Basic Study of a New Denture Base Resin Applying Hydrophobic Methacrylate Monomer

Kozo UMEMOTO and Shigeaki KURATA

Department of Dental Materials and 1Department of Dental Biotechnology and Bioengineering, Kanagawa Dental College, 82, Inaoka-cho, Yokosuka, Kanagawa 238, Japan

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To improve the water sorption of poly(methyl methacrylate), new hydrophobic monomers, such as norboneyl and phenyl methacrylate, were studied to determine the resin with lower water sorption with no decrease in mechanical property. Water sorption of the copolymers of the hydrophobic monomers and MMA decreased with the increase in the concentration of the monomers. Compressive and bending strength of the copolymers were higher than that of PMMA, and the elastic modulus in bending was the same as that of PMMA. In addition, the transverse-deflection values satisfied ADA specifications. Dynamic mechanical thermal analysis of the copolymers showed a similar tendency to that of PMMA in spite of the introduction of bulky groups, such as norboneyl and phenyl, in the polymer molecule. The polymerization shrinkage in volume was in the following order: norboneyl < phenyl < methyl methacrylate.

Key words: Denture base resin, Copolymer, Hydrolytic stability

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is used widely in prosthetic, orthodontic and restorative dentistry. However, there are a few problems to be solved clinically. One disadvantage 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. Dentists can choose other denture base resins which have lower water sorption compared with PMMA resin. However, PMMA has many useful advantages for example, processing techniques are easy, special equipment is not necessary, repair and adjustment are easy.

A cross-linking agent has been used for the alteration of the PMMA mechanical properties, the water sorption and resistance to solvents. For example, ethylene glycol dimethacrylate (EGDMA) has been used generally as a cross-linking agent for PMMA dentures. Masuhara and Hirasawa reported that the addition of EGDMA did not improve the water sorption of PMMA. Wolff reported that the tensile strength of resin containing EGDMA changed a little with up to 25 percent addition, but the Knoop hardness number did not show any significant change. Therefore, the usefulness of EGDMA as a cross-linking agent may be low.

It has been reported that a hydrophobic methacrylate, such as octafluoropentylmethacrylate, decreases water sorption of resin material. However, resin consisting
of octafluoropentyl methacrylate showed poor mechanical properties\textsuperscript{8}). Kojima et al., reported that the application of vinylmethysiloxane as a cross-linking agent in MMA was very useful in improving hardness, water resistance and solvent resistance\textsuperscript{9}). Greenly reported that the reactivity of the vinyl group was lower than that of a methacryloxy group\textsuperscript{10}). The authors reported that the addition of 1,3-bis (methacryloxypropyl) tetramethylidisiloxane (BMPMS) as a cross-linking agent could improve the water sorption of PMMA\textsuperscript{11}), but the mechanical properties of BMPMS-copolymer at a concentration 10 mole % or above of BMPMS in copolymer decreased.

The purpose of the present study was to improve the water sorption of PMMA by the addition of norbornyl and phenyl methacrylate in MMA. These monomers have a hydrophobic group and the homopolymers have a high glass transition point, 155 and 110°C, respectively, and to estimate the water sorption and the mechanical properties of the resin improved.

MATERIALS AND METHODS

\textit{Synthesis and analysis of phenyl methacrylate monomer}

The phenol (Wako Pure Chemical Industries, Osaka, Japan) and methacryloyl chloride (Wako Pure Chemical Industries, Osaka, Japan) were used to synthesize phenyl methacrylate monomer. The mixture of phenol (0.538 mol), the methacryloyl chloride (0.548 mol) and 50 ml dry diethyl ether was added in a Pyrex flask equipped with a dropping funnel and a reflux condenser, and was stirred at room temperature, and then triethylamine was added to the mixture via the funnel for 1 hour. The mixture was stirred overnight. Benzene was added to the mixture, and the mixture was washed with aqueous sodium hydroxide solution and then with distilled water until the washed water was neutral. Benzene was removed under reduced pressure and phenyl methacrylate was obtained by fractional distillation. The synthesized phenyl methacrylate monomer was indentified by infrared spectroscopy (Model FT-4000, Shimadzu, Co., Ltd., Kyoto, Japan) and H-NMR spectroscopy (Model R-90H, Hitachi, Ltd., Tokyo, Japan). A H-NMR spectrometer was used under the following conditions: Solvent; CDCls, Concentration of specimen; 10 weight percent.

\textit{Preparation of bulk polymerization specimen}

The chemical formulas and codes of norbornyl methacrylate (NBMA) (Mitsubishi rayon Co., Ltd., Tokyo, Japan) and phenyl methacrylate (PHMA) are listed in Table 1. The mixture of NBMA or PHMA and MMA (Wako Pure Chemical Industries, Osaka, Japan), and benzoyl peroxide (0.5 wt%) as an initiator were placed into a glass tube of 4 mm inside diameter and 80 mm length and then the tube was sealed. The mixture was polymerized at 55°C for 24 hrs in a water bath and then at 100°C for 1 hr in dry oven. The concentration of the NBMA and PHMA in the copolymer was 10, 20, 30 and 40 wt%, respectively.
Compressive and bending strengths
The compressive and bending test specimens were fabricated from the polymerized bulks using a diamond cutter machine (Isomet, Buehler LTD., ILL., USA) under running water. The cutting surfaces of the compressive and bending specimens were polished using No.1000 water–proof paper under running water and the dimensions of the compression test pieces were 4 mm in diameter and 8 mm in length. The specimens were stored in 37°C water for 1 week prior to the test. Compressive strength was measured using a universal testing machine (AGS-500, Simadzu, Co., Ltd., Kyoto, Japan) at a cross-head speed of 2 mm/min. The dimensions of the bending test pieces were 4 mm in diameter and 25 mm in length. To determine bending strength, each specimen was placed in a 3-point bending fixture with a span of 20 mm, which was loaded by the universal testing machine at a cross-head speed of 1 mm/min. The load at fracture was recorded at a chart speed of 100 mm/min. The elastic modulus in bending was calculated from the straight portion up to the proportional limit of the load–time curve of the bending test. The loads of NBMA and PHMA homopolymers were 1–3 kgf and the loads of copolymers and PMMA were 1–8 kgf.

Water sorption test
The specimens were fabricated from the polymerized bulks using a diamond cutter machine described above. Specimens measuring 10 mm in diameter and 1 mm in thick-
ness were used. The specimen surfaces were polished by No.1000 water-proof paper under running water, and were stored in the desiccator at room temperature until a constant weight was reached (A mg). The specimens were immersed in 37°C water for 1 week prior to the measurement (B mg). The water sorption (C mg/cm²) was calculated by the following equation:

\[ C \text{ (mg/cm}^2\text{)} = \frac{[B - A] \text{ (mg)}}{\text{the surface area of the specimen (cm}^2\text{)}} \]

**Transverse-deflection test**

The mixture of NBMA and MMA and PHMA and MAA was placed into a stainless-steel mold and polymerized in an oven under the curing condition described above, respectively. The specimen surfaces were polished by No.1000 water-proof paper under running water and rectangular-shaped plates measuring 60 × 10 × 2.5 mm were used. Testing was carried out in accordance with American Dental Association Specification No.12. The specimens were stored in 37°C water for 50±2 hrs prior to the test. The specimens were placed in a 3-point bending fixture with a span of 50 mm and a universal testing machine was used to determine the bending strength at a cross-head speed of 1 mm/min. The transverse-deflection values were calculated from the bending strength results.

**Dynamic mechanical thermal analysis (DMTA)**

The specimens were fabricated from the polymerized bulks using a diamond cutter machine described above. The specimen surfaces were polished by No.1000 water-proof paper under running water and rectangular-shaped plates measuring 20 × 10 × 0.7 mm were used. The visco-elastic properties were measured using a dynamic mechanical thermal analyzer (PL-DMTA, Thermal Sciences, Loughborough, UK). The specimens were clamped with the single cantilever sample arrangement in the apparatus and the sinusoidal driving flexural stress was applied to a clamped specimen. The sample span of the cantilever was 5 mm. DMTA was used under the following conditions: Temperature range; from -50 to +150°C, Heating rate; 3°C/min, Frequency; 1 Hz, Strain; 64μm. Storage modulus (E') was collected.

**Polmerization shrinkage**

Testing was carried out along the lines of polymerization shrinkage tests according to the Japan Industrial Standard K7112 A. Volume contraction was measured.

**RESULTS**

The IR and NMR spectrum of synthesized PHMA are shown in Figs. 1 and 2, respectively. The bands at 2990, 1720 and 1640 cm⁻¹ were assigned to the CH₃, the C=O, C=C stretching mode, respectively. The bands at 845 and 690 cm⁻¹ were based on the phenyl group. The resonances at approximately 7.5–6.9, 6.5–5.6 and 2 ppm were based on phenyl, vinyl, methyl group protons, respectively. It was confirmed by NMR spectra and the high yield (>98%) that the phenol gave the corresponding PHMA almost
Table 2 Effect of addition of NBMA and PHMA on the mechanical property and water sorption of PMMA

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Water sorption (mg/cm³)</th>
<th>Compressive strength (MPa)</th>
<th>Bending strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% NBMA-copolymer</td>
<td>0.77±0.05*</td>
<td>112±2*</td>
<td>163±14*</td>
</tr>
<tr>
<td>20% NBMA-copolymer</td>
<td>0.71±0.04*</td>
<td>113±4*</td>
<td>153±12*</td>
</tr>
<tr>
<td>30% NBMA-copolymer</td>
<td>0.61±0.02*</td>
<td>114±6</td>
<td>116±15*</td>
</tr>
<tr>
<td>40% NBMA-copolymer</td>
<td>0.49±0.00*</td>
<td>116±3*</td>
<td>106±9*</td>
</tr>
<tr>
<td>NBMA homopolymer</td>
<td>0.12±0.02*</td>
<td>65±12*</td>
<td>27±5*</td>
</tr>
<tr>
<td>10% PHMA-copolymer</td>
<td>0.80±0.03*</td>
<td>90±5</td>
<td>123±16</td>
</tr>
<tr>
<td>20% PHMA-copolymer</td>
<td>0.60±0.03*</td>
<td>105±7</td>
<td>130±13</td>
</tr>
<tr>
<td>30% PHMA-copolymer</td>
<td>0.58±0.02*</td>
<td>118±4*</td>
<td>179±15*</td>
</tr>
<tr>
<td>40% PHMA-copolymer</td>
<td>0.47±0.04*</td>
<td>121±2*</td>
<td>147±6*</td>
</tr>
<tr>
<td>PHMA homopolymer</td>
<td>0.19±0.00*</td>
<td>126±5*</td>
<td>61±12*</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.94±0.06</td>
<td>107±3</td>
<td>134±6</td>
</tr>
</tbody>
</table>

* Asterisk shows significant difference between PMMA and specimen groups at 95% confidence level.

Water sorption, compressive and bending strengths of NBMA-MMA copolymer (NBMA-copolymer), and PHMA-MMA copolymer (PHMA-copolymer) and NBMA, PHMA homopolymer and PMMA are shown in Table 2. The water sorption of NBMA- and PHMA-copolymers decreased clearly with increasing amounts of NBMA and PHMA and there was a significant difference between the copolymers and PMMA, respectively. The compressive strengths of all NBMA-copolymers were slightly higher than that of PMMA, despite the lower strength of the NBMA homopolymer. The compressive strengths of PHMA-copolymers and PHMA homopolymer were markedly higher than that of PMMA, except for 10% and 20% PHMA-copolymer.
Fig. 3 The load-time curves of NBMA and homopolymer and 10% NBMA-copolymer.  
---, Homopolymer;  
-----, Copolymer.

Fig. 4 Effect of addition of NBMA and PHMA on the bending modulus of elasticity of NBMA and PHMA homopolymer and NBMA- and PHMA-copolymer.  
\[ \text{Bending modulus of elasticity (Pa)} \]  
\[ \text{Concentration of hydrophobic monomer in MMA (wt%)} \]  
\[ \begin{array}{c} \text{PMMA}, \text{NBMA homopolymer and copolymer;} \\
\text{PHMA homopolymer and copolymer;} \\
\text{PMMA.} \end{array} \]

Fig. 5 Plots of $E'$ versus temperature for various NBMA-copolymer specimens and PMMA.  
---, 10% NBMA-copolymer;  
-----, 20% NBMA-copolymer;  
-----, 30% NBMA-copolymer;  
-----, 40% NBMA-copolymer;  
-----, PMMA.

Fig. 6 Plots of $E'$ versus temperature for various PHMA-copolymer specimens and PMMA.  
---, 10% PHMA-copolymer;  
-----, 20% PHMA-copolymer;  
-----, 30% PHMA-copolymer;  
-----, 40% PHMA-copolymer;  
-----, PHMA.
Table 3 Transverse-deflection value of 20% NBMA- and 20% PHMA-copolymer and PMMA which made by use of bulk polymerization

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Transverse-deflection value (mm) 1.5-3.5 kgf</th>
<th>1.5-5.0 kgf</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBMA-copolymer</td>
<td>1.38±0.03</td>
<td>2.55±0.07</td>
</tr>
<tr>
<td>PHMA-copolymer</td>
<td>1.45±0.12</td>
<td>2.08±0.70</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.77±0.06</td>
<td>3.48±0.08</td>
</tr>
</tbody>
</table>

Table 4 Polymerization shrinkage of NBMA, PHMA and MMA

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Polymerization shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBMA</td>
<td>7.1±0.1</td>
</tr>
<tr>
<td>PHMA</td>
<td>12.5±0.1</td>
</tr>
<tr>
<td>MMA</td>
<td>21.0±0.1</td>
</tr>
</tbody>
</table>

The load–time curves of NBMA homopolymer and 10% NBMA-copolymers are shown in Fig. 3. The bending strengths of NBMA-copolymers in the range from 10 to 20% were higher than PMMA and there was a significant difference between the strengths of those copolymers and PMMA. The strengths of NBMA-copolymers at a concentration of 30% or above were lower than PMMA. The strength of NBMA homopolymer was remarkably low. The bending strengths of PHMA-copolymer in the range 10 to 20% were similar to that of PMMA. However, strength increased gradually with an increase in PHMA in copolymer and 30% PHMA-copolymer exhibited the highest bending strength. The bending strength of PHMA homopolymer was remarkably low compared with that of PMMA.

The elastic modulus in bending of NBMA- and PHMA-copolymers and NBMA and PHMA homopolymer are shown in Fig. 4. The moduli of NBMA and PHMA homopolymer are slightly high compared with that of PMMA. The moduli of NBMA- and PHMA-copolymers approach those of NBMA and PHMA homopolymer with increases in amount of NBMA and PHMA in the copolymer, respectively. The storage moduli (E') of NBMA- and PHMA-copolymers measured by DMTA are shown in Figs. 5 and 6, respectively. All E' values of NBMA- and PHMA-copolymers were similar to that of PMMA and decreased rapidly at temperatures above 100°C. The transverse-deflection values of both 20% NBMA-copolymer and 20% PHMA-copolymer are shown in Table 3. The transverse-deflection value of the copolymer satisfied the requirements of ADA specification. The polymerization shrinkages of NBMA, PHMA and MMA are shown in Table 4. The polymerization shrinkage of NBMA and PHMA was markedly smaller than that of MMA.
DISCUSSION

Denture base resin is affected by biochemical mechanism and mechanical stress within the oral environment. Saliva is absorbed into the denture base resin and weakens the resin through plasticization. Long-term water sorption decreases the mechanical property of PMMA. Unpleasant smell of the denture base is induced by the saliva and water absorbed in PMMA. Moreover, according to manufacturers, the water sorption of PMMA resin is much higher than that of polycarbonate and polysulphone resin. It is desirable to diminish the water sorption in PMMA dentures. Denture base resin made of very high hydrophobic polymer has poor affinity to the tissues that support the denture compared with resin of hydrophilic polymer. We suggest that resin obtained by the optimum concentration of hydrophobic monomers and MMA will show good tissue affinity and hydrolytic stability. The addition of hydrophobic NBMA or PHMA in MMA clearly reduced the water sorption of the copolymers compared with that of PMMA, and the value of the sorption was controlled by the NBMA and PHMA content in those copolymers.

The Tgs of NBMA and PHMA homopolymer were 155 and 110°C, respectively (Table 1), and their moduli were higher than that of PMMA. However, our findings show that the homopolymers were brittle when compared with PMMA. In contrast, the compressive and bending strengths of PHMA homopolymer were high compared with NBMA homopolymer because of π-π interaction of phenyl groups and/or hindrance of mobility of the polymer-chain due to bulky phenyl groups. For the copolymers of hydrophobic monomers and MMA below 20 wt% of NBMA, the addition of NBMA to MMA gives high mechanical strength. However, NBMA (30 wt% or above), the bending resistance decreased, because the brittle nature of NBMA-copolymer increases with an increase in the amount of NBMA. The mechanical strengths of 30 and 40% PHMA-copolymers were higher than PMMA, because of π-π interaction of the phenyl group or hindrance of mobility of the polymer-chain due to bulky phenyl groups. The storage moduli (E’) values of NBMA- and PHMA-copolymers were similar to that of PMMA, therefore, the addition of NBMA and PHMA has little effect on the glass transition temperature of the copolymers up to 40 wt%.

Transverse deflection performance is an important characteristic in denture base resin. According to ADA specifications, the requirements of the deflection limits of denture base polymers do not allow more than 2.5 mm deflection in the load range from 1.5 to 3.5 kgf and require a deflection of between 2.0 and 5.5 mm from a load 1.5 to 5.0 kgf. Both the transverse-deflection values of 20% NBMA- and of PHMA-copolymer satisfied the requirements of ADA specifications.

The polymerization shrinkages of NBMA and PHMA are shown in Table 3. The shrinkage of NBMA and PHMA with bulky bicyclo and aromatic rings showed less than that of MMA with the methyl group. Use of those hydrophobic monomers and/or a mixture of those monomers and MMA as denture base monomer will lessen the polymerization shrinkage of dentures.
CONCLUSION

The water sorption of copolymers containing hydrophobic monomers, such as NBMA and PHMA, decreased significantly compared with that of PMMA. The mechanical performance of the copolymers was higher than that of PMMA. The transverse-deflection values of the copolymers had the satisfactory requirement of ADA specifications. The polymerization shrinkage of NBMA and PHMA was markedly smaller than that of MMA. The addition of norbonyl or phenyl methacrylate into MMA was useful for improving the hydrophobicity of PMMA.

ACKNOWLEDGMENTS

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REFERENCES

本号掲載論文の和文抄録

各種コラーゲン強化法のコラーゲン薄膜の
機械的強さに及ぼす影響について

小出 武, 大槻道治
大阪歯科大学小児歯科学講座

各種コラーゲン強化法と象牙質強化との関連性を検討
している。本研究ではI型コラーゲンを主成分としたコ
ラーゲン薄膜を用い、紫外線照射、タンニン酸およびグル
タルアルデヒド溶液浸漬後、引張試験、彫刻性試験
および抗酸素性試験を実施した。作用時間の延長ととも
に引張弾性率は大きくなったが、引張破壊伸びは小さく
なり、脆くなった。この傾向は紫外線照射で著明であっ
た。また、タンニン酸は、他の2方法と比べると架橋の
進行速度は遅かった。抗酸素性はタンニン酸およびグル
タルアルデヒド作用で著明に上昇した。

歯科修復物製作用CAD/CAM システム
—ブリッジ修復用のCADについて—

庄村泰治, 高橋純造
大阪大学歯学部歯科理工学講座

ブリッジ修復用のCADプロセスを開発し、それを用
いて上顎の3番ブリッジのCADによる修復を試みた。
まず、標準的な第二小臼歯および大臼歯の三次元形状
計測データを変形して支台歯に適応させ、ついで計測し
たポンティックのデータをその間に挿入した。ここに対合歯
ピットデータを取り込んで、試験した冠部データとの咬合
関係を調整した。その後、ピットデータをFGPデータに取
り替え、FGPデータと干渉する冠部の部分は取り除いた。

次いで、連結プロセスを行った。つまり、ポンティッ
クと隣接歯冠の間隔をデータ補間によって連結した。そ
して試験した第二小臼歯と大臼歯クラウンの端部と各々
の支台歯のマージンとを連結した。

最後に各々の支台歯のマージンより上部を抽出して、
ブリッジのクラウン内冠部のデータとして用いた。

このようにして今回開発したプログラムでブリッジ全
体の設計が行えるようになった。

疎水性メタクリレートモノマーを応用した新規床用レジンの基礎的研究

樫本貢三, 倉田茂昭

神奈川歯科大学歯科理工学教室

PMMA レジン材料の臨床上の欠点である吸水性を改
善するために、ノルボルニル基（NBMA）やフェニル
基（PHMA）をもつ新規疎水性モノマーを用い、
MMA との共重合により、ポリマーの主鎖中へ疎水性
基を導入し、レジンの機械的強さを損なうことなく、吸
水性を低下（制御）する可能性を検討した。その結果、
これらコポリマーの吸水量は疎水性モノマーの添加量と
共に大幅に減少した。また、圧縮および曲げ強さは
PMMA レジンと比較し優れ、曲げ弾性率は PMMA と同様であり、たわみ量は ADA の規格値を満たしていた。動的貯蔵弾性率に変化は認められず、コポリマー化による分子の運動性への影響は認められなかった。各モノマーの中等収縮量は、MMA＞PHMA＞NBMA の順に減少した。

メチルシクロヘキサンジオンを用いた象牙質接着用の新しい重合開始剤

今井庸二、石川美保
東京医科歯科大学医学部研究室

象牙質の接着において重合開始剤の役割を調べる研究の一環として、2-メチル-1,3-シクロヘキサンジオン（MCHD）と塩化第二鉄からなる新しい重合開始剤の効果を、象牙質の前処理とレジン中の塩化第二鉄の濃度の影響について調べたものである。0.001-0.03%の塩化第二鉄を含む MMA と 2%の MCHD を含む PMMA から成るレジンを用いて、硬化時間と牛骨象牙質に対する引張り接着強さを測定した。象牙質表面は、0-3%の塩化第二鉄あるいは塩化第二鉛を含む10%リン酸あるいはクエン酸の前処理剤で処理した。適切な条件下では約10MPa の接着強さが得られ、この値は現在最も効果的な接着性レジンであるトリプチルボルタンを開始剤とする MMA レジンに匹敵するものであった。このように、MCHD/塩化第二鉄の重合開始剤を用いたレジンは象牙質の接着に非常に効果的であることがわかった。

1 ステップボンディングシステムのエナメル質、象牙質に対するせん断接着強さ

二階堂徹、中島正俊、東高士、金村信晴、
パトリシア H.R. ベイラ、田上順次
東京医科歯科大学医学部歯科保存学第一講座

1 ステップで接着操作を完了できる試作プライマーが開発された。このプライマーを用いて、光硬化型グラスアイオノマーセメントならびにコンポジットレジンの歯質接着性について検討した。せん断接着試験の結果、エナメル質に対する良好な接着性が確認されたが（＞11MPa）、象牙質に対する接着性は低かった。しかし、試作プライマーの塗布、光照射の操作を 2 回繰り返すことにより、象牙質に対する接着強さの向上が認められた（＞8MPa）。SEM 観察の結果、試作プライマーは、エナメル質、象牙質に対して、マイルドな脱灰効果を有し、さらに光硬化型グラスアイオノマーセメントと象牙質との接着界面には、樹脂含浸層の形成が確認された。以上の結果から、1 ステップのボンディングシステムにおいても良好な歯質接着性が得られる可能性が強く示唆された。

石こう系クリストパライト埋没材における異方性膨張

渋谷昌史、大澤雅博、松元仁、久恒邦博、安田克広

長崎歯学部歯科保存学第一講座
1長崎歯学部歯科理工学講座

石こう系クリストパライト埋没材による部材内部の膨張について検討した。アスベストリボンを裏装した製造