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Effect of Methacrylated Hyperbranched Polymers on the Fracture Properties of Denture Base Materials

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Hyperbranched polymers have the potential to reinforce crosslinked polymeric materials. In this study several concentrations of a methacrylated hyperbranched polyether are formulated with a denture base resin and cured. The denture base resin is a polymethyl methacrylate based resin. The fracture toughness of each of these concentrations was measured and compared to control. Only the 1% concentration had a significantly higher fracture toughness compared to the control. This is similar to other results that are found in the literature.

Keywords dental materials, denture base materials, polymethyl methacrylate, hyperbranched polymers, fracture toughness

Introduction

Polymethyl methacrylate resin (PMMA) was introduced as a material for removable dentures bases in 1935 (1) and remains the most widely used denture material. Due to its superior physical, biological and esthetic properties, PMMA has replaced previous denture materials such as vulcanite, nitrocellulose, phenol formaldehyde, vinyl plastics and porcelain (2). Pure PMMA resin is a colorless, transparent solid, which may be tinted to provide any shade and degree of translucency to achieve proper esthetics for dental applications (3).

Despite PMMA's wide use as a main component of denture bases, this material will sometimes fracture during clinical use due to their low resistance to impact, flexural or fatigue stresses (4). Poor fabrication technique (5) can also play a role in decreased clinical longevity.

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The susceptibility of denture base materials to fracture demonstrates the need to improve to increase clinical longevity. There are two approaches, which can be used to improve the strength of PMMA. The first approach is adding a polyfunctional crosslinking agent such as polyethylene glycol dimethacrylate (6). The second approach is to reinforce denture base polymers by incorporating a rubber phase (7, 8), metal, metal wire (9, 10) or fibers (11).

Strengthening by fiber reinforcement is based on the principle that a relatively soft ductile polymer matrix is fully capable of transferring an applied load to the fibers via shear forces at the interface. The fibers will be the main load bearing constituents while the matrix forms a continuous phase to surround and hold the fibers in place (12).

Several different fibers have been explored to reinforce denture base materials. Investigations have shown that carbon fibers produced a significant increase in the flexural strength of polymers (13, 14). However, their black color limits their use in esthetic dental applications. Transverse strength was not improved by polyethylene fibers in the absence of surface treatment due to poor adhesion between the fibers and the polymer matrix (15). When plasma treated polyethylene fibers were used, a significant increase in strength was shown (16). Silanized glass fibers are promising due to their good adhesion to the polymer matrix, high esthetic quality and increased strength of the resulting composite (17, 18).

Hyperbranched polymers have been successfully used to reinforce crosslinked dental resins (19–21). Increases in flexural strength and a decrease in polymerization shrinkage was observed. Hyperbranched polymers have a more globular structure than linear polymers (Figure 1) imparting several properties useful in crosslinked systems. Hyperbranched polymers have lower viscosity per molecular weight compared to linear polymers (22). This allows for the reinforcement of polymeric resin without significantly increasing the viscosity. Large numbers of surface functional groups also result from its globular structure. This allows the attachment of functional or polymerizable groups to the hyperbranched polymer.

In work discussed above, hyperbranched polyesters from Perstorp Corporation, (Perstorp, Sweden) were used. This project uses a polyether based hyperbranched polymer Boltorn EO3000 from Perstorp Corporation because it is expected that the ether linkages will be more hydrolytically stable than the ester linkages. The EO3000 was subsequently methacrylated as part of this project.

The fracture mechanics approach is considered a more reliable indicator of the performance of brittle materials (23, 24). Fracture toughness is the ability of a material to resist crack propagation and may more accurately determine the likelihood of fracture of PMMA in clinical practice (25).

The purpose of this study was to compare the effect of a different concentration of the methacrylated hyperbranched polymer (MA-HB) on the fracture toughness and water sorption of PMMA based denture base materials. Our hypothesis is that MA-HB will increase the fracture toughness and decrease the water sorption of denture base materials.

Experimental

This study involves the synthesis of MA-HB using Boltorn EO3000 as a starting material. The MA-HB will be formulated with a denture base resin in four different concentrations (0, 1, 5, and 10% by weight). The fracture toughness, water sorption and water solubility of each formulation will be evaluated.

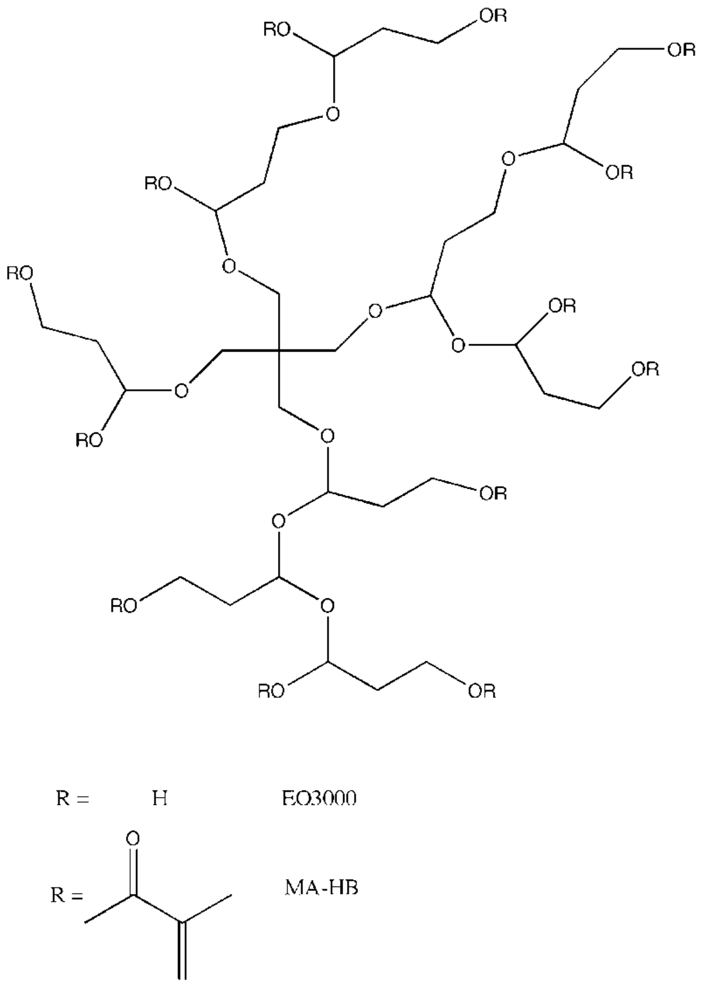

Figure 1. Structure of EO3000 and MA-HB. Note that both materials have a large number of structural isomers and this figure is only one possible representation.

Synthesis of MA-HB

Materials. Boltorn E03000 was supplied by Perstorp Coporation, methacrylic anhydride (MAA), dimethyl amino pyridine (DMAP), 4-methoxy phenol (MEHQ) were purchased from Aldrich Chemical and used as received. Solvents were of reagent grade and used as provided. The denture base material used was Lucitone Fastpor, Dentsply International (York, PA).

Procedure. 10 g of EO3000, 7.7 g of MAA, 0.0611 g of DMAP, and 0.031 g of MEHQ were dissolved in 50 ml of tetrahydrofuran (THF) and heated at 60°C in an oil bath under inert atmosphere. After 12 h, the polymer was purified by removing the THF under reduced pressure, dissolving the polymer in ethyl acetate. The organic solution was washed with 5% NaOH to remove any excess acrylic acid. The ethyl acetate was removed under reduced pressure to yield the methacrylated hyperbranched polymer.

For the fracture toughness test, a total of 20 compact test specimens were fabricated following ASTM no E 399-83 (26) recommendations. Specimens were divided according to the MA-HB concentration in four groups (0%, 1%, 5%, and 10%). Each specimen was in the form of a double cantilever beam, with a slot that originated from the center of one edge extending along the block's center line to a 60 degree terminal apex located slightly beyond the mid point of the block. Two loading holes pierced the block (23).

A specially designed stainless steel mold (Figure 2) was used to fabricate specimens in this study. The design of the assembled mold provided three triangular ports, which allowed the escape of excess resin during mold assembly and exposure to pressure during polymerization.

PMMA control (0% MA-HB) specimens were fabricated at room temperature by mixing 1.53 g polymer and 1 g monomer in a clean glass jar with a stainless steel spatula for 60 sec. When the mix reaches the dough stage, it was packed into the mold cavity slowly to avoid entrapping of air, then the mold was assembled, placed in a hand press and compressed to allow the material to completely flow into the mold then allowed to cure under 20 PSI in a pressure container for 20 min. The detail of the specimen preparation for the reinforced groups was similar except that MA-HB was added with different concentration (0%, 1%, 5%, and 10% by wt).

After the resin had completely set, the specimens were separated from the mold and the flash removed using a razor blade. The specimens were examined for any voids and any defective specimens were discarded. Specimens were stored in 37°C water for 24 h before testing.

A pre-crack was placed in the compact test specimens by putting a sharp scalpel at the end of the slot and hand pressure applied. Measurements of the dimensional parameters (a, W, b) for each specimen were recorded using a measuring microscope (Nikon Measurescope Model MM-11, Nikon Corporation, Tokyo, Japan).

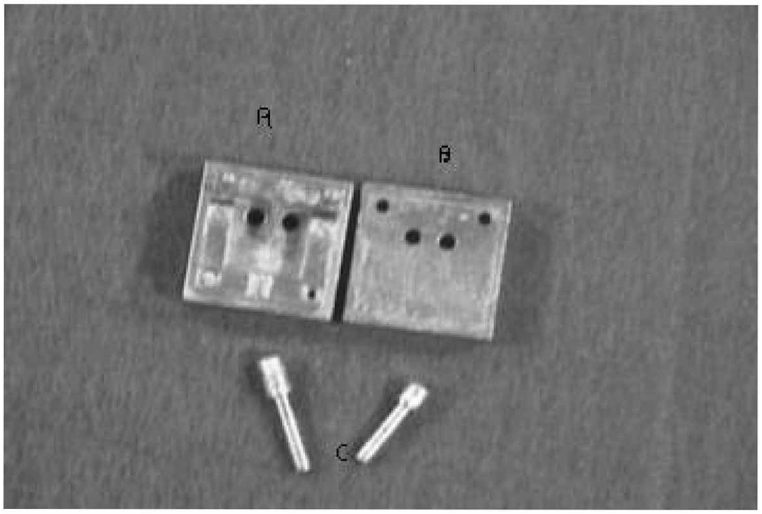

Figure 2. A photograph representing the mold to produce the compact test specimens. A: Base containing the mold cavity B: Cover, which fit over the base C-Two circular rods.

The specimens were tested in tension in a universal-testing machine (Instron Corp. 4204, Canton, MA) with the direction of the force perpendicular to the plane of the performed crack. Each specimen was held in a specially designed tension device in the machine, and tension force was applied with a crosshead speed of 5 mm/min.

The peak force in Newton, which caused fracture of the specimens was recorded and used to calculate the fracture toughness in $\mathrm{MPa \cdot m^{1/2}}$ from the following equation:

$$K_{1c} = pc/bw^{1/2}\ F(a/w)$$

where:

pc is the maximum load prior to crack advance in (KN)
b is the average specimen thickness in (cm)
w is the width of the specimen in (cm)

and

$$F(a/w) = \frac{(2 + a/w)\ (0.886 + 4.64a/w - 13.32a^2/w^2 + 14.72a^3/w^3 - 5.6a^4/w^4)}{(1 - a/w)^{1/2}}$$

where (a) = crack length in (cm).

For the water sorption test, the recommendations (R) of the ISO14077 (27) was used as a guide. A total of 20 disc-shaped polymer-based resin specimens were fabricated using specially prepared stainless steel molds. The unreinforced specimens were prepared by packing a mixture of 1 ml of PMMA monomer and 1.53 grams of polymer powder in the mold to a slight excess avoiding air bubbles, then covered with a glass cover plate.

Once the material was polymerized, the specimen was separated from the mold, polished on both sides using a fine sand paper to a thickness of (1.0 ± 0.2) mm. The same techniques were used to fabricate PMMA specimens reinforced with a different concentration of hyperbranched polymer (1%, 5%, and 10% by weight).

The diameter and thickness in the center and at four points at the periphery of each test specimen was measured to an accuracy of ±0.01 mm using digital calipers (description) then the volume (V) was determined using the formula:

$$\pi r^2 h$$

where: r = diameter, h = height.

For the purpose of drying, the specimens were stored in a desiccator at (37 ± 1)°C for 23 h, then stored in a second desiccator for 1 h at (23 ± 1)°C. Each specimen was weighed to an accuracy of ±0.2 mg. and the drying procedure was repeated until the loss in weight become less than 0.2 mg within 24 h (m_1).

All test specimens were stored in 20 ml water at (37 ± 1)°C for 7 days. Separately each test specimen was removed, washed with water and dabbed with blotting paper until free from visible moisture. Then waved in air for 15 sec and weighed 1 min after removal from the water (m_2).

After weighing, the test specimens were reconditioned in the desiccator to a constant mass until the loss is less than 0.2 mg within 7 days using the cycle described above. This is m_3.

Water absorption was calculated using the following formula:

$$(m_2 - m_3)/V$$

Table 1
Mean values, standard deviations and Tukey's standardized range test (HSD) of the fracture toughness of PMMA with different MA-HB concentrations

MA-HB concentration	Mean fracture toughness ($MPa \cdot m^{1/2}$)	Standard deviation	Tukey grouping[a]
1%	1.81	0.11	A
0%	1.45	0.06	B
5%	1.44	0.07	B
10%	1.17	0.17	C

[a] Groups with different letter are significantly different.

while the water solubility is calculated from the equation:

$$(m_1 - m_3)/V$$

The mean and standard deviation values for each group were calculated. The data was analyzed for difference by using one-way ANOVA followed by Tukey-Kramer HSD (honestly significant difference) using a confidence level of 0.05 to determine the mean differences.

Results and Discussion

The results of this study are elaborated in Table 1. The one-way ANOVA showed a statistically significant difference between the four groups ($P < 0.0001$). The post-hoc test showed that the addition of 1% of MA-HB to the polymethyl methacrylate resin significantly increased the fracture toughness, whereas increasing the concentration of MA-HB to 10% significantly decreased the fracture toughness (Table 1).

While all the 20 specimens had water absorption values well within the specified limit of $32\,g/mm^3$, there was no significant difference between the mean water absorption among the four groups. Water solubility tests showed that all the specimens had solubility values less than the specified $5\,g/mm^3$ and no significant difference was found between the means of the four groups (Tables 2 and 3).

Table 2
Mean values, standard deviations and Tukey's standardized range test (HSD) of water absorption of PMMA with different MA-HB concentrations

MA-HB concentration	Mean water absorption ($\mu g/mm^3$)[a]	Standard deviation	Tukey grouping[b]
0%	22.27	1.49	A
1%	21.34	1.62	A
5%	19.78	1.02	A
10%	20.56	1.3	A

[a] Differences among the means were significantly different ($P < 0.0001$).
[b] Groups with different letter are significantly different.

Table 3
Mean values, standard deviations and Tukey's standardized range test (HSD) of water solubility of PMMA with different MA-HB concentrations

MA-HB concentration	Mean water solubility ($\mu g/mm^3$)[a]	Standard deviation	Tukey grouping[b]
0%	1.55	0.86	A
1%	2.51	1.00	A
5%	2.12	0.96	A
10%	2.24	0.92	A

[a] Differences among the means were significantly different ($P < 0.0001$).
[b] Groups with different letter are significantly different.

The hypothesis of this study was that the addition of MA-HB to the PMMA denture resin would increase the fracture toughness of the denture base material. The results of the fracture toughness test showed that the use of 1% MA-HB supported this hypothesis. However, as the amount of MA-HB concentration increased there was a decrease in the fracture toughness values of the PMMA. One possible explanation for this is that the hyperbranched polymer will make the resin more ductile, which in low concentrations could increase the fracture toughness of the cured resin. However, at higher concentrations the cured resin becomes more ductile causing a decrease in the fracture toughness.

Previous studies have shown that functionalized hyperbranched polymers can improve the properties of several polymer systems. Epoxy systems have been studied by Ratna (28) and Mezzenga (29). Methacrylated hyperbranched polyesters have been used to reinforce dental resins based on the BisGMA-TEGDMA system (19–21). Flexural, compressive and diametral strength were improved in these systems, however, beyond loading levels of 10%, mechanical properties begin to decrease. Similar results were found by Dodiuk-Kenig (30) who found that the optimal concentrations of a hyperbranched polymer in a composite system was about 0.1–0.3%. At higher concentrations the properties were similar or lower than the control. Future work will involve optimizing hyperbranched levels and exploring concentrations below 1%.

Conclusions

The results of the water sorption and solubility studies was unexpected because the hyperbranched polymer is hydrophilic. The unmodified hyperbranched polymer is soluble in water alcohol mixtures. It would be expected that the water sorption would increase as the MA-HB concentration increased because the ethylene oxide repeat units of the hyperbranched polymer are hydrophilic. This could be due to the increased crosslinking density because the MA-HB has such a high density of methacrylate groups.

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References

1. Phillips, R.W. (1982) *Skinner's Science of Dental Materials*; Saunders: Philadelphia, 300.
2. Woelfel, J.B. (1971) *Dent. Clinc. North Am.*, 15 (1): 67–79.
3. Craig, R.G. and Powers, J.M. (2002) *Restorative Dental Materials*; Mosby, Inc: St. Louis; Vol. 11, 501.
4. Abou-Tabl, Z.M., Tidy, D.C., Combe, E.C., and Grant, A.A. (1983) *J. Biomed. Mater. Res.*, 17 (5): 885–898.
5. Schneider, R.L. (1985) *J. Prosth. Dent.*, 54 (6): 809–814.
6. Kanie, T., Fujii, K., Arikawa, H., and Inoue, K. (2000) *Dent. Mater.*, 16 (2): 150–158.
7. Knott, N.J. (1989) *Quintessence Int.*, 20 (5): 341–343.
8. Stafford, G.D., Bates, J.F., Huggett, R., and Handley, R.W. (1980) *J. Dent.*, 8 (4): 292–306.
9. Ruffino, A.R. (1985) *J. Prosthet. Dent.*, 54 (1): 75–78.
10. Teraoka, F., Nakagawa, M., and Takahashi, J. (2001) *J. Oral Rehab.*, 28 (10): 937–942.
11. Goldberg, A.J. and Burstone, C.J. (1992) *Dent. Mater.*, 8 (3): 197–202.
12. Freilich, M.A., Meiers, J.C., Duncan, J.P., and Goldberg, A.J. (2000) Quintessence Publishing: Illinois, 9–23.
13. Schreiber, C.K. (1971) *Br. Dent. J.*, 130 (1): 29–30.
14. Yazdanie, N. and Mahood, M.J. (1985) *Prosth. Dent.*, 54 (4): 543–547.
15. Vallittu, P.K. (1997) *Dent. Mater.*, 13 (6): 381–382.
16. Ramos, V., Jr., Runyan, D.A., and Christensen, L.C. (1996) *J. Prosth. Dent.*, 76 (1): 94–96.
17. Aydin, C., Yilmaz, H., and Caglar, A. (2002) *Quintessence Int.*, 33 (6): 457–463.
18. Solnit, G.S. (1991) *J. Prosth. Dent.*, 66 (3): 310–314.
19. Gao, F., Schricker, S.R., Tong, Y., and Culbertson, B.M. (2002) *J. Macromol. Sci. Pure and Appl. Chem.*, A39 (4): 267–286.
20. Wan, Q., Schricker, S.R., and Culbertson, B.M. (2000) *J. Macromol. Sci. Pure and Appl. Chem.*, A37 (11): 1317–1331.
21. Wan, Q., Schricker, S.R., and Culbertson, B.M. (2000) *J. Macromol. Sci. Pure and Appl. Chem.*, A37 (11): 1301–1315.
22. Frechet, J.M.J. and Hawker, C.J. (1995) *React. Funct. Poly.*, 26 (1–3): 127–136.
23. Gegauff, A.G. and Pryor, H.G. (1987) *J. Prosthet. Dent.*, 58 (1): 23–29.
24. Kovarik, R.E. and Muncy, M.V. (1995) *Am. J. Dent.*, 8: 145–148.
25. Craig, R.G. and Powers, J.M. (2002) *Restorative Dental Materials*; Mosby, Inc: St. Louis; Vol. 11, 57–74.
26. ASTM Standard E-399-83 (1992) Standardized test method for plane-strain fracture toughness of metallic materials. In *1992 Annual Book of ASTM*; 676–706.
27. ISO10477. (1992) *Dentistry-Polymer Based Crown and Bridge Materials*; International Organization for Standardization: Geneva, Switzerland, 3–6.
28. Ratna, D., Varley, R., Raman, R.K.S., and Simon, G.P. (2003) *J. Mater. Sci.*, 38 (1): 147–154.
29. Mezzenga, R. and Manson, J.A.E. (2001) *J. Mater. Sci.*, 36 (20): 4883–4891.
30. Dodiuk-Kenig, H., Lizenboim, K., Eppelbaum, I., Zalsman, B., and Kenig, S. (2004) *J. Adhes. Sci. Tech.*, 18 (15–16): 1723–1737.