Chemical properties of 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane - methyl methacrylate copolymer

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This study evaluated the chemical properties such as water sorption, water solubility and solvent resistance of a new resin material consisting of 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane (BMPMS) and methyl methacrylate (MMA). Water sorption was evaluated by immersing the specimens in water at 37±1°C for 1 week, water solubility was evaluated by keeping the specimens in a desiccator under dry conditions at 37±1°C until the weight became constant, and solvent resistance was evaluated by immersing the specimens in acetone for 1 week and measuring the dissolved weight of acetone volatilized from those liquids. The water sorption and solvent resistance of the new resin were improved with increasing amount of BMPMS, whereas the water solubility remained the same value and did not depend on the amount of BMPMS.

Keywords: Rebase material, Cross-linking agent, Siloxane oligomer

INTRODUCTION

In prosthetic dentistry, dentures are made by using polymethyl methacrylate (PMMA), nylon, poly-carbonate, acetal and poly(ethylene terephthalate)1). Dentures are required to have certain mechanical properties such as strength and elasticity to protect against fractures, and must also be easy to repair, such as for rebase and fracture repairs. However, there have been few studies that clearly identified the required mechanical strength of a denture base, and some resin-based materials, such as nylon, poly-carbonate, acetal, and poly(ethylene terephthalate), do not efficiently bond to PMMA and so dentures made from these resin-based materials cannot be easily repaired. The repair, such as rebase and relining, is very important treatment in prosthodontics. Meanwhile, PMMA has a serious problem with percolated saliva and water which cause an unpleasant smell and a decline in mechanical properties2,3). In a previous study, a new soft resin material (MMA-BMPMS copolymer) consisting of 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane (BMPMS) and methyl methacrylate (MMA) monomer was reported4,5). BMPMS, which is a siloxane oligomer, has two methacryloxy groups at both ends of the molecule and shows high hydrophobicity6). Therefore, the MMA-BMPMS copolymer is expected to show hydrophobic properties compared with PMMA and to be suitable for repairing the PMMA denture. These advantages will give a possibility of MMA-BMPMS copolymer using as a rebase material and/or a denture material. The present study evaluated the effect of BMPMS addition to MMA on the chemical properties such as water sorption, water solubility and solvent resistance of the MMA-BMPMS copolymer.

MATERIALS AND METHODS

Preparation of the MMA-BMPMS copolymer

The MMA-BMPMS copolymer components used in the present study are listed in Table 1. The benzoyl peroxide (BPO) was recrystallized commercially-produced BPO from chloroform two times.

The MMA-BMPMS copolymers were prepared by the same method as in the previous paper4,5) through the following steps. BMPMS monomer was mixed with MMA monomer at molar ratios of 0, 10, 30, 50 and 70 mol% and 0.5 mass% of BPO was added to the monomer mixtures. Then the mixture was poured into a poly(propylene) tube (A18, Maruemu, Osaka, Japan; 16 mm diameter) and both ends of the tube were sealed by blowing hot air. Polymerization was done at 53°C for 5 days in a water bath followed by at 100°C for 1 h in a dry oven.

Specimen preparation

Disc-shaped specimens (16 mm diameter, 1.0 mm thickness) were cut from the cylindrical copolymer block by a linear precision saw (Isomet, Buehler Ltd., IL, USA) for the measurement of water sorption, water solubility and solvent resistance. The BMPMS monomer was mixed with MMA monomer at molar ratios of 0, 10, 30, 50 and 70 mol% and 0.5 mass% of BPO was added to the monomer mixtures. Then the mixture was poured into a poly(propylene) tube (A18, Maruemu, Osaka, Japan; 16 mm diameter) and both ends of the tube were sealed by blowing hot air. Polymerization was done at 53°C for 5 days in a water bath followed by at 100°C for 1 h in a dry oven.

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Water sorption measurements

Five specimens were prepared for each composition. The specimens were immersed in 30 mL of water at 37±1°C for 1 week, and then the weight was measured. The water sorption (mg/cm²) was calculated as described in a previous paper\(^5\) using the formula:

\[
C = \frac{(B - A)}{S}
\]

where,

- \(C\): water sorption (mg/cm²)
- \(B\): specimen weight immersed in water for 1 week (mg)
- \(A\): sample weight dried in desiccator for 1 week (mg)
- \(S\): surface area of the specimen (cm²)

Water solubility measurements

The specimens after the water sorption measurements were kept in the desiccator under dry conditions at 37±1°C for 1 week, and then the weight was measured daily until a constant weight was confirmed by the digital analytical balance. Water solubility (%) was calculated by subtracting the lost weight using the formula:

\[
E = \left(\frac{A - F}{A}\right) \times 100
\]

where,

- \(E\): water solubility (%)
- \(F\): specimen weight dried in desiccator for 1 week after the water sorption measurements (mg)

Solvent resistance measurements

Five specimens were prepared for each composition. The specimens were immersed in 20.0 mL of acetone (purity: 99.5%, Wako Pure Chemical Industries Ltd., Osaka, Japan) in a vial (size: 50 mL, I bottle, As one, Osaka, Japan) for 1 week. The liquids were filtrated by a solvent resistance filter (ShodexDT ED-25CR, Showa Denko Ltd., Tokyo, Japan), and then 10.0 mL of the liquid was taken with a pipette (Pipetman P-5,000, Gilson, WI, USA). The acetone was distilled from the taken liquid, and solvent resistance (%) was determined by measuring the dissolved weight in acetone and using the formula:

\[
G = \left(\frac{100 - (I \times 2/H)}{100}\right) \times 100
\]

where,

- \(G\): solvent resistance (%)
- \(H\): specimen weight before immersed in acetone (mg)
- \(I\): dissolved weight in 10 mL acetone (mg)

Statistical analysis

All measurements of water sorption, water solubility and solvent resistance were analyzed statistically by one-way analysis of variance and Tukey HSD test using statistics software (JMP 8.0, SAS Institute Inc., NC, USA).

RESULTS

Water sorption of the MMA-BMPMS copolymer

Figure 1 shows change in the water sorption with the content of BMPMS in the MMA-BMPMS copolymers. Even a small amount of BMPMS addition as low as 10 mol% caused a significant decrease in water absorption by almost one third (\(p<0.05\)). At concentration more than 10 mol% of BMPMS, water sorption almost linearly decreased with the BMPMS concentration, however, the decreasing amount is not so large only by 20 to 30% between 10 mol% and 70 mol%.

Water solubility of the MMA-BMPMS copolymer

The water solubility values are shown in Table 2. There was no significant difference between the PMMA and MMA-BMPMS copolymers.

Solvent resistance of the MMA-BMPMS copolymer

The solvent resistance values are shown in Table 3. The
PMMA completely was dissolved in acetone. The solvent resistance of the MMA-BMPMS copolymers was significantly higher than that of the PMMA (p<0.05). As seen in the water sorption, only 10 mol% of BMPMS addition to MMA drastically improved the solvent resistance. More addition of BMPMS slightly increased the solvent resistance, though there is no significant difference among 30, 50 and 70 mol% addition.

**DISCUSSION**

In prosthetic dentistry, various silicone materials are widely used such as for taking impressions, rebasing and tissue conditioning. Silicone materials are easy to handle and are water resistant compared with PMMA. However, silicone materials have low mechanical properties as a denture base material and do not efficiently bond to PMMA. Compared to silicone materials, PMMA has good mechanical properties and bonds to PMMA, but one of the biggest disadvantages of PMMA is water and saliva sorption, which cause an unpleasant smell and a decline in the mechanical properties. This study aimed to evaluate the water sorption, water solubility, and solvent resistance of the MMA-BMPMS copolymers by using BMPMS with high hydrophobicity in order to apply as a rebase material. It is especially examined that the influence of adding a large amount of BMPMS to MMA on chemical properties such as water absorption, and solubility in water and acetone. The results suggested that water sorption and solvent resistance were improved as the amount of BMPMS increased compared to those of PMMA, and the water solubility was almost the same as that of PMMA. Yamaga reported that adding hydrophobic resin to hydrophilic resin reduced the water sorption. BMPMS has hydrophobic characteristics, and so the MMA-BMPMS copolymer is more hydrophobic than PMMA alone. Miyasaka reported that silyldimethacrylates were effective as additional monomers in dental composites to improve water repellency. The longer the siloxane chain was, the lower the water sorption and Vickers hardness were, and the siloxane chain is one of the reasons for the hydrophobic properties of MMA-BMPMS copolymer. Sakai reported that adding 3-chloro-2-hydroxypropyl methacrylate to MMA effectively improved the solubility in acetone, however, the water sorption was increased. The hydroxy and chloro group have hydrophilic properties, so the water sorption of the new denture base materials developed by Sakai was increased. Sakai suggested that the cross-linked structure improved the solubility in acetone. BMPMS with two methacryloxy groups can form cross-linked structures and so the copolymer of BMPMS and MMA showed an excellent solvent resistance.

On the other hand, the MMA-BMPMS copolymer has some disadvantages. The first disadvantage is the decrease in mechanical properties depending on the amount of BMPMS added. It is suggested that the silicone conformation of BMPMS reduces the mechanical properties because the free energy rotation of Si is low, and therefore the MMA-BMPMS copolymer is softer than PMMA. This disadvantage suggests that the MMA-BMPMS copolymer, as seen in this case, is not suitable as a clinical denture resin. Increasing the amount of BMPMS in the MMA-BMPMS copolymer increases the hydrophobic properties, but the mechanical properties of the MMA-BMPMS copolymer decline. This suggests that the MMA-BMPMS copolymer is suitable as a rebase material rather than as a denture base material. The second disadvantage is the difficulty of making objects. In this study, the MMA-BMPMS copolymer was made from a liquid, but this bulk polymerization method cannot be used to form prostheses having a complicated shape such as a denture base, and the polymerization shrinkage is greater than that by ordinary powder-liquid polymerization. In prosthetic dentistry, denture resins are produced from a powder with a liquid medium for case of use and to decrease the curing shrinkage. Therefore, it is desirable to change the technique for making large prosthesis.

**CONCLUSION**

The solvent resistance of the MMA-BMPMS copolymers was significantly higher than that of the PMMA and the water sorption of the MMA-BMPMS copolymers was significantly lower than that of the PMMA, furthermore, the water sorption decreases significantly as the amount of BMPMS increases. These advantages suggested that the MMA-BMPMS copolymer is suitable as a rebase material.
REFERENCES