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

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ARTICLE INFO

Article history:

Received 3 September 2006

Accepted 14 May 2007

Keywords:

Nanofilled composites

Poisson's ratio

Elastic modulus

Temperature

Water storage

ABSTRACT

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

Methods. Three nanofilled 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 polymer-

ization shrinkage [1,2] and stress [3], viscoelastic properties [1,4], thermal properties [4], incorporation of filler [5] and biocompatibility [6] and on the filler content [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 [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-

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doi:10.1016/j.dental.2007.05.009

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 ($\nu=0.5$) 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: $E=6B(0.5-\nu)$ 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 (Coltolux 4 light, Coltene Whaledent, Dentalbertriebs GmbH Kostanz/Germany). The light output was tested before use with the radiometer included in the Coltolux 4 (600 mW/cm^2). 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 $D=745 \text{ cm}$. The mirror rotation angle, ϕ ,

Table 1 – Composition of tested materials

Materials	Matrix	Filler	Fillers (wt%)	Filler (vol.%)	Manufacturer
Grandio (Nano-hybrid)	Bis-GMA, dimethacrylate, urethane dimethacrylate and triethyleneglycol dimethacrylates	Glass-ceramic (Microfiller) 1 μm , SiO ₂ (Nanofiller) 20–60 nm	87%	71.4%	Voco Postfach 767, Cuxhaven, Germany
Supreme (Nano-hybrid)	Triethyleneglycol dimethacrylate, urethane dimethacrylate and Bis-EMA	Zirconia-silica (Microfiller) 0.6–1.4 μm , silica (Nanofiller) 5–20 nm	78.5%	57.7%	3M Dental Products, St. Paul, MN, USA
Simile (Nano-hybrid)	Difunctional methacrylate of PCBIS-GMA, Bis-GMA, UDMA and HDDMA	Barium boro-silicate glass, nanoparticulate silica, zirconium silicate (Nanofiller) 5–20 nm	75%	68%	Pentron Clinical Technologies, 53 N Plains Indrl, Wallingford, CT
Admira (Ormocer)	Ormocer, Bis-GMA, urethane dimethacrylate and triethyleneglycol dimethacrylate	Glass-ceramic SiO ₂ (Microfiller) 0.7 μm	78%	56%	Voco Postfach 767, Cuxhaven, Germany
Filtek P60 (Packable)	Bis-GMA, UDMA and Bis-EMA	Zirconia/silica 0.04–3.5 μm	83%	61%	3M Dental Products, St. Paul, MN, USA

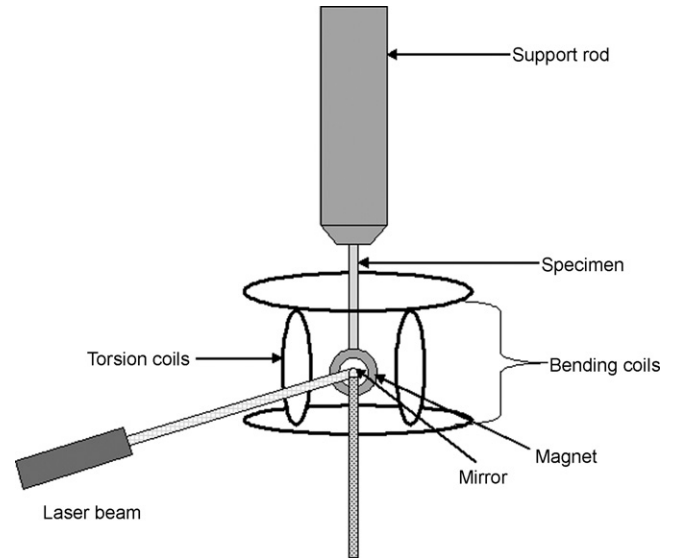


Fig. 1 – Laser based testing apparatus.

is given by $\varphi = X/2D$, 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, γ , in a circular cylinder in torsion is

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

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

$$\text{Stress } \sigma = \frac{MR}{\pi R^4/2}$$

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 10s, the angular displacement was recorded (at 10s) and then the torque was 'instantaneously' released. The shear modulus $G = \sigma/\gamma$ was calculated from the

equation:

$$G = \frac{2ML}{\pi R^4 \varphi}$$

The distribution of flexural strain, ε , in a circular cylinder in bending is

$$\text{Strain } \varepsilon = \frac{r\varphi}{L}$$

For the determination of Young's modulus of elasticity (E) the coil was rotated for 90° in order to achieve bending, and a constant torque was applied to the specimen for a time for 10 s, the angular displacement was recorded (at 10 s) and then the torque was 'instantaneously' released. Young's modulus $E = \sigma/\varepsilon$ was calculated from the equation:

$$E = \frac{64ML}{\pi d^4 \varphi}$$

where d is the diameter of the cylinder.

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 sinusoidally 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 δ is the phase angle between stress and strain sinusoids. The loss tangent is proportional 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 displacement or amplitude was measured on the chart for each frequency. 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 was obtained from the relation $\tan \delta = (1/\sqrt{3})\Delta\nu/\nu_0$. The storage shear modulus, G_1 , was calculated from the relation $\nu_0 = (1/2\pi)\sqrt{G_1\pi r^4/2LI}$, where r is the radius of the specimen, L is its length and I is the moment of inertia of the magnet that was measured to be $4 \times 10^{-7} \text{ kgm}^2$. The loss modulus was calculated from $G_2 = G_1 \tan \delta$. The dynamic viscosity was obtained from the equation $n^* = (1/\omega_0)\sqrt{G_1^2 + G_2^2}$, 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, α , indicates the magnitude of width between the frequencies at one half the resonance peak of the compliance curve and is $\alpha = 2\pi\nu_0$. 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 $Q = \sqrt{3}\nu_0/\Delta\nu$. Some authors

use a measure ψ known as the specific damping capacity. ψ refers to the energy ratio for a full cycle and is meaningful for non-linear materials as well as linear ones since the energies 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 $E = 2G(1 + \nu)$, using the values of G and E calculated in static measurements.

2.3. Statistical analysis

Mean values of shear modulus, elastic modulus and loss tangent 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 different 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 calculated 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 materials 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 conditions; 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 temperatures 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.

Filtek 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

Table 2 – Results of materials stored and tested dry

Materials	Static case (torsion). Specimens dry at room temp. 21 °C				Dynamic case (torsional vibration). Specimens dry at room temp. 21 °C						
	Age of specimen	Shear mod., G (GPa)	Young's mod., E (GPa)	Poisson's ratio, ν	Shear mod., G ₁ (GPa)	Shear mod., G ₂ (MPa)	Dynamic viscosity, η^* (MPa)	Loss tangent, $\tan \delta$	Quality factor, Q	Coeff. of decay, α	Specific damping, ψ
Grandio	24 h	7.62	20.4	0.33	9.7	0.34	24.7	0.350	28.42	12.00	0.22
	1 month	7.69	20.5	0.33	10.6	0.25	25.9	0.023	42.57	8.39	0.14
Simile	24 h	4.68	12.5	0.33	6.5	0.29	19.8	0.044	22.51	12.63	0.27
	1 month	5.31	14.2	0.33	6.6	0.24	20.3	0.036	27.9	10.05	0.22
Supreme	24 h	4.72	12.7	0.35	6.13	0.22	19.6	0.036	27.81	9.74	0.22
	1 month	4.68	12.6	0.35	6.22	0.22	19.8	0.036	28.01	9.74	0.22
Admira	24 h	4.99	13.4	0.34	5.5	0.27	18.7	0.049	20.49	12.57	0.3
	1 month	5.03	13.5	0.34	6.32	0.28	20.7	0.044	22.69	11.66	0.27
Filtek P60	24 h	7.3	19.5	0.33	7.94	0.23	22.3	0.030	33.82	9.11	0.18
	1 month	7.41	19.7	0.32	7.9	0.24	22.3	0.030	33.52	9.17	0.18

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

Materials	Temperature (°C)	Shear mod., G (GPa)	Young's mod., E (GPa)	Poisson's ratio				
Specimens age: 24 h wet, measured under static torsion at different temperatures								
Grandio	21	7.52	20.20	0.34				
	37	7.09	19.30	0.36				
	50	5.1	15.00	0.46				
Simile	21	4.63	12.50	0.35				
	37	3.66	10.00	0.36				
	50	2.64	7.60	0.43				
Supreme	21	4.51	12.40	0.37				
	37	3.53	9.78	0.38				
	50	2.78	7.90	0.42				
Admira	21	4.42	12.00	0.36				
	37	3.73	10.03	0.38				
	50	2.62	7.42	0.41				
Filtek P60	21	6.69	18.30	0.36				
	37	5.07	14.00	0.37				
	50	3.66	10.40	0.41				
Specimens age: 1 month wet, measured under static torsion at different temperatures								
Grandio	21	7.27	19.60	0.34				
	37	6.98	19.10	0.36				
	50	5.37	15.50	0.44				
Simile	21	4.69	12.80	0.35				
	37	4.26	11.80	0.38				
	50	3.15	8.91	0.41				
Supreme	21	4.51	12.10	0.35				
	37	3.5	9.69	0.39				
	50	2.55	7.35	0.44				
Admira	21	4.5	12.30	0.36				
	37	3.39	9.45	0.39				
	50	2.55	7.19	0.42				
Filtek P60	21	7.08	19.30	0.36				
	37	5.8	16.10	0.38				
	50	4.19	11.90	0.42				
Materials	Temperature (°C)	Shear mod., G ₁ (GPa)	Shear mod., G ₂ (GPa)	Dynamic viscosity, n* (MPa s)	Loss tangent (tan δ)	Quality factor, Q	Coeff. of decay, α	Specific damping, ψ
Specimens age: 24 h wet, measured under dynamic torsion at different temperatures								
Grandio	21	8.5	0.34	23.1	0.040	24.78	12.88	0.25
	37	7.4	0.36	21.6	0.049	20.36	14.61	0.31
	50	5.7	0.33	18.9	0.058	17.27	15.08	0.36
Simile	21	6	0.24	19	0.040	25.06	10.87	0.25
	37	3.6	0.24	14.7	0.067	14.86	14.20	0.42
	50	3	0.26	13.5	0.088	11.38	16.96	0.55
Supreme	21	5.9	0.26	19.2	0.044	22.83	11.62	0.28
	37	4.4	0.30	16.7	0.068	14.69	15.65	0.43
	50	2.8	0.32	13.4	0.112	8.90	20.70	0.71
Admira	21	5	0.29	17.8	0.058	17.37	14.14	0.36
	37	4.2	0.32	16.3	0.077	12.97	17.28	0.49
	50	3	0.29	13.8	0.097	10.35	18.38	0.61
Filtek P60	21	6.91	0.24	20.8	0.035	28.59	10.05	0.22
	37	5.7	0.30	19	0.052	19.12	13.70	0.33
	50	4.4	0.33	16.6	0.076	13.09	17.44	0.48
Specimens age: 1 month wet, measured under dynamic torsion at different temperatures								
Grandio	21	7.5	0.24	21.8	0.031	32.10	9.36	0.20
	37	7.2	0.29	21.2	0.040	24.85	11.78	0.25
	50	6	0.33	19.5	0.054	18.53	14.51	0.34

Materials	Temperature (°C)	Shear mod., G ₁ (GPa)	Shear mod., G ₂ (GPa)	Dynamic viscosity, n* (MPa.s)	Loss tangent (tan δ)	Quality factor, Q	Coeff. of decay, α	Specific damping, ψ
Simile	21	6.2	0.27	19.7	0.044	22.60	12.00	0.28
	37	5	0.29	17.7	0.058	17.16	14.20	0.37
	50	3.7	0.29	15.2	0.079	12.67	16.52	0.50
Supreme	21	4.9	0.21	17.6	0.042	23.55	10.30	0.27
	37	4	0.26	15.9	0.066	15.10	14.48	0.42
	50	3.1	0.32	14.1	0.103	9.71	19.92	0.65
Admira	21	5.4	0.28	19.2	0.052	19.20	12.79	0.33
	37	4	0.29	16.5	0.073	13.69	15.36	0.46
	50	3.3	0.31	15.0	0.095	10.47	18.19	0.60
Filtek P60	21	7.2	0.27	21.3	0.038	26.31	11.15	0.24
	37	5.9	0.31	19.2	0.053	18.74	14.17	0.34
	50	4.2	0.34	16.3	0.081	12.36	18.13	0.51

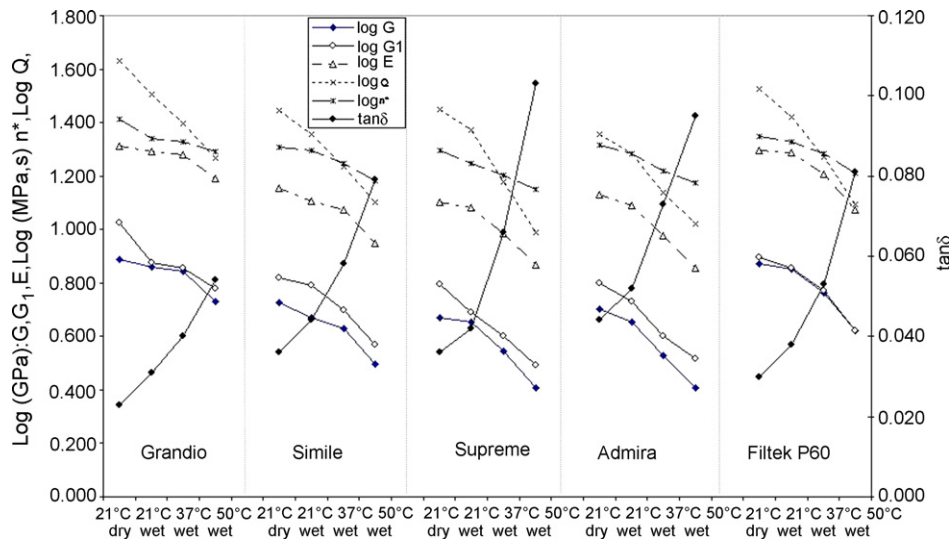


Fig. 2 – The viscoelastic parameters of the tested materials under different temperatures.

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.

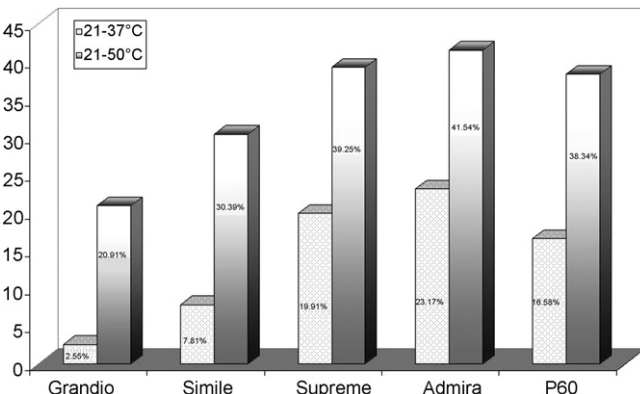


Fig. 3 – The % loss of Young's modulus between different temperatures in materials stored wet for 1 month.

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. *Grandio*, *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 nano-scale 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

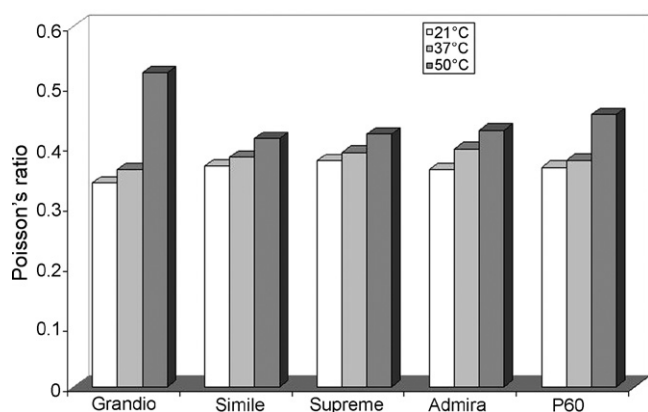


Fig. 4 – The effect of temperature on Poisson's ratio.

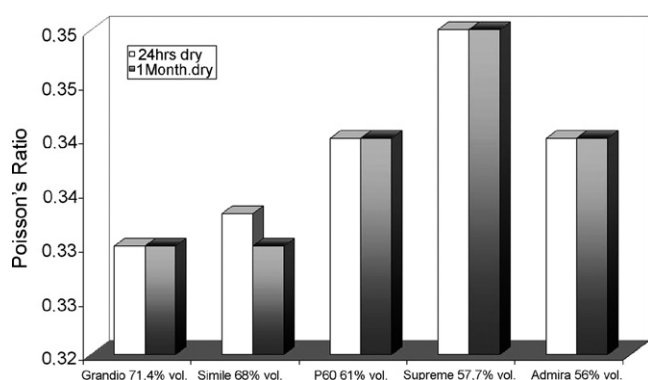


Fig. 5 – The Poisson's ratio and the filler volume content of the materials tested.

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.

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