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Dynamic viscoelastic behavior of resin cements measured by torsional resonance

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Abstract

Objective. The purpose of the study was to measure the viscoelastic properties of four dental resin composite cements using a dynamic mechanical analysis technique.

Methods. Dynamic torsional loading was conducted in the frequency range from 1 to 80 Hz. Cement specimens were tested after storage in 37 °C water for 24 h. One group was thermal cycled prior to testing. Measurements were taken at 21, 37, and 50 °C. Storage modulus, loss tangent and other viscoelastic parameters were determined from the amplitude/frequency curves.

Results. Storage moduli of the cements ranged from 2.9 to 4.1 GPa at 37 °C. Loss tangents ranged from 0.054 to 0.084. Storage moduli decreased in a regular way with increasing temperature, whereas, loss tangents increased. Thermal cycling caused small decreases in storage moduli.

Significance. Resin cements with higher filler loading were found to have higher storage moduli and lower loss tangents. Since these properties have been associated with better clinical performance in the areas of retention and prevention of fracture of porcelain and resin restorations, the more highly filled cements may be recommended. Temperature variations influenced viscoelastic behavior of the cements. However, within the temperature range studied no sharp drop in modulus was seen, so the materials should function satisfactorily in the oral cavity.

Keywords: Dental materials; Resin cements; Mechanics; Elastic modulus; Viscoelasticity

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1. Introduction

Dynamic mechanical analysis is a method that has been used to acquire useful information about viscoelastic properties of dental resins [1–5]. The technique gives information about elastic modulus (storage modulus) that defines the energy stored in a specimen due to an applied strain. In a dynamic experiment, when equilibrium is reached and viscoelastic behavior is linear, both stress and strain vary sinusoidally, but strain lags behind stress. The storage modulus G_1 is in phase with the strain, whereas, the loss modulus G_2 is 90° out of phase with the strain and is related to dissipation of energy. The ratio of loss modulus to elastic modulus is referred to as internal damping or the loss tangent. The loss tangent is a measure of the ratio of energy lost to energy stored and it determines properties such as damping of free vibrations, attenuation of propagated waves and the frequency width of a resonance response.

The influence of properties of cements has been reviewed by Rosenstiel et al. [6]. High elastic modulus of the substrate has been shown to be an important factor in fracture resistance of ceramic crowns [7]. Creep of the cement may influence retention of crowns by dental cements [6,8]. Creep is a time-dependent deformation under constant or cyclic load and it is related to the loss tangent measured by dynamic mechanical testing.

The purpose of the present study was to determine some viscoelastic functions of resin cements under varying conditions of temperature and with and without thermal cycling. The materials were selected so that effects of filler loading could be evaluated. Two hypotheses were statistically tested. The first was that cements with different filler concentrations will have different viscoelastic properties.

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Table 1
Resin cements used in the study

Material	Manufacturer	Description
Duo Cement	Coltene/Whaledent, 750 Corporate Drive, Mahwah, NJ, USA	Dual cured, 72 wt% filler
Lute-It!	Pentron Clinical Technologies, Wallingford, CT, USA	Light-cured/dual-cured, 65 wt% filler, 0.8 μm
Rely-X ARC	3M Dental Products, St Paul, NM, USA	Dual-cured, 67.5 wt% filler, 1.5 μm
Variolink II	Ivoclar Vivadent, Bendererstrasse 2, FL-9494, Schaan, Liechtenstein	Light-cured/dual-cured 74 wt% filler, 0.7 μm

The second hypothesis was that different test conditions of temperature and thermocycling will affect viscoelastic properties of resin cements. An experimental method was used that is capable of measuring viscoelastic behavior in a variety of ways, including: creep, constant load rate, sub-resonant dynamic and resonant dynamic experiments in bending and torsion. The resonant dynamic method was used in this study.

2. Materials and methods

Four dimethacrylate-based dental cements were investigated (Table 1). Two cements (Variolink II and Lute-It!) were light cured/dual cured and two (Rely X Arc and Duo Cement) were dual cured only. As shown in Table 1 the filler loading varied from 65 to 74 wt%.

Specimen preparation was the same as described in an earlier article [9]. The cements were injected into glass capillary tubes, resulting in finished specimens that were 0.85 mm in diameter and 18 mm in length. The resins were photopolymerized with a Coltolux light directed at the side of the capillary tube using 40 s exposure time for each 5 mm of length of the tube. Thorough curing was achieved because of the small diameter of the specimens. The specimens were mounted using a jig for centering between a Plexiglas disc (0.5 mm thick) and a rod by means of a composite filling material. A water-tight chamber with a heating unit and thermocouple surrounded the specimen during testing under wet conditions.

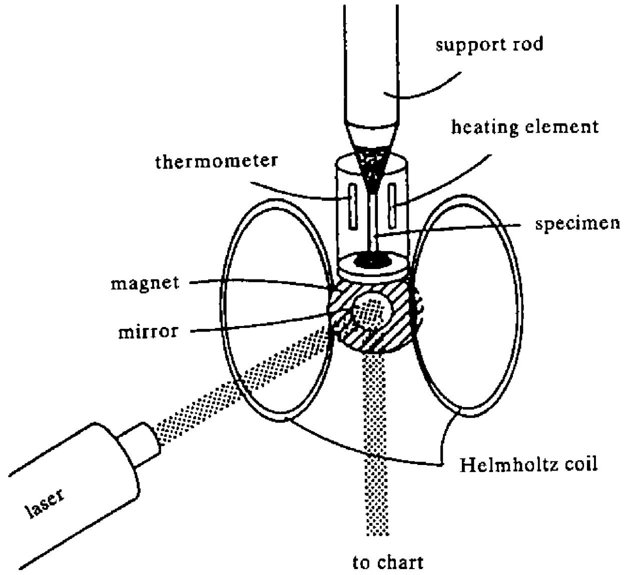

Fig. 1. Diagram of the apparatus used to measure dynamic torsional vibration.

Each of the four cements was tested under four different conditions so that there were 16 experimental groups with five specimens in each. The test conditions were (1) Dry at 21 °C: these specimens were stored in a dry beaker at 37 °C for 24 h after fabrication and subsequently tested dry at 21 °C. This was the control group. (2) Wet at 37 °C: these specimens were stored in distilled water for 24 h at 37 °C and then they were tested in distilled water at 37 °C. (3) Thermocycled: these specimens were stored in distilled water for 24 h at 37 °C and then cycled 3000 times in baths with temperatures of 37, 50, 37, 5 °C with a 15 s immersion time in each bath. After cycling, the specimens were tested wet at 37 °C. (4) Wet at 50 °C: specimens were stored in distilled water for 24 h at 37 °C and tested in distilled water at 50 °C.

The apparatus (Fig. 1) for measuring torsional resonance has been described by Lakes [10]. Torque was generated by a permanent samarium cobalt magnet fixed to the end of the specimen. The magnet produced a torque of 0.00247 N m/A at the center of a Helmholtz coil. A thin mirror 8.2 mm in diameter and 1.5 mm thick was cemented to the magnet to reflect a laser beam to a chart at a distance, D, of 941 cm. The mirror rotation angle, φ, is given by $\varphi = X/2D$, where X is the chart displacement of the laser beam. Steady-state dynamic torsional vibration was applied by driven frequencies ranged from 1 to 80 Hz. The displacement or amplitude was measured on the chart for each frequency and the compliance curve was constructed (Fig. 2).

Viscoelastic parameters were calculated from the resonance frequency, ν_0, corresponding to the peak amplitude and the resonance full width, $\Delta\nu$, that is the difference between the two frequencies at which the amplitude is half of the maximum. The loss tangent is obtained from the relation $\tan\delta = [1/\sqrt{3}]\Delta\nu/\nu_0$. The storage shear modulus, G_1, was calculated from the relation $\nu_0 = [1/2\pi]\sqrt{[G_1\pi r/2LI]}$, where r is the specimen radius, L is its length, and I is the moment of inertia of the magnet that was measured to be 4×10^{-7} kg m^2. The loss modulus was calculated from $G_2 = G_1\tan\delta$. The dynamic viscosity was obtained from the equation $[\eta^*] = (1/\omega_0)\sqrt{(G_1^2+G_2^2)}$, where $\omega_0 = 2\pi\nu_0$. The above simple data reduction is valid for a small loss, i.e. $\tan\delta \ll 1$. The coefficient of decay is $\alpha = \pi\Delta\nu$ and indicates

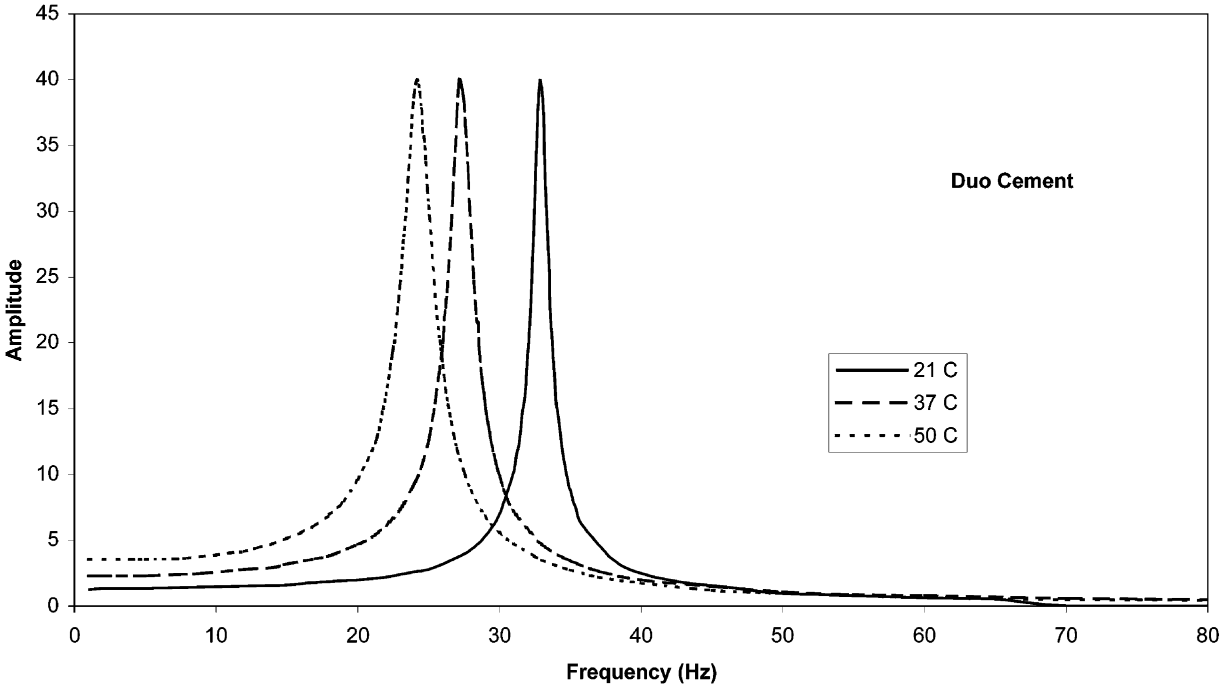

Fig. 2. Compliance versus frequency curves for Duo Cement at 21, 37 and 50 °C. The decrease of the resonant frequency corresponds to a decrease in the modulus. The broadening of the peaks corresponds to an increase in the loss tangent.

the magnitude of the width between the frequencies at one half the resonance peak of the compliance curve. The quality factor, $Q = \nu_0/\Delta\nu$, indicates the shape of the resonance curve. A high value of Q correlates with a peaked resonance curve and little damping.

Storage modulus and loss tangent for the four groups of specimens of each material were analyzed by means of one-way analysis of variance (ANOVA). The Student–Newman–Keuls test was used for post-hoc multiple comparisons of means.

3. Results

The viscoelastic functions measured in this study are given in Table 2. The compliance versus frequency curves

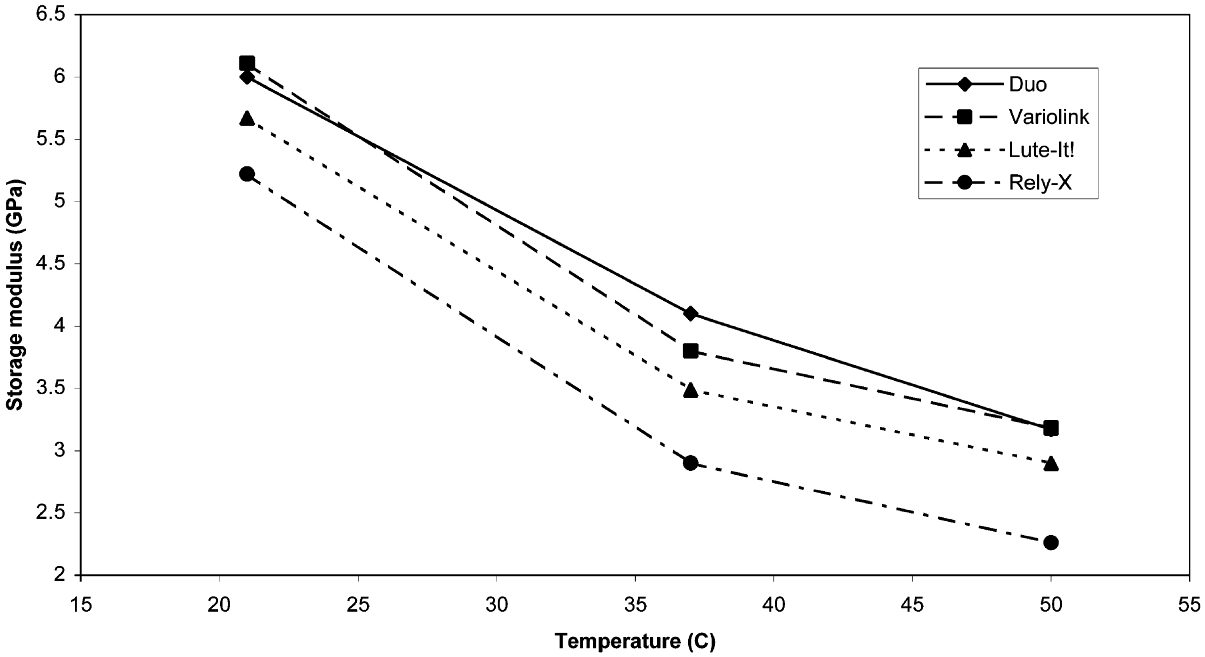

Fig. 3. Storage moduli of the four resin cements decreased similarly with temperature.

Table 2
Viscoelastic parameters of resin cements

Material	Test temp. (°C)	Test condition	Loss tangent tan δ mean (SD)	Storage modulus GPa (SD)	Loss modulus GPa (SD)	Dynamic viscosity MPa s	Coeff. of decay	Quality factor
Duo	21	Dry	0.0294 (0.0007)	6.004 (0.008)	0.171 (0.004)	29.1	5.09	20.30
Cement	37	Wet	0.0532 (0.0024)	4.103 (0.021)	0.222 (0.010)	24.0	8.01	10.67
	37	TC/wet	0.0546 (0.0008)	3.381 (0.004)	0.186 (0.003)	21.8	7.38	10.51
	50	Wet	0.0942 (0.0005)^a	3.171 (0.003)^b	0.254(0.002)	21.4	10.30	7.38
Lute-It!	21	Dry	0.0293 (0.0004)	5.673 (0.003)	0.164 (0.002)	28.2	5.03	19.98
	37	Wet	0.0543 (0.0004)	3.492 (0.005)	0.190 (0.001)	22.2	7.45	10.59
	37	TC/wet	0.0587 (0.0001)	3.216 (0.002)	0.189 (0.001)	21.3	7.70	9.83
	50	Wet	0.0796 (0.0003)	2.902 (0.003)	0.231 (0.001)	20.3	9.90	7.26
Rely-X	21	Dry	0.0369 (0.0001)	5.222 (0.004)	0.192 (0.001)	27.1	6.13	15.74
	37	Wet	0.0843 (0.0017)^c	2.903 (0.021)	0.246 (0.005)	20.3	10.52	6.84
	37	TC/wet	0.0818 (0.0004)	2.759 (0.001)	0.227 (0.001)	19.8	9.99	7.01
	50	Wet	0.0970 (0.0021)^c	2.260 (0.017)	0.218 (0.005)	17.9	10.59	5.99
Variolink	21	Dry	0.0347 (0.0007)	6.110 (0.012)	0.210 (0.004)	29.3	6.22	16.742
	37	Wet	0.0663 (0.0023)	3.801 (0.024)	0.239 (0.009)	23.2	8.95	9.193
	37	TC/wet	0.0674 (0.0001)	3.409 (0.004)	0.230 (0.001)	21.9	9.08	8.581
	50	Wet	0.0951 (0.0009)^a	3.179 (0.013)^b	0.298 (0.003)	21.2	12.25	6.128

TC/wet: specimens were thermocycled then tested in water. *N*, five specimens per group. Homogeneous statistical groups ($\alpha = 0.05$) are shown by superscript letters.

of one of the cements is shown in Fig. 2. All the materials showed significant differences ($p < 0.001$) in storage moduli and the loss tangents at the four different conditions, except for Rely-X, which had no significant difference ($p > 0.05$) in loss tangent at 37 versus 50 °C. The storage moduli of the materials decreased with temperature, as is shown in Fig. 3. The loss tangents of the cements increased with temperature (Fig. 4). The effect of thermal cycling was a decline in storage moduli (Fig. 5). But it did not uniformly affect the loss tangents of the materials (Fig. 6). Loss tangent of two of the cements increased. It decreased slightly for one cement and showed no change for the remaining cement.

When the storage moduli and loss tangents were statistically compared among materials, there were also significant differences ($p < 0.001$) in conditions examined, except for the specimens of Variolink versus Duo cement, where there were no significant differences ($p > 0.05$) between specimens examined at 50 °C.

4. Discussion

All the cements tested in this study showed stable viscoelastic behavior in the temperature range of 21–50 °C, that is, no large shifts indicative of the glass transition were seen. This indicates that these cements should maintain their properties in the temperature range found in the mouth. All materials showed similar decreases in storage moduli and increases in loss tangents consistent with temperature dependence of these parameters. Storage moduli dropped from 16 to 23% in the temperature range of 37–50 °C. Since materials are equilibrated at 37 °C in the mouth and are not thermal conductors, temperature changes from 37 °C are expected to be small and should lead to only modest changes in modulus.

Thermal cycling between 5 and 50 °C for 3000 cycles had only a slight effect on the cements. Two potential effects of cycling on elastic modulus can be anticipated. Some additional polymerization may occur due to the elevated temperature and this would increase the modulus. On the other hand, the additional exposure to water would allow for more water absorption that has a plasticizing effect on composites and lowers the elastic modulus. In the present study, storage moduli were lower after thermal cycling, so water absorption appeared to have predominated. Two of the cements showed the expected increase in loss tangent after cycling, but the remaining two did not.

Elastic moduli of composites depend on the concentration of filler particles [11] and this dependence was seen in this study. The cements with the highest filler loading, Duo (72 wt%) and Variolink (74 wt%), had higher storage moduli than Lute-It! (65 wt%) and Rely-X (67.5%). The relationship between storage modulus and filler loading was not seen for small changes in filler concentration. Variolink had lower modulus than Duo, though its filler loading was

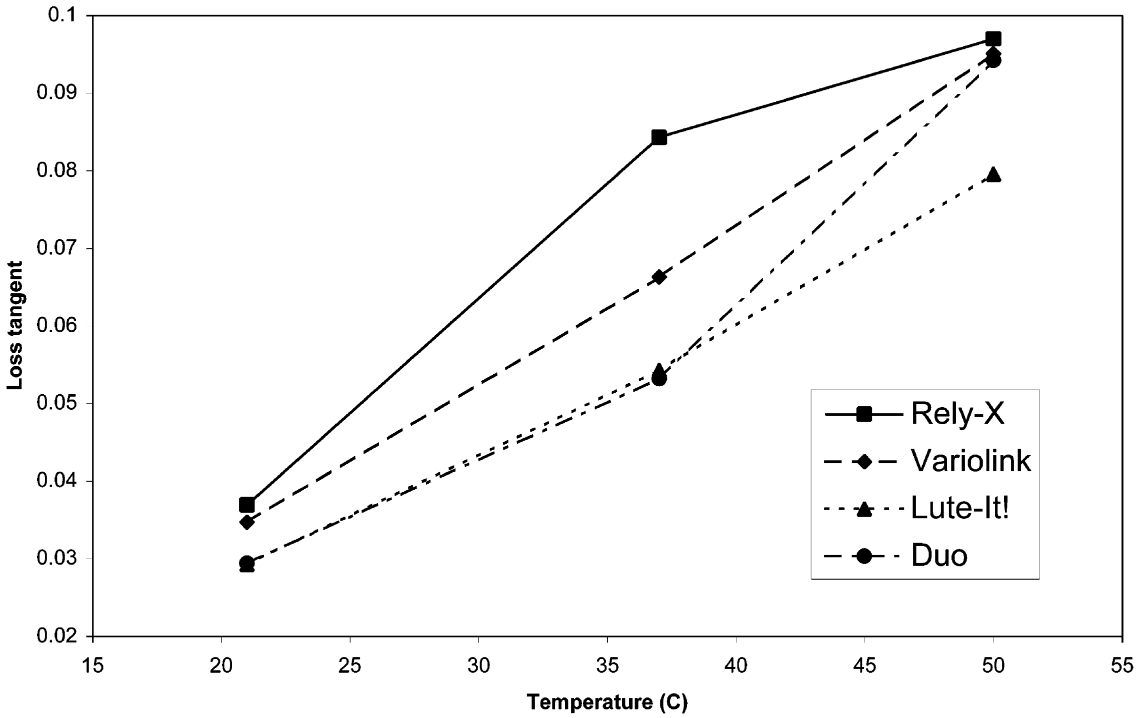

Fig. 4. Loss tangents of the four resin cements increased with temperature.

slightly higher. The same was true comparing Lute-It! and Rely-X. Small differences in filler loading were probably outweighed by differences in polymer conversion and crosslinking of the different products. The loss tangent was expected to show lower values in materials with higher filler loading. In general this was true except that Lute-It!, with a low filler content, also had a relatively low loss tangent.

Storage moduli of the cements were lower than those of more highly filled composites reported in an earlier study of viscoelastic properties measured using the same apparatus [5]. Hybrid composite restorative materials with filler

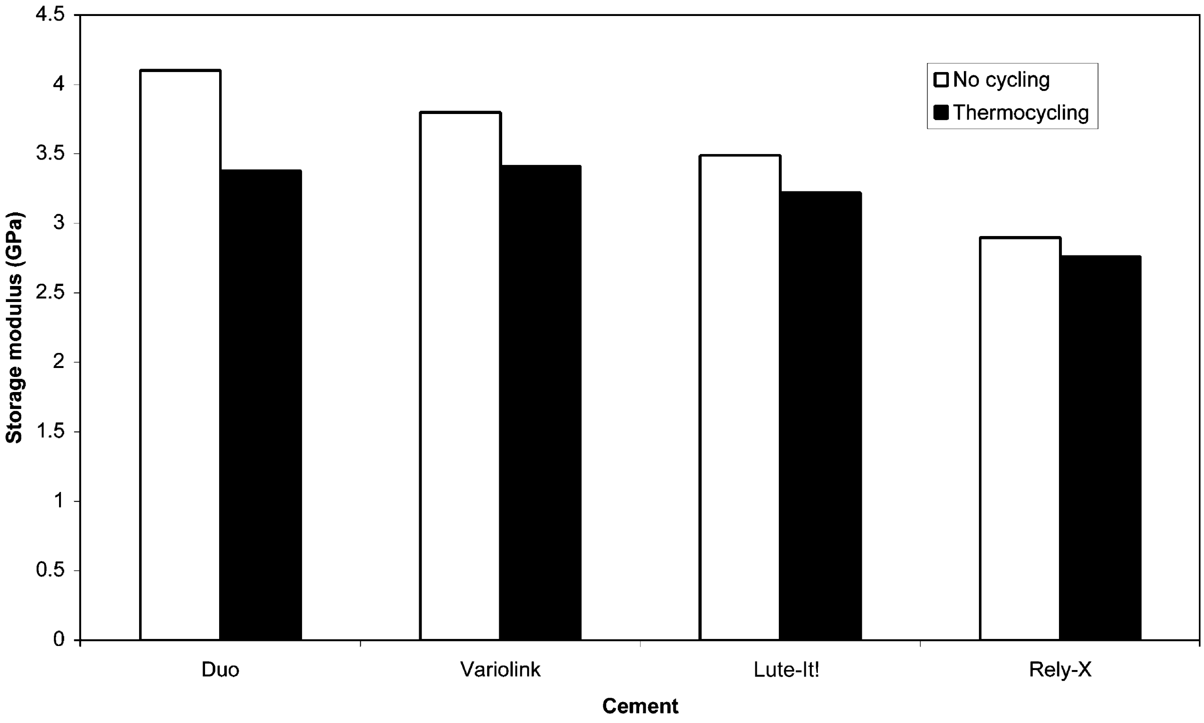

Fig. 5. Thermocycling between 5 and 50 °C for 3000 cycles with 15 s immersion time caused storage moduli of the resin cements to decline.

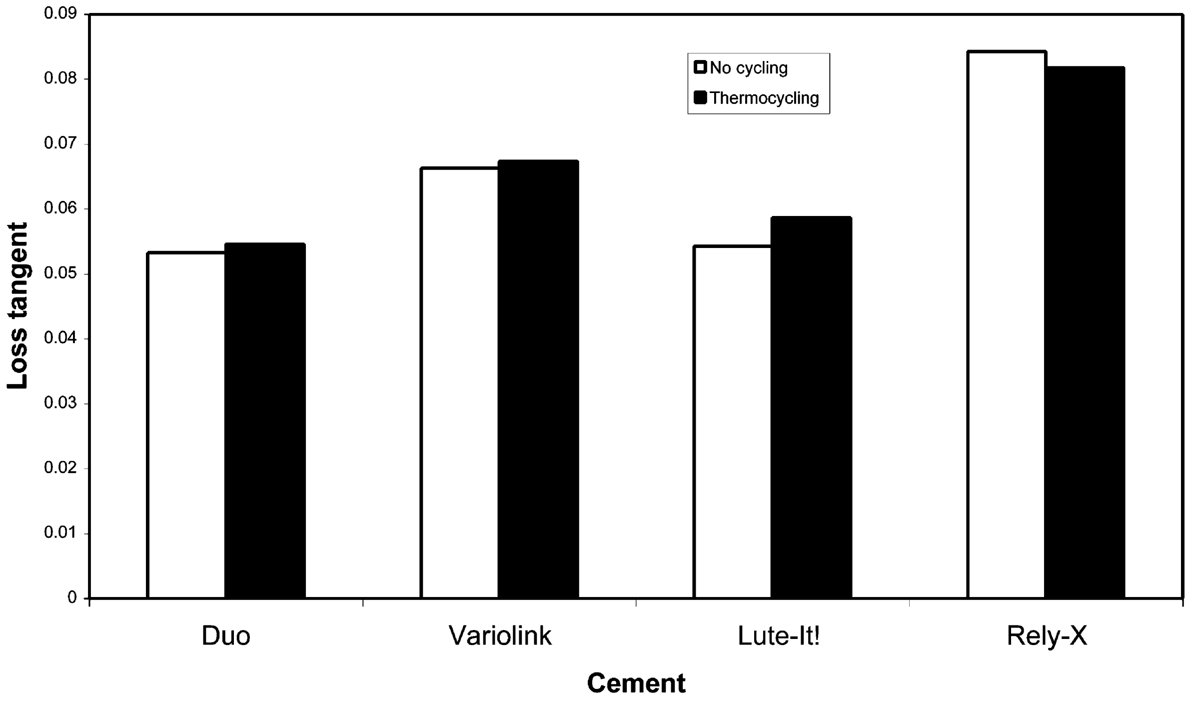

Fig. 6. Thermocycling did not affect loss tangents of the resin cements uniformly. Some increased, and one decreased, however, differences were relatively small.

loading of 78 and 87.5 wt% had storage moduli ranging from 7.9 to 9.6 GPa compared to the values of 2.9–4.1 GPa at 37 °C found for the resin cements in this study. However, these cements have storage moduli greater than the microfilled composites reported in the earlier study, ranging from 2.57 to 2.58 GPa. The latter have lower filler loading of 52 wt%. Loss tangents of the cements in the present study ranged from 0.054 to 0.084 at 37 °C and were very similar to those measured by the same method for composite restorative materials, ranged from 0.049 to 0.080 [5].

Elastic modulus and creep are two of many properties that are thought to influence clinical performance of dental cements [6]. Porcelain crowns have been shown to have better fracture resistance when placed over higher modulus substrates [7]. Elastic modulus of the cement is important since fracture resistance of porcelain crowns was found to be higher over hardened cement than try-in paste [12]. Fracture resistance of ceramic and composite inlays and onlays may be expected to be similarly influenced by resin cement properties. Required values of elastic modulus are not known, however, loss rates of crowns cemented with a high modulus cement, zinc phosphate (12 GPa), are less than when polycarboxylate cement (3 GPa) is used [13]. It can be speculated that resin cements with high elastic moduli, consistent with acceptable viscosity and film thickness, would be the best performers.

It has been suggested that creep (plastic strain) may influence capability of cements to retain crowns [8]. The loss tangent determined in this study is related to the slope of the creep compliance curve $J(t)$ by the following: $\tan \times \delta \approx (\pi/2) d \ln J(t)/d \ln t$. For example, in a power-law creep, $J(t) = At^n$, the loss angle is $\delta = n\pi/2$. So, for $\tan \delta = 0.05$, representative of these cements, $n = 0.0318$, then creep is 7.6% per decade (factor of ten in time).

Cements function by micromechanical interlocking of cement tags in rough surfaces of the tooth and crown. Deformation of these tags could reduce the retentive ability of the cement layer [13]. These investigators found that creep of a composite resin cement was greater than zinc phosphate cement, but lower than polycarboxylate cement. Creep of glass ionomer cement was similar to composite resin [14]. It can be speculated that resin cements with low loss tangents might show better clinical performance.

In summary, viscoelastic properties of resin cements measured by a torsion resonance method varied among materials and among test conditions. Cements with higher filler loading had higher storage moduli and lower loss tangents, although the relationship was not shown between materials with small differences in filler loading. Viscoelastic properties varied with temperature levels (21, 37, 50 °C), but changes were not indicative of a glass transition in this region. Thermocycling had a plasticizing effect on materials, probably due to increased water sorption.

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