Dynamic mechanical properties of hard, direct denture reline resins

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Statement of problem. Dynamic mechanical properties of hard, direct reline resins are important factors in the clinical success of dentures. However, little information is available on the nature of these properties.

Purpose. This study evaluated the dynamic mechanical properties of a variety of hard, direct reline resins: (1) visible light-polymerized, powder-liquid type, (2) visible light-polymerized, paste-type, (3) autopolymerized, powder-liquid type, as classified by component composition and mode of polymerization activation, namely, type of delivery system, and (4) heat-polymerized denture base materials.

Material and methods. The dynamic mechanical analysis (DMA) of 8 commercial hard denture reline materials (HDR) (2 visible light-polymerized, powder-liquid type, 4 visible light-polymerized, paste-type, and 2 autopolymerized, powder-liquid type), and 2 heat-polymerized denture base materials was obtained at a frequency of 1 Hz at 37°C. Five specimens of each material, 40.0 x 7.0 x 2.0 mm, were made to measure the elastic (storage) ($E'$) and inelastic (loss) ($E''$) moduli, and loss tangent (tan $\delta$). These parameters were compared with MANOVA and Student-Newman-Keuls test ($\alpha=.05$).

Results. The $E'$ values of 3 visible light-polymerized, paste-type reline resins were significantly higher than those of the other 5 reline resins. However, the $E'$ values of all reline resins were significantly lower than those of the 2 heat-polymerized denture base resins. Except for 1 autopolymerized reliner, all reline materials had significantly lower $E''$ than the heat-polymerized denture base resins. The tan $\delta$ values of all but 1 visible light- and autopolymerized reliners were significantly higher than those of the heat-polymerized denture base materials.

Conclusions. Three visible light-polymerized, paste-type reline resins showed greater stiffness than the visible light- or autopolymerized, powder-liquid type reline resins. However, all of the hard, direct reline resins, including the 3 paste-type materials, exhibited greater flexibility compared to the heat-polymerized denture base resins. (J Prosthet Dent 2007; 98:319-326)

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Hard, direct reline resins are used to improve the stability and retention of ill-fitting complete and removable partial dentures and as interim liners for immediate dentures. Several types of these resins are available, including autopolymerized and visible light-polymerized materials. These so-called “chairside reline systems” are more convenient than those processed in a laboratory, because the direct method is faster and does not cause clinically significant dimensional changes of the reline resins.\(^1\) However, when autopolymerized reline resins are used with a direct method, several problems can occur, including a burning sensation caused by monomers, an exothermic heat reaction, and an unpleasant odor.\(^2,6\) There is also a risk that the relined denture cannot be removed from the mouth, if the excess reline resin flows and polymerizes into undercuts of abutment teeth and soft tissue. Use of visible light-polymerized reline resin systems avoids such problems, because the resins have flow or viscoelastic properties prior to the final polymerization using visible light,\(^1\) as well as diminished thermal irritation,\(^7\) little release of residual monomer,\(^1,8\) a longer working time,\(^7\) and allow for easier trimming of excess material.\(^1,8\)

Visible light-polymerized, hard, direct reline resins can be divided into 2 groups according to the supplied form: a powder-liquid type and a paste-type. Some visible light-polymerized reline resins are dual-polymerized. The powder form of the visible light-polymerized and autopolymerized, powder-liquid type materials consists of poly (ethyl methacrylate), poly (methyl methacrylate), or poly (ethyl methacrylate/ethyl methacrylate), along with a peroxide initiator and pigment.\(^4,6,8\) The liquid components are mixtures of methacrylate-based monomers: methyl methacrylate, n-butyl methacrylate, or cyclohexyl methacrylate, along with a cross-linking agent (ethoxylated bisphenol A dimethacrylate or 1,6-hexanediol dimethacrylate).\(^4,6,8\) In addition, the liquid forms of the visible light-polymerized materials and the autopolymerized materials include a photoinitiator, such as camphorquinone, and a chemically activated accelerator, such as N,N-dimethyl p-toluidine, respectively.\(^4,6,8\) The dual-polymerized materials contain both compounds. The visible light-polymerized, paste-type materials are a mixture of methacrylate copolymers, a polyfunctional monomer (such as urethane dimethacrylate), and a silica filler,\(^7,8\) which acts as a thickening agent.\(^9\) The differences in composition and structure influence the mechanical properties of the resulting polymer. Previous studies\(^5,9\) indicate that increased cross-linking and microfine silica may result in higher flexural modulus values. The degree of cross-linking of heat-polymerized denture base resins is higher than that of direct reline resins.\(^3\) The paste-type materials include the silica filler.

Previous studies of visible light-polymerized, hard, direct reline resins examined their chemical compositions,\(^6\) physical properties (such as hardness, tensile strength, transverse strength, and polymerization shrinkage), and bond strength to heat-polymerized denture base resins,\(^1,8\) as well as color stability\(^7\) and biocompatibility.\(^10,11\) Mechanical tests provide useful information regarding behavior of these materials; however, in clinical situations, reline materials used with dentures are subjected to instantaneous and cyclic stresses caused by mastication.\(^12\) To simulate the clinical performance of reline materials more precisely, it is necessary to measure the material response to cyclic stress. For this reason, a dynamic viscoelasticometer based on the principle of nonresonance-forced vibration is well suited to apply such stresses, while also measuring dynamic mechanical properties.

Using this device, a sinusoidal tensile strain is added to 1 end of a specimen and the stress response is detected at the other end (Fig. 1). Amplitude attenuation of the sinusoidal strain and delay of the strain wave are known to be dependent on the viscoelastic properties of the material.\(^13\) Dynamic mechanical analysis (DMA) determines viscoelastic properties over a wide range of frequencies and temperatures, and has been used to evaluate the properties of various dental materials.\(^9,12,14–18\) The test frequency of 1 Hz is important in analysis of dental materials, as this value simulates behavior during mastication.\(^16,18\) Three rheological parameters are generally studied in DMA: tensile storage modulus (\(E’\)), tensile loss modulus (\(E''\)), and loss tangent (tan \(\delta\)). \(E’\) describes elastic deformation under stress, whereas \(E''\) exhibits viscous (inelastic) deformation.\(^13\) Tan \(\delta\) provides an indication of the relative contribution of the elastic and inelastic components that account for overall material behavior.\(^13\) An “ideal” hard denture reliner material would demonstrate a high stiffness (\(E’\)) and a moderate deformation with stress (\(E''\)), but a low tan \(\delta\), as it is preferable that the material return to its original shape shortly after the load is removed.

The flexural strength of autopoly-
merized reline resins is lower than that of heat-polymerized denture base resins, and denture bases with reline resins have a lower resistance to failure than the original, intact denture bases. The reline resins and denture base resins should be sufficiently stiff and behave in the same manner during mastication.

The purpose of this study was to compare the dynamic mechanical properties of a variety of commercial hard, direct reline resins to those of commercial denture base materials, as well as to determine the effect of the type of delivery system on their properties. The materials examined were classified into 4 delivery system types: (1) visible light-polymerized, powder-liquid type reline resin; (2) visible light-polymerized, paste-type reline resin; (3) autopolymerized, powder-liquid type reline resin; and (4) heat-polymerized denture base resin. It was expected that a wide range of dynamic mechanical properties would be found among the 4 types of delivery systems due to differences in composition and polymer structure.

It was also hypothesized that these reline resins would have a more viscous component (increased flexibility), as compared to the heat-polymerized denture base resins, because of the lower degree of cross-linking. It was further hypothesized that the visible light-polymerized, paste-type reline resins would exhibit greater stiffness than the visible light-polymerized and autopolymerized, powder-liquid type reline resins, due to the presence of a silica filler.

MATERIAL AND METHODS

Table I lists the materials used, and characterizes them as to use (hard reliner or denture base) and delivery system (power/liquid or paste, and polymerization type, light-, auto-, or heat- polymerized). Five specimens of each material were prepared in the form of rectangular blocks (40.0 x 7.0 x 2.0 mm) by use of a polytetrafluoroethylene (PTFE) mold, in accordance with the manufacturers’ processing instructions. For the powder-liquid type reline resins, immediately after mixing the components by hand, each mixture was poured into a PTFE mold. The manufacturers’ recommended powder/liquid ratios were used. For the paste-type reline resins, except for Triad DuaLine, each paste was placed into the PTFE mold by hand using polyethylene film. The paste of Triad DuaLine was automatically mixed and extruded using the dual paste cartridge and dispenser, and was expressed directly into the mold. For all the materials, a flat glass plate was immediately placed on the mold top and pressed onto the mass, then removed 15 minutes later. In addition, for the visible light-polymerized reline resins, the specimens were exposed to a light-polymerizing source (Triad II, light intensity 65 mW/cm²; Dentply Trubyte, York, Pa) from one side, then turned over and irradiated from the other side for the periods of time recommended by the manufacturers. The irradiation time of Astron LC (Hard), Light Liner (Hard), Lightdon-U, and Triad DuaLine was 5 minutes, and that of Triad Hi-Flow Reline Material and Triad VLC Reline Material...
The complex dynamic tensile modulus \( E' \) (Pa) of each material was determined as follows\(^{12}\):

\[ |E'| = \frac{\Delta F}{S \times L_t \times \Delta L} \]  

\[ E' = |E'| \cos \delta \]  

\[ E'' = |E'| \sin \delta \]  

\[ \tan \delta = \frac{E''}{E'} \]  

where \( \Delta F \) is the dynamic load (N), \( S \) the cross-sectional area of the specimen (m\(^2\)), \( L_t \) the length of the specimen (m), and \( \Delta L \) the dynamic displacement (m). \( E' \) was resolved into 2 components: \( E' \) and \( E'' \). \( E' \) (Pa) and \( E'' \) (Pa) were calculated using the following formulae:\(^{12}\):

\[ E' = E' + iE'' \]  

\[ E'' = \frac{E'}{\cos \delta} \]  

\[ \tan \delta = \frac{E''}{E'} \]  

\[ E'' = \frac{E'}{\sin \delta} \]

was 10 minutes, which represents the combination of both exposures. The heat-polymerized denture base resin specimens were prepared in a preformed plaster mold, and polymerized according to the manufacturers’ recommended procedures. All polymerized specimens were abraded on both sides with 600-grit silicon-carbide paper, and then stored in air at 23 ±2°C for 24 hours to allow post-polymerization to complete.

Following storage, the dynamic mechanical properties of the test materials were obtained using an automatic dynamic viscoelastometer (Rheovibron DDV-25FP; Orientec Co Ltd, Tokyo, Japan), based on the principle of nonresonance forced vibration.\(^{12}\) Three rheological parameters were obtained: tensile storage modulus \( E' \), tensile loss modulus \( E'' \), and loss tangent \( (\tan \delta) \). The tests were performed at 37°C over a frequency range of 0.1 to 100 Hz (at 28 different frequencies) in dry conditions. Specimen ends were held at a 20-mm separation. The strain applied to the specimen was 0.05%, which was based on the theory of linear viscoelasticity.

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Table II. MANOVA results for storage modulus ($E'$), loss modulus ($E''$), and loss tangent ($\tan \delta$) of materials tested at 1 Hz.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Test Name</th>
<th>Value</th>
<th>Approximate F</th>
<th>Hypothesis $df$</th>
<th>Error $df$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Pillai’s trace</td>
<td>2.951</td>
<td>152.583</td>
<td>27</td>
<td>120</td>
<td>&lt;.001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>Rheological Parameter</th>
<th>$df$</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Storage modulus ($E'$)</td>
<td>9</td>
<td>208.4</td>
<td>23.151</td>
<td>630.5</td>
<td>&lt;.001</td>
</tr>
<tr>
<td></td>
<td>Loss modulus ($E''$)</td>
<td>9</td>
<td>0.2</td>
<td>2.163x10^{-2}</td>
<td>181.6</td>
<td>&lt;.001</td>
</tr>
<tr>
<td></td>
<td>Loss tangent ($\tan \delta$)</td>
<td>9</td>
<td>0.4</td>
<td>4.121x10^{-2}</td>
<td>580.6</td>
<td>&lt;.001</td>
</tr>
<tr>
<td>Residual</td>
<td>Storage modulus ($E'$)</td>
<td>40</td>
<td>1.5</td>
<td>3.672x10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss modulus ($E''$)</td>
<td>40</td>
<td>4.8x10^{-3}</td>
<td>1.191x10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss tangent ($\tan \delta$)</td>
<td>40</td>
<td>2.8x10^{-3}</td>
<td>7.098x10^{-3}</td>
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<td></td>
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<tr>
<td>Total</td>
<td>Storage modulus ($E'$)</td>
<td>49</td>
<td>209.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss modulus ($E''$)</td>
<td>49</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Loss tangent ($\tan \delta$)</td>
<td>49</td>
<td>0.4</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Storage ($E'$) and loss moduli ($E''$) at 1 Hz of materials tested. Specimens per experimental group: n=5. Vertical bar represents +1 standard deviation. Within test parameter, values having similar uppercase letters ($E'$) or lowercase letters ($E''$) are not statistically different. Within each material type, $E' > E''$.

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Loss tangent (tan δ) at 1 Hz for materials tested; n=5 specimens per experimental group. Vertical bar represents +1 standard deviation. Within test parameter, values having similar letters are not statistically different. Increase in tan δ values indicates material is better able to absorb more energy without elastically returning it, acting more as shock absorber.

The MANOVA results indicated significant differences among the materials (P<.001) for storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) (Pillai's trace statistic, P<.001) (Table II). The values of E', E'', and tan δ for the 10 materials tested at 1 Hz are shown in Figures 2 and 3, respectively. The denture base resins had significantly higher E' values (Student-Newman-Keuls test, P<.001) than the visible light-polymerized and autopolymerized reline resins. The E' values of the 3 visible light-polymerized, paste-type reline resins (Triad DuaLine, Triad Hi-Flow Reline Material, and Triad VLC Reline Material) were significantly higher (Student-Newman-Keuls test, P<.001 to P=.017) than those of the other 5 reline resins. All of the direct reline resins, except for New Truliner, had significantly lower E'' values (Student-Newman-Keuls test, P<.001) than the denture base resins. Within each material, E' values were significantly higher than E'' values (t test, P<.0005). The tan δ values of all of the heat-polymerized denture base resins were significantly lower (Student-Newman-Keuls test, P<.001) than those of the reline resins, except for 1 visible light-polymerized, paste-type reline resin (Triad DuaLine) which was not different. The hard, direct reline resins were found to exhibit more viscous characteristics and greater flexibility than either of the heat-polymerized denture base resins evaluated.

DISCUSSION

The hypothesis that the hard, direct reline resins would have more viscous components than the heat-polymerized denture base resins was supported by the results. Furthermore, large differences in dynamic mechanical properties were found among the reline resins. Three of the 4 visible light-polymerized, paste-type reline resins showed greater stiffness than the visible light-polymerized and autopolymerized, powder-liquid type reline resins.

Rheological parameters obtained at 1 Hz are considered to be most important for clinical assessment of hard reline resins, as compared to the other frequencies measured (Figs. 2 and 3). Thus, the frequency value of 1 Hz was selected in the present study. At this frequency, visible light-polymerized and autopolymerized, hard, di-
rect reline resins with lower $E'$ values, which ranged from 0.63 to 3.17 GPa, were less stiff than the heat-polymerized denture base resins (6.37 to 6.88 GPa). Although there were significant differences in $E'$ among the materials (ranging from 0.12 to 0.32 GPa), the differences may not be large enough to influence clinical behavior. New Truliner and Light Liner (Hard) had significantly higher tan $\delta$ values (0.302 to 0.257) than the other materials (0.042 to 0.126). Because of their higher tan $\delta$ values, the reline materials New Truliner and Light Liner (Hard) show much greater ability to absorb a load and not return to original dimensions (higher tan $\delta$) than all other materials, because these 2 materials have greater viscous components.

Three of the 4 visible light-polymerized, paste-type reline resins (Triad DuaLine, Triad Hi-Flow Reline Material, and Triad VLC Reline Material) were stiffer than the visible light-polymerized and autopolymerized, powder-liquid type reline resins. This finding may be attributed to the presence of silica fillers in these products, which act to reinforce the resin. For example, Triad VLC Reline Material contains 14.7% silica. A previous study reported that a visible light-polymerized, paste-type reline resin had higher transverse strength and Knoop hardness compared to visible light-polymerized, powder-liquid type reline resins. These findings are consistent with those of the present study. Differences in dynamic mechanical properties are most likely due to differences in material composition and character of the resulting polymerized network. For example, the type, molecular weight, and particle size of the polymer powder, the type and content of the monomer and crosslinking agent, and the powder/liquid ratio may all have an influence on the mechanical properties of the polymerized material. In the case of the paste-type materials, type, concentration, and particle size of the filler may also have a significant effect on the properties. A lower degree of crosslinking and a smaller quantity of silica filler in the reline resins may result in increased flexibility characteristics. However, the influence of product composition and the characteristics of the polymerized network on material properties was not determined in the present study, because this information is considered proprietary. Analysis of the chemical composition and polymer structure of hard, direct denture reline resins should be performed in future studies.

In some clinical situations, the thickness of a denture base is much greater than that of the reline resin. Differences in dynamic mechanical properties between these materials would potentially influence interfacial stresses. These differences could result in debonding between the 2 materials during long-term function, resulting in liner loss and gap formation with ingress of bacteria and fungus. This difference would only weakly influence overall denture strength. However, denture bases relined with autopolymerized reline resins (New Truliner and Tokuyama Rebase II (Fast)) have lower maximum fracture load values than intact denture bases. The 2-mm-thick denture bases were relined with 1 mm of autopolymerized reline resin in that study. For the previously mentioned reasons, a hard direct reline resin should have dynamic mechanical properties comparable to those of a denture base resin. From this standpoint, Triad DuaLine (visible light-polymerized, paste-type), with high $E'$ and lower tan $\delta$ values (more stiff), may better meet the requirements of a hard, direct reline resin when compared with the other 7 reline resins tested. From the aspect of manipulation, Triad DuaLine paste is easier to use than the powder-liquid type (hand-mixed type) and 1 paste-type (sheet-type) reline resins because this material is supplied in a form that allows direct injection of automixed material (paste system) onto the prepared denture. Therefore, the visible light-polymerized, paste-type reline resins delivered by means of a self-mixing, 2-paste cartridge (Triad DuaLine) may be more efficacious for direct lining of dentures than the other types of delivery systems: powder-liquid types of visible light- or autopolymerized reline resins and the paste-type (sheet-type) of visible light-polymerized reline resins. However, none of the products tested demonstrated “ideal” properties of the hard, direct reline resins. The large differences in the dynamic mechanical properties of hard, direct reline resins and denture base resins prevent this goal from being achieved. Furthermore, there are many factors involved with the mechanical properties of reline resins, including the influences of water immersion, thermal cycling, and masticatory force. The present testing did not completely simulate clinical behavior because specimens were tested in the dry state. Additional study of the relationships between dynamic mechanical properties of hard, direct reline resins and their compositions and polymerized networks is necessary, as well as focused clinical studies to help clarify the specifics of these differences.

CONCLUSIONS

Within the limitations of the present study, the following conclusions were drawn:

1. Hard, direct reline resins showed significantly more viscous characteristics and greater flexibility ($P<.001$) than did the heat-polymerized denture base resins at a frequency of 1 Hz, which reflected masticatory conditions.

2. Three visible light-polymerized, paste-type reline resins (Triad DuaLine, Triad Hi-Flow Reline Material, and Triad VLC Reline Material) demonstrated significantly higher stiffness ($P<.001$ to $P=.017$) than did the visible light-polymerized and autopolymerized, powder-liquid type reline resins evaluated.
REFERENCES