Influence of monomer type, plasticizer content, and powder/liquid ratio on setting characteristics of acrylic permanent soft denture liners based on poly(ethyl methacrylate/butyl methacrylate) and acetyl tributyl citrate

Tomoyasu MORI, Kazuma TAKASE, Kazuhiro YOSHIDA, Hitomi OKAZAKI and Hiroshi MURATA

Department of Prosthetic Dentistry, Graduate School of Biomedical Sciences, Nagasaki University, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan
Corresponding author, Kazuma TAKASE; E-mail: ktakase@nagasaki-u.ac.jp

We evaluated the influence of monomer type, plasticizer content, and powder/liquid (P/L) ratio on the setting characteristics of light-cured acrylic permanent soft denture liners based on poly(ethyl methacrylate/butyl methacrylate). Two monomers, iso-butyl methacrylate (i-BMA) and 2-ethylhexyl methacrylate (2-EHMA), that contained various concentrations of the plasticizer acetyl tributyl citrate (ATBC) and trace amounts of the photo initiator and reducing agent were used. The P/L ratio was 1.0 or 1.2. The gelation time was measured using a controlled stress rheometer. Materials with i-BMA had shorter gelation times than those for materials with 2-EHMA. The gelation time increased exponentially with increasing plasticizer content. A higher P/L ratio led to a shorter gelation time. The effects of monomer type and plasticizer content were larger than that for the P/L ratio. These results show that 2-EHMA is a suitable monomer for soft denture liners and that the setting characteristics can be controlled via ATBC content.

Keywords: Soft denture liners, Gelation time, Dynamic viscoelasticity, Acetyl tributyl citrate, Monomer

INTRODUCTION

It is expected that the number of elderly denture wearers will increase as society ages1 even though the number of remaining teeth has been increasing. Some denture wearers suffer from masticatory pain and denture ulcers under the basal seat mucosa because they have severe alveolar resorption and/or a thin and relatively non-resilient mucosa2. Such a basal seat mucosa cannot easily dissipate the masticatory forces. Permanent soft denture liners are widely used to compensate the thickness and/or viscoelastic properties of the basal seat mucosa3 to relieve masticatory pain during function4-6. Such soft denture liners are mainly made of an acrylic material or silicone, which vary in terms of some mechanical properties, such as viscoelastic properties2,8,9, hardness11,12, cushioning effect13, and bond strength to denture base resins14,15. Mechanical properties, especially viscoelastic properties and their durability, are very important for the clinical efficacy of soft denture liners. A previous study found that the improvement in the masticatory function of complete denture wearers who cannot tolerate a hard denture base and complain of masticatory pain was greater with acrylic permanent soft denture liners than silicone ones because acrylic materials exhibit viscoelastic properties and better relieve the stress caused by masticatory forces whereas silicone exhibits elastic properties8,9.

Two methods are used for applying permanent soft denture liners to dentures, namely the chairside technique and the laboratory reline technique. In a clinical situation, it is necessary to reline dentures with soft denture liners at a thickness of approximately 1.5 to 2 mm to achieve a cushioning effect2,16. Furthermore, heat-cured materials are preferred over cold-cured materials from the viewpoint of durability. Thus, it is desirable to apply heat-cured materials using the laboratory reline technique to obtain the optimal lining layer thickness. However, this requires patients to leave their dentures at the laboratory for a while. The laboratory reline technique is thus only applicable to patients with spare dentures. In contrast, with the chairside technique, the reline can be completed in one office visit; however, only cold-cured materials, whose physical properties have lower durability, can be applied. The chairside technique can be used for home-visit dental treatment, which has seen increasing demand. In this technique, a soft denture liner is applied to the intaglio surface of the dentures after the powder and liquid or base and catalyst pastes have been mixed. It is difficult to obtain an appropriate layer thickness because the materials easily flow out from the intaglio surface of the dentures if the patient strongly bites the dentures. It is important to understand the setting characteristics and initial flow properties just after mixing, and to manipulate the soft denture liner to obtain the optimal layer thickness. These characteristics are closely related to the working time for insertion and seating into the mouth, border molding, and the fit between the intaglio surface of the dentures and the basal seat mucosa.

Both acrylic and silicone permanent soft denture liners are applied to dentures in the chairside technique. Although acrylic materials that exhibit viscoelastic behavior have been reported to improve the masticatory function of complete denture wearers compared with that obtained with silicone, which exhibits elastic behavior2, the properties of acrylic materials show a more marked change over time16. To overcome these drawbacks, we plan to develop a light-cured acrylic permanent soft denture liner that has viscoelastic properties and high...
durability.

It is first necessary to evaluate the relationship between the composition and setting characteristics of a material. Several studies have reported the relationship between the composition and that of tissue conditioners and hard, direct denture reline resins. However, little information is available on permanent soft denture liners. In addition, there is no ISO standard for the setting characteristics and initial flow just after the mixing of the powder and liquid of permanent soft denture liners, i.e., soft lining materials for long-term use, even though one exists for hardness, bond strength to the denture base, sorption, and solubility.

The purpose of the present study was to evaluate the influence of monomer type, plasticizer content, and the powder/liquid (P/L) ratio on the setting characteristics of light-cured acrylic permanent soft denture liners based on poly(ethyl methacrylate/butyl methacrylate) (poly(EMA/BMA), 50/50) and acetyl tributyl citrate (ATBC). We hypothesize that the type of monomer, plasticizer content, and the P/L ratio influence the gelation time and that soft denture liners with iso-butyl methacrylate (i-BMA), lower plasticizer content, and a higher P/L ratio will exhibit a shorter gelation time.

**MATERIALS AND METHODS**

Table 1 lists the commercial acrylic denture liners used in the present study together with the polymerization type, manufacturer, composition of the powder and liquid, the powder/liquid (P/L) ratio recommended by the manufacturer. These commercial products were applied for the chairside technique in a clinical situation. They exhibit elastic properties just after the powder and liquid have been mixed. Bio Liner (BL) and Comfortner (CO) are soft denture liners, and the other materials are hard denture liners. CO exhibits more elastic properties after light curing, whereas DIL (DI) and DYNAMIC LINER (DL), and FDr (FD) and Fdr-PERI (FP), became hard 1–2 weeks after insertion in the mouth, and after light curing, respectively. The materials were evaluated to determine a clinically acceptable gelation time.

After the evaluation of the commercial products, the relationship between the composition and setting characteristics of the light-cured acrylic permanent soft denture liners was determined. Poly(ethyl methacrylate/butyl methacrylate) (poly(EMA/BMA), 50/50) was used as the powder. The ratio of 50/50 is based on the unit of 2 monomers of EMA and BMA, and the ratio is 1:1 in this copolymer. The weight average molecular weight, number average molecular weight, and polydispersity were $5.52 \times 10^5$, $1.51 \times 10^5$, and 3.7, respectively. The average particle size was approximately 70 µm. The main liquid components were a monomer and a plasticizer. Trace amounts of camphorquinone and ethyl p-dimethylaminobenzoate were added as the photo initiator and reducing agent, respectively, to produce the photo initiator and reducing agent, respectively.
the light-cured material (Table 2). In the present study, two kinds of monomer, namely iso-butyl methacrylate (i-BMA) and 2-ethylhexyl methacrylate (2-EHMA), that contained a plasticizer, acetyl tributyl citrate (ATBC), at concentrations of 0, 25, 50, and 75 wt% were used. The powder/liquid (P/L) ratio was 1.0 or 1.2 by weight. The composition of the trial soft denture liners is shown in Table 3.

**Setting characteristics**

The setting characteristics of the soft denture liners were evaluated in terms of the gelation time obtained from the measurement of dynamic viscoelasticity. The gelation time was determined at 37°C using a controlled stress rheometer (AR-G2, TA Instruments-Waters LLC, New Castle, DE, USA) with a parallel plate test configuration (diameter: 20 mm; gap: 1,000 µm) in oscillatory mode. The powder and liquid were mixed for 15 s at 23±1°C. The resulting plate was placed on the plate of the rheometer, and the parallel plate was set to automatically produce a constant gap of 1,000 µm. Measurements were performed every 15 s at constant oscillation frequency (1 Hz) and angular displacement (3 mrad) 5 times for each materials.

The complex dynamic shear modulus (G*), shear storage modulus (G'), shear loss modulus (G''), and loss tangent (tan δ) are defined as follows:

\[
|G^*| = \tau / \gamma \\
G^* = G' + i G'' \\
G' = |G^*| \cos \delta \\
G'' = |G^*| \sin \delta \\
tan \delta = G'' / G'
\]

where \(i^2 = -1\) and \(\delta\) is the phase angle between stress and strain.

The gelation time was defined as the time at which tan \(\delta=1\) (\(G'=G''\)) was reached, that is, the gel point.

**Statistical analysis**

A comparison of gelation time for the six commercial acrylic denture liners and trial materials was performed using one-way analysis of variance (ANOVA) combined with a Student-Newman-Keuls test. That of the trial soft denture liners was also performed using three-way ANOVA. The contribution ratios (\(\rho\)) of monomer type, plasticizer content, and the P/L ratio, as well as their interactions, were determined. Regression analysis was

### Table 2 Liquid components used

| Material                                      | Batch no. | Manufacturer                                      |
|-----------------------------------------------|-----------|---------------------------------------------------|
| Iso-butyl methacrylate                        | OZPUJOF   | Tokyo Chemical Industry, Tokyo, Japan             |
| 2-Ethylhexyl methacrylate                     | AGNO1     | Tokyo Chemical Industry                           |
| Acetyl tributyl citrate (tributyl O-acetylcitrate) | USBNCNE   | Tokyo Chemical Industry                           |
| Camphorquinone                                | DPJ7702   | Wako Pure Chemical Industries, Osaka, Japan       |
| Ethyl p-dimethylaminobenzoate                 | M8T2170   | Nacalai Tesque, Kyoto, Japan                      |

### Table 3 Composition of trial soft denture liners

| Monomer type | P/L ratio | Composition of liquid (wt%) | Code |
|--------------|-----------|----------------------------|------|
|              |           | Monomer | Plasticizer (ATBC) |      |
|              | 1.0       |         |                   |      |
| i-BMA        | 25        | 75      | A                  |
|              | 50        | 50      | B                  |
|              | 75        | 25      | C                  |
|              | 100       | 0       | D                  |
|              | 1.2       |         |                   |      |
|              | 25        | 75      | A'                 |
|              | 50        | 50      | B'                 |
|              | 75        | 25      | C'                 |
|              | 100       | 0       | D'                 |
|              | 1.0       |         |                   |      |
| 2-EHMA       | 25        | 75      | E                  |
|              | 50        | 50      | F                  |
|              | 75        | 25      | G                  |
|              | 100       | 0       | H                  |
|              | 1.2       |         |                   |      |
|              | 25        | 75      | E'                 |
|              | 50        | 50      | F'                 |
|              | 75        | 25      | G'                 |
|              | 100       | 0       | H'                 |
used to determine the correlation between gelation time and plasticizer content. A comparison between P/L ratios of 1.0 and 1.2 was performed using the Student t-test. The level of statistical significance for all tests was set at \( p<0.05 \). SPSS Statistics version 17.0 (SPSS, Chicago, IL, USA) was used for all statistical analyses.

**RESULTS**

**Commercial acrylic denture liners**

Figure 1 shows the variations of shear storage modulus \( (G') \), shear loss modulus \( (G'') \), and loss tangent (\( \tan \delta \)) with time for the six commercial acrylic denture liners at 37°C. All commercial materials showed increases in \( G' \) and \( G'' \) with time. BL exhibited an exponential increase in these values approximately 400 s after the mixing of the powder and liquid. The \( \tan \delta \) values of all materials except for BL increased with time until approximately 80–140 s after mixing, and then decreased. That of BL decreased with time just after mixing. The gelation time of the six commercial materials is shown in Fig. 2. The shortest mean gelation time (128 s) was recorded for BL, and the longest one (652 s) was recorded for DL \( (p<0.05) \). The gelation times followed the order DL>FD>DI>FP>CO>BL.

**Influence of composition on gelation time of trial acrylic permanent soft denture liners**

The results of three-way ANOVA indicated that all examined factors, except for the interaction between monomer type and the powder/liquid (P/L) ratio and that between plasticizer content and the P/L ratio, had a significant influence on gelation time for the light-
cured acrylic permanent soft denture liners based on poly(ethyl methacrylate/butyl methacrylate) (poly(EMA/BMA)) and acetyl tributyl citrate (ATBC) (Table 4). The contribution ratio of monomer type was highest ($\rho$=50.7%), followed by that of plasticizer (ATBC) content ($\rho$=41.4%). The contribution ratio of the P/L ratio was the lowest ($\rho$=1.2%).

The relationship between the variations of $G'$, $G''$, and $\tan \delta$ of the trial soft denture liners with time and each factor at 37°C are shown in Figs. 3–5, respectively. The $G'$ and $G''$ values of all materials increased with time, whereas the $\tan \delta$ values decreased with time. The trial soft denture liners that included iso-butyl methacrylate (i-BMA) had a greater rate of increase of $G'$ and $G''$ with time compared to that for those that included 2-ethylhexyl methacrylate (2-EHMA). Although the $\tan \delta$ values of the materials that included 2-EHMA just after the mixing of the powder and liquid were higher

### Table 4  Three-way ANOVA results for the gelation time of 16 tested materials

| Source                              | df  | Sum of squares | Mean square | F            | Significance of F | Contribution ratio, $\rho$ (%) |
|-------------------------------------|-----|----------------|-------------|--------------|------------------|-------------------------------|
| Monomer type                        | 1   | 589,781.098    | 589,781.098 | 788.996      | 0.000            | 50.7                          |
| Plasticizer content                 | 3   | 483,647.19     | 161,215.73  | 215.671      | 0.000            | 41.4                          |
| P/L ratio                           | 1   | 14,444.103     | 14,444.103  | 19.323       | 0.000            | 1.2                           |
| Monomer type×plasticizer content    | 3   | 15,404.064     | 5,134.688   | 6.869        | 0.000            | 1.1                           |
| Monomer type×P/L ratio              | 1   | 831.579        | 831.579     | 1.112        | 0.296            | 0.0                           |
| Plasticizer content×P/L ratio       | 3   | 3,361.092      | 1,120.364   | 1.499        | 0.223            | 0.1                           |
| Monomer type×P/L ratio×plasticizer content | 3   | 7,195.315      | 2,398.438   | 3.209        | 0.029            | 0.4                           |
| Error                               | 64  | 47,840.529     |             |             |                  | 5.1                           |
| Corrected total                     | 79  | 1,162,504.969  |             |             |                  |                               |

### Table 5  Gelation times of trial soft denture liners

| Monomer type | P/L ratio | Composition of liquid (wt%) | Code | Gelation time (s) | Evaluation of manipulation |
|--------------|-----------|-----------------------------|------|-------------------|----------------------------|
|              |           | Monomer | Plasticizer (ATBC) |      |                  |                            |
| i-BMA        | 1.0       | 25      | 75                  | A    | 241 (10)$^{bc}$  | +                          |
|              |           | 50      | 50                  | B    | 111 (10)$^a$     | –                          |
|              |           | 75      | 25                  | C    | 78 (4)$^{ab}$    | –                          |
|              |           | 100     | 0                   | D    | 70 (5)$^{ab}$    | –                          |
|              | 1.2       | 25      | 75                  | A'   | 213 (35)$^{d}$   | +                          |
|              |           | 50      | 50                  | B'   | 87 (17)$^{ab}$   | –                          |
|              |           | 75      | 25                  | C'   | 66 (2)$^{ab}$    | –                          |
|              |           | 100     | 0                   | D'   | 53 (11)$^{a}$    | –                          |
| 2-EHMA       | 1.0       | 25      | 75                  | E    | 424 (46)$^b$     | +                          |
|              |           | 50      | 50                  | F    | 301 (19)$^a$     | +                          |
|              |           | 75      | 25                  | G    | 259 (30)$^{d}$   | +                          |
|              |           | 100     | 0                   | H    | 228 (27)$^{ab}$  | +                          |
|              | 1.2       | 25      | 75                  | E'   | 437 (64)$^a$     | +                          |
|              |           | 50      | 50                  | F'   | 282 (32)$^{ab}$  | +                          |
|              |           | 75      | 25                  | G'   | 197 (27)$^{a}$   | +                          |
|              |           | 100     | 0                   | H'   | 164 (7)$^a$      | +                          |

Mean (SD)
+ : acceptable
− : unacceptable
Identical letters indicate no statistical differences.
Fig. 3 Variations of shear storage modulus ($G'$), shear loss modulus ($G''$), and loss tangent (tan δ) of trial soft denture liners with time and monomer type at 37°C. The material with the median value of gelation time was selected from the five measured materials. Poly(EMA/BMA) was mixed with various monomers/25 wt% ATBC at a P/L ratio of 1.0.

and decreased more rapidly than those of the materials that included i-BMA, the time at which tan δ = 1 ($G' = G''$) was reached was shorter for the latter materials (Fig. 3). A greater rate of increase of $G'$ and $G''$ and a decrease of tan δ with time were noted for materials with lower plasticizer (ATBC) content and a higher P/L ratio (Figs. 4 and 5). The other materials exhibited the same tendencies in setting characteristics.

Table 5 shows the gelation times of the trial soft denture liners and their evaluation in terms of manipulation. The trial materials that had gelation times comparable to those of the six commercial acrylic denture liners tested (128–652 s) were considered clinically acceptable. The shortest gelation times were observed for the materials that consisted of 75 wt% i-BMA/25 wt% ATBC at a P/L ratio of 1.0 or 1.2, 100 wt% i-BMA at a P/L ratio of 1.0 or 1.2, and 50 wt% i-BMA/50 wt% ATBC at a P/L ratio of 1.2 (53–87 s) ($p < 0.05$). The longest gelation times were observed for those that consisted of 25 wt% 2-EHMA/75 wt% ATBC at a P/L ratio of 1.0 or 1.2 (424–437 s) ($p < 0.05$). The materials made with a liquid that contained i-BMA as the monomer exhibited shorter gelation times than those of materials made with a liquid that contained 2-EHMA for given plasticizer (ATBC) content and P/L ratio. The gelation times of the trial soft denture liners made with a liquid that contained lower plasticizer content (i.e., higher monomer content) decreased exponentially. A positive linear relationship was found between the log of the gelation time and plasticizer content ($r = 0.900–0.948$, $p < 0.0005$) (Fig. 6).
The material with the median value of gelation time was selected from the five measured materials. Poly(EMA/BMA) was mixed with 75 wt% 2-EHMA/25 wt% ATBC at two P/L ratios.

**DISCUSSION**

The present findings confirm our hypothesis that monomer type, plasticizer content, and the powder/liquid (P/L) ratio influence the setting characteristics of light-cured acrylic permanent soft denture liners based on poly(ethyl methacrylate/butyl methacrylate) (poly(EMA/BMA)) and acetyl tributyl citrate (ATBC), and that materials with iso-butyl methacrylate (i-BMA), lower plasticizer (ATBC) content (i.e., higher monomer content), and a higher P/L ratio exhibit a shorter gelation time.

Permanent soft denture liners with viscoelastic properties are used as a shock absorber to relieve the pain caused by mastication due to remarkable alveolar resorption and/or a thin basal seat mucosa2,27. These materials distribute the transmitted masticatory forces equally on the residual ridge. They should have adequate setting characteristics when used with the chairside technique to obtain the optimal lining layer thickness, which influences the cushioning effect29. Chemical- and light-cured materials are available for cold-cured acrylic permanent soft denture liners, which are applied for the chairside technique. Light-cured materials are advantageous in terms of manipulation after the mixing of the powder and liquid compared with chemical-cured materials because the final setting does not occur before exposure to a polymerizing light source. Therefore, the setting characteristics of light-cured acrylic permanent soft denture liners were the initial focus in the present study.

The setting characteristics of denture liners and tissue conditioners have been determined using a reciprocating rheometer28, an oscillating rheometer17,21,22, and a displacement rheometer29. Reciprocating and oscillating rheometers measure a complex combination of dynamic viscosity and storage modulus29. Although these rheometers allow a comparative evaluation of the setting characteristics of different materials, they do not provide the absolute values of elasticity and viscosity. A displacement rheometer monitors the developing elastic recovery during the setting of materials. However, the viscosity that reflects the adaptation between the intaglio surface of the dentures and the basal seat

**Fig. 5** Variations of shear storage modulus ($G'$), shear loss modulus ($G''$), and loss tangent (tan $\delta$) of trial soft denture liners with time and P/L ratio.

The gelation times of the materials with a P/L ratio of 1.2 were shorter than those of materials with a P/L ratio of 1.0 ($p<0.05$) except for the materials that consisted of 25 wt% i-BMA/75 wt% ATBC, 25 wt% 2-EHMA/75 wt% ATBC, and 50 wt% 2-EHMA/50 wt% ATBC.

**Fig. 6** Relationship between the gelation times of trial soft denture liners and plasticizer (ATBC) content at 37°C.
mucosa is not determined. In the present study, a controlled stress rheometer was employed to evaluate the dynamic viscoelastic properties during the setting of soft denture liners. This rheometer determines three rheological parameters, namely the shear storage modulus (G'), shear loss modulus (G''), and loss tangent (tan δ). G' and G'' represent elastic deformation and viscous deformation under stress, respectively. The tan δ value indicates the relative contribution of the elastic and viscous components to material behavior.

Polymers such as soft denture liners undergo a phase transition from a liquid to a solid during setting. The G' and G'' values of polymers increase with time. The degrees of elasticity and viscosity are equal at the time at which tan δ=1 (G''=G'); this critical point is called the gel point. A method based on the gel point reflects both the elasticity and viscosity during setting and thus allows a scientifically rigorous evaluation of setting characteristics. The setting characteristics and gelation time of permanent soft denture liners are not specified in an ISO standard even though the consistency just after the mixing of the powder and liquid of tissue conditioners, i.e., soft lining materials for short-term use, is specified. The consistency test can determine the initial flow properties of a material just after mixing but not the gelation time. Therefore, the gel point obtained from a measurement of dynamic viscoelasticity was applied for the evaluation of gelation time in the present study. Both soft denture liners and hard denture liners were used to determine the clinically acceptable gelation time because all materials exhibited viscoelastic properties after the mixing of the powder and liquid. The hard denture liners used in this study do not become hard before 1–2 weeks after insertion in the mouth or before light curing. Thus, a clinically acceptable gelation time for the trial acrylic permanent soft denture liners was defined as a time comparable to those of the tested commercial acrylic materials (128–652 s).

Wide ranges of gelation time were found for the tested commercial acrylic materials. A liquid that consists of a monomer and a plasticizer penetrates and diffuses into the polymer, leading to polymer chain entanglement or chemical curing. Bio Liner (BL) showed a greater increase in G' and G'' and a greater decrease in tan δ with time (i.e., faster setting behavior) compared with those for the other five products. The tan δ of the products except for BL increased with time for a while just after the mixing of the powder and liquid, and then decreased. The flow properties of the materials except for BL and the resultant tan δ values were initially low because the penetration of the liquid into the polymer was slower than that for BL and not complete. After complete penetration and diffusion, the pastes had higher flow properties and higher tan δ values. Then, the entanglement or chemical curing of all the materials accelerated with time. The compatibility of the powder and liquid of BL was highest among the materials. Furthermore, there were differences in variations of G', G'' and tan δ with time among the materials. This was due to the differences in composition, such as powder type, powder molecular weight and particle size, monomer type, and plasticizer type, of the liquids among the materials. Further studies on commercial acrylic permanent soft denture liners and the relationship between composition and setting characteristics are necessary.

The present study evaluated the relationship between composition and setting characteristics to develop a light-cured acrylic permanent soft denture liner using iso-butyl methacrylate (i-BMA) or 2-ethylhexyl methacrylate (2-EHMA) as the monomer and acetyl tributyl citrate (ATBC) as the plasticizer. These monomers only slightly irradiate the mucosa. ATBC is a citric acid but not a phthalate ester that has been found to show estrogenicity. ATBC is recognized as a safe plasticizer by the U.S. Food and Drug Administration and applied as a plasticizer for food packing film. The above liquid components were thus selected in this study.

Several types of polymer such as poly(ethyl methacrylate) and poly(methyl methacrylate) are used as the powder of denture liners and denture bases. However, it is necessary to apply the polymer with lower glass transition temperature to produce the softer materials. Thus, poly(EMA/BMA), that has lower glass transition temperature than poly(ethyl methacrylate) and poly(methyl methacrylate), were used in this study. Copolymerization changes the glass transition temperature of polymers.

The gelation times of the soft denture liners that include i-BMA were shorter than those of the liners that include 2-EHMA for given plasticizer content and P/L ratio. The penetration and diffusion of the solvent into the polymer are influenced by the molar volume, which is the ratio of molecular weight to density. The molar volume of i-BMA is 160.5 cm³/mol and that of 2-EHMA is 225.4 cm³/mol. i-BMA has a lower molar volume and thus more easily penetrates and diffuses into the polymer than does 2-EHMA, resulting in faster polymer chain entanglement and a shorter gelation time. The clinically acceptable gelation time was found to be between approximately 130 and 650 s. Thus, 2-EHMA is a more suitable monomer than i-BMA for soft denture liners based on poly(EMA/BMA) and ATBC because the materials with i-BMA except for 25 wt% i-BMA/75 wt% ATBC at a P/L ratio of 1.0 or 1.2 had gelation times outside the clinically acceptable range, making them difficult to manipulate.

The gelation times increased exponentially with increasing plasticizer (ATBC) content. A plasticizer, which has a low molecular weight, penetrates and diffuses into the polymer together with the monomer, and then enters the gaps in the polymer because of its affinity. This reduces the intermolecular force and local friction coefficient of entanglement of the molecular chains. For a given material, the glass transition temperature decreases and flexibility increases with the addition of a plasticizer. The molar volume of ATBC is 384.8 cm³/mol, which is higher than those of i-BMA and 2-EHMA. Higher plasticizer (ATBC) content in the liquid leads to higher molar volume and softness. A liquid with a higher
molar volume takes longer to penetrate and diffuse into the polymer. Therefore, the liquid penetration into the polymer and thus the increase in the material elastic modulus with time will be slow, resulting in a longer gelation time. The contribution ratio (ρ) of plasticizer content to gelation time (ρ=41.4%) was slightly lower than that of monomer type (ρ=50.7%) probably because influence of change of plasticizer content on molar volume of the liquids mixed with monomer and plasticizer would be less than that of change of monomer type.

A higher P/L ratio (i.e., higher powder content) led to a greater rate of increase of $G'$ and $G''$ and a greater decrease of tan δ with time, resulting in faster gelation, which was likely due to a greater entanglement of polymer chains\(^\text{24}\). Although the P/L ratio had a significant influence on gelation time, its contribution ratio (ρ=1.2%) was lower than those of monomer type (ρ=50.7%) and plasticizer content (ρ=41.4%).

The gelation times of the acrylic permanent soft denture liners evaluated in the present study were thus less controlled by the P/L ratio compared with monomer type and plasticizer content.

In clinical practice, some working time just after the mixing of the powder and liquid of a soft denture liner is necessary to remove air bubbles, apply the denture liner to the intaglio surface of the dentures, insert the dentures into the mouth, conduct border molding, remove the dentures from the mouth, and trim redundant material. A wide range of setting characteristics was found among the trial acrylic permanent soft denture liners. When a soft denture liner with a relatively long gelation time is applied, dentists should delay the placement of the materials on the intaglio surface of the dentures and insertion into the mouth until the flow lessens to obtain the optimal lining layer thickness. Conversely, dentists should manipulate a soft denture liner with a relatively shorter gelation time more quickly and skillfully. The clinically acceptable gelation time of the trial soft denture liners for the chairside technique was defined as a time comparable to those of the commercial materials. Although the trial acrylic materials that were judged to be acceptable in the present study can be applied in a clinical situation from the standpoint of manipulation, it is necessary to determine a more rigorous definition of acceptable gelation time based on various viewpoints, such as the relationship between viscosity and evaluation of manipulation by dentists. Furthermore, an ISO standard for the setting characteristics and initial flow just after the mixing of the powder and liquid of permanent soft denture liners should be specified.

In the present study, the relationship between the setting characteristics of the trial acrylic permanent soft denture liners and composition was evaluated. We plan to evaluate the dynamic viscoelastic properties after light curing, their durability, cytotoxicity and biocompatibility of the trial soft denture liners. The results of the present study will contribute to the development of light-cured acrylic permanent soft denture liners.

**CONCLUSIONS**

Within the limitations of this study, the following conclusions can be made:

1. The clinically acceptable gelation time of the trial acrylic permanent soft denture liners was between approximately 130 and 650 s according to an evaluation of the gel point.
2. The gelation times of the trial soft denture liners that included i-BMA were shorter than those of liners that included 2-EHMA.
3. The gelation times of the trial soft denture liners increased exponentially with increasing plasticizer (ATBC) content in the liquid.
4. The gelation times of the trial soft denture liners with a P/L ratio of 1.2 tended to be shorter than those with a P/L ratio of 1.0.
5. The influence of monomer type and plasticizer (ATBC) content on the gelation times of the trial soft denture liners was greater than that of the P/L ratio.
6. 2-EHMA is a more suitable monomer than i-BMA for light-cured acrylic permanent soft denture liners based on poly(EMA/BMA) and ATBC in terms of setting characteristics. The setting characteristics can be controlled by ATBC content.

**ACKNOWLEDGMENTS**

This work was supported by JSPS KAKENHI Grant Number JP20H03880.

**REFERENCES**

1. Ministry of Health, Labour and Welfare. Survey of Dental Diseases. 2016; https://www.mhlw.go.jp/toukei/Ihat/62-17. html.
2. Murata H, Taguchi N, Hamada T, Kawamura M, McCabe JF. Dynamic viscoelasticity of soft liners and masticatory function. J Dent Res 2002; 81: 123-128.
3. Schmidt WF Jr, Smith DE. A six-year retrospective study of Molloplast-B-lined dentures. Part I: Patient response. J Prosthet Dent 1983; 50: 308-313.
4. Duncan JD, Clark LL. The use of a soft denture liner for chronic residual ridge soreness. J Am Dent Assoc 1985; 111: 64-65.
5. Williamson RT. Clinical application of a soft denture liner: a case report. Quintessence Int 1995; 26: 413-418.
6. Kimoto S, So K, Yamamoto S, Ohno Y, Shinomiya M, Ogura K, et al. Randomized controlled clinical trial for verifying the effect of silicone-based resilient denture liner on the masticatory function of complete denture wearers. Int J Prosthodont 2006; 19: 593-600.
7. Kimoto S, Kimoto K, Gunji A, Kawai Y, Murakami H, Tanaka K, et al. Clinical effects of acrylic resilient denture liners applied to mandibular complete dentures on the alveolar ridge. J Oral Rehabil 2007; 34: 862-869.
8. Kimoto S Yamamoto S, Shinomiya M, Kawai Y. Randomized controlled trial to investigate how acrylic-based resilient liner affects on masticatory ability of complete denture wearers. J Oral Rehabil 2010; 37: 533-539.
9. Waters M, Jagger R, Williams K, Jerolimov V. Dynamic mechanical thermal analysis of denture soft lining materials.
10) Murata H, Taguchi N, Hamada T, McCabe JF. Dynamic viscoelastic properties and the age changes of long-term soft denture liners. Biomaterials 2000; 21: 1421-1427.

11) Dootz ER, Koran A, Craig RG. Physical property comparison of 11 soft denture lining materials as a function of accelerated aging. J Prosthet Dent 1993; 69: 114-119.

12) McCabe JF, Basker RM, Murata H, Wollwage PG. The development of a simple test method to characterise the compliance and viscoelasticity of long-term soft lining materials. Eur J Prosthodont Restor Dent 1996; 4: 77-81.

13) Kawano F, Ohguri T, Koran A III, Matsumoto N, Ichikawa T. Influence of lining design of three processed soft denture liners on cushioning effect. J Oral Rehabil 1999; 26: 962-968.

14) Kawano F, Dootz ER, Koran A 3rd, Craig RG. Bond strength of six soft denture liners processed against polymerized and unpolymerized poly(methyl methacrylate). Int J Prosthodont 1997; 10: 178-182.

15) Aydin AK, Terzioglu H, Akinay AE, Ulubayram K, Hasirci N. Bond strength and failure analysis of lining materials to denture resin. Dent Mater 1999; 15: 211-218.

16) Wright PS. Soft lining materials: their status and prospects. J Dent 1976; 4: 247-256.

17) Murata H, Iwanaga H, Shigeto N, Hamada T. Initial flow of tissue conditioners - influence of composition and structure on gelation. J Oral Rehabil 1993; 20: 177-187.

18) Parker S, Braden M. The effect of particle size on the gelation of tissue conditioners. Biomaterials 2001; 22: 2039-2042.

19) Yang TC, Cheng KC, Huang CC, Lee BS. Development of new tissue conditioner using acetyl tributyl citrate and novel hyperbranched polyester to improve viscoelastic stability. Dent Mater 2015; 29: 695-701.

20) Saito Y. Polymerization characteristics of EMA-based resin. Dent Mater J 2004; 23: 14-18.

21) Yoshida K, Kurogi T, Torisu T, Watanabe I, Murata H. Effects of 2,2,2-trifluoroethyl methacrylate on properties of autopolymerized hard direct denture reline resins. Dent Mater J 2013; 32: 744-752.

22) Okuyama Y, Shiraishi T, Yoshida K, Kurogi T, Watanabe I, Murata H. Influence of composition and powder/liquid ratio on setting characteristics and mechanical properties of autopolymerized hard direct denture reline resins based on methyl methacrylate and ethylene glycol dimethacrylate. Dent Mater J 2014; 33: 522-529.

23) International Organization for Standardization (2016) ISO 10139-2. Dentistry –Soft lining materials for removable dentures– Part 2: Materials for long-term use.

24) Murata H, Chimori H, Hamada T, McCabe JF. Viscoelasticity of dental tissue conditioners during the sol-gel transition. J Dent Res 2005; 84: 376-381.

25) Winter HH, Chambon F. Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. J Rheol 1986; 30: 367-382.

26) Nielson LE, Landel RF. Mechanical properties of polymers and composites. 2nd ed. New York: Marcel Dekker Inc; 1994. p. 167-175.

27) Jepson NJ, McCabe-JF, Storer R. Evaluation of the viscoelastic properties of denture soft lining materials. J Dent 1993; 21: 163-170.

28) Jones DW, Sutow EJ, Graham BS, Milne EL, Johnston DE. Influence of plasticizer on soft polymer gelation. J Dent Res 1986; 65: 634-642.

29) Murata H, McCabe JF, Jepson NJ, Hamada T. The determination of working time and gelation time of temporary soft lining materials. Dent Mater 1997; 13: 186-191.

30) International Organization for Standardization (2018) ISO 10139-1. Dentistry –Soft lining materials for removable dentures– Part 2: Materials for short-term use.

31) Mir GN, Lawrence WH, Autian J. Toxicological and pharmacological actions of methacrylate monomers I: Effects on isolated, perfused rabbit heart. J Pharm Sci 1973; 62: 778-782.

32) Hashimoto Y, Kawaguchi M, Miyazaki K, Nakamura M. Estrogenic activity of tissue conditioners in vitro. Dent Mater 2003; 19: 341-346.

33) Hong G, Maeda T, Li Y, Sadamori S, Hamada T, Murata H. Effect of PMMA polymer on the dynamic viscoelasticity and plasticizer leachability of PEMA-based tissue conditioners. Dent Mater J 2010; 29: 374-380.

34) Arias V HA, Odelius K, Albertsson AC. Polylactides with “green” plasticizers: Influence of isomer composition. J Appl Polym Sci 2013; 130: 2962-2970.