Effect of PMMA filler particles addition on the physical properties of resin composite

Yoshiko KONDO¹, Tomohiro TAKAGAKI¹, Makoto OKUDA¹, Masaomi IKEDA², Yoshinori KADOMA³, Junichi YAMAUCHI⁴, Koichi OKADA⁴, Alireza SADR⁵, Toru NIKAI¹ and Junji TAGAMI^{1,5}

¹Cariology and Operative Dentistry, Department of Restorative Sciences, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University, 5-45 Yushima 1-chome, Bunkyo-ku, Tokyo 113-8549, Japan.

²Faculty of Dentistry, School for Dental Technology, Tokyo Medical and Dental University, 5-45 Yushima 1-chome, Bunkyo-ku, Tokyo 113-8549, Japan.

³Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 3-10 Kanda-Surugadai 2-chome, Chiyoda-ku, Tokyo 101-0062, Japan.

⁴Kuraray Medical Inc, 2045-1 Sakazu, Kurashiki, Okayama 710-8691, Japan.

⁵Global Center of Excellence Program, Tokyo Medical and Dental University, 5-45 Yushima 1-chome, Bunkyo-ku, Tokyo 113-8549, Japan.

Corresponding author, Tomohiro TAKAGAKI; E-mail: takagaki.ope@tmd.ac.jp

The aim of this study was to evaluate the effect of additional polymethyl methacrylate (PMMA) fillers on the physical properties of experimental resin composites. PMMA particles ($d=30\ \mu\text{m}$) were added to an experimental methacrylate-based resin composite in five concentrations of 0, 2.0, 4.8, 9.1, and 23.1 wt%. Properties such as contact angle, water sorption and compressive strength were measured and the fractured specimens were observed with a scanning electron microscope. The results showed that a small amount (2 wt%) of additional PMMA fillers inhibited the crack propagation and enhanced compressive strengths of the resin composites, without a significant change in water contact angle of surface or increased water sorption. However, in higher portions, the mechanical properties were not improved as a debonding at the interface between untreated fillers and the matrix, or failure within the organic filler could reduce the compressive yield strength of the composite.

Keywords: PMMA, Resin composite, Filler

INTRODUCTION

Recent advances in resinous restorative materials, as well as an increased demand for esthetics, have stimulated a great increase in the use of resin-based composite in dental restorations^{1,2}.

Methacrylate resins are found in a variety of dental materials including denture base polymers, synthetic teeth, provisional and definitive fixed prostheses, sealants, dentin adhesives, luting agents for crowns and fixed partial dentures, and tooth-colored restorative materials. A number of properties have been introduced as determinant factors of the final success of these materials; mechanical properties³⁻⁶, handling⁷, water sorption and biofilm adherence and esthetics^{8,9} have been among the most investigated factors.

Dental composites have been demonstrating continual improvement; however, the resin technology for dentistry is far from perfect. For example, it is known that the stress induced by excessive polymerization shrinkage of resin composite in a directly restored cavity, may result in interfacial gap formation and microleakage at the margins, which will eventually lead to secondary caries. In an attempt to resolve the problem, Weinmann *et al.*¹⁰ reported that a silorane-based composite (3M ESPE, St. Paul MN, USA), which polymerized by a cationic ring opening process, exhibited the lowest polymerization shrinkage and stress.

Another example for shortcomings of the current dental resin is the attachment of bacterial biofilms on the surface. In an attempt to improve surface resistance of composite against biofilm formation, Gyo *et al.*¹¹ developed an experimental methacrylate-based resin composite with incorporated polytetrafluoroethylene (PTFE) particles. In their experiment, the hydrophobicity of the resin composite was improved by incorporation of PTFE fillers; however, surface resistance against biofilm formation was not improved.

PMMA has been widely used in dentistry¹². It is the most commonly used material in denture fabrication, and adequately satisfies the esthetic demands. However, a few problems remain to be solved for this material. One disadvantage of the PMMA-based resins is water sorption. Denture base resin made of PMMA takes up saliva and water, which percolate over time toward the inside of the denture causing the mechanical properties of the material to decrease and the roughness of the surface to increase producing an unpleasant smell^{13,14}. Meanwhile PMMA denture based has several advantages. For example, processing techniques are easy, special equipment is not necessary, repair and adjustment are easy.

To increase mechanical properties of resin composite, a conventional approach has been the addition of high concentration of filler particles, such as glass and silica in the composite. Moreover, the adhesion between resin matrix and filler, and thus the final mechanical properties of the composite, is

improved by silane treatment. Nevertheless, fillers in low concentrations have also been effective in improvement of the mechanical properties. It was found that 2 vol% admixtures of mineral oxide or glass particles in a PMMA resin matrix significantly improved the mechanical properties of the acrylic resin¹⁵⁾.

In contrast to the conventional inorganic filler, organic fillers are a further new approach in the filler technology. Atsuta *et al.*¹⁶⁾ evaluated the mechanical strength of networks formed from mixtures of PMMA powder and ethylene glycol dimethacrylate (EGDM) with azobisisobutyronitrile as a chemical initiator over the widest practicable range of compositions. It was discovered that doping with as little as 1% PMMA significantly increased flexural strength without causing turbidity. However, the addition of soft polymer particles into a resin matrix has not been adequately investigated to date.

Therefore, the aim of this study was to evaluate mechanical properties of experimental resin-based materials containing PMMA.

MATERIALS AND METHODS

Materials used in this study

Compositions of the experimental resin composites are listed in Table 1. The PMMA filler particles (Fujikura Kasei, Tokyo, Japan) used in this study were spherical with average size of 30 μm in diameter. The composition of the control group without the PMMA filler particles (PM0) was a mixture of multifunctional methacrylates, photo-initiator, and micro-filler. Either 2.0, 4.8, 9.1, or 23.1 wt% of the PMMA filler particles were incorporated into the PM0 (PM2, PM5, PM10, and PM30).

Contact angle measurement

The experimental resin composites (PM0, PM2, PM5, PM10, and PM30) were dispensed from each syringe onto a glass plate. Composite plates (approximately 2.0×2.0×1.5 mm) were prepared by pressing another clean glass plate on top of the dispensed resin, and light-curing by a visible light curing unit (Optilux 501; Sybron Kerr Corp., Orange, CA, USA) from the top and bottom sides at 600 mW/cm² for 40 sec each. The

surface of the sample was then ground flat using #600-grit SiC paper under running water. The specimens were then kept in a desiccators (DRY) or in distilled water (WET) for 7 days. The surface was gently air-dried prior to contact angle measurements. The relative hydrophobicity of the material surfaces was determined by measuring the contact angle using a drop shape analysis system (FTÅ32 First Ten Angstroms, Portsmouth, UK); the image of a drop was detected with a CCD camera, and the captured images were subsequently analyzed on a personal computer. Deionized water (3.0 μL) was used as the test fluid for contact angle measurements. The surface of the drop was constantly monitored and the contact angle was measured just after 20 sec, when the droplet was stabilized. The contact angle was defined as the angle at which the liquid interface met the solid surface of the composite block. The number of these specimens was 5 for each group.

Water sorption measurement

The experimental resin composites were inserted into a stainless steel mold (4 mm diameter, 6 mm height), pressed with a plastic strip, and light-cured by using a visible light curing unit (Optilux 501; Sybron Kerr Corp. West Collins Orange, CA, USA) from the top and bottom sides for 40 sec each. The surface of each sample was then ground flat using #600-grit SiC paper under running water, and the samples were kept in a desiccator for 1 week and then stored in 37°C distilled water. Water sorption was then measured at 1, 2, 3, 5, 7, 14, 21, 30, and 60 days of storage in water.

Water sorption was calculated from the following formula;

$$\alpha = 100(W_n - W_0) / W_0$$

where α is water sorption (%), W_n is weight of specimen at each measurement period (in mg) and W_0 is weight of specimen just before storing in 37°C distilled water (in mg). The number of these specimens was 10 for each group.

Compressive strength measurement

Experimental resin composite blocks (PM0, PM2, PM5, PM10 and PM30) were fabricated in the same manner

Table 1 Experimental resin composites used in this study

Code	Lot No.	Composition
PM0	MH-101-12	97 unit: multifunctional methacrylates, 3 unit: photo-initiator, 20 unit: micro-filler
PM2	MH-101-12	100 unit: PM0+2 unit: PMMA [2.0 wt% PMMA]
PM5	MH-101-12	100 unit: PM0+5 unit: PMMA [4.8 wt% PMMA]
PM10	MH-101-12	100 unit: PM0+10 unit: PMMA [9.1 wt% PMMA]
PM30	MH-101-12	100 unit: PM0+30 unit: PMMA [23.1 wt% PMMA]

Unit: Parts by weight

as described for the water sorption measurement. After polishing, the specimens were stored in a desiccator (DRY) or in distilled water (WET) for 7 days. Compressive strengths were measured using a universal testing machine (Autograph AGS-1000A, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min. The number of these specimens was 10 for each group.

The fractured surface of specimens after the compressive strength measurements were gold sputter-coated and observed with a scanning electron microscope (JSM-5310LV, JEOL, Tokyo, Japan).

Statistical analysis

The data were statistically analyzed using the Statistical Package for the Medical Science (SPSS Ver.11 for Windows, SPSS Inc., Chicago, IL, USA). The data for contact angles were analyzed by two-way analysis of variance (ANOVA) and Tukey's HSD at 95% level of confidence. The data for water sorption were analyzed by two-way analysis of variance (ANOVA), Tukey's HSD or Dunnett T3 at 95% level of confidence. The data for compressive strength were analyzed by two-way analysis of variance (ANOVA) and Dunnett T3 at 95% level of confidence. For the two-way analyses, the two factors examined were the moisture condition or water storage and the PMMA content.

RESULTS

Contact angle measurement

Figure 1 shows some examples of surface contact angle measurement in this study (1a: PM0, 1b: PM2, 1c: PM30). The results of contact angle measurement of the materials surface are summarized in Table 2. Two-way ANOVA showed significant difference between DRY and WET groups ($p < 0.05$); the PMMA composition ratio significantly affected the contact angle ($p < 0.05$). PM0 and PM2 showed significantly smaller contact angles compared to other groups ($p < 0.05$). The contact angles of the surfaces gradually increased from PM0 to PM30 in both the DRY and WET groups.

Water sorption measurement

The results of water sorption measurement of the materials are summarized in Figure 2. One day after immersion, there was no significant difference in water uptake between any groups. Groups with higher PMMA concentrations tended to have an increased water sorption at each immersion period. There was statistically significant difference between PM0, PM2, and PM5. However, from day 14, PM30 showed significantly higher water sorption compared to the other groups ($p < 0.05$).

Compressive strength measurement

Figure 3 illustrates the results of compressive strength measurements. The highest compressive strengths values were obtained for PM2 in both DRY and WET, which were significantly different from all other groups.

Fig. 1 Video pictures of de-ionized water droplet on surface at the time of contact angle measurement. (a) PM0, (b) PM2, and (c) PM30

In addition, the compressive strength of PM2 was significantly higher in DRY group than in WET group ($p < 0.05$). There were no significant differences between other groups ($p > 0.05$).

Table 2 Contact angle of the experimental materials ($n=5$)

Code	Contact angle (θ)	
	DRY	WET
PM0	43.0 (3.5) ^a	34.9 (3.5) ^d
PM2	41.8 (2.2) ^a	40.6 (3.3) ^d
PM5	43.0 (6.9) ^b	45.4 (3.4) ^e
PM10	53.6 (10.2) ^{b, c}	45.6 (2.8) ^{e, f}
PM30	53.7 (5.4) ^c	54.9 (3.8) ^f

Mean (S.D.)

Groups with the same superscript letter shows statistically insignificant difference ($p>0.05$)

Fig. 2 Water sorption of the experimental materials.

Morphological study of fractured surfaces after compressive strength test by the SEM observations

SEM photographs of the material after compressive strength measurement are summarized in Figure 4. The fractured surface of PM0 (Figure 4a), showed progression of many cracks on the surface, forming “river markings”. Fractured surface of PM2 (Figure 4b) exhibited growth of a crack due to compressive stress centered at the PMMA filler particles. In the PM30 (Figure 4c), highly concentrated PMMA particles were observed on the fractured surface, where the crack progression was observed through the PMMA particles. Crater-like void structures were created due to the detachment of PMMA particles was also observed on the surface.

Fig. 3 Compressive strength of the experimental materials. Within each chart, different letters indicate statistically significant differences ($p<0.05$).

DISCUSSION

In the present study, the surface properties of PMMA incorporated resin composite were investigated. Measuring contact angle at the solid-air-liquid meeting point is a widely known technique used to investigate wettability of solid substrates¹⁷. Contact angles change with surface topography, surface tension of the liquid, surface energy of the substrate, and level of interaction between the liquid and solid¹⁷. Lower wettability of composite resin surface and less water sorption contribute to the reduction of staining¹⁸. However, no conclusive correlation was found between surface wettability of composite resin and biofilm formation¹¹. Adherence of oral pathogens to the biomaterial surfaces is affected by chemical composition, surface energy, surface roughness, and presence of functional groups on the surface, which will eventually result in biofilm formation.

Yokoyama *et al.*¹⁹ reported that the contact angle of pure PMMA plate is 65.5°. In the present study, the contact angle of the experimental materials tended to increase with incorporation of PMMA fillers in the resin composite in both DRY and WET conditions (Table 2), which indicated that surface hydrophobicity increased with addition of PMMA fillers.

For PM0, there was a remarkable difference in contact angle between DRY and WET conditions. It has been reported that water contact angles on the moist material surface is less than that of dry condition¹⁷.

Fig. 4 SEM pictures of fracture surface after compressive strength test. (a) PM0 (×350) Progression of many cracks on the surface were observed, (b) PM2 (×350) The growth of a crack due to compressive stress was centered at the PMMA filler particles and (c) PM30 (×350) Highly concentrated PMMA particles were observed on the fractured surface, the crack progression was observed through the PMMA particles. A crater-like void structure due to dropped PMMA particles was also observed on the surface.

Addition of PMMA fillers resulted in decreased surface wettability, while in the long-term, water sorption of material was increased. The increased water sorption may be due to difference in water sorption between PMMA and the polymer from the multifunctional methacrylates in the experimental materials. Intrinsically, addition of PMMA particles in the materials tended to increase the hydrophilicity (Figure 2). Moreover, since there was no surface treatment for PMMA particles to promote adhesion to the resin matrix, it is likely that increased water sorption was due to the increased porosity of the resulting polymer. Additional amount of water can be accommodated at the interface between the particles and the matrix if the particles are loosely embedded in the matrix.

Compressive strength and flexural strength tests are important to determine the mechanical properties for *in vitro* testing of the dental restorative materials. Fatigue studies showed a correlation between the compressive strength and the fatigue limit, indicating that a composite with a high compressive strength will withstand fatigue better²⁰.

PM2 demonstrated higher compressive strength than PM0 in both DRY and WET groups. It is noteworthy that 2% PMMA caused a marked increase in strength, even though there was no good adhesion between the resin matrix and PMMA filler particles, as confirmed by the voids observed in fracture patterns.

The crack progression patterns indicated the possibility that the plastic deformation capacity was increased by mixing a small quantity of PMMA. It was speculated that without the PMMA fillers, the crack under the compressive stress initiated quickly after the loading, and propagated drastically inside the polymer; however, with the smaller amounts of PMMA particles added, the crack propagation could be hindered at the interface between the PMMA particles and resin matrix, resulting in higher compressive strength.

The mechanical property of the PMMA particles is relatively lower than those of the other ingredients, such as the resin matrix and micro-fillers. Moreover, there is no bonding between the resin matrix and the PMMA particles; therefore, stress release and/or slide friction effects against the compressive stress may occur by adding the PMMA particle. When a large amount of PMMA particles were contained in the composites, the crack propagation easily occurred at the interface between PMMA fillers and resin matrix, resulting in decrease of compressive strength.

The findings of this study were in line with those of a previous study; which revealed quite interesting results on the relationship between volume fraction of inorganic filler with/without silane treatment and the compressive strength. The volume fraction of untreated filler materials showed a negative correlation with compressive strength²¹. The presence of a small quantity of untreated filler enhances the slide friction; however, in higher portions, a debonding at the interface between untreated fillers and the matrix, or

failure within the organic filler, will reduce the compressive yield strength of the composite.

From the current results, small amount of PMMA fillers dramatically increased the compressive strength of the resin composite. This finding may also suggest that the addition of PMMA particles may improve the mechanical resistance of the surface; however, further studies are required to evaluate the wear resistance of the experimental materials. The organic particle-incorporated resin composites are expected to contribute to development of new bioactive restorative materials in the future.

ACKNOWLEDGMENTS

This work was supported by the grant from the Japanese Ministry of Education, Global Center of Excellence (GCOE) Program, "International Research Center for Molecular Science in Tooth and Bone Diseases", and by a Grant-in-Aid for Young Scientists (B) (No. 21791839).

REFERENCES

- 1) Sakaguchi RL. Review of the current status and challenges for dental posterior restorative composites: clinical, chemistry, and physical behavior considerations. Summary of discussion from the Portland Composites Symposium (POCOS) June 17-19, 2004, Oregon Health and Science University, Portland, Oregon. *Dent Mater* 2005; 21: 3-6.
- 2) Sarrett DC. Clinical challenges and the relevance of materials testing for posterior composite restorations. *Dent Mater* 2005; 21: 9-20.
- 3) Suzuki S, Suzuki SH, Charles F. Evaluation the antagonistic wear of restorative material. *J Am Dent Assoc* 1996; 127: 74-80.
- 4) Suzuki S. Simulated enamel wear during occlusal contact. *Am J Dent* 2004; 17: 373-377.
- 5) Suzuki S, Minami H. Evaluation of toothbrush and generalized wear of luting materials. *Am J Dent* 2005; 18: 311-317.
- 6) Suzuki S, Wood MB. Mutual wear evaluation of resin composites when opposing enamel and dentin. *J Biomed Mater Res B* 2007; 81: 76-81.
- 7) Ferrari M, Kugel G. Handling characteristics of resin composites in posterior teeth. *Compend Contin Educ Dent* 1998; 19: 879-886.
- 8) Francci C, Loguercio AD, Reis A, Carrilho MR. A novel filling technique for packable composite resin in Class II restorations. *J Esthet Restor Dent* 2002; 14: 149-157.
- 9) Sadowsky SJ. An overview of treatment considerations for esthetic restorations: a review of the literature. *J Prosthet Dent* 2006; 96: 433-442.
- 10) Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. *Dent Mater* 2005; 21: 68-74.
- 11) Gyo M, Nikaido T, Okada K, Yamauchi J, Tagami J, Matin K. Surface response of fluorine polymer-incorporated resin composites to cariogenic biofilm adherence. *Appl Environ Microbiol* 2008; 74: 1428-1435.
- 12) Schildknecht CE. Vinyl and related polymers. London: John Wiley & Sons, Inc; 1952. p. 179-255.
- 13) Engelhardt JP. The microbial decomposition of dental resins and its importance to the microbial balance of the oral cavity. *Int Dent J* 1974; 24: 376-386.
- 14) Ruyter IE, Svendsen SA. Flexural properties of denture base polymers. *J Prosthet Dent* 1980; 43: 95-104.
- 15) Zuccari AG, Oshida Y, Moore BK. Reinforcement of acrylic resins for provisional fixed restorations. Part I: Mechanical properties. *Biomed Mater Eng* 1997; 7: 327-343.
- 16) Atsuta M, Turner DT. Increased strength of polyethylene glycol dimethacrylate doped with polymethyl methacrylate. *J Mater Sci* 1983; 18: 1675-1690.
- 17) Namen FM, Galan J Jr., De Oliveira JF, Cabreira RD, Costa E Silva-Filho F, Balduino A, De Deus G. Surface properties of dental polymers: measurements of contact angles, roughness and fluoride release. *Mater Res* 2008; 11: 239-243.
- 18) Satou N, Khan AM, Matsumae I, Satou J, Shintani H. *In vitro* color change of composite-based resins. *Dent Mater* 1989; 5: 384-387.
- 19) Yokoyama Y, Kadoma Y, Masuhara E. Properties of 2, 2, 2-trifluorethyl methacrylate copolymers. *Rep Inst Med Dent Eng* 1984; 18: 1-9.
- 20) Draughn RA. Compressive fatigue limits of composite restorative materials. *J Dent Res* 1979; 58: 1093-1096.
- 21) Söderholm KJ. Relationship between compressive yield strength and filler fractions of PMMA composites. *Acta Odontol Scand* 1982; 40: 145-150.