

## Evaluation of glass transition temperature and dynamic mechanical properties of autopolymerized hard direct denture reline resins

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This study assessed methods for evaluation of glass transition temperature ( $T_g$ ) of autopolymerized hard direct denture reline resins using dynamic mechanical analysis and differential scanning calorimetry in addition to the dynamic mechanical properties. The  $T_g$  values of 3 different reline resins were determined using a dynamic viscoelastometer and differential scanning calorimeter, and rheological parameters were also determined. Although all materials exhibited higher storage modulus and loss modulus values, and a lower loss tangent at 37°C with a higher frequency, the frequency dependence was not large.  $T_g$  values obtained by dynamic mechanical analysis were higher than those by differential scanning calorimetry and higher frequency led to higher  $T_g$ , while more stable  $T_g$  values were also obtained by that method. These results suggest that dynamic mechanical analysis is more advantageous for characterization of autopolymerized hard direct denture reline resins than differential scanning calorimetry.

**Keywords:** Reline resin, Glass transition temperature, Dynamic mechanical analysis, Differential scanning calorimetry

### INTRODUCTION

Autopolymerized hard direct denture reline resins are widely used to provide accurate adaptation between the denture intaglio surface of complete and removable partial dentures and denture foundation areas<sup>1)</sup> changed due to residual ridge resorption<sup>2)</sup>. A procedure of reline improves the stability and retention of ill-fitting dentures. Although an indirect (laboratory-processed reline system) method has also been used, the direct method (chair-side reline system) using autopolymerized hard direct denture reline resins is applied in nearly all clinical situations, because sending the denture to a dental laboratory is not required and the procedure is easier than that of an indirect method<sup>3)</sup>.

In general, the powder component used in autopolymerized reline resins is based on poly(methyl methacrylate), poly(ethyl methacrylate), or poly(methyl methacrylate/ethyl methacrylate), while the liquid component consists of a monofunctional methacrylate monomer, polyfunctional monomer (cross-linking agent), or those in combination<sup>4)</sup>. A chemically activated accelerator such as tertiary amine is also added to the liquid to produce the autopolymerization reaction<sup>5)</sup>. The differences in composition and structure among the available materials have great influence on mechanical properties<sup>3,6-8)</sup>, manipulation<sup>3)</sup>, durability<sup>3)</sup>, water absorption and solubility of the liquid components<sup>3,6,7,9)</sup>, bond strength to denture base resins<sup>10-12)</sup> and exothermic reactions during polymerization<sup>13-15)</sup> with mechanical properties especially important for the lifetime of dentures with denture reline resins. The properties of denture reline resins have been determined by findings obtained in a 3-point bending test<sup>6,7)</sup>, Knoop hardness test<sup>12)</sup> and dynamic mechanical test<sup>4,3,8,15,16)</sup>. Furthermore,

glass transition temperature ( $T_g$ ) has great significance from a practical point of view, as polymers generally exhibit a large variation of mechanical properties with temperature. At sufficiently low temperature, amorphous polymers, which are widely used in dental materials, behave as rigid solids, and when the temperature is increased they behave as flexible solids, rubber, or viscous liquid<sup>5)</sup>. The transition from hard brittle to soft flexible material is shown by  $T_g$ <sup>17)</sup>. Large polymer chains can move freely at  $T_g$ <sup>18)</sup> though such movement is dependent on the molecular structure, as well as degree of cross-linking and branching<sup>5)</sup>.

Thermal properties including the  $T_g$  values of materials used for dentures have primarily been investigated by dynamic mechanical analysis (DMA)<sup>3,8,15,18-20)</sup> and differential scanning calorimetry (DSC)<sup>18,21,22)</sup>. Dynamic mechanical analysis is one of the most useful techniques available for evaluating the mechanical properties of materials with cyclic applications of stress and temperature. In a dynamic mechanical test, sinusoidal tensile strain is applied to one end of a specimen and stress response is measured at the other end. When the specimen is a perfectly elastic solid, the strain is in exact phase with the applied stress, while the strain is 90° out of phase in a perfectly viscous liquid. For a viscoelastic material, the strain is somewhere in between ( $\pi/2 > \delta > 0$ )<sup>16,23)</sup>. Generally, 3 rheological parameters, storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ), are determined for evaluation of the dynamic mechanical properties of the tested material.  $E'$  shows elastic deformation under stress and corresponds to completely recoverable energy, while  $E''$  shows viscous deformation and corresponds to energy loss from heat dissipation, and  $\tan \delta$  shows the relative contributions of the elastic and viscous

components, that is, a measure of the ratio of energy lost to energy stored during cyclic deformation. This parameter reveals overall material behavior<sup>16,23</sup>. The  $T_g$  value of a tested material can be determined from a graphic representation of  $\tan \delta$  or  $E''$ <sup>3,20,24-26</sup>.

Differential scanning calorimetry is essentially a thermal analysis technique used to measure temperatures and heat flow related to the thermal transition of materials<sup>24,27,28</sup>. When using a differential scanning calorimeter, 2 pans are connected to the heater. The specimen is placed into 1 and the remaining pan is used as a reference. Heat flow to each pan is monitored, and the differential between the specimen and the reference is determined, which provides variations in heat capacity with temperature of the tested material<sup>18</sup>. The  $T_g$  value can be determined as a downward step in heat flow using a differential scanning calorimetry trace<sup>18</sup>.

A previous study evaluated  $T_g$  of mouthguard materials by both dynamic mechanical analysis and differential scanning calorimetry<sup>28</sup>, and found no significant differences among various commercial materials for mean  $T_g$  values. On the other hand, differences between the  $T_g$  values obtained from dynamic mechanical analysis and differential scanning calorimetry were noted for all of the tested materials. Those findings will indicate that the  $T_g$  value of other dental materials such as autopolymerized hard direct denture reline resins may vary based on the test method used. Furthermore, for a dynamic mechanical test, it is necessary to evaluate the influence of frequency on calculated  $T_g$  values, because rheological parameters such as  $E'$ ,  $E''$ , and  $\tan \delta$  vary based on the frequency applied to the materials<sup>25,29</sup>. However, there is scant information regarding  $T_g$  evaluation methods for use with autopolymerized hard direct denture reline resins.

The purpose of the present study was to assess evaluation methods for  $T_g$  values of autopolymerized hard direct denture reline resins obtained using dynamic mechanical analysis and differential scanning calorimetry. In addition, the dynamic mechanical

properties of the tested reline resins and influence of frequency on those properties were also determined. Prior to performing the study, we speculated that differences in the obtained  $T_g$  values would be found between these 2 methods and that frequency applied in the dynamic mechanical test would have an influence on determination of  $T_g$ .

## MATERIALS AND METHODS

Table 1 shows the autopolymerized hard direct denture reline resins used in the present study, together with manufacturer and general composition. The glass transition temperatures ( $T_g$ ) values of the tested materials were determined by means of dynamic mechanical analysis and differential scanning calorimetry.

### Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis of the materials was performed using an automatic dynamic viscoelastometer (Rheovibron DDV-25FP, A&D Co. Ltd., Tokyo, Japan) based on the principle of nonresonance forced vibration<sup>3,16</sup>. Five samples of each material were prepared in the form of rectangular blocks (25.0×7.0×2.0 mm) using a metal mold. Tests for temperature dependence of the dynamic mechanical properties were conducted at 0.1, 0.2, 1, 5 and 10 Hz over a temperature range of 25–200°C at 2 h after sample preparation to determine the glass transition temperature ( $T_g$ ) of the tested material. The ends of the samples were held with a span of 15 mm and strain amounting to 0.05% was added<sup>16</sup>. The rheological parameters tensile storage modulus ( $E'$ ), tensile loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were then calculated using the following the equations:

$$\begin{aligned} E^* &= E' + iE'' \\ E' &= |E^*| \cos \delta \\ E'' &= |E^*| \sin \delta \\ \tan \delta &= E''/E' \end{aligned}$$

Table 1 Autopolymerized hard direct denture reline resins tested

Material	Batch no	Manufacturer	Composition*	
			Powder	Liquid
Kurarebase	Powder: 00076A, Liquid: 00026A	Kuraray Noritake Dental Inc., Tokyo, Japan	Poly(ethyl methacrylate)	Fluorinated monomer, Other methacrylate monomer
New Truliner	Powder: 1205-188, Liquid: 1204-150	The Harry J. Bosworth Co, Skokie, IL, USA	Poly(ethyl methacrylate)	Iso-butyl methacrylate Dibutyl phthalate
Rebaron	Powder: 1211021, Liquid: 1106011	GC Corp., Tokyo, Japan	Poly(methyl methacrylate)	Methyl methacrylate Dibutyl sebacate

\*Composition as given by manufacturers and reference 4)

Where  $E^*$  is the complex dynamic tensile modulus,  $i\sqrt{1}$  and  $\delta$  the phase angle between stress and strain.  $T_g$  was defined as the temperature corresponding to the maximum of the  $\tan \delta$  peak position<sup>3,8,20,26</sup>.

#### Differential scanning calorimetry (DSC)

Differential scanning calorimetry was conducted using a differential scanning calorimeter (DSC-60, Shimadzu Corp., Kyoto, Japan) to determine  $T_g$ . Each specimen was placed into an aluminum pan and the tests were performed under a nitrogen purge with a flow rate of 50 mL/min. The scan speed for thermal heating was 2°C/min and the temperature range was from 25–200°C. The heat flow of each material was plotted against the temperature (time) (DSC curve). The  $T_g$  values of the test materials were determined according to JIS (Japanese Industrial Standards) K 7121:1987<sup>30</sup> with 5 tests conducted for each material.

#### Statistical analyses

Five tests were carried out for each measurement and material. Comparisons of  $T_g$  values obtained by dynamic mechanical analysis at various frequencies and differential scanning calorimetry were subjected to one-way analysis of variance (ANOVA), and the mean values were compared using Tukey's method at a 5% level of significance. The above statistical analyses of  $E'$ ,  $E''$ , and  $\tan \delta$  values at 1 Hz and 37°C were also conducted to determine differences among the materials. A  $t$ -test was used to determine whether statistically significant differences existed between  $E'$  and  $E''$  for 1 Hz and 37°C. For all statistical analyses, a statistical analysis software (SPSS Statistics version 17.0, SPSS Inc., Chicago, IL, USA) was used.

## RESULTS

There were variations in the obtained storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with changes in temperature for the 3 autopolymerized hard direct denture relines resins at various frequencies (Figs. 1–3). The  $E'$  values for Kurarebase, New Truliner, and Rebaron were greatly decreased at approximately 50°C, 60°C, and 40°C, respectively, while their  $E''$  values were also greatly decreased at ranges of approximately 60–70°C, 70–80°C, and 90–100°C, respectively. Both the  $E'$  and  $E''$  values of the 3 materials tended to be higher at higher frequencies. As shown in the figures, the curves of  $E'$  and  $E''$  became shifted to the right side with increasing frequency. Furthermore, the  $\tan \delta$  values for the 3 materials were increased with increasing temperature until the maximum level was reached, then decreased. The peak of  $\tan \delta$ , namely glass transition temperature ( $T_g$ ), for Kurarebase at 0.1, 0.2, 1, 5, and 10 Hz was observed at approximately 70°C, 70°C, 73°C, 77°C, 85°C, and 89°C, respectively, while those for New Truliner were observed at approximately 62°C, 64°C, 68°C, 72°C, 79°C, and 84°C, respectively, and for Rebaron were observed at approximately 86°C, 87°C, 89°C, 92°C, and 99°C, respectively. The peak of  $\tan \delta$  ( $T_g$ )

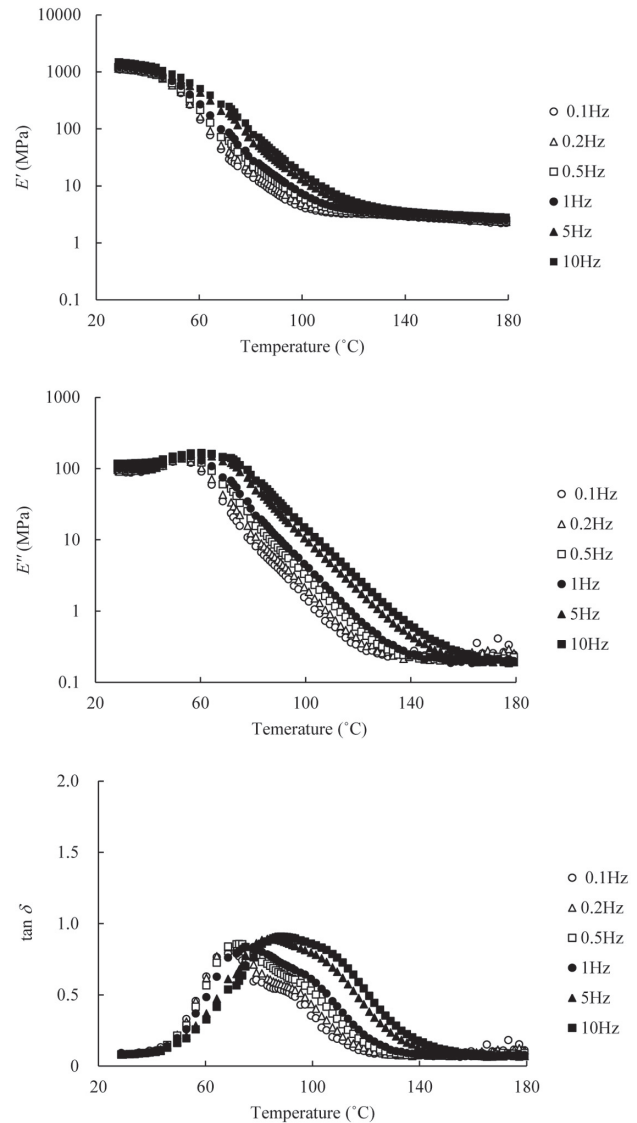


Fig. 1 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with temperature for Kurarebase at various frequencies.

of the materials demonstrated a tendency to shift to the right side, that is to higher temperature, with increasing frequency, as shown in the figures.

Figure 4 shows variations in the  $E'$ ,  $E''$  and  $\tan \delta$  values with different frequencies for the 3 tested materials at 37°C. The values for  $E'$  and  $E''$  increased with increasing frequency, whereas  $\tan \delta$  tended to decrease with increased frequency.

Figure 5 shows the  $E'$ ,  $E''$ , and  $\tan \delta$  values for the 3 tested materials at 1 Hz and 37°C. The values of  $E'$  were significantly higher ( $p < 0.01$ ) than  $E''$  for all materials. Rebaron had the highest  $E'$  value ( $p < 0.05$ ) among the test materials, while there was no significant

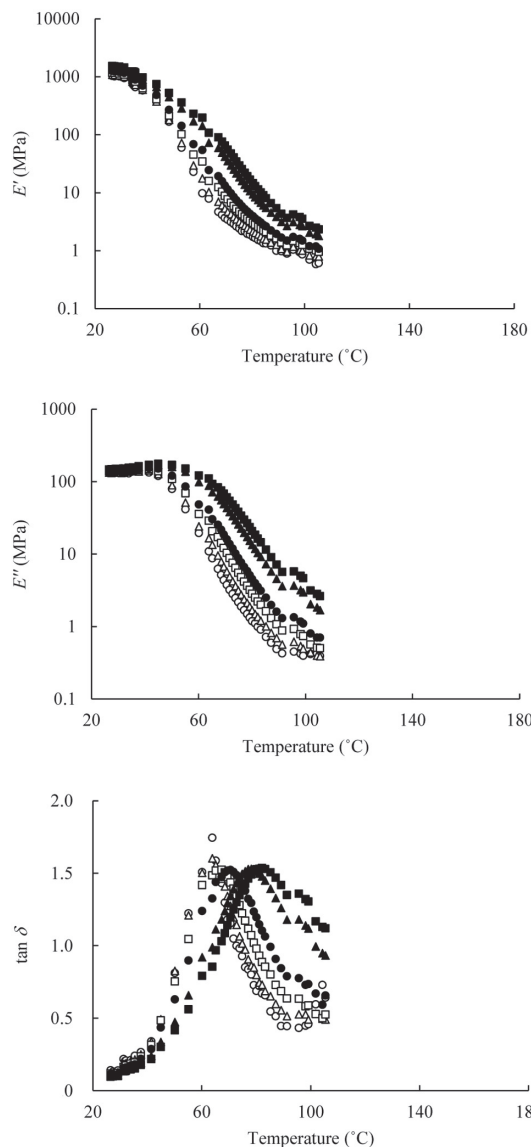


Fig. 2 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with temperature for New Truliner at various frequencies.

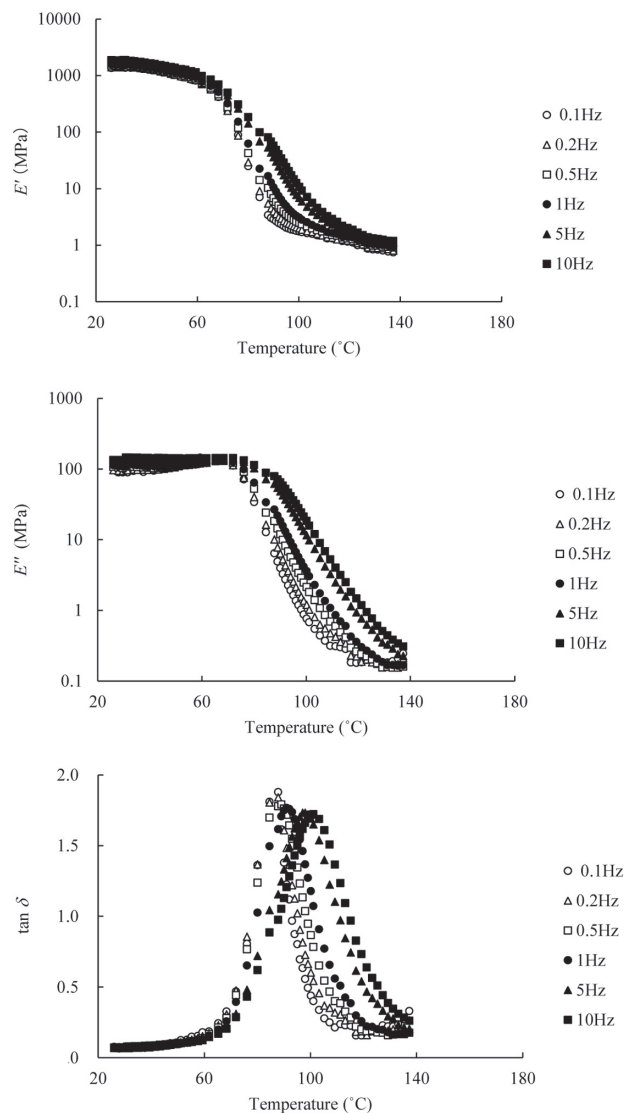


Fig. 3 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with temperature for Rebaron at various frequencies.

difference between the  $E'$  values for Kurarebase and New Truliner. As for  $E''$  values, significant differences were found among the materials ( $p < 0.05$ ) in the order of New Truliner > Rebaron > Kurarebase. Also, New Truliner had the highest  $\tan \delta$  value ( $p < 0.05$ ) among the test materials, while there was no significant difference between the  $\tan \delta$  values for Kurarebase and Rebaron.

$T_g$  values obtained by dynamic mechanical analysis at various frequencies and differential scanning calorimetry for the 3 tested materials are presented in Fig. 6. Significant differences were found for  $T_g$  values with the different frequencies applied in the dynamic mechanical analysis of all of the tested materials.  $T_g$

values were higher with higher frequencies. That for Rebaron was higher than that for Kurarebase, which in turn was higher than that for New Truliner at all frequencies ( $p < 0.05$ ). There were also differences for the  $T_g$  values among the materials in the differential scanning calorimetry measurements. Rebaron had a significantly higher  $T_g$  value than New Truliner and Kurarebase ( $p < 0.05$ ). Although  $T_g$  of New Truliner was also higher than that of Kurarebase, the difference was not significant.  $T_g$  values obtained by dynamic mechanical analysis tended to be higher than those by differential scanning calorimetry for all of the materials.

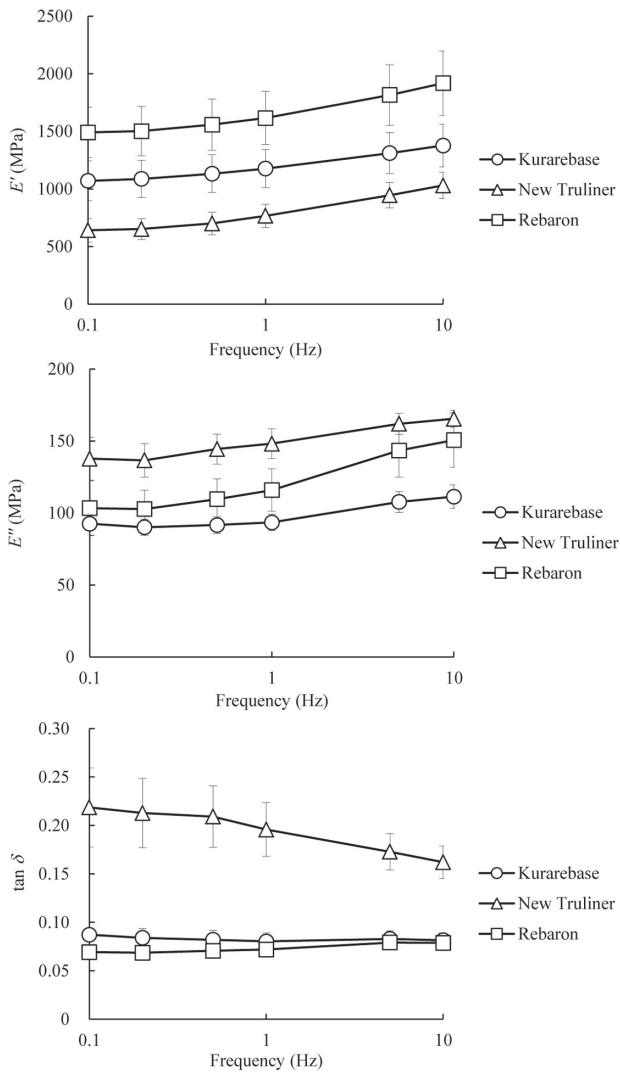


Fig. 4 Variations in storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values with frequency for the 3 tested materials at 37°C.

DISCUSSION

The present findings confirmed our speculation that the glass transition temperatures ( $T_g$ ) values for autopolymerized hard direct denture relining resins would vary between dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). In addition, they confirmed that the experimental condition of applied frequency would influence  $T_g$  in a dynamic mechanical test. We found significant differences for both  $T_g$  values and dynamic mechanical properties among the denture relining resins tested.

A direct method (chair-side relining system) using autopolymerized hard direct denture relining resins is more often applied for relining of ill-fitting dentures in clinical situations as compared with an indirect method (laboratory-processed relining system) using

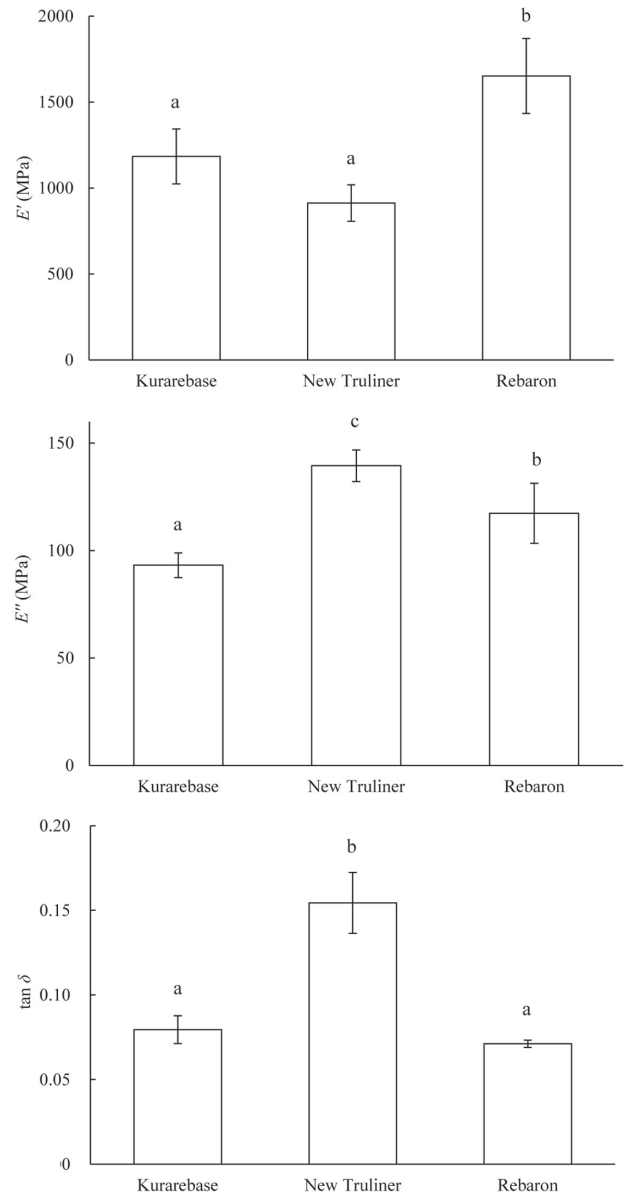


Fig. 5 Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) values for the 3 tested materials at 1 Hz and 37°C.

Identical letters indicate no statistically significant difference.

heat-polymerized denture base resins, because the former does not require sending the denture to a dental laboratory, and is also less time consuming and more convenient<sup>3,4</sup>. However, autopolymerized hard direct denture relining resins have a lower level of stiffness than heat-polymerized denture base resins, as well as unpleasant taste and odor, and cause irritation of the oral mucosa from the monomer components<sup>1,3-5,13,14,31</sup>. Ideally, an autopolymerized hard direct denture relining resin should have the same dynamic mechanical



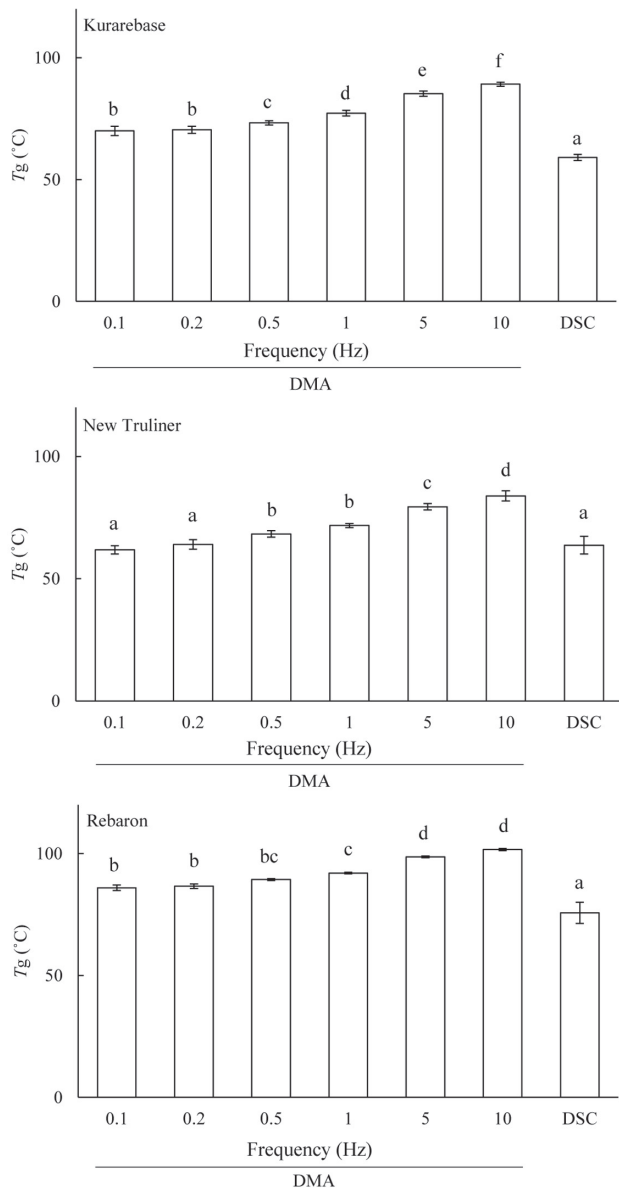


Fig. 6 Glass transition temperature ( $T_g$ ) values obtained by dynamic mechanical analysis (DMA) at various frequencies and differential scanning calorimetry (DSC) for the 3 tested materials.

properties and  $T_g$  value as a heat-polymerized denture base resin<sup>15,16,31</sup>.

Differences in dynamic mechanical properties and  $T_g$  were found among the tested denture relines. All also exhibited higher values for storage modulus ( $E'$ ) and loss modulus ( $E''$ ), and lower values for loss tangent ( $\tan \delta$ ) with higher frequency at 37°C, which indicates greater stiffness. These findings may be explained by the fact that polymers generally behave in a more elastic manner in response to a rapidly applied force, *i.e.*, at higher frequency, and more viscously in response to a

slowly applied force, *i.e.*, at lower frequency<sup>29</sup>. Although the hard relines resins behaved in a more elastic manner with higher frequency, the influence of frequency on their dynamic mechanical properties was less than that on the soft relines resins. In our previous experiments, we evaluated the influence of rheological parameters on frequency for soft denture liners<sup>29</sup>. In that study, an acrylic soft relin resin exhibited great changes with approximately 7-, 25-, and 4-fold increases in  $E'$ ,  $E''$  and  $\tan \delta$ , respectively, when the frequency changed from 0.1 to 10 Hz. On the other hand, the hard relines resins examined in the present study exhibited small increases of approximately 1.3- to 1.6-, 1.2- to 1.5-, and 0.7- to 1.1-fold in  $E'$ ,  $E''$  and  $\tan \delta$ , respectively, when the frequency was changed from 0.1 to 10 Hz. This difference in dependence on frequency between soft and hard relines resins may be due to the degree of crosslinking and polymerization.

Rheological parameters at 1 Hz are considered to be most important for clinical assessment of relin resins among the frequencies measured, because the masticatory cycle is approximately 1 Hz and the condition of the materials at that frequency simulate behavior occurring with mastication<sup>3</sup>. There were significant differences for the rheological parameters at 1 Hz among the autopolymerized hard direct denture relin resins tested. Rebaron with higher  $E'$  and lower  $\tan \delta$  values was stiffer than Kurarebase and New Truliner. Also, the  $T_g$  value of Rebaron tended to be higher than that of Kurarebase, which in turn was higher than that of New Truliner, while New Truliner had a higher  $\tan \delta$  value, that is higher  $E''$  and lower  $E'$  values. Thus, New Truliner with greater viscosity would have lower dimensional stability based on its greater ability to absorb load during mastication. The principal composition of Rebaron is similar to that of general heat-polymerized denture base resins; *i.e.*, poly(methyl methacrylate) as the powder and methyl methacrylate as the liquid components. Aliphatic ester dibutyl sebacate is also contained at approximately 10 wt% in the liquid<sup>4</sup>. In the case of New Truliner, the powder consists of poly(ethyl methacrylate), and the liquid portion consists of 92 wt% iso-butyl methacrylate and 8 wt% aromatic esters dibutyl phthalate<sup>4</sup>. As for Kurarebase, the powder is also poly(ethyl methacrylate), while the liquid components are fluorinated monomer and another methacrylate monomer. The  $T_g$  of poly(methyl methacrylate), the main powder component of Rebaron, is 105°C, and that of poly(ethyl methacrylate), the main powder component of Kurarebase and New Truliner, is 65°C<sup>17</sup>. The  $T_g$  value for Rebaron (75.7°C) was found to be approximately 29°C below that of poly(methyl methacrylate) when measured by differential scanning calorimetry, while that of Kurarebase (59.1°C) and New Truliner (63.7°C) was approximately 6°C and 1°C, respectively, lower than that of poly(ethyl methacrylate). The plasticizers (dibutyl sebacate, dibutyl phthalate) in the liquids likely caused the decrease in  $T_g$  value for the present relin resins<sup>17</sup>. In addition, other factors such as the type of monomers and residual monomer content

also may influence  $T_g$ . Methyl methacrylate monomer causes irritation to oral mucosa and occasionally allergic responses in patients, whereas iso-butyl methacrylate monomer is far less irritating to oral mucosa and causes fewer exothermic reactions during polymerization<sup>4,5,32</sup>. A fluorinated monomer was also reported to have satisfactory biocompatibility in addition to chemical stability, water and oil repellency and contamination resistance<sup>3,12,33</sup>. From this perspective, relene resins comprised of iso-butyl methacrylate (New Truliner) or fluorinated monomer (Kurarebase) as the liquid component are thought to be advantageous as compared to those comprised of methyl methacrylate (Rebaron). However, Rebaron has better mechanical properties than the other 2 relene resins tested, probably due to the difference in powder composition of poly(methyl methacrylate) and poly(ethyl methacrylate). When considering both mechanical properties and biocompatibility, a relene resin comprised of fluorinated monomer may be preferable.

The  $T_g$  of an autopolymerized hard direct denture relene resin is an important factor in addition to its mechanical properties when attempting to characterize and develop an ideal material. In the present study, the  $T_g$  values of relene resins were evaluated. Our findings demonstrated that the evaluation methods of dynamic mechanical analysis and differential scanning calorimetry had significant influence on calculation of those values. With dynamic mechanical analysis, the frequency applied to the specimen was also found to have an influence on  $T_g$ . The higher frequencies produced higher  $T_g$  values in all materials. When the frequency changed from 0.1 to 10 Hz, the increase in  $T_g$  for the tested relene resins ranged from approximately 16°C to 22°C. The dynamic mechanical properties of the relene resins were influenced by the frequency used for testing, as a higher frequency led to higher values for  $E'$  and  $E''$ .  $\tan \delta$  values, calculated as  $E''/E'$ , were also influenced by frequency.  $T_g$  values show relaxation of the molecular of polymeric materials, which generally exhibit stiffer properties at higher frequencies. Therefore,  $T_g$ , *i.e.*, the temperature corresponding to the peak position of  $\tan \delta$ , shifted to a higher temperature with higher frequency in all of the tested relene resins. A similar phenomenon has been observed with other polymeric materials such as polyisobutylene<sup>25</sup>.

In the present study,  $T_g$  measured by dynamic mechanical analysis was higher than that by differential scanning calorimetry with the differences in  $T_g$  values between dynamic mechanical analysis at 0.1 Hz and 1 Hz, and differential scanning calorimetry ranging from approximately 2°C to 11°C and 8°C to 18°C, respectively. This may have been due to differences among the tested parameters, such as mechanical properties in dynamic mechanical analysis and heat flow in differential scanning calorimetry. A previous report noted that the  $T_g$  values of polymeric materials determined by  $\tan \delta$  peak were also higher than those determined by dilatometry or differential thermal analysis<sup>25</sup>. Furthermore, there were differences in the standard

deviations of  $T_g$  values between the evaluation methods. The standard deviations of  $T_g$  by differential scanning calorimetry were larger than those by dynamic mechanical analysis for the tested relene resins, except for Kurarebase at 0.1 and 0.2 Hz. The dynamic mechanical analysis obtained more stable  $T_g$  values than the differential scanning calorimetry for the autopolymerized hard direct denture relene resins. The degree of shift of the DSC curve from the baseline for the relene resins was quite small, whereas the peak of the  $\tan \delta$  curve was clear. Thus, the dispersion of  $T_g$  values measured by differential scanning calorimetry was larger than that of those by dynamic mechanical analysis. Furthermore, dynamic mechanical analysis is able to evaluate mechanical properties in addition to the glass transition of the materials.

In the present study, evaluation of analytical techniques for determination of  $T_g$  was conducted by using autopolymerized hard direct denture relene resins. However, findings obtained by measurements of other materials utilized for dentures, such as heat-polymerized denture base acrylic resins, acrylic soft liners, silicone soft liners, and tissue conditioners, may not concur with the present findings. Additional studies are necessary to establish effective methods to evaluate the  $T_g$  values of materials used exclusively for dentures. The present results suggest that dynamic mechanical analysis is more advantageous as compared to differential scanning calorimetry for characterization of autopolymerized hard direct denture relene resins, as that method more accurately determine  $T_g$  values in addition to mechanical properties.

## CONCLUSIONS

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

1. Differences in dynamic mechanical properties were found among the autopolymerized hard direct denture relene resins tested.
2. Although all of the relene resins demonstrated higher values for storage modulus ( $E'$ ) and loss modulus ( $E''$ ), and lower values for loss tangent ( $\tan \delta$ ) with the higher frequency at 37°C, the influence of frequency on dynamic mechanical properties was not large.
3. The glass transition temperatures ( $T_g$ ) values of the tested relene resins determined by dynamic mechanical analysis were higher than those determined by differential scanning calorimetry.
4. With dynamic mechanical analysis, a higher frequency applied to the relene resins led to higher  $T_g$  values.
5. Dynamic mechanical analysis obtained more stable  $T_g$  values than differential scanning calorimetry for the present relene resins.
6. Dynamic mechanical analysis is more advantageous for characterization of autopolymerized hard direct denture relene resins as compared to differential scanning calorimetry.

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