Comparison of the visco-elastic behavior of a pre-impregnated reinforced glass fiber composite with resin-based composite

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ABSTRACT

Objectives. The visco-elastic behavior of a pre-impregnated reinforced glass fiber composite (everStick®) was compared with a resin-based particulate composite (Filtek™ P60) by using dynamic mechanical analysis (DMA) to determine their storage modulus (E') and damping ratio ($\tan \delta$).

Methods. These materials were subjected to three-point bend tests using a PerkinElmer DMA7. In temperature mode, the temperature was increased from 26 to 140 °C at 1 Hz. In frequency mode, the range was 1–10 Hz at a constant temperature of 37 °C.

Results. In both temperature and frequency modes, E' for everStick® was significantly higher and $\tan \delta$ was significantly lower than those for Filtek™ P60, indicating that the stiffness of the pre-impregnated glass fiber composite was higher and its damping property was lower than those for resin-based particulate composite.

Significance. The glass fiber restorative composite appears to absorb less energy in repeated stress and is less likely to retain external energy as residual stress.

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1. Introduction

Resin-based particulate composites (RBCs) are well-established restorative materials [1–4]. Fiber reinforced resins have also been used for a variety of applications; these have included carbon fibers [5–8], ultra high modulus polyethylene fiber [9–12], and latterly glass fibers [13–18]. Particulate composites are heterogeneous and isotropic materials, while fiber reinforced composites (FRCs) are heterogeneous and often anisotropic if long fibers are packed in one direction. In the latter case, the modulus and strength enhancement will be in the direction of the fibers. Such systems are used for endodontic posts [17,19]. However, if woven fabric or chopped fibers are used, then the composite is more homogeneous. Such systems have been used for denture bases [11,20–22]. One form of FRC employs densely packed silanated glass fibers pre-impregnated in a polymer–monomer gel consisting of a light cure dimethacrylate monomer resin (Bis-GMA) and a linear polymer (PMMA). When this composite is polymerized, a semi-interpenetrating polymer network (semi-IPN) is formed [23,24].

In the present study, the visco-elastic properties of one FRC (everStick®, Batch Number: 2040413-EO-040, Stick Tech Oy, Finland) and one RBC (Filtek™ P60, Batch Number: 4720 A3, 3M ESPE, Germany) were measured by dynamic mechanical analysis (DMA) with respect to temperature and frequency.

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Visco-elastic measurements are useful in that information can be obtained about the polymeric system on which the material is based, and on the propensity of the material to creep under load. Visco-elastic solids differ from elastic solids in that [25]:

(i) on application of a constant stress, after the instantaneous strain, the strain increases with time (creep);
(ii) on application of a constant strain, after the instantaneous stress, the stress decreases with time (stress relaxation);
(iii) if an alternating (sinusoidal) stress or strain is applied, stress and strain are out of phase. This phase angle is denoted by δ. In the corresponding theory, the Young's modulus (E) of classical elasticity is replaced by the so-called complex modulus (E^*), where E^* is given by

$$E^* = E' + iE'' \tag{1}$$

where E' is the storage modulus, and represents the elastic component of deformation, E'' is the loss modulus, and represents the viscous (inelastic) component, and $i = \sqrt{-1}$. These are related to δ:

$$\tan\delta = \frac{E''}{E'} \tag{2}$$

$\tan\delta$ is a measure of energy loss, sometimes referred to loosely as damping capacity. It is related to the fraction of energy retained, resilience (R):

$$R = \exp(-\pi\tan\delta) \tag{3}$$

At the glass transition temperature (T_g), E' decreases dramatically over a short temperature range, E'' decreases initially and then increases, and $\tan\delta$ go through maxima, consequent on the enhanced molecular mobility; some polymers show secondary transitions. Beyond T_g the polymer is in the rubber-like state, where deformation is a function of entropy only. Visco-elastic properties of polymeric dental materials have been occasionally studied in the literature [26–29]. DMA measures the ratio of the amplitudes of stress to the applied strain, and the phase angle δ, and computes E', E'', and $\tan\delta$. In the current study the samples were tested in the three-point bending mode.

2. Materials and methods

The everStick® is a light cured, radiopaque unidirectional continuous fiber composite containing E-glass fibers (55% SiO_2, 15% CaO, 15% Al_2O_3, 6% B_2O_3, 0.5% MgO, and 1.0% $Fe + Na + K$). The glass fibers are pre-impregnated with a silane coupling agent and a dimethacrylate resin matrix that is surrounded by a coating of PMMA and Bis-GMA. The Filtek™ P60 is a visible-light activated, radiopaque, restorative composite. The fillers are zirconia/silica (61% by volume without silane treatment). The filler particle size ranges from 0.01 to 3.5 μm with an average particle size of 0.6 μm. The resins are Bis-GMA, urethane dimethacrylate (UDMA) and bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA).

2.1. Sample preparation

Polytetrafluorethylene (PTFE) molds were made in order to manufacture test samples (24 mm × 2 mm × 1.5 mm in length, width and height, respectively). Prior to use the FRC specimens were stored at 4 °C and it was maintained to avoid them from direct light source. The samples were cut with sharp scalpel and were soaked in a dimethacrylate monomer (Scotchbond Multipurpose Adhesive, 3M ESPE, USA) in a Petri dish for 10 min in a low light environment. Prior to polymerization, excess resin was removed with soft tissue paper. The specimens were then placed in the mold and were polymerized using blue visible light (DeTrey, Dentsply, Germany, wavelength ≈ 470 nm) for 60 s. The distance of blue visible light was maintained constant for all samples. After removing the sample from the mold, the edges and the rough surfaces were polished by dry silica paper using 400 grade followed by 800 and 1000 grades to improve the surface finish. Twelve rectangular-shaped beam specimens were prepared and were stored in a low light environment before DMA testing. For the RBC sample, the samples were used as it was received from the manufacturer and were handled according to manufacturer's instruction. The material was injected directly into the PTFE mold (24 mm × 2 mm × 1.5 mm) without soaking in a monomer and 12 specimens were prepared. The specimens were polymerized by using blue visible light (DeTrey, Dentsply, Germany, wavelength ≈ 470 nm) for 60 s. The distance of blue visible light was constant for all samples. After removing the sample from the mold, the edges and the rough surfaces were polished by dry silica paper using 400 grade followed by 800 and 1000 grades to improve the surface finish.

2.2. DMA

A PerkinElmer DMA7 (PerkinElmer Corp., USA) in three-point bending mode was used to measure the dynamic mechanical properties of the two materials. For a specimen of known geometry if, L = distance between the two supports, b = width, and t = depth, the oscillating strain (ε_o) is given by

$$\varepsilon_o = \frac{3ty_0}{L^2} \tag{4}$$

where y_0 is the displacement amplitude.

The maximum oscillating stress (σ_o) occurs on the upper and lower surfaces and was given by

$$\sigma_o = \frac{3F_0L}{2bt^2} \tag{5}$$

where F_0 is the axial force amplitude. Therefore, by substituting for stress and strain, the complex modulus (E^*) was given by

$$E^* = \frac{F_0L^3}{2y_0bt^3} \tag{6}$$

The support separation in three-point bend test was 20 mm and the specimen length was 24 mm. The width and height were nominally 1.60 and 0.8 mm, respectively for everStick®. For Filtek™ P60, the nominal width and height were 1.72 and

Table 1 – Parameters used in temperature and frequency scan modes

Parameters	Conditions
Temperature	
Initial temperature (°C)	26
Final temperature (°C)	140
Static force (mN)	400
Dynamic force (mN)	380
Frequency (Hz)	1
Heating rate (°C min^{-1})	10
Frequency	
Initial frequency (Hz)	1
Final frequency (Hz)	10
Static force (mN)	400
Dynamic force (mN)	380
Temperature (°C)	37

1.05 mm, respectively. Prior to testing, specimen dimensions (width and depth) for each specimen were measured at three different points and averaged.

Testing was performed in the temperature and frequency scan modes using the parameters and conditions shown in Table 1. The temperature was measured with a thermocouple positioned approximately 1 mm away from the sample. Helium gas at a rate of 30 ml min^{-1} was used in the furnace and cooling water maintained the isothermal environment outside the furnace. The measured data were automatically saved at the end of each test using the Pyris Manager software.

The difference between the measured values of FRC and RBC were tested using unpaired Student's t-test with significant given by $p \leq 0.05$.

3. Results

The typical behavior of everStick® and Filtek^{TM} P60 for both E' and tan δ with reference to (a) temperature and (b) frequency is shown in Fig. 1.

3.1. Temperature

The effect of temperature on the E' and tan δ values for all the samples is summarized in Fig. 2. E' for Filtek^{TM} P60 decreased consistently with increasing temperature; but for everStick® E' decreased initially up to 50 °C and the values remained relatively constant in higher temperature. At 37 °C, E' for everStick® was significantly higher than that for Filtek^{TM} P60 ($p \leq 0.01$). Tan δ for Filtek^{TM} P60 could be observed to be increasing with temperature, with a broad peak at ~95 °C (Fig. 1). For everStick®, the tan δ appeared to peak at ~55 °C. Above 26 °C, tan δ for Filtek^{TM} P60 was significantly higher than that for everStick® ($p \leq 0.01$).

3.2. Frequency

The effect of frequency on E' and tan δ values are summarized in Fig. 3 E' for both Filtek^{TM} P60 and everStick® increased consistently with increasing frequency and the values for everStick® were significantly higher than Filtek^{TM} P60 at all frequencies ($p \leq 0.01$). Similar trends were observed for tan δ,
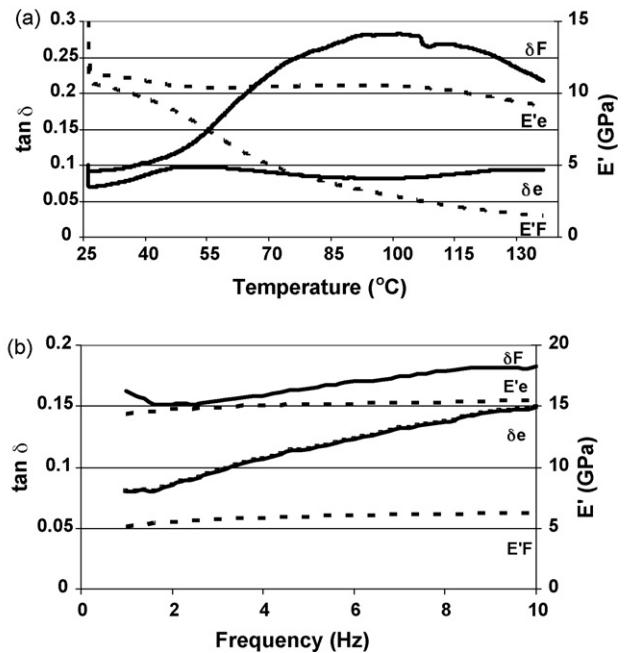

Fig. 1 – Variation of storage modulus for Filtek P60^{TM} ($E'F$) and everStick® ($E'e$) and tan δ for Filtek P60 (δF) and everStick® (δe) with (a) temperature and (b) frequency.

which increased with increasing frequency. In all frequencies, tan δ for Filtek^{TM} P60 was significantly higher than that for everStick® ($p \leq 0.01$).

4. Discussion

Filtek^{TM} P60 is an isotropic standard composite restorative material, whereas everStick® is a highly anisotropic reinforced
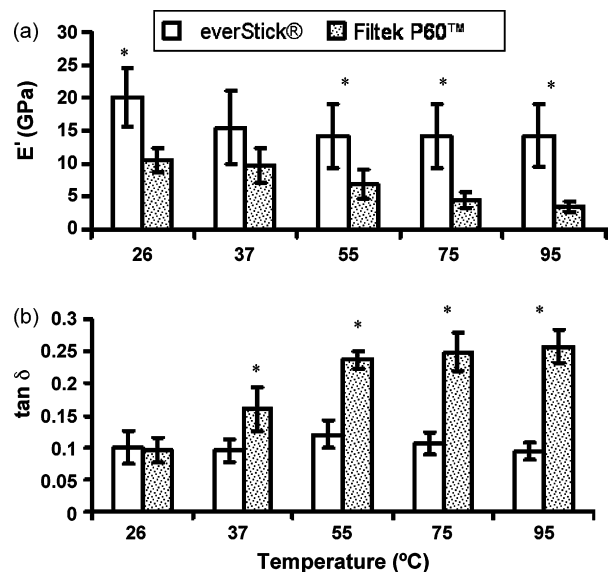
Fig. 2 – Comparison of (a) E' and (b) tan δ for Filtek P60^{TM} and everStick® with reference to temperature, statistically significant difference are shown by *$p \leq 0.01$.
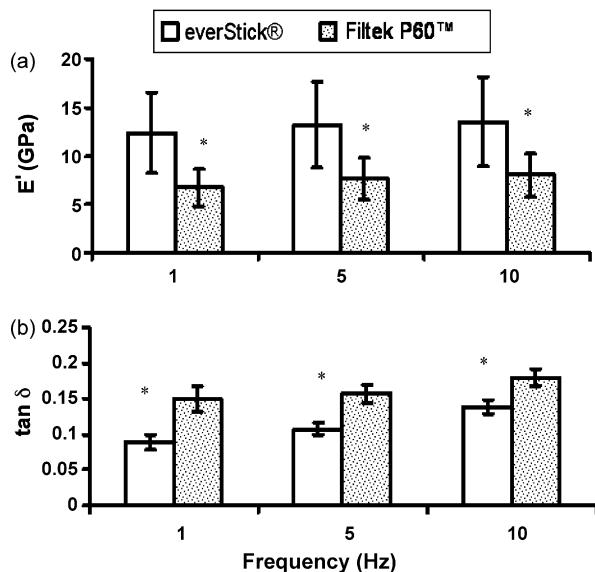
Fig. 3 – Comparison of (a) E' and tan δ (b) for Filtek P60^{TM} and everStick® with reference to frequency, statistically significant difference are shown by $^*p \leq 0.01$.

fiber material, thus direct comparison of their visco-elastic properties is difficult. In the present study, the three-point bending test was used, therefore, the comparison of the modulus values for everStick® are limited to only those in the axial direction. The direction of the testing load means that the materials were subjected to tension in the lower surface and compression in the upper surface. The significantly higher E' and lower tan δ values found in everStick®, comparing to Filtek P60, indicate that the FRC absorbs less energy in repeated stress, and the external energy is less likely to be dissipated within the material as residual stress.

The variation of E' and tan δ with temperature presumably reflects the changes in modulus of the resin phase. Although the E' decreased with increasing temperature for both materials (Fig. 2), the values for Filtek^{TM} P60 decreased more severely (71% decrease from 11.8 GPa at 26 °C to 3.4 GPa at 95 °C) than that for everStick® (32% decrease from 20.1 GPa at 26 °C to 14.3 GPa at 95 °C). The temperature dependence of E' and tan δ for Filtek^{TM} P60 and everStick® are markedly different. It is of interest to note that tan δ had a peak at ~95 °C for Filtek^{TM} P60 and at ~55 °C for everStick®. The principal tan δ peak for Bis-GMA (2,2-bis-4-(2-hydroxy-methacryloyloxy-propoxy)-phenyl-propane) is at 160 °C, with a secondary peak at 120 °C [27,28]. Karacaer et al. [30] observed two tan δ peaks for a glass-fiber reinforced PMMA material, one at 60 °C and other at 134 °C. Hence, the tan δ peak for everStick® observed in the present study might correspond to the secondary relaxation of PMMA. This means clinically, everStick® should not be exposed directly in the oral environment because hot beverage or food might exceed this temperature and the material might become rubbery.

The increase in E' with frequencies is the result of the well-known equivalence of an increase of frequency and a decrease in temperature, as exemplified by the Williams–Landel–Ferry equation [31].

The high standard deviation of the measured values in the present study might be attributed to the variation in the roughness of the specimen surface because all the specimens were prepared manually, and the testing configuration is sensitive to surface flaws and defects. However, this feature appears to be consistent with previous mechanical and thermal studies [32–35].

It would be of interest to compare the visco-elastic moduli of these materials to those of natural tooth tissue. It has been shown that the relaxation modulus of human dentin has a linear dependence on the logarithm of time [36], indicating that dentin is also a visco-elastic material. The linear dependence of relaxation or creep on log time has been shown by Gent [37] to be applicable for elastomers and Braden and Wilson [26] for glass ionomer cements to be predicted by applying the Fourier integral to systems where the dependence of E' and E'' on frequency is small. The authors were unable to find any report that used DMA to measure the visco-elastic moduli for dentin in order to make direct comparison. The Young's modulus for dentin, measured by simple bending technique, was reported to be in the range of 11.4–19.3 GPa [38] which compares well with the storage modulus of everStick® at 37 °C. This value is lower than the E' for intertubular dentin, 21 GPa (range 17–23 GPa), measured by combining a nano-indentation technique with Atomic Force Microscopy [39].

Acknowledgements

REFERENCES

[1] Lutz F, Krejci I. Resin composites in the post-amalgam age. Compend Contin Educ Dent 1999;20:1138–44.
[2] Tyas MJ, Anusavice KJ, Frencken JE, Mount GJ. Minimal intervention dentistry—a review. FDI Commission Project 1-97. Int Dent J 2000;50:1–12.
[3] Bogacki RE, Hunt RJ, de Aguila M, Smith WR. Survival analysis of posterior restorations using an insurance claims database. Oper Dent 2002;27:488–92.
[4] Yashida Y, Shirai K, Nakayama Y, Itoh M, Okazaki M, Shintani H, et al. Improved filler-matrix coupling in resin composites. J Dent Res 2002;81:270–3.
[5] Kilfoil BM, Hesby RA, Pelleu Jr GB. The tensile strength of a composite resin reinforced with carbon fibers. J Prosthet Dent 1983;50:40–3.
[6] Malquarti G, Berruet RG, Bois D. Prosthetic use of carbon fiber-reinforced epoxy resin for esthetic crowns and fixed partial dentures. J Prosthet Dent 1990;63:251–7.
[7] Viguie G, Malquarti G, Vincent B, Bourgeois D. Epoxy/carbon composite resins in dentistry: mechanical properties related to fiber reinforcements. J Prosthet Dent 1994;72:245–9.
[8] Sidoli GE, King PA, Setchell DJ. An in vitro evaluation of a carbon fiber based post and core system. J Prosthet Dent 1997;78:5–9.
[9] Braden M, Davy KW, Parker S, Ladizesky NH, Ward IM. Denture base poly(methyl methacrylate) reinforced with ultra-thin modulus polyethylene fibers. Br Dent J 1988;164:109–13.

[10] Goldberg AJ, Burstone CJ. The use of continuous fiber reinforcement in dentistry. Dent Mater 1992;8:197–202.

[11] Ladizesky NH, Chow TW. The effect of interface adhesion, water immersion and anatomical notches on the mechanical properties of denture base resins reinforced with continuous high performance polyethylene fibers. Aust Dent J 1992;37:277–89.

[12] Ellakwa AE, Shortall AC, Shehata MK, Marquis PM. The influence of fiber placement and position on the efficiency of reinforcement of fiber reinforced composite bridgework. J Oral Rehabil 2001;28:785–91.

[13] Vallittu PK. Comparison of two different silane compounds used for improving adhesion between fibers and acrylic denture base material. J Oral Rehabil 1993;20:533–9.

[14] Vallittu PK. Some aspects of the tensile strength of unidirectional glass fiber polymethyacrylate composite used in dentures. J Oral Rehabil 1998;25:100–5.

[15] Nohrstrom TJ, Vallittu PK, Yli-Urpo A. The effect of placement and quantity of glass fibers on the fracture resistance of interim fixed partial dentures. Int J Prosthodont 2000;13:72–8.

[16] Behr M, Rosentritt M, Latzel D, Kreisler T. Comparison of three types of fiber reinforced composites molar crowns on their fracture resistance and marginal adaptation. J Dent 2001;29:187–96.

[17] Mannocci F, Sherriff M, Watson TF. Three-point bending test of fiber posts. J Endodont 2001;27:758–61.

[18] Vallittu PK. Use of woven glass fibers to reinforce a composite veneer. A fracture resistance and acoustic emission study. J Oral Rehabil 2002;29:423–9.

[19] Maccari PC, Conceicao EN, Nunes MF. Fracture resistance of endodontically treated teeth restored with three different prefabricated esthetic posts. J Esthet Restor Dent 2003;15:25–30 [discussion 31].

[20] Ladizesky NH, Cheng YY, Chow TW, Ward IM. Acrylic resin reinforced with chopped high performance polyethylene fiber—properties and denture construction. Dent Mater 1993;9:128–35.

[21] Ladizesky NH, Chow TW, Cheng YY. Denture base reinforcement using woven polyethylene fiber. Int J Prosthodont 1994;7:307–14.

[22] Vallittu PK. Flexural properties of acrylic resin polymers reinforced with unidirectional and woven glass fibers. J Prosthet Dent 1999;81:318–26.

[23] Lastumaki TM, Lassila LV, Vallittu PK. The semi-interpenetrating polymer network matrix of fiber-reinforced composite and its effect on the surface adhesive properties. J Mater Sci Mater Med 2003;14:803–9.

[24] Narva KK, Lassila LV, Vallittu PK. The static strength and modulus of fiber reinforced denture base polymer. Dent Mater 2005;21:421–8.

[25] Aklonis JJ, MacKnight WJ. Introduction to polymer viscoelasticity. New York: Wiley; 1983. p. 10–24.

[26] Braden M, Wilson AD. Relationship between stress relaxation and viscoelastic properties of dental materials. J Dent 1982;10:181–6.

[27] Clarke RL. The viscoelastic nature of polymers related to dentistry. PhD Thesis. University of London; 1988.

[28] Clarke RL. Dynamic mechanical thermal analysis of dental polymers. II. Bisphenol A-related resins. Biomaterials 1989;10:549–52.

[29] Tanimoto Y, Nishiwaki T, Nemoto K. Dynamic viscoelastic behavior of dental composites measured by Split Hopkinson pressure bar. Dent Mater J 2006;25:234–40.

[30] Karacaer O, Dogan A, Dogan OM, Usanmaz A. Dynamic mechanical properties of dental base material reinforced with glass fiber. J Appl Polym Sci 2002;85:1683–97.

[31] Williams ML, Landel RF, Ferry JD. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass forming liquids. J Am Chem Soc 1955;77:3701–7.

[32] Musanje L, Shu M, Darvell BW. Water sorption and mechanical behavior of cosmetic direct restorative materials in artificial saliva. Dent Mater 2001;17:394–401.

[33] Tezvergil A, Lassila LVJ, Vallitu PK. The shear bond strength of bidirectional and random-oriented fiber-reinforced composite to tooth structure. J Dent 2005;33:509–16.

[34] Tezvergil A, Lassila LVJ, Vallitu PK. The effect of fiber orientation on the thermal expansion co-efficient of fiber-reinforced composite. Dent Mater 2003;19:471–7.

[35] Gohring TN, Gallo L, Luthy H. Effect of water storage, thermocycling, the incorporation and site of placement of glass-fibers on the flexural strength of veneering composite. Den Mater 2005;21:761–72.

[36] Trengrove HG, Carter GM, Hood JAA. Stress relaxation properties of human dentin. Dent Mater 1995;11:305–10.

[37] Gent AN. Relaxation processes in vulcanized rubber. I. Relation among stress relaxation, creep, and hysterisis. J Appl Polym Sci 1962;6:433–41.

[38] Renson CE, Braden M. Experimental determination of the rigidity modulus Poisson's ratio and elastic limit in shear of human dentin. Arch Oral Biol 1975;20:43–7.

[39] Balooch M, Marshall GW, Marshall SJ, Warren OL, Asif SAS. Evaluation of a new modulus mapping technique to investigate microstructural features of human teeth. J Biomech 2004;37:1223–32.