

## Effects of 2,2,2-trifluoroethyl methacrylate on properties of autopolymerized hard direct denture reline resins

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This study evaluated the effects of the fluorinated monomer of 2,2,2-trifluoroethyl methacrylate (TFEMA) on the properties of autopolymerized hard direct denture reline resins. Iso-butyl methacrylate (i-BMA) and 2-hydroxyethyl methacrylate (2-HEMA) containing 30% TFEMA by weight were used as monomers, while poly(ethyl methacrylate) was used as a powder. Setting characteristics, dynamic mechanical properties, and changes over time, as well as wettability were determined by use of an oscillating rheometer, dynamic viscoelastometer, and contact angle meter. Water absorption and solubility were also measured according to ISO specifications. The reline resin based on i-BMA had greater elasticity and stiffness properties, while that based on 2-HEMA showed fewer dynamic mechanical property changes over time with the addition of TFEMA. Furthermore, water absorption and solubility tended to be reduced and contact angle increased. The results of this study suggest that TFEMA improves mechanical properties and durability of reline resins over time.

**Keywords:** Reline resin, Fluorinated monomer, 2,2,2-trifluoroethyl methacrylate, Dynamic mechanical properties, Water absorption and solubility

### INTRODUCTION

With long-term use of removable dentures, adaptation between the denture intaglio surface and denture-bearing mucosa is gradually reduced when physiological bone resorption occurs<sup>1,2</sup>. Hard denture reline resins are used to improve the adaptation of ill-fitting complete and removable partial dentures, and enhance stability and retention<sup>3</sup>. Reline methods are classified into indirect and direct method. In the indirect method, there is no stimulus to the oral mucosa by the monomers in the materials or temperature during polymerization, because the reline is conducted in a dental laboratory. However, the denture must be kept from the patient for a few days. In addition, the laboratory procedure is complicated and includes investing, heat curing, and removal of the stone from around the denture. In contrast, the direct method is performed chairside using autopolymerized reline resins and widely applied for relining of ill-fitting dentures. Furthermore, it is not a complicated procedure and there is no need to keep the denture at the dental laboratory. On the other hand, when reline resins are used with the direct method, various clinical problems occur, such as unpleasant odor and taste, and irritation to the oral mucosa caused by the monomers contained in the direct reline resins and exothermic reaction during polymerization<sup>4-8</sup>. A high solubility of the monomers has also been observed with autopolymerized reline resins. Additionally, it has been reported that water absorption acts as a plasticizer, leading to a decrease in mechanical properties and increase in dimensional changes<sup>9-11</sup>, and that the solubility of the components can irritate the oral

mucosa<sup>12-14</sup>.

Generally, the powder form of autopolymerized hard direct denture reline resins consists of poly(ethyl methacrylate), along with a peroxide initiator and pigment<sup>7,14,15</sup>. The liquid components, which vary among reline resins, are mixtures of iso-butyl methacrylate, 2-hydroxyethyl methacrylate, methyl methacrylate, and 2-ethyl hexyl methacrylate, along with a chemically activated accelerator<sup>7,14,15</sup>.

Several studies have been conducted to examine improvements in the durability of denture base resins including reline resins. Addition of glass fiber to acrylic resins was found to decrease polymerization shrinkage, though water absorption in the tested resins was not improved<sup>16</sup>. Cross-linking agents such as ethylene glycol dimethacrylate in the liquid have also been shown effective for improving mechanical properties such as craze resistance, stiffness, and surface hardness<sup>17,18</sup>. As for water absorption, the value decreases by increasing the concentrations of the cross-linking agents<sup>18</sup>. However, the solubility characteristics of liquid components differ from those of water absorption, as solubility tends to exhibit a small decrease up to approximately 40%, followed by a much greater increase as the concentration of the cross-linking agent increases, *i.e.*, solubility is not improved<sup>18</sup>. Although the addition of cross-linking agents has some effects on improvement of autopolymerized reline resins in regard to their mechanical properties and water absorption, it is considered necessary to examine the development of ideal reline resins from a different viewpoint.

In the present study, a new type of fluorinated monomer was focused on as the liquid component of reline

resin. Fluorinated monomer and fluorocarbon polymers have advantages, including water and oil repellency, contamination resistance, and chemical stability<sup>19-21</sup>, and have been used in various biomaterials such as arterial and venous prostheses<sup>22,23</sup>. In the field of dentistry, a commercial hard denture lining material consisting of fluorocarbon polymer has been introduced<sup>24</sup>. However, scant information is available concerning the effects of fluorinated monomer and fluorocarbon polymers on reline resins in regard to water absorption, solubility, and mechanical properties such as rheology, as well as durability over time.

The purpose of the present study was to evaluate the effect of the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) in liquid on the above-mentioned properties of autopolymerized hard direct denture reline resins. It was hypothesized that the addition of TFEMA to reline resins would reduce water absorption and solubility, resulting in improved durability.

## MATERIALS AND METHODS

Poly(ethyl methacrylate) powder with a weight average molecular weight of  $50.0 \times 10^4$  and containing a trace of benzoyl peroxide as a polymerization initiator was used. The liquid components and chemical formulas of the monomers used in this study are listed in Table 1 and Fig. 1, respectively. Iso-butyl methacrylate (i-BMA) and 2-hydroxyethyl methacrylate (2-HEMA) containing the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) at 30% by weight were used as monomers. A trace of p-tolyldiethanolamine was added as a polymerization accelerator to produce autopolymerized materials. These materials without the fluorinated monomer were also evaluated. The powder/liquid ratio was 1.6 by weight. Setting characteristics, dynamic mechanical properties and their changes with time, water absorption, solubility, and contact angle for each material were measured.

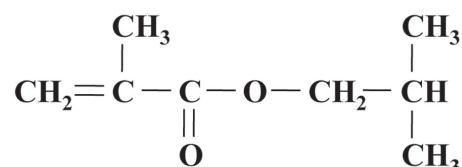
### Setting characteristics

An oscillating rheometer (Seiki Co., Tokyo, Japan) that records the time course of amplitude of the lower platen with change of viscosity of the tested material, which determines the resistance received from the material, was used to determine the setting characteristics of the materials<sup>25</sup>. The amplitude of the rheometer trace decreases as the material sets. The lower platen is fixed to 3 sheet springs connected to the driver shaft and the upper platen to the arm. The platens are 10 mm in diameter and the distance between each is 1.0 mm. Torsional deformation is applied to the sample through the sheet springs at a speed of 10 rpm. The oscillating movement of the lower platen without a sample is  $1.45^\circ$ . A hybrid recorder (AL371P-N00-01A, Chino Corp., Tokyo, Japan) was also used to record the output from the rheometer.

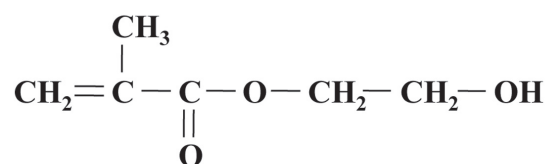
After mixing the powder and liquid for 30 s at  $23 \pm 1^\circ\text{C}$ , the paste was placed in the rheometer and the relative change of viscosity over time was recorded at

Table 1 Composition of experimental monomer liquids

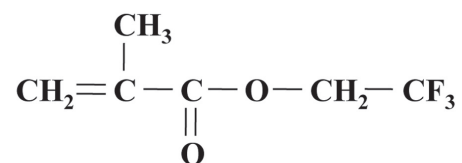
| Code         | Composition  |
|--------------|--|
| i-BMA        | 100% iso-butyl methacrylate  |
| i-BMA/TFEMA  | 70% iso-butyl methacrylate<br>30% 2,2,2-trifluoroethyl methacrylate      |
| 2-HEMA       | 100% 2-hydroxyethyl methacrylate   |
| 2-HEMA/TFEMA | 70% 2-hydroxyethyl methacrylate<br>30% 2,2,2-trifluoroethyl methacrylate |



iso-butyl methacrylate (i-BMA)



2-hydroxyethyl methacrylate (2-HEMA)



2,2,2-trifluoroethyl methacrylate (TFEMA)

Fig. 1 Chemical formulae of monomers used in this study.

a temperature of  $37^\circ\text{C}$ . The setting time was defined as that required for a 75% reduction in width of the rheometer amplitude, as previously reported<sup>25</sup>.

### Dynamic mechanical properties

The dynamic mechanical properties of the test materials were determined using an automatic dynamic viscoelastometer (Rheovibron DDV-25FP, A&D Co. Ltd., Tokyo, Japan) based on the principle of nonresonance forced vibration<sup>15</sup>. With this device, sinusoidal tensile strain is added to one side of the sample and stress

response is detected on the other side. Delay of the strain wave is dependent on the viscoelastic properties of the material.

Five samples for each material were prepared in the form of rectangular blocks (20.0×7.0×0.6 mm) using a metal mold. Measurements were performed to examine 2 experimental conditions; time dependence and temperature dependence of the dynamic mechanical properties.

A series of tests for time dependence were conducted at 1 Hz and 37°C at 24 h, and 1, 2, 4, 6, 9 and 12 months after preparation of the sample. The samples were stored in distilled water at 37°C except during the measuring period. The rheological parameters tensile storage modulus ( $E'$ ), tensile loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were calculated using the following equations<sup>26)</sup>:

$$E^* = E' + iE''$$

$$E' = |E^*| \cos \delta$$

$$E'' = |E^*| \sin \delta$$

$$\tan \delta = E''/E'$$

where  $E^*$  is the complex dynamic tensile modulus,  $i = \sqrt{-1}$ , and  $\delta$  the phase angle between stress and strain.

Tests for temperature dependence were conducted at 1 Hz over a temperature range of -150°C to 150°C at 24 h after sample preparation to determine the glass transition temperature ( $T_g$ ) of the tested material.  $T_g$  was defined as the temperature corresponding to the maximum of the  $\tan \delta$  peak position<sup>27,28)</sup>. The ends of the samples were held with a separation of 15 mm and the strain added to the sample was 0.05% in both tests<sup>15)</sup>.

#### Water absorption and solubility

Water absorption and solubility tests were carried out according to ISO specification 20795-1 (2008)<sup>29)</sup>. Each sample was made into a disc measuring 50±1 mm in diameter and 0.5±0.1 mm thick, with the dimensions checked with a micrometer. They were stored in a desiccator containing freshly dried silica gel at 37±1°C for 23±1 h and then at 23±1°C for 60±10 min. The samples were then weighed to an accuracy of 0.2 mg using a micro balance (AEM-5200, Shimadzu Corp., Kyoto, Japan). The cycle described above was repeated until a constant mass ( $m_1$ ) was obtained. Conditioned samples were immersed in distilled water at 37°C for 7 days±2 h, removed from water and weighed to obtain the  $m_2$  value, then reconditioned to a constant mass ( $m_3$ ) using the desiccator. Water absorption and solubility of the tested materials were determined using the following formulae:

$$\text{Absorption } (\mu\text{g}/\text{mm}^3) = (m_2 - m_3)/V$$

$$\text{Solubility } (\mu\text{g}/\text{mm}^3) = (m_1 - m_3)/V$$

where  $V$  is the volume of the sample ( $\text{mm}^3$ )

#### Wettability

Wettability was evaluated as a contact angle of distilled water on the sample surface using a contact angle meter (CA-DT type, Kyowa Interface Science Co. Ltd., Saitama, Japan). Five samples of each material were prepared in the form of rectangular blocks

(60.0×10.0×3.0 mm) using a metal mold. 2  $\mu\text{L}$  of distilled water was then dropped onto the sample and the contact angle was determined at 23±1°C.

#### Statistical analyses

Five tests were carried out for each measurement and material. Student's  $t$ -test was performed to determine whether statistically significant differences were present between the materials with and without TFEMA. A one-way analysis of variance (ANOVA) was also conducted to find whether statistically significant differences were present among the times for  $E'$ ,  $E''$  and  $\tan \delta$  of each material. For all statistical analyses, SPSS Statistics version 17.0 was used.

## RESULTS

Figure 2 shows the influence of the fluorinated monomer TFEMA on the setting times of the autopolymerized hard direct denture reline resins. The setting times were decreased significantly by addition of TFEMA both in reline resin based on i-BMA and in that based on 2-HEMA ( $p < 0.01$ ). However, the setting speed of the reline resin based on 2-HEMA was more influenced by TFEMA than that on i-BMA.

The values for  $E'$ ,  $E''$ , and  $\tan \delta$  of the 4 tested materials at 1 Hz and 37°C at 24 h after preparation, namely, before immersion in water, are shown in Fig. 3. The i-BMA/TFEMA sample had significantly higher  $E'$  ( $p < 0.05$ ), and lower  $E''$  and  $\tan \delta$  ( $p < 0.01$ ) values than the i-BMA sample. On the other hand, the 2-HEMA/TFEMA sample had a significantly lower  $E'$  and higher  $\tan \delta$  ( $p < 0.01$ ) value than the 2-HEMA material. There was no significant difference between the  $E''$  values of these samples.

Figure 4 shows the variations of  $E'$ ,  $E''$ , and loss  $\tan \delta$  values with time of immersion in distilled water for the

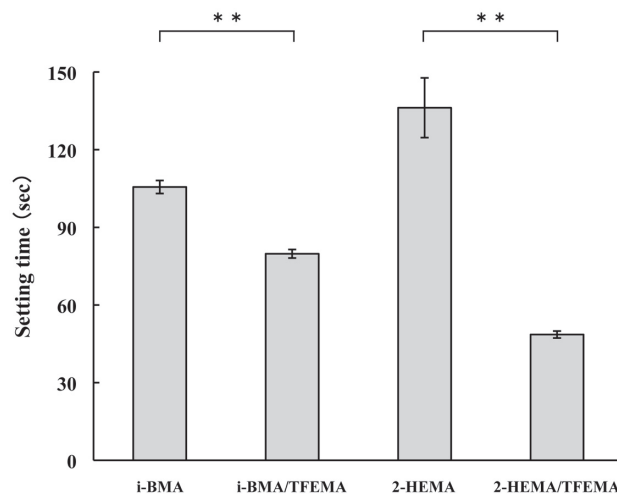


Fig. 2 Setting times for the 4 tested materials at 37°C. \*\* $p < 0.01$

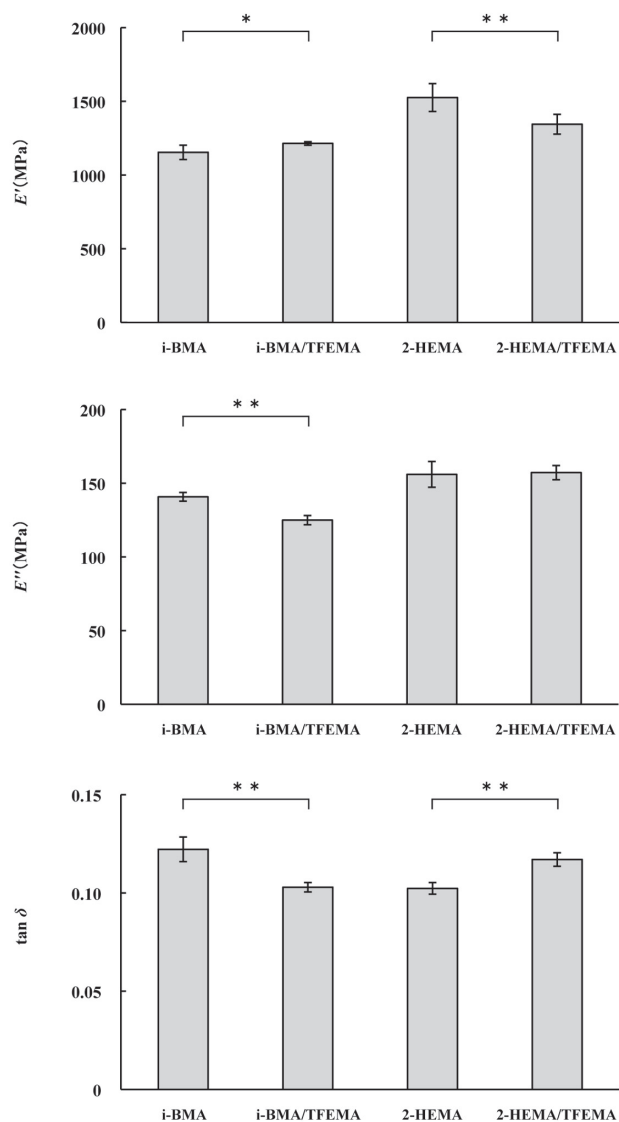


Fig. 3 Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values for the 4 tested materials at 1 Hz and 37°C at 24 h after preparation, namely, before immersion in water. \* $p < 0.05$ , \*\* $p < 0.01$

4 tested materials at 1 Hz and 37°C. Changes for all of the rheological values of the i-BMA and i-BMA/TFEMA samples were slight though significant differences were found among times for these values ( $p < 0.05$ ) except for  $E'$  of the i-BMA and i-BMA/TFEMA samples ( $p = 0.110$  and  $p = 0.056$ , respectively). The values for  $E''$  and  $\tan \delta$  gradually decreased during 1 year in water. The i-BMA/TFEMA sample showed higher  $E'$  and lower  $E''$  and  $\tan \delta$  values than the i-BMA sample throughout the 1-year test period ( $p < 0.05$ ) except for  $E'$  at 12 months ( $p = 0.085$ ). On the other hand, significant differences were found among times for the rheological values of the 2-HEMA and 2-HEMA/TFEMA samples ( $p < 0.01$ ). All values for these two samples except for  $\tan \delta$  of 2-HEMA/TFEMA

tended to change until 2 months of water immersion, after which the rate of changes was slight. The 2-HEMA/TFEMA sample also showed higher  $E'$  and lower  $\tan \delta$  values during 1 year than the 2-HEMA sample ( $p < 0.01$ ) except for  $E'$  at 1 and 6 months ( $p = 0.847$  and  $p = 0.078$ , respectively), and  $\tan \delta$  at 1 month ( $p = 0.259$ ), though the  $E'$  and  $\tan \delta$  values of the 2-HEMA/TFEMA sample were lower and higher, respectively, than those of the 2-HEMA sample at 24 h after preparation ( $p < 0.01$ ). No significant differences were found between the  $E''$  values of the 2-HEMA and 2-HEMA/TFEMA samples at all time points after water immersion ( $p = 0.280$ – $0.841$ ). The rates of change for the  $E'$  and  $\tan \delta$  values for the 2-HEMA/TFEMA sample during 1 year of water immersion were smaller as compared to 2-HEMA.

Values for temperature dependence of  $E'$ ,  $E''$  and  $\tan \delta$  for the 4 tested materials at 1 Hz at 24 h after preparation are shown in Fig. 5.  $E'$  and  $E''$  of the i-BMA and i-BMA/TFEMA samples, and those of the 2-HEMA and 2-HEMA/TFEMA samples were greatly decreased at approximately 50°C and 70–80°C, respectively. The  $\tan \delta$  values for the i-BMA and i-BMA/TFEMA samples were increased with increasing temperature and yielded maximum levels at approximately 80°C, namely, glass transition temperature ( $T_g$ ), then decreased with temperature. The peaks of  $\tan \delta$  for 2-HEMA and 2-HEMA/TFEMA samples were observed at approximately 105°C and 95°C, respectively.

The  $T_g$  values of the 4 tested materials are shown in Fig. 6. i-BMA/TFEMA had a slightly higher  $T_g$  than i-BMA, though the difference was not significant.  $T_g$  of the 2-HEMA sample was significantly higher than that of the 2-HEMA/TFEMA sample ( $p < 0.05$ ).

Water absorption and solubility for the 4 tested materials are listed in Table 2. Samples composed of i-BMA had lower absorption and solubility than those composed of 2-HEMA. There were no significant differences in absorption and solubility between i-BMA and i-BMA/TFEMA samples. On the other hand, the 2-HEMA/TFEMA samples showed significantly lower absorption and solubility than the 2-HEMA samples ( $p < 0.01$ ).

Figure 7 shows the results of contact angle for the 4 tested materials. Samples containing i-BMA tended to have a higher contact angle than those containing 2-HEMA. The contact angle of 2-HEMA/TFEMA was significantly higher than that of 2-HEMA ( $p < 0.01$ ), whereas no significant difference was noted between the contact angles of the i-BMA and i-BMA/TFEMA samples.

## DISCUSSION

The present findings confirmed our hypothesis that addition of the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) would improve the mechanical properties and durability of autopolymerized hard direct denture relines over time. However, the influence of the monomer on some of the resin properties varied between the main monomers iso-butyl methacrylate

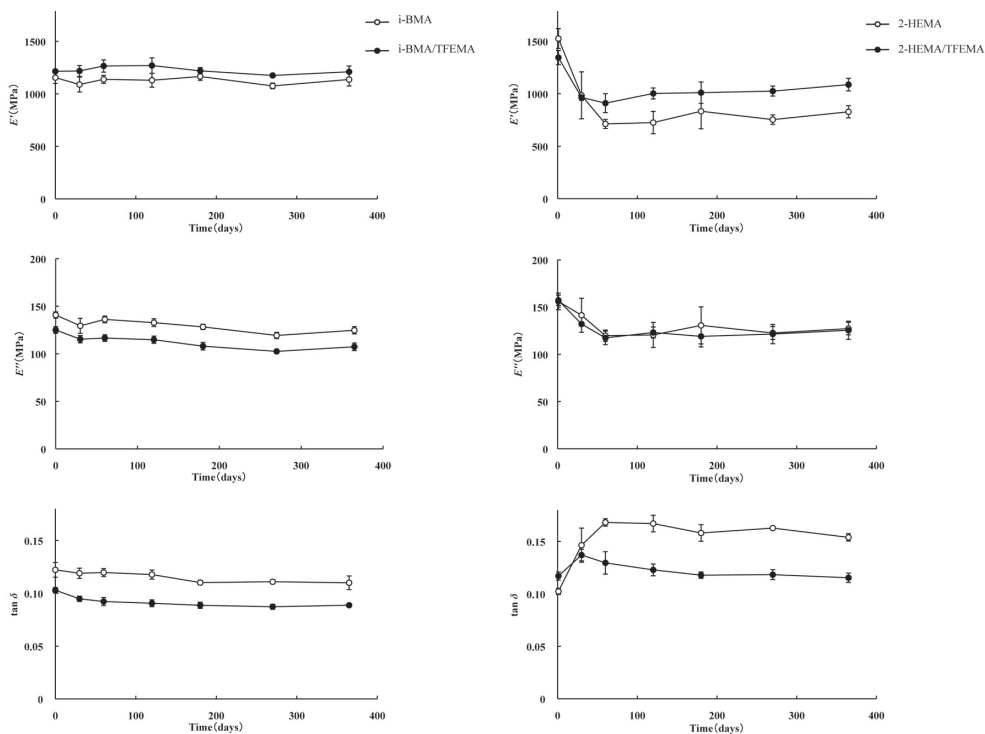


Fig. 4 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values over time for the 4 tested materials with immersion in distilled water at 1 Hz and 37°C.

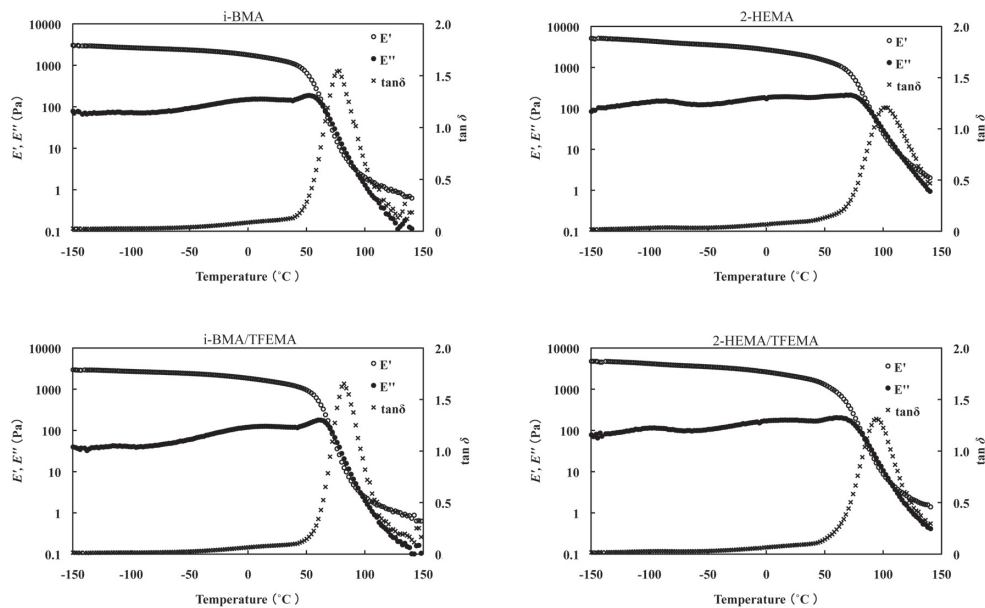


Fig. 5 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with temperature for the 4 tested materials at 1 Hz at 24 h after preparation, namely, before immersion in water.

(i-BMA) and 2-hydroxyethyl methacrylate (2-HEMA).

Ideal characteristics of hard direct denture relines would include mechanical properties similar to

denture base resins, such as higher storage modulus ( $E'$ ), lower loss tangent ( $\tan \delta$ ), lower water absorption and solubility, and higher durability over time<sup>15,30</sup>. In

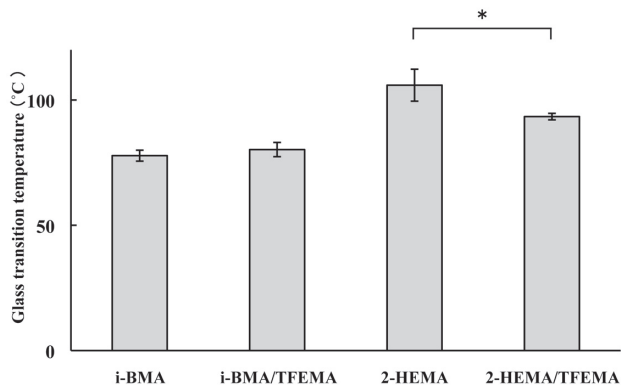


Fig. 6 Glass transition temperature ( $T_g$ ) for the 4 tested materials. \* $p < 0.05$

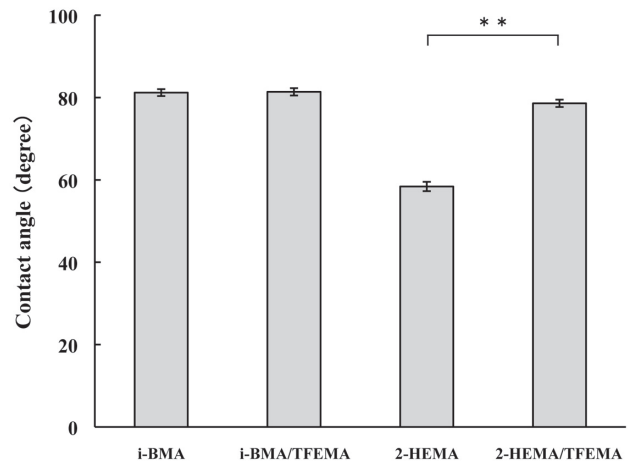


Fig. 7 Contact angle for the 4 tested materials. \*\* $p < 0.01$

Table 2 Water absorption and solubility for the 4 tested materials

| Materials    | Water absorption ( $\mu\text{g}/\text{mm}^3$ ) | Solubility ( $\mu\text{g}/\text{mm}^3$ ) |
|--------------|--|--|
| i-BMA        | 8.16 (0.88)                                    | 2.60 (0.25)                              |
| i-BMA/TFEMA  | 7.30 (0.78)                                    | 2.02 (0.49)                              |
| 2-HEMA       | 163.47 (8.14)                                  | 28.29 (1.22)                             |
| 2-HEMA/TFEMA | 78.84 (2.59)                                   | 11.93 (1.14)                             |

\*\* $p < 0.01$

the present study, a fluorinated monomer, TFEMA, was applied as a liquid component to the relines to evaluate its efficacy for improvement of mechanical properties and durability. Although further studies will be necessary to develop the ideal relines, the relines containing the fluorinated monomer would exhibit higher durability with time and reduce the risk of fracture of denture, roughness of denture surface and adherence of denture plaque, resulting in longer lifetime of the denture.

Several types of monomers are available commercially for autopolymerized hard direct denture relines, with methyl methacrylate (MMA) monomer previously used widely as a liquid component. However, that monomer is an irritant and sensitizes patients, who suffer allergic responses<sup>31</sup>. In recent years, i-BMA monomer has become popular, because it is far less irritating to oral mucosa, and has caused fewer exothermic reactions during curing and lower solubility than MMA<sup>7,31,32</sup>. 2-HEMA is also used as a liquid component of relines because of its biocompatible characteristics including lack of odor. In the field of ophthalmology, 2-HEMA polymer is utilized for producing soft contact lenses. However, water absorption occurs due to the hydrophilic nature caused by the hydroxyl group<sup>18</sup>. Thus i-BMA and

2-HEMA were used as the main liquid components in the present study.

Addition of TFEMA influenced the properties of the relines evaluated in the present study. TFEMA has 3 fluorine atoms in a single molecule. The main characteristic of these atoms is high electronegativity in all elements, and the C-F bond is extremely high (bond dissociation energy: 116 kcal/mol). Thus, the fluorocarbon polymer demonstrates water- and oil-repellent properties, low surface tension, and non-adhesion. Furthermore, it has been reported that a polymer with a larger number of fluorine atoms became softer and demonstrated lower mechanical properties because the intermolecular distance is greater<sup>20</sup>. Therefore, TFEMA with a short carbon chain and intermolecular distance was selected as an additive from the various fluorinated monomers available in the present study. The larger percentage of TFEMA will have the larger effect on improvement in mechanical properties and durability of the relines. However, addition of more than 30% of TFEMA has been found to lead to so short setting time that the samples cannot be prepared in the preliminary experiment. It is not also possible to apply the relin resin with more than 30% of TFEMA in the liquid in clinical situations from the standpoint of manipulation. Thus monomers containing TFEMA at 30% was used to obtain the greater possible advantage of TFEMA in this study.

Setting characteristic is an important factor to consider when evaluating the handling of autopolymerized hard denture relines used in a direct method. The setting time in the present study was determined as the time required for a 75% reduction in width of the amplitude of the oscillating rheometer, because the materials were considered to be elastic enough to be removed from the mouth when a 75% reduction occurred<sup>25</sup>. Addition of TFEMA (molecular weight: 168.12) accelerated the setting and produced shorter setting times for both the relines

resin based on i-BMA (molecular weight: 142.20) and on 2-HEMA (molecular weight: 130.14). TFEMA with a higher-molecular-weight monomer produces a faster increase of elasticity by crosslinking, resulting in faster setting time.

Determination of dynamic mechanical properties is also important because reline resins are subjected to instantaneous and cyclic stress such as mastication. In general, the masticatory cycle is approximately 1 Hz<sup>33</sup>. It has been reported that a dynamic mechanical test that measures the response of the material to sinusoidal or other cyclic stress is more suitable for clinical situations than static tests, such as creep and stress relaxation tests<sup>26</sup>.

Therefore, the dynamic mechanical testing at a frequency of 1 Hz was performed in the present study. Addition of TFEMA caused the reline resin based on i-BMA to gain more elastic and stiffer properties, while addition to 2-HEMA led to a more viscous property. However, materials that consisted of 2-HEMA/TFEMA liquid exhibited higher  $E'$  and lower  $\tan \delta$  values after 2 months of storage, namely, they were more elastic than the 2-HEMA sample. The glass transition temperature ( $T_g$ ) also has great significance from a practical point of view. Large changes occur in the mechanical properties of polymeric materials before and after  $T_g$  due to micro-Brownian motion of the segment, which is affected by intermolecular force and the size of the side chain<sup>34</sup>. Addition of TFEMA produced higher  $T_g$  in the reline resin based on i-BMA and lower  $T_g$  in that based on 2-HEMA. This result was consistent with that of the  $E'$  values obtained in the dynamic mechanical test, that is samples with higher  $E'$  values exhibited higher  $T_g$ . The above phenomena can be attributed to the length of the side chain, intermolecular forces induced by the polarizability of the monomers, compatibility between the polymer and monomer, homogeneity of the autopolymerized resins, and degree of polymerization, all factors that intricately influence the mechanical properties<sup>35,36</sup>.

Durability of the resins utilized is relevant for the continued function of relined dentures. The dynamic mechanical properties of the reline resins that consisted of i-BMA with and without TFEMA remained stable during 1 year of water immersion. Although addition of TFEMA did not have a large influence on the changes in rheological parameters of the reline resin based on i-BMA over time, it led to a higher  $E'$  value and lower values for  $\tan \delta$  and  $E''$ , namely, to greater elasticity and stiffness. On the other hand, in the case of reline resin based on 2-HEMA, addition of TFEMA resulted in higher durability, as shown by the results that the rates of change of  $E'$  and  $\tan \delta$  of the 2-HEMA/TFEMA sample over time were smaller than those of the 2-HEMA sample, though the addition of TFEMA gave a viscous property in the initial stage. Notably,  $\tan \delta$  of the 2-HEMA/TFEMA sample remained unchanged during 1 year of water immersion. Reline resins that consisted of 2-HEMA containing TFEMA tended to remain more stable than those without TFEMA.

Reline resins undergo 2 processes when immersed in water; as some monomer components are leached out into the water and water is absorbed into the structure of the resins. Water absorption and the wettability of the materials can be measured to evaluate hydrophilicity and hydrophobicity. Furthermore, water absorption and solubility are deeply involved in degradation of the materials over time. The results of this study showed the decreases in water absorption and solubility, and an increase in contact angle significantly when TFEMA was added to 2-HEMA. The effect of the fluorinated monomer varied between the monomers used as a base. Reline resin based on 2-HEMA, which was more hydrophilic, was influenced more than that based on i-BMA. The surface of materials that contain fluorine atoms has a lower level of surface energy<sup>20</sup> and exhibits a higher value for contact angle, resulting in higher water repellency. Thus, the decrease in water absorption by addition of TFEMA was considered due to the higher hydrophobicity of the fluoroalkyl group<sup>36</sup>. In addition, the decrease in solubility of the components in water might be also due to hydrophobicity or the degree of polymerization. The present results showed that addition of TFEMA improves the durability of reline resins over time.

In order to evaluate the durability of reline resins in clinical settings, it is necessary to determine their mechanical properties under conditions more similar to the oral cavity, such as thermal cycling, masticatory force, and saliva. Furthermore, the influence of denture cleansers and especially adhesion to denture base acrylic resins are also important. The adhesion of the reline resins to denture base resins is generally dependent on formation of an interpenetrating polymer network (IPN) that is formed by diffusion of monomers into the polymers and polymerization of diffused monomers<sup>37</sup>. The monomer having higher molecular weight tends to show the lower permeability. Thus there is a possibility that the addition of TFEMA would reduce the bond strength to the denture base resins because the molecular weight of TFEMA is higher than those of i-BMA and 2-HEMA. The specific primer for this kind of reline resin would be necessary. Additional studies focused on these factors are necessary.

An ideal hard reline resin would have high  $E'$  and low  $\tan \delta$  values, low water absorption and solubility, and excellent durability over time<sup>15,30</sup>. The results of the present study suggest that addition of TFEMA to autopolymerized hard direct denture reline resins is effective for improving mechanical properties and durability, and should contribute to development of such denture reline resins with ideal characteristics.

## CONCLUSION

Within the limitations of the present study, the following conclusions can be drawn:

1. Addition of the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) to autopolymerized hard direct reline resins based

- on iso-butyl methacrylate (i-BMA) or 2-hydroxyethyl methacrylate (2-HEMA) accelerated the setting behavior.
2. Reline resin based on i-BMA was more elastic and stiffer, while that based on 2-HEMA showed a more viscous property with addition of TFEMA. Over time, the 2-HEMA/TFEMA sample developed more elasticity and stiffness as compared to the 2-HEMA sample.
  3. The glass transition temperature of reline resin based on i-BMA tended to be slightly higher with addition of TFEMA, while that based on 2-HEMA showed a significant decrease.
  4. Changes in the dynamic mechanical properties of reline resin based on 2-HEMA containing TFEMA tended to be smaller over time as compared to resin containing no TFEMA.
  5. Water absorption and solubility for reline resin based on i-BMA, and especially on 2-HEMA were reduced with addition of TFEMA.
  6. The wettability of reline resin based on 2-HEMA was significantly decreased when TFEMA was added.
  7. Addition of TFEMA to autopolymerized hard direct denture reline resins led to improvements in mechanical properties and durability over time.

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