The effect of temperature on the viscoelastic properties of nano-hybrid composites

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ABSTRACT

Objectives. The purpose of this study was to examine the viscoelastic properties of nano-filled dental composites under both static and dynamic testing and to determine the influence of temperature, medium of storage and storage time.

Methods. Three nano-filled composites, one packable and one ormocer were tested. The specimens were examined dry at 21 °C and wet at 21, 37 and 50 °C after being stored for 24 h and 1 month under both static and dynamic testing. Shear modulus, elastic modulus, loss tangent, Poisson’s ratio and other viscoelastic parameters were calculated. Data were analyzed with one-way and two-way analysis of variance (ANOVA) (p = 0.05).

Results. All materials tested showed a significant decrease in their moduli with the increase of temperature, while the effect of water storage was different among the composites. Grandio was the composite with the highest Young’s modulus followed by Filtek P60.

Significance. Most of the materials tested did not have elastic moduli near to that of dentin, making them less satisfactory in posterior restorations. The materials possessing nano-sized filler particles had different elastic properties among them and this implies that filler size is not the only factor that affects the elastic behavior of dental composites.

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1. Introduction

Although composite resins were first used as anterior restorative materials they are now being used in stress-bearing posterior restorations with increased frequency. Since 1960, when they were introduced in dentistry, they have undergone a lot of changes in order to become restorative materials with acceptable aesthetic properties and mechanical properties comparable to those of dental amalgam. The research on the composition of composite materials is focused on the resin matrix monomers in order to improve properties like polymerization shrinkage \cite{1,2} and stress \cite{3}, viscoelastic properties \cite{1,4}, thermal properties \cite{4}, incorporation of filler \cite{5} and biocompatibility \cite{6} and on the filler content \cite{7} which plays a major role in properties like compressive strength, hardness, flexural strength and elastic modulus.

The ongoing demand for better mechanical and aesthetic properties promoted a subdivision of direct restoratives for specific applications \cite{8}. Packable composites, also called condensable, were presented as amalgam alternatives. Their high-filler load along with their filler distribution gives them improved handling properties, easier establishment of inter-
proximal contacts and the ability of bulk curing of the restoration. Also, flowable composites were introduced with low-filler load resulting in a less viscous material. Flowable composites were introduced as liners in deep cavities or pit and fissure sealants.

One of the most recent advancements in the direct dental restorative materials is the incorporation of nanotechnology. Nanotechnology is the understanding and control of matter at dimensions of roughly 1–100 nm and the engineering of functional systems at the molecular scale. It refers to the construction of items from the bottom up, using techniques and tools to make complete products.

A number of nanofilled restorative materials have been produced [9] by various manufacturers with a filler size ranging from 5 to 100 nm. Nanofilled composite resins are claimed to have improved properties in both aesthetics [7,8,10] and mechanical performance. The superior mechanical properties [7,8] like high flexural strength, low abrasion, low polymerization shrinkage and resistance to fracture are attributed to the high-filler load of these materials because of the small size the fillers possess.

The elastic properties of the resin-based restorative materials are very important in order to predict their behavior in the oral environment. The elastic modulus quantifies the relative stiffness or rigidity of a material within the elastic range and may be described as the ratio of uniaxial stress to strain at small strain levels [11]. It represents the slope of the elastic portion of the stress–strain curve [12]. The stress–strain ratio is sometimes constant over a range of strain and then Hooke’s law applies. Depending on the different modes and geometries of stress application different moduli as flexural or shear arise [12]. These moduli can be related under elastic deformation with a mechanical parameter known as Poisson’s ratio, ν, which can be defined as the ratio of transverse contraction strain to the longitudinal extension strain [13] and is also a measure of the relative resistance to dilatation and shearing [14]. The value of ν can be between −1 and +0.5 where at one extreme (ν = 0.5) a material is incompressible and has a high bulk modulus relative to Young’s modulus [15]. Young’s modulus (E), bulk modulus (B) and shear modulus (G) are related with ν through the following relationships: \( E = 6\nu(0.5 - \nu) \) and \( E = 2G(1 + \nu) \). These relationships apply to isotropic materials and cannot be used for anisotropic like oriented fibrous materials.

The elastic parameters of a material are indicative of the deformation of the material under external forces. Dental restorative materials must withstand the masticatory forces in the oral cavity and their elastic modulus is of great importance for the longevity of both the restoration and the surrounding dental tissue. If the composite has a low modulus, it will deform more under the functional stresses and it is possible that the tooth structure will suffer from a catastrophic fracture or that the bond between tooth and restoration will be compromised [16] leading to marginal gap deformation, post-operative sensitivity and secondary caries. Also, the stresses at the post-gel phase of polymerization which are extremely important for the polymerization shrinkage and the cuspal strain are related to the elastic modulus of the composite [17] and its ability to flow [16,18,19]. Ideally, the elastic properties of the restorative materials should be close to those of the tooth structure resulting in a more uniform distribution of stresses [15]. However, the tooth consists of enamel and dentin that elastically are very different [20]. If they were both to be replaced, two distinct restorative materials should be used [16] and so, one of them should be chosen as a standard. Dentin is a composite structure that consists of hydroxylapatite crystals embedded in a collagen matrix and its viscoelastic behavior at body temperature is similar to that of dental polymers [12,16] so it is used as the golden standard.

The purpose of this study was to determine the viscoelastic properties of nanofilled and conventional composite resins by using both static and dynamic tests under different temperatures and conditions of storage.

2. Materials and methods

Three nanofilled composite resins (Grandio, Simile, Filtek Supreme), one packable (Filtek P60) and an ormocer (Admira) were investigated in this study (Table 1). The uncured composites were injected into glass capillary tubes, resulting in specimens of 1.04 mm in diameter and 18 mm in length. The volume of the specimens is similar to small dental restorations. The specimens were photopolymerized (Coltulox 4 light, Coltene Whaledent, Dentalbertriebs GmbH Kostanz/Germany). The light output was tested before use with the radiometer included in the Coltulox 4 (600 mW/cm²). The light was directed toward the side of the capillary tube with an exposure time of 40 s for each 5 mm length of the tube. The cylindrical specimens ended in small spheres that were mounted using a jig for centering, between a Plexiglas disc (0.5 mm thick) and a rod, by means of a self-cured composite (Concise, 3M Dental Products). The specimens tested under wet conditions were surrounded by a watertight chamber with a heating unit and thermocouple.

Four groups consisting of four specimens from each of the five composites were tested. The specimens in the first group were stored in a dry beaker at 21 °C for 24 h after fabrication and were then tested dry at 21 °C. The specimens in the second group were stored in a dry beaker at 21 °C for 1 month and then were tested dry at 21 °C. The specimens in the third group were stored in distilled water for 24 h at 37 °C and then were tested wet at three temperatures (21, 37 and 50 °C). The fourth group consisted of specimens stored in distilled water for 1 month at 37 °C and then tested wet at three temperatures (21, 37 and 50 °C).

The apparatus used in this study (Fig. 1) is described by Lakes [21] and it has since been modified in order to enable the study of microsamples of foams and composites. The apparatus is capable of torsion or bending tests upon cylindrical specimens, following static or dynamic methods. Torque was generated by a permanent samarium cobalt magnet fixed to the end of the specimen. The magnet (19.06 mm in diameter and 6.35 mm thick) produced a torque of \( 2.47 \times 10^{-3} \text{ N m/A} \) at the center of a Helmholtz coil. A thin mirror (3 mm in diameter and 1 mm thick) was cemented onto the magnet to reflect the spot of a low power helium neon laser beam on a calibrated chart at a distance of \( D = 745 \) cm. The mirror rotation angle, ϕ,
Table 1 – Composition of tested materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Matrix</th>
<th>Filler (wt%)</th>
<th>Filler (vol.%)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grandio (Nano-hybrid)</td>
<td>Bis-GMA, dimethacrylate and methacrylic urethane dimethacrylate and bis-acrylamide UDMA and bis-EMA</td>
<td>87%</td>
<td>71.4%</td>
<td>Voco Postfac 767, Cuxhaven, Germany</td>
</tr>
<tr>
<td></td>
<td>Glass–ceramic (Microfiller) 1.0 mm, SiO₂</td>
<td>87.5%</td>
<td>71.4%</td>
<td>3M Dental Products, St. Paul, MN, USA</td>
</tr>
<tr>
<td></td>
<td>Zirconia–silica (Nanofiller) 5–20 nm</td>
<td>87.5%</td>
<td>71.4%</td>
<td>Voco Postfac 767, Cuxhaven, Germany</td>
</tr>
<tr>
<td>Supreme (Nano-hybrid)</td>
<td>Triethyleneglycol dimethacrylate, urethane dimethacrylate and Bis-EMA</td>
<td>87%</td>
<td>71.4%</td>
<td>3M Dental Products, St. Paul, MN, USA</td>
</tr>
<tr>
<td></td>
<td>Glass–ceramic SiO₂ (Microfiller) 0.7 mm</td>
<td>87%</td>
<td>71.4%</td>
<td>Voco Postfac 767, Cuxhaven, Germany</td>
</tr>
<tr>
<td>Simile (Nano-hybrid)</td>
<td>Bis-GMA, dimethacrylate and methacrylic urethane dimethacrylate and bis-acrylamide UDMA and bis-EMA</td>
<td>87%</td>
<td>71.4%</td>
<td>3M Dental Products, St. Paul, MN, USA</td>
</tr>
<tr>
<td></td>
<td>Barium borosilicate glass, silica (Nanofiller) 5–20 nm</td>
<td>87%</td>
<td>71.4%</td>
<td>Voco Postfac 767, Cuxhaven, Germany</td>
</tr>
<tr>
<td>Admira (Ormocer)</td>
<td>Ormocer, Bis-GMA, urethane dimethacrylate and bis-acrylamide UDMA and bis-EMA</td>
<td>87%</td>
<td>71.4%</td>
<td>3M Dental Products, St. Paul, MN, USA</td>
</tr>
<tr>
<td>Filtek P60 (Packable)</td>
<td>Bis-GMA, UDMA and Bis-EMA Zirconia/silica 0.04–3.5 μm</td>
<td>87%</td>
<td>71.4%</td>
<td>3M Dental Products, St. Paul, MN, USA</td>
</tr>
</tbody>
</table>

Fig. 1 – Laser based testing apparatus.

is given by $\psi = X/2D$, where $X$ is the displacement of the laser beam on the chart.

The weight of the magnet resulted in a constant small axial tensile stress on the specimen. There was no constraint on the specimen for either torsion or extension. In principle, a torsional load will generate an axial deformation in a specimen; however, this has a non-linear effect, which is negligible at the small torque levels used. Moreover, the method for measuring torsional angular displacement is totally insensitive to any axial deformation that may occur [22].

2.1. Static shear moduli ($G$) and Young’s moduli ($E$) measurements

The distribution of shear strain, $\gamma$, in a circular cylinder in torsion is

$\text{Strain } \gamma = \frac{r \psi}{L}$

where $r$ is the radial distance from the centerline and $L$ is the length of the cylinder. The distribution of the shear stress, $\sigma$, depends on the material properties. If it is linearly elastic or linearly viscoelastic, the shear stress is given by

$\text{Stress } \sigma = \frac{MR}{\pi R^3/2}$

where $M$ is the torque of the magnet and $R$ is the radius of the specimen. Interpretation of torsion results is straightforward when the stress is sufficiently small for the specimen to be linearly viscoelastic. At higher stress, caution is required, since only the outer layers of the specimen experience the peak stresses. Consequently the intrinsic material non-linearity is underestimated in the results.

For the determination of the shear moduli of elasticity ($G$) of the tested materials, a constant torque was applied to the specimen for a time of 10 s, the angular displacement was recorded (at 10 s) and then the torque was ‘instantaneously’ released. The shear modulus $G = \sigma/\gamma$ was calculated from the
The relation \( \tan \) half of the maximum. The loss tangent was obtained from between the two frequencies at which the amplitude is
titude and the resonance full width,
lus
G
and is related to the dissipation of energy. In most cases of
G
soidally and strain lags behind the stress. The storage modulus
viscoelastic behavior is linear, both stress and strain vary sinu-
260
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2

\[ \tan \] is the moment of inertia of the magnet that was mea-

is the diameter of the cylinder.

\begin{align*}
\text{Strain } \epsilon &= \frac{r \phi}{L} \\
\text{where } d \text{ is the diameter of the cylinder.}
\end{align*}

2.2. Dynamic experiments—storage \((G_1)\) and loss \((G_2)\) shear moduli measurements

In a dynamic experiment, when equilibrium is reached and
viscoelastic behavior is linear, both stress and strain vary sinu-
soidally and strain lags behind the stress. The storage modulus
\(G_1\) (the real part of the complex modulus \(G^*\)) is in phase
with strain, whereas the loss modulus \(G_2\) (the imaginary part of
the complex modulus \(G^*\)) is 90° out of phase with the strain
and is related to the dissipation of energy. In most cases of
stiff materials \(G_2\) is small compared to \(G_1\) and therefore \(G^*\) is
approximately equal to \(G_1\) and is loosely referred as modulus \(G\).
The ratio of the imaginary part to the real part of the complex
modulus \(G^*\) is referred to as internal damping or loss
tangent (tan \(\delta\)). The loss tangent is a measure of the ratio of
energy lost to energy stored. The angle \(\delta\) is the phase angle
between stress and strain sinusoids. The loss tangent is propor-
tional to the energy loss per cycle within the framework of
linear viscoelasticity.

Steady-state dynamic torsional vibration was applied by
driven frequencies that ranged from 1 to 100 Hz. The dis-
placement or amplitude was measured on the chart for each
frequency. Viscoelastic parameters were calculated from the
resonance frequency, \(v_0\), corresponding to the peak amplitude
and the resonance full width, \(\Delta v\), that is the difference
between the two frequencies at which the amplitude is
half of the maximum. The loss tangent was obtained from the
relation \(\tan \delta = (1/\sqrt{3})\Delta v/v_0\). The storage shear modulus,
\(G_1\), was calculated from the relation \(v_0 = (1/2\pi)\sqrt{G_1\pi^4/2L}\),
where \(r\) is the radius of the specimen, \(L\) is its length and
\(L\) is the moment of inertia of the magnet that was mea-
sured to be \(4 \times 10^{-7}\) kg m². The loss modulus was calculated
from \(G_2 = G_1 \tan \delta\). The dynamic viscosity was obtained from
the equation \(n^* = (1/v_0)\sqrt{G_1^2 + G_2^2}\), where \(v_0 = 2\pi v_0\).
The above simple data reduction is valid for a small loss, i.e. \(\tan \delta \ll 1\).
The coefficient of decay, \(\alpha\), indicates the magnitude of width
between the frequencies at one half the resonance peak of the
compliance curve and is \(\alpha = 2\pi v_0\). The quality factor, \(Q\),
indicates the shape of the resonance curve. A high value of \(Q\)
correlates with a peaked resonance curve and little damping. \(Q\)
was calculated from the equation \(Q = \sqrt{3v_0/\Delta v}\). Some authors
use a measure \(\psi\) known as the specific damping capacity. \(\psi\)
refers to the energy ratio for a full cycle and is meaningful
for non-linear materials as well as linear ones since the ener-
gies can be calculated from the stress–strain loop even if its
shape is not elliptical. It was calculated from the equation
\(\psi = 2\pi \tan \delta\). Poisson’s ratio was calculated from \(E = 2G(1+\psi)\),
using the values of \(G\) and \(E\) calculated in static measurements.

2.3. Statistical analysis

Mean values of shear moduli, elastic modulus and loss tan-
gent for every material were compared with two-way ANOVA
and Bonferroni post-tests at \(p = 0.05\) level in the dry specimens
in order to find the effect of storage time and the differences
between the materials. In the case of wet specimens where dif-
ferent testing temperatures were used, two-way ANOVA was
used for each storage time separately in order to find the effect
of temperature and the differences between the materials.
One-way ANOVA was used in order to determine the effect
of storage time and the effect that the environment of storage
had. Linear regression analysis was used and \(r^2\) was calcu-
lated in order to study the correlation of static shear moduli
and dynamic storage moduli in the same temperature and
storage time. One-way ANOVA was used in order to compare
the Poisson’s ratio of the different materials under the same
conditions.

3. Results

The mean values of shear moduli, Young’s moduli, Poisson’s
ratio and loss tangent are shown in Tables 2 and 3. Grandio
exhibited the highest Young’s modulus among the materi-
als tested, under all temperatures and storage conditions.
It was significantly higher than Filtek P60 (\(p < 0.01\)) and also
Simile, Supreme and Admira (\(p < 0.001\)). Filtek P60 had the
second highest Young’s modulus, significantly higher than
Simile, Supreme and Admira (\(p < 0.001\)). Between the other
three materials the values differed depending on the condi-
tions; however in the wet specimens Simile had a significantly
higher elastic modulus (\(p < 0.001\)) than the other two materials.

Grandio also had the highest shear modulus in all tem-
peratures and storage conditions (\(p < 0.001\)) and Filtek P60 was
second (\(p < 0.001\)). The differences between the shear moduli
of Simile, Admira and Supreme varied in the different storage
times, temperatures and conditions of testing.

Filtrek P60 had the lowest loss tangent in both dry and wet
specimens stored for 24 h and tested in 21 °C. Grandio had the
lowest loss tangent in the dry specimens stored for 1 month
and in the specimens stored in water for 24 h and tested in
temperatures of 37 and 50 °C and those stored in water for 1
month. Admira was the material with the highest loss tangent
(\(p < 0.001\)) in all conditions.

Poisson’s ratio ranged from 0.33 to 0.36 in the dry specimens
stored for 24 h and from 0.327 to 0.35 in the dry specimens
stored for 1 month. In the dry specimens Poisson’s ratio
decreased with storage time, while in the wet specimens it
increased.

Temperature had an extremely significant effect (\(p < 0.001\))
on all the properties tested (Fig. 2). Shear modulus, Young’s
modulus and the quality factor of all materials decreased with the gradual increase of temperature from 21 to 37 and 50 °C. Loss tangent, Poisson’s ratio, dynamic viscosity, coefficient of decay and specific damping increased with the increase of temperature.

The effect of storage time was not significant in the majority of the materials stored and tested dry. Only Simile was affected between 24 h and 1 month with an increase in both shear and flexural moduli. The rest of the materials showed no difference after 1 month of dry storage. The effect of storage time in the wet specimens was not universal. Admira, Grandio and Supreme showed no difference in their properties after 1 month of wet storage, while Filtek P60 and Simile exhibited an increase in their moduli.

The elastic properties under the two storage environments (dry and wet) were compared for every material tested at 24 h and 1 month. This was done only for 21 °C because dry specimens were tested at this temperature. Admira exhibited statistically significant lower moduli under wet storage \((p<0.001)\), while Supreme did not exhibit any difference in its properties because of the storage environment. Simile did not show any difference between dry and wet specimens stored for 24 h, but after 1 month of storage the wet specimens had lower values \((p<0.001)\) than the dry ones.

Linear regression analysis revealed significant correlation between the dynamic and static shear moduli \((r^2 = 0.9)\) for all ages and temperatures tested.

4. Discussion

From the findings of this study it is clear that the values obtained for most of the materials are not close to those of dentin. Only Grandio and Filtek P60 have Young’s moduli close to that of dentin, however in the case of Filtek P60 there was a decline in its elastic properties when the temperature was increased. At the temperature of 37 °C where testing results are very important [23] in order to predict the clinical performance of a composite resin, Filtek P60 had a lower modulus than that of dentin. In large stress-bearing restorations like those in anterior teeth most of the materials tested would absorb the majority of the masticatory stresses and would deform because of the difference of their modulus with that of dentin. This could eventually lead to marginal fractures and microleakage and to the failure of the restoration.

The effect of temperature on the viscoelastic properties of the materials was investigated in the case of the wet specimens and was found to be extremely significant. All materials tested wet showed a decrease in their moduli (Fig. 3) and their quality factor when the testing temperature rose from 21 to 37 and 50 °C. This was expected because these parameters investigated are temperature dependent. The data collected do not indicate the existence of glass transition because there was no corresponding fall to the moduli that would imply a transition to the rubber state of the composites. Such a transition is expected at higher temperatures. The changes observed in the moduli in the present study may be characteristic of minor or secondary transitions [24]. As mentioned before, the properties of the tested materials, with the exception of Grandio, are not close to the properties of dentin in the range of the
Table 3 – Results of materials stored and tested wet

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Shear mod., $G_1$ (GPa)</th>
<th>Shear mod., $G_2$ (GPa)</th>
<th>Dynamic viscosity, $n^*$ (MPa s)</th>
<th>Loss tangent (tan $\delta$)</th>
<th>Quality factor, $Q$</th>
<th>Coeff. of decay, $\alpha$</th>
<th>Specific damping, $\psi$</th>
</tr>
</thead>
</table>

Specimens age: 24 h wet, measured under static torsion at different temperatures

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Shear mod., $G_1$ (GPa)</th>
<th>Shear mod., $G_2$ (GPa)</th>
<th>Dynamic viscosity, $n^*$ (MPa s)</th>
<th>Loss tangent (tan $\delta$)</th>
<th>Quality factor, $Q$</th>
<th>Coeff. of decay, $\alpha$</th>
<th>Specific damping, $\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grandio</td>
<td>21</td>
<td>8.5</td>
<td>0.34</td>
<td>23.1</td>
<td>0.040</td>
<td>24.78</td>
<td>12.88</td>
<td>0.25</td>
</tr>
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<td></td>
<td>37</td>
<td>7.4</td>
<td>0.36</td>
<td>21.6</td>
<td>0.049</td>
<td>20.36</td>
<td>14.61</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.7</td>
<td>0.33</td>
<td>18.9</td>
<td>0.058</td>
<td>17.27</td>
<td>15.08</td>
<td>0.36</td>
</tr>
<tr>
<td>Simile</td>
<td>21</td>
<td>6</td>
<td>0.24</td>
<td>19</td>
<td>0.040</td>
<td>25.06</td>
<td>10.87</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>3.6</td>
<td>0.24</td>
<td>14.7</td>
<td>0.067</td>
<td>14.86</td>
<td>14.20</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3</td>
<td>0.26</td>
<td>13.5</td>
<td>0.088</td>
<td>11.38</td>
<td>16.96</td>
<td>0.55</td>
</tr>
<tr>
<td>Supreme</td>
<td>21</td>
<td>5.9</td>
<td>0.26</td>
<td>19.2</td>
<td>0.044</td>
<td>22.83</td>
<td>11.62</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>4.4</td>
<td>0.30</td>
<td>16.7</td>
<td>0.068</td>
<td>14.69</td>
<td>15.65</td>
<td>0.43</td>
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<tr>
<td></td>
<td>50</td>
<td>2.8</td>
<td>0.32</td>
<td>13.4</td>
<td>0.112</td>
<td>8.90</td>
<td>20.70</td>
<td>0.71</td>
</tr>
<tr>
<td>Admira</td>
<td>21</td>
<td>5</td>
<td>0.29</td>
<td>17.8</td>
<td>0.058</td>
<td>17.37</td>
<td>14.14</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>4.2</td>
<td>0.32</td>
<td>16.3</td>
<td>0.077</td>
<td>12.97</td>
<td>17.28</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3</td>
<td>0.29</td>
<td>13.8</td>
<td>0.097</td>
<td>10.35</td>
<td>18.38</td>
<td>0.61</td>
</tr>
<tr>
<td>Filtek P60</td>
<td>21</td>
<td>6.91</td>
<td>0.24</td>
<td>20.8</td>
<td>0.035</td>
<td>28.59</td>
<td>10.05</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>5.7</td>
<td>0.30</td>
<td>19</td>
<td>0.052</td>
<td>19.12</td>
<td>13.70</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.4</td>
<td>0.33</td>
<td>16.6</td>
<td>0.076</td>
<td>13.09</td>
<td>17.44</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Specimens age: 1 month wet, measured under dynamic torsion at different temperatures

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Shear mod., $G_1$ (GPa)</th>
<th>Shear mod., $G_2$ (GPa)</th>
<th>Dynamic viscosity, $n^*$ (MPa s)</th>
<th>Loss tangent (tan $\delta$)</th>
<th>Quality factor, $Q$</th>
<th>Coeff. of decay, $\alpha$</th>
<th>Specific damping, $\psi$</th>
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<td>0.24</td>
<td>21.8</td>
<td>0.031</td>
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<td>0.33</td>
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Table 3 – (Continued)

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<th>Materials</th>
<th>Temperature (°C)</th>
<th>Shear mod., $G_1$ (GPa)</th>
<th>Shear mod., $G_2$ (GPa)</th>
<th>Dynamic viscosity, $n^*$ (MPa s)</th>
<th>Loss tangent (tan δ)</th>
<th>Quality factor, $Q$</th>
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<td>16.3</td>
<td>0.081</td>
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Fig. 2 – The viscoelastic parameters of the tested materials under different temperatures.

Fig. 3 – The % loss of Young’s modulus between different temperatures in materials stored wet for 1 month.

temperatures that may be encountered in the clinical service. However, the changes in the elastic properties observed may not be of clinical relevance in most cases because temperature changes from 37°C are usually small and lead to modest changes of modulus due to the fact that composites are not thermal conductors. Only when consumption of very hot or very cold foods and beverages occurs, substantial temperature changes may happen.

While the effects of temperature were extremely significant, storage time did not have the same effect on all materials. When materials were stored dry for 1 month, only Simile presented a significant increase in its static shear modulus and its Young’s modulus, while the rest remained unaffected. Although dry storage cannot be considered as a stable condition [16], the majority of the materials retained their properties after 1 month. In the case of storage in water there is no agreement among researchers about its effect on the properties of composite resins. Gladys et al. [25] found a slight increase in the moduli of composite resins in the period of 1 month and then a slight decrease. They attributed the initial increase to the fact that the polymerization continues for up to 1 month. Sabbagh et al. [26] also observed an increase in the moduli of most materials in 1 month, followed by a relative stability. A small reduction in the flexural modulus of some composites was observed in other studies [20,27], while
other researchers [28,29] did not find any effect of the water storage on the flexural modulus of resin composites tested. The variety of the results could be explained by the different testing conditions in every experiment and especially the storage medium which as has been shown is important [30]. The degrading effect of water on the composites has been explained in the past with two different mechanisms. The first one is the plasticizing role of the water molecule [16,30] which creates more volume in the matrix and enhances the movement of the chain segments, resulting in the decrease of the stiffness of the material. The other mechanism [30] is the leaching of the composite’s components in the water. In the present study Admira was the only material that exhibited different values when wet and dry specimens were compared in both storage times, with lower moduli when tested wet. Among the rest of the materials, Simile showed a significant difference between wet and dry, but only after 1 month because of the great increase in the dry moduli, so wet storage did not have any major effect. None of the materials exhibited a decline in their properties after 1 month of wet storage compared to the values after 1 day. Grando, Admira and Supreme did not show any difference between 24 h and 1 month, while Filtek P60 and Simile exhibited an increase in their moduli. It seems that the effect of water is material specific and not universal like that of temperature and this could also explain the different results between the various studies. According to Ferracane et al. [27] the fact that the modulus of some materials is unaffected by water sorption may mean that the filler level is more important in determining rigidity and that variables affecting the polymer matrix play a less important role.

In this study, Grandio was found to have the best results among the nanofilled composites, but also among all other materials. Its flexural modulus was the highest with a value around that of dentin at the temperature of 37 °C, which may mean that it has the desirable elastic properties in order to match the behavior of the tooth and it also had the highest shear modulus. This comes in agreement with the findings of Mesquita et al. [16], according to which Grandio approaches the rigidity of dentine. The high elastic properties and the lowest Poisson’s ratio (0.33 when tested dry) could be attributed to the high-filler load of Grandio (71.4% volume) and also to the small size that these fillers possess. What is more important though, is the fact that Grandio exhibited the best behavior under both the effects of storage time and temperature. This is apparent in its loss tangent, which was the second highest in the dry specimens tested after 1 day but was the highest after 1 month and also the highest in all the wet specimens stored for 1 month. The decrease exhibited in its elastic properties because of the influence of temperature changes was the smallest. Young’s modulus decreased by 2.55% from 21 to 37 °C and by 20.91% from 21 to 37 °C, while shear modulus decreased by 5.8 and 22.2%, respectively. The fact that Grandio showed a relative stability in its properties could be crucial in its clinical performance.

Filtek P60 had the second highest values in this study surpassing the rest of the nanofilled composites and the ormocer. These values come in accordance with the findings of other studies [20,26]. Filtek P60 is a packable composite with a high-filler load which probably is the reason it exhibited a modulus close to that of dentin. It possesses the second highest filler load in weight (83%) and the third in volume (61%) among the materials tested and this could well be the reason for the high values obtained. However while its values were close to that of Grandio in the dry specimens and in the wet specimens tested at 21 °C, the rise of temperature caused a severe decline of both shear and Young’s moduli, a fact that could be attributed to differences in the composition of their matrix.

None of the other three materials had elastic properties near to that of dentin making them less satisfactory for posterior restorations. Supreme and Simile despite being nanofilled composites did not achieve the values that Grandio did. This could well mean that the size of the fillers may not be the deciding factor in elastic properties when there is an important difference in filler load. Supreme and Simile have smaller nanofillers than Grandio, however Grandio has a high-filler load, while the other two nanofilled composites have lower filler loads (Supreme 57.7% and Simile 68%). The maximum filler concentration depends on particle shape and not size, since concentration has no units of length. Reduction of filler size therefore does not increase the maximum concentration [31]. It is possible that nanoscale inclusions may have other benefits, perhaps in the view of their large surface area. High-filler concentrations can be achieved by using particles of different sizes. It appears that this hierarchical multi-scale packing is not yet used in dental composites.

Supreme exhibited stability in its properties and was not affected by the storage medium or the time of storage, but only by temperature changes. Simile on the other hand exhibited the greatest increase in its properties while stored dry. Its Young’s modulus increased from 12.5 to 14.2 GPa during the 1 month of dry storage. It also showed an increase in its properties, although smaller, when stored wet for 1 month, implying that polymerization continues for up to 1 month. Admira exhibited values close to that of the other two nanofilled composites, but had the highest loss tangent among the materials tested. It also exhibited a lower Young’s modulus (p<0.05) when tested and stored wet compared to the dry specimens in the temperature of 21 °C. This is in agreement with another study [20] that found a 4.9% difference among 24 h stored specimens. In the present study there was a 5.5% difference among dry and wet after 24 h and 8.2% after 1 month of storage. Admira is an ormocer (organically modified ceramic) and it is based on a different matrix composition consisting of chains of ceramic polysiloxane that could be affected by hydrolysis [20], thus explaining the differences between dry and wet specimens.

The Poisson’s ratio is a parameter that is greatly affected by the testing procedure and different values can be obtained with a change of the strain rate. However, the values obtained from the materials in this study are in a rather narrow and reasonable range that was expected for composites and calculated by other researchers [15]. In the dry specimens the Poisson’s ratio ranged from 0.32 to 0.35 at 21 °C, while in the wet specimens it ranged from 0.34 to 0.36 in the same temperature. The increase of temperature in the case of the composites tested wet resulted in an increase of the Poisson’s ratio (Fig. 4), something that was expected. Materials with higher filler volume content exhibited lower Poisson’s ratio (Fig. 5). This comes in accordance with previous studies [15,32] where composites...
Fig. 4 – The effect of temperature on Poisson’s ratio.

Fig. 5 – The Poisson’s ratio and the filler volume content of the materials tested.

with lower filler fraction exhibited lower elastic modulus and higher Poisson’s ratio.

5. Conclusions

The majority of the materials tested in this study did not approach the ideal values of elastic properties for posterior restorations, with the exception of Grandio. The nanofilled composites did not behave in a similar way and exhibited differences in their behavior, which may be the result of different filled loads. This finding shows that the reduction of filler size achieved by nanotechnology must be combined with other factors in order to result in better performance of the material. The effect of temperature was extremely significant and was the same on all materials, while the medium and the time of storage affected each material differently.

REFERENCES


