Evaluation of the frequency and temperature dependence of the dynamic mechanical properties of acetal resins

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The purpose of this study was to evaluate and compare the dynamic mechanical properties of two acetal resins (different colored samples of the same resin), an autopolymerized reline resin, and a heat-polymerized denture base resin. Measurements were obtained in two conditions, the frequency- and temperature-dependent conditions, using a dynamic viscoelastometer. The acetal resins exhibited lower loss tangent values than the autopolymerized reline resin and heat-polymerized denture base resin. With respect to temperature dependence, all of the materials displayed stable viscoelastic properties in the temperature range found in the oral environment. The acetal resin had both a glass transition temperature and a melting point, whereas the autopolymerized reline resin and heat-polymerized denture base resin had only glass transition temperatures. The results of this study suggest that acetal resin displays elastic properties when compared with the other 2 materials.

Keywords: Acetal resin, Dynamic mechanical properties, Frequency dependence, Temperature dependence, Glass transition temperature

INTRODUCTION

In view of the aging society in Japan3, the number of patients who need prostheses is expected to rise in the future. In addition, the esthetic requirements for prostheses, including removable partial dentures, have also been increasing in recent years. In removable partial dentures in which other forms of attachment are not used, the clasps are always visible. The most common alloys used for such clasps are cobalt-chromium alloys and gold alloys, but they can be unsightly2. Various methods, such as clasps painted with tooth-colored resin3,4, lingually or gingivally positioned clasps5,6, and mesial rather than distal undercuts7, have been employed in order to solve these problems. While these methods are effective to some extent, it has not yet been possible to develop esthetically ideal dental clasps. Many thermoplastic resins have been approved for use as denture bases, and the use of thermoplastic resins has become common in the past few years. Furthermore, there is anxiety about metal allergies arising from denture use. The first thermoplastic resin used as a denture base material was polyamide resin, which was developed to deal with the problem of allergic reactions to residual acrylic resin monomers8. It has also been used to avoid metal allergies. Thus, there is an increasing expectation that non-metal materials will be used in denture bases.

In the present study, we focused on acetal resins. Acetal resins have been used as an alternative denture base and clasp material since 19869. In addition to clasps, acetal resins are used to produce partial denture frameworks, provisional bridges, occlusal splints, and implant abutments. Acetal resins are thermoplastic resins composed of polymerized formaldehyde and contain a chain of alternating methyl groups linked by an oxygen molecule. They have been reported to have sufficiently high resilience and elasticity modulus values to allow their use in the manufacturing of retentive clasps, connectors, and support elements for removable partial dentures10. They are also biocompatible11 and so can be used in patients that suffer allergic reactions to metal alloys. Due to these properties, acetal resins have been employed in the prostheses used in total hip replacement12 as well as in artificial heart valve occluders13.

In the clinical setting, dental clasps are often subjected to sudden stress, such as during mastication, and the insertion and removal of the denture. It is reported that dynamic tests are more effective than static tests at determining the mechanical properties of materials in such situations14. However, the dynamic mechanical properties of acetal resin have not been fully elucidated.

In this study, we evaluated the dynamic mechanical properties of acetal resin and compared them with those of an autopolymerized reline resin and a heat-polymerized denture base resin. It was hypothesized that acetal resins would exhibit more elastic properties than denture base resins.

MATERIALS AND METHODS

The materials used in this study are listed in Table 1. One acetal resin (T.S.M.) with two kinds of color, an autopolymerized reline resin (KU), and a heat-polymerized denture base resin (UR) were selected for this study. The acetal resins came in two colors, A1 and C4. The color of acetal resin is comparable to the
vita color scale of crown color. As for the color in this study, two acetal resins in large different colors were arbitrarily chosen. Five specimens of each material, measuring 20.0 mm long×7.0 mm wide×0.6 mm thick, were prepared at 23±2°C in accordance with the manufacturer’s instructions. The surfaces of the specimens were polished with waterproof abrasive paper #800 and #1000. The dynamic mechanical properties, frequency dependence, and temperature dependence of the viscoelastic properties of the resins were assessed.

The dynamic mechanical properties of the test material were evaluated using an automatic dynamic viscoelastometer (Rheovibron DDV-25FP, A&D, Tokyo, Japan). This device is based on the principle of non-resonance forced vibration\(^\text{15}\) and can be used to measure dynamic mechanical properties at a wide range of temperatures and frequencies and in the presence of various amounts of strain. In this study, tensile strain was applied to the test materials. By evaluating the delay in the stress response detected on the opposite side, the rheological parameters of each material were calculated. The complex dynamic tensile modulus \(E^*\), tensile storage modulus \(E'\), tensile loss modulus \(E''\), and loss tangent \((\tan \delta)\) of the 4 tested materials at 37°C. The \(E'\) of T.S.M. was stable at all frequencies. On the other hand, the \(E''\) and \(\tan \delta\) of T.S.M. decreased sharply between about 0.01 and 0.1 Hz, and then decreased slowly. Both colors of T.S.M., A1 and C4, exhibited the same tendency. The KU and UR displayed a similar tendency. Specifically, \(E'\) remained stable at all frequencies, and \(E''\) and \(\tan \delta\) gradually increased as the frequency rise from 0.1 Hz.

The \(E', E''\), and \(\tan \delta\) values of the materials at 1 Hz and 37°C are shown in Fig. 2. The T.S.M. and UR exhibited significantly higher \(E'\) values than the KU \((p<0.05)\). The T.S.M. displayed significantly lower \(E''\) and \(\tan \delta\) values than the UR and KU \((p<0.05)\). There was no significant difference in \(E', E''\), or \(\tan \delta\) between the two colors of acetal resin.

The temperature dependence of the viscoelastic properties

The temperature dependence of the viscoelastic properties; i.e., \(E', E''\), and \(\tan \delta\), of the test materials is shown in Fig. 3. In the tests of T.S.M., \(\tan \delta\) demonstrated two sharp peaks while \(E'\) and \(E''\) exhibited large reductions from −80 to −50°C and 100 to 150°C. The first \(\tan \delta\) peak indicated the glass transition temperature.
Fig. 1 Variations in the storage modulus ($E'$), loss modulus ($E''$), and loss tangent ($\tan \delta$) values of the tested materials according to frequency.

Fig. 2 Storage modulus ($E'$), loss modulus ($E''$), and loss tangent ($\tan \delta$) values of the tested materials at 1 Hz and 37ºC. Identical letters indicate no significant difference ($p>0.05$).

of T.S.M., and the second peak represented its melting point. On the other hand, the $\tan \delta$ values of KU and UR only exhibited one sharp peak and their $E'$ and $E''$ values decreased rapidly from 50 to 120ºC and from 110 to 150ºC, respectively. The $\tan \delta$ peaks for these materials were indicative of their glass transition temperatures. Table 2 shows the glass transition temperature and melting point data obtained from the temperature
dependence of the viscoelastic properties of the tested materials. T.S.M. had by far the lowest glass transition temperature in the materials tested, and KU showed a significantly lower glass transition temperature than UR ($p<0.05$). The glass transition temperature of T.S.M. was about $-65^\circ$C. All of the materials exhibited stable viscoelastic properties at the temperature found in the oral environment.

**DISCUSSION**

The hypothesis that acetal resins would exhibit more elastic properties than denture base resins was supported by the present study. The use of polyacetal resin as a denture base material was considered by Smith over 40 years ago$^9$. Some properties of acetal resins, such as their flexural properties$^{18}$, transverse strength$^{19}$, biocompatibility$^{11}$, color stability$^{20}$, and water sorption and solubility$^{21}$, have been reported previously. However, the viscoelastic properties of acetal resins have not been clarified. So, we focused on these properties in this study.

Evaluating the viscoelastic properties of materials used in the oral environment is very important. The mechanical properties of such materials can be assessed by examining their viscoelastic properties. Evaluating the viscoelastic properties of the materials used in dental prostheses is very important because such materials are subjected to sudden bouts of stress in the clinical setting, such as during mastication. There are two types of test that can be used to assess viscoelastic properties, static tests and dynamic tests. Static tests, e.g., the creep test, measure the strain induced by a constant stress level over long periods. However, the materials tested in this study

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**Table 2** Glass transition temperature and melting point for the tested materials

| Materials                        | Glass transition temperature ($^\circ$C) | Melting point ($^\circ$C) |
|----------------------------------|----------------------------------------|---------------------------|
| T.S.M. Acetal Dental (A1)        | $-67.4$ (0.9)                          | 126.6 (5.0)               |
| T.S.M. Acetal Dental (C4)        | $-67.4$ (1.7)                          | 127.0 (3.0)               |
| Kurarebase                       | $80.7$ (1.7)                           | —                         |
| Urban                            | $135.4$ (1.1)                          | —                         |

Mean (SD)
are subjected to very short periods of stress, e.g., during mastication and the insertion/removal of removable dentures, and static tests are not suitable for examining the behavior of materials over periods of less than a few seconds\textsuperscript{14}. It has also been reported that dynamic tests are especially sensitive tools for evaluating the chemical and physical structures of polymeric materials and provide more information about materials than other tests\textsuperscript{14}. Thus, dynamic tests were performed using an automatic dynamic viscoelastometer in the present study.

It has been reported that conditions associated with mastication and exposure to continuous weak pressure levels are reflected by frequency values of 1 Hz and <1 Hz, respectively\textsuperscript{15}. Therefore, the rheological parameters obtained at 37°C and a frequency of 1 Hz are considered to be the most important when assessing materials for use in oral prostheses\textsuperscript{16,22}. Hence, in this study these conditions were employed during the experiments examining the frequency dependence of the viscoelastic properties of the tested materials. Large differences in the dynamic mechanical properties of the tested materials were detected. The T.S.M. had higher $E'$ and lower $E''$ values at 1 Hz, which resulted in it exhibiting a lower tan $\delta$ value than the other materials. This indicates that because of its lower tan $\delta$ value, T.S.M. is less likely to absorb loads, and hence, is affected less by deformation. That is, acetal resins have high elastic recovery, which means that this materials deform when an external force is applied to them, and immediately recover to its original shape with permanent deformation when external force is removed from them. As acetal resins are used to produce dental clasps, these viscoelastic properties are very important; i.e., it is appropriate to produce dental clasps, which are repeatedly opened and closed, from acetal resin. It was reported that direct relining resins displayed significantly greater viscosity and flexibility than heat-polymerized denture base resins at a frequency of 1 Hz\textsuperscript{17}. This trend agrees with the findings of the current study, in which KU, a reliner resin, was found to be less stiff than UR, a heat-polymerized denture base resin. A material's rheological parameters at 0.1 Hz are indicative of its behavior under continuous weak pressure. T.S.M. displayed a lower tan $\delta$ value; i.e., elastic behavior, as the frequency was increased from 0.1 to 1 Hz. On the other hand, KU and UR demonstrated higher tan $\delta$ values; i.e., viscous behavior, as the frequency was increased from 0.1 to 1 Hz.

Polymers have crystalline and/or amorphous regions. Polymers with crystalline portions are known as crystalline polymers. Crystalline polymers have some amorphous regions, which is why they have both a glass transition temperature and a melting point, whereas amorphous polymers only have a glass transition temperature. The physical properties of polymer materials can vary markedly above and below the glass transition temperature due to micro-Brownian motion, which is affected by intermolecular forces and the size of any side chains, but not by molecular weight or the degree of polymerization\textsuperscript{23}. During glass transition, the polymer chains in the amorphous portions of polymers start to move. When the melting point, which is higher than the glass transition temperature, is reached, the polymer chains in the crystalline portion start to move, too. Rapid changes in rheological parameters, such as $E'$, $E''$, and tan $\delta$, are indicative of rapid changes in physical properties; i.e., glass transition and melting. Thus, the glass transition temperature of a material can be calculated by evaluating the temperature dependence of its viscoelastic properties; i.e., it is defined as the temperature at which the maximum tan $\delta$ value is obtained\textsuperscript{24}. The chemical components of KU included polyethyl methacrylate as a polymer and methacrylate monomer as a monomer, whereas UR contained polymethyl methacrylate as a polymer and methyl methacrylate as a monomer. Except for their glass transition temperatures, the viscoelastic properties of KU and UR (amorphous methacrylate polymers) exhibited similar temperature dependence. UR displayed a significantly higher glass transition temperature than KU. This is because the differences in the monomer and polymer components of KU and UR affected the glass transition temperatures of the materials. T.S.M., a crystalline polymer, had both a glass transition temperature and a melting point. Most of the viscoelastic properties of the materials remained stable at the temperature of the oral environment (below the glass transition temperatures of KU and UR; above the glass transition temperature of T.S.M., but below its melting point).

The present study revealed large differences among the viscoelastic properties of acetal resins, a reliner resin, and a denture base resin. Many of the thermoplastic resins applied to dental clasps are crystalline polymers similar to the acetal resin used in this study. Therefore, the present study selected a reliner resin and a denture base resin that are amorphous polymers to compare crystalline polymers and amorphous polymers. Acetal resin have the dynamic mechanical properties which means difficulty to deform by external force in oral environment, temperature and frequency. The fatigue of a denture claps is occurred by the repeated deflection during insertion and removal of the removable partial denture\textsuperscript{25}. So, acetal resins are suitable for the application to dental clasps. For acetal resin, both colors showed the same tendency of viscoelastic properties, and their frequency and temperature dependence. So, it was found that the pigments of acetal resin did not affect the viscoelastic properties. However, considering that these materials are used in the oral cavity, this study did not perfectly simulate their clinical behavior. Varius factors can influence viscoelastic properties, such as water sorption, thermal cycling, and masticatory function. Acetal resins are used to produce clasps for partial dentures. Therefore, it will be necessary to compare the viscoelastic properties of acetal resins with those of cobalt-chromium alloys and gold alloys, which are also used to produce clasps for dentures. So, additional studies examining these issues will be required.
CONCLUSIONS

The results of this study are summarized as follows:

1. The acetal resin displayed more elastic behavior, whereas the autopolymerized reline resin and heat-polymerized denture base resin demonstrated more viscous behavior, at the frequency range from 0.1 to 1 Hz (clinically relevant values).

2. The acetal resin exhibited higher $E'$ and lower $E''$ and tan $\delta$ values than autopolymerized reline resin and heat-polymerized denture base resin at 1 Hz. As a result, it was demonstrated that acetal resin tends to be more elastic in the oral environment.

3. The rheological parameters of all of the examined materials remained relatively stable in the temperature range found in the oral environment.

4. The acetal resin had both a glass transition temperature and a melting point, whereas the autopolymerized reline resin and heat-polymerized denture base resin only had a glass transition temperature.

From the standpoint of dynamic mechanical properties, the acetal resin can be used as clasps for removable partial dentures.

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