requirement at a 5000 Gm load.

There was little or no difference among the four materials in hardness, indentation and recovery, water sorption, and color stability. The solubility of the glass-containing specimens was slightly greater than that of the specimens containing no glass. The addition of glass extended the time required to reach the packing stage.

The addition of 30% glass to the resin caused a slight reduction in transverse strength while the addition of 50% glass slightly increased the transverse strength; addition of 40% glass yielded specimens having transverse strength equal to that of the resin with no glass. The strength of specimens made with glass that had not been treated with silane was significantly lower.

The materials were repairable by commonly used methods. The use of heat-cure repairs gave higher strengths than cold-cure repairs.

The density of the glass-containing materials was significantly greater and would result in heavier dentures that might be objectionable clinically.

The drop impact resistance as measured by a falling steel ball indicates that there was little difference among the four compositions.

The coefficients of linear thermal expansion were decreased by addition of the glass but the decrease would not be large enough to visibly affect the clinical fit of dentures.

Young's, bulk, shear, and flexural moduli were all increased as the amount of glass was increased. This would result in dentures having a greater resistance to deformation from the various types of stress.

The 24-hour water solubility of the glass powder was 0.24% and about 4 times that of powdered porcelain teeth. The major soluble constituents of the glass powder were barium, calcium, aluminum, and silicon. Solubility of the silane-treated glass powder increased to about 0.55% after 5 days. However, the water solubility of the radiopaque composite denture base material (resin plus radiopaque, silane-treated, powdered glass) was very low.

Within the foregoing limitations it is believed that an acceptable radiopaque denture base composite material has been described.

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Legends

Fig 1: Apparatus for measuring drop impact resistance. A, channel for directing the falling ball; B, ball catcher; C, specimen holder; D, specimen; E, steel ball, 20.64 mm in diameter.

Fig 2: Higher magnification of the specimen holder seen in Fig. 1. Distance AB = 3.43 mm; BC = 3.17 mm; AD = 38.1 mm.

Fig 3: Cumulative percent glass dissolved in a mixture containing 10% by weight of the silane treated glass and water.

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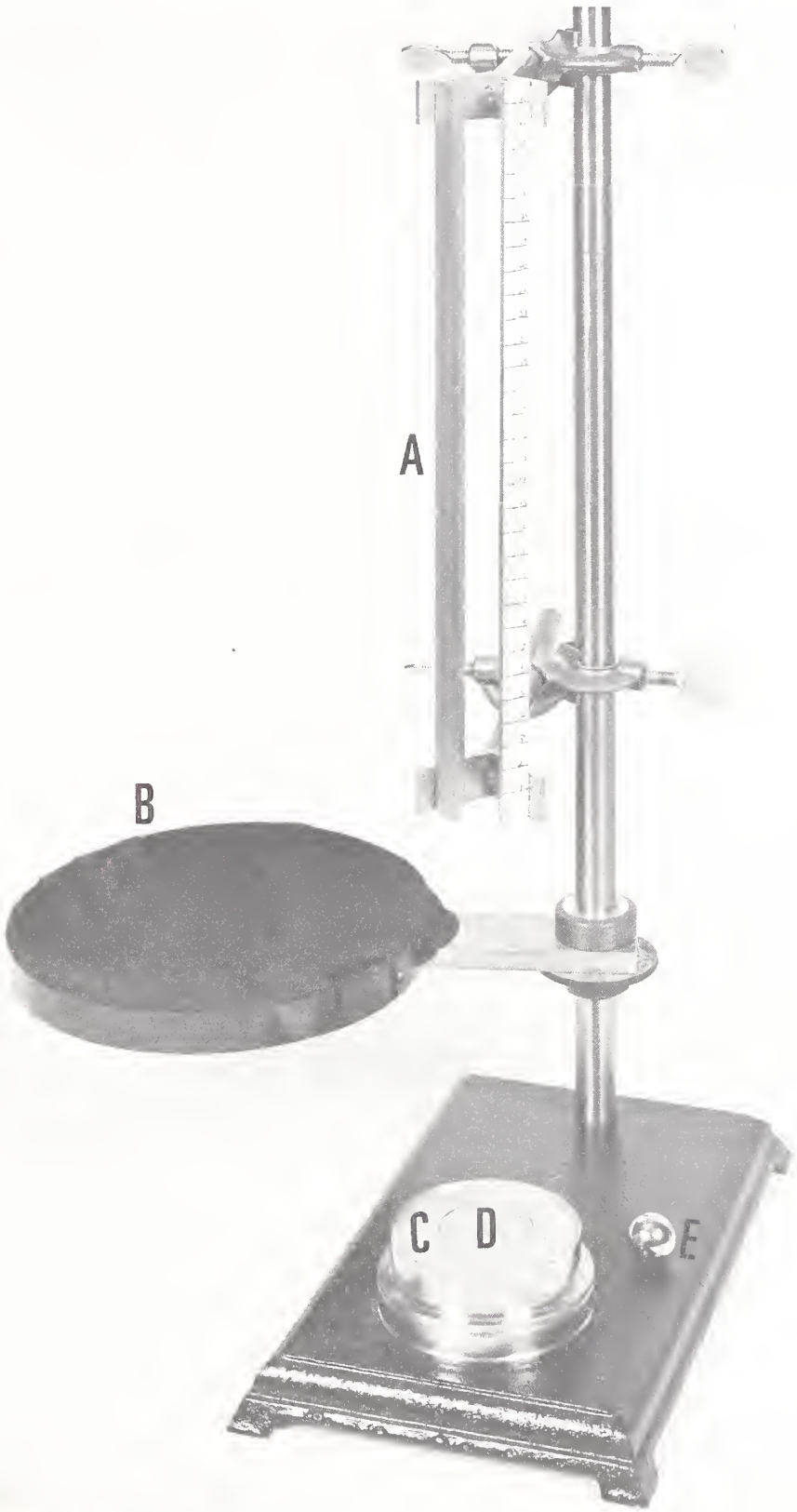

fig 1

fig 2

fig 3