Thermal Properties of Nanofilled and Microfilled Restorative Composites

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The thermal properties of nanofilled and microfilled restorative composites (Filtek Supreme XT and Filtek Z250) are studied in comparison with the ones of teeth. Our results show slightly decreased values of the thermal constants of Filtek Supreme XT with respect of Filtek Z250, due to the smaller filler particle size. Both analyzed composite materials have the values of the thermal conductivity and diffusivity very close to the one of enamel, with the better fitting in the case of Filtek Supreme XT. Comparing with the values for dentin, the thermal conductivity is about two times higher, while the thermal diffusivity is three times higher.

Keywords: thermal properties, thermal conductivity, restorative composites

Dental composites consisting of polymeric resin matrices and inorganic fillers have been available for over four decades. Compared to dental amalgams, the composites possess better esthetic property, have less safety concern, and have shown reasonably satisfactory clinic results. They have been widely adopted by the dental profession as the restorative material of choice.

The latest development in the field has been the introduction of nanofilled materials by combining nanometric particles and nanoclusters in a conventional resin matrix. Nanofilled materials are believed to offer excellent wear resistance, strength and ultimate esthetics due to their exceptional polishability, polish retention and lustrous appearance [1]. The essence of nanotechnology is in the creation and utilization of materials and devices at the level of atoms, molecules, and supramolecular structures, and in the exploitation of unique properties and phenomena of particles [2] with size ranging from 0.1 to 100 nanometers. The compressive and diametral strengths and the fracture resistance of the nanocomposite materials are equivalent to or higher than those of the other commercial composites tested (hybrids, microhybrids and microfill) [3].

In the last few years the effects of thermal transients on teeth have received international attention. The emphasis has been on protecting the tooth from thermal shock. Moreover, the compatibility between the thermal properties of the teeth and of the restorative materials plays a key role in preventing the effects of thermal stress on teeth caused by abrupt temperature change due to drinking or eating hot or cold substances. In such context, in the present paper the experimental results on the thermal properties of nanofilled and microfilled restorative composites (Filtek Supreme XT and Filtek Z250) are studied in comparison with the ones of teeth.

Experimental part

Restorative composites structure

Dental resins are usually cured (hardened) by photoinitiated free radical polymerization. Camphorquinone (CQ) is a commonly used visible-light initiator and ethyl-4-(*N*,*N*_- dimethylamino) benzoate (4EDMAB) is a commonly used co-initiator. The monomer 2,2_-bis-[4-(methacryloxypropoxy)- phenyl]-propane (Bis-GMA) has been widely used as an important dental base monomer since it was invented in early 1960s [4,5]. Bis-GMA is a very viscous liquid. To improve the handling qualities, a low viscosity diluent monomer, such as tri (ethylene glycol) dimethacrylate (TEGDMA), is added to thin the resin. In Bis-GMA/TEGDMA dental resin, Bis-GMA functions to limit the photopolymerization induced volumetric shrinkage and to enhance resin reactivity, while TEGDMA provides for the increased vinyl double bond conversion (fig. 1) [6,7].

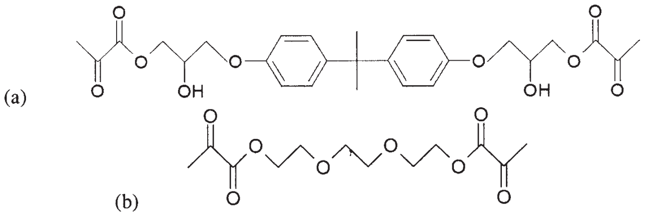

Fig. 1. Chemical structures of bis-GMA (a) and TEGDMA (b)

In Filtek Z250 restorative, the majority of TEGDMA has been replaced with a blend of UDMA (urethane dimethacrylate) and Bis-EMA(6)1 (Bisphenol A polyethylene glycol diether dimethacrylate) [8] (fig. 2). Both of these resins are of higher molecular weight and therefore have fewer double bonds per unit of weight. The high molecular weight materials also influence the measurable viscosity. Despite this large disparity, dentists may not distinguish any difference in handling viscosity. However, the higher molecular weight of the resin results in less shrinkage, reduced aging and a slightly softer resin matrix. Additionally these resins exhibit a higher hydrophobicity and are less sensitive to changes in atmospheric moisture.

While dental resins have been reinforced with inorganic fillers such as silanized glass/ceramic particles for years, the relatively low strength and durability of the composites have limited their uses [9-12]. For example, in Filtek Z250 composite material, the filler consists in zirconia and silica particles of average size of 0.6 μm. Reinforcement with high-strength fibers/whiskers [13-17] has been shown to

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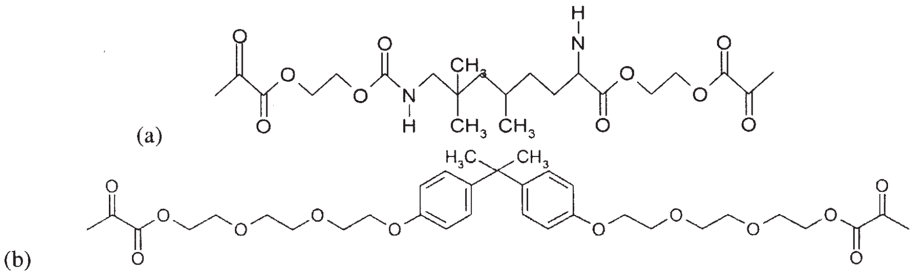

Fig. 2. Chemical structures of UDMA (a) and Bis-EMA(6) (b)

result in dramatic improvements on the properties of dental composites [18-20].

3M ESPE Filtek Supreme XT Universal Restorative material [21] is a visible-light activated, direct restorative nanocomposite designed to deliver optimized esthetic properties for both single or multi-shade restorations. The resin system is the same reduced shrinkage resin as found in 3M ESPE's Filtek Z250. Translucent shades contain a combination of a non-agglomerated/non-aggregated, 75 nm silica nanofiller, and a loosely bound agglomerate silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4 microns. The filler loading is 72.5% by weight. The Translucent shades are not radiopaque. All of the remaining shades contain a combination of a non-agglomerated/non-aggregated, 20 nm nanosilica filler, and loosely bound agglomerated zirconia/silica nanocluster, consisting of agglomerates of primary zirconia/silica particles with size of 5-20 nm fillers. The cluster particle size range is 0.6 to 1.4 microns. The filler loading is 78.5% by weight.

Filtek Supreme XT and Filtek Z250 dental materials were supplied by 3M ESPE Romania and used as received.

Experimental technique

Ten cylindrical samples 30 mm in diameter and 5 mm in width were prepared for each tested composite material (Filtek Supreme XT and Filtek Z250). The specimens were polymerized using high intensity visible light (COE-LITE, model 400, Imperial Chemical Industries PLC, Macclesfield, Cheshire, England) for a minimum of 10 min. to ensure maximum polymerization.

To measure the thermal properties, the TCi Mathis non-destructive testing technology was used. There are no limitations as to how large a sample can be due to the transient method of measurement the system employs. Testing times are typically within a few seconds and automated testing remains a key convenience.

The device consists in a temperature sensor (fig. 3) whose electrical resistance *R* is temperature dependent, ΔR = A . ΔT, with *A* a constant. Considering a constant supply of heat per sec per volume *G'*, the heat equation is given by:

$$c\rho\frac{\partial T}{\partial t}=k\frac{\partial^2 T}{\partial x^2}+G' \qquad (1)$$

where *c* is the specific heat, ρ the density and *k* the thermal conductivity.

Let's assume two semi-infinite media in contact with heat generated at the interface at a constant rate per unit area per unit time. Further assume that the effusivity sensor represents one medium, and the other medium is the tested material, and both are at the same temperature and in equilibrium after contact between them has been established. The solution of equation (1) follows these expressions:

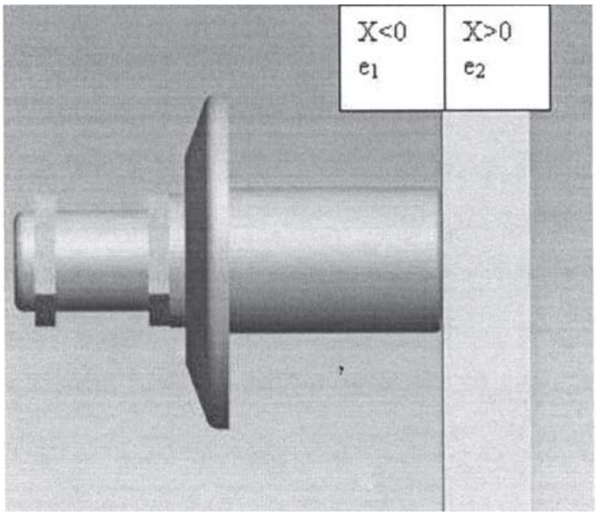

Fig. 3. Schematic view of the temperature sensor

$$\Delta T_1(x,t)=\frac{2G\sqrt{t}}{e_1+e_2}ierfc\frac{|x|}{2\sqrt{\alpha_1 t}}\text{, for } x<0,\ t>0 \qquad (2)$$

$$\Delta T_2(x,t)=\frac{2G\sqrt{t}}{e_1+e_2}ierfc\frac{|x|}{2\sqrt{\alpha_2 t}}\text{, for } x>0,\ t>0 \qquad (3)$$

where:

ΔT= change in sensor surface temperature (°C),

G = power flux supplied to sensor (W/m^2)

t = time measured from start of process (s),

e_1, e_2= equivalent effusivities of sensor and of measured material($\sqrt{k\cdot c\cdot\rho}$, $\left|W\sqrt{s}/(m^2K)\right|$), α_1 α_2 are the equivalent diffusivities of sensor and of measured material, ($k/(c\cdot\rho)$, [m^2/s])

We consider that the sensor and the measured material are in equilibrium and at the same temperature when the measurement starts. If no contact resistance exists at the interface, T_1 = (x=0, t) = T_2(x=0,t) at all points with x=0. For x = 0 equations (2) and (3) are reduced to:

$$\Delta T(x=0,t)=\frac{2G\sqrt{t}}{e_1+e_2}\cdot 0.5642=\frac{1.1284G\sqrt{t}}{e_1+e_2} \qquad (4)$$

Previously, we saw the connection between sensor temperature and resistance. The resistance change of the sensor is:

$$\Delta R=R(t)-R(t=0)=A\cdot\Delta T(x=0,t) \qquad (5)$$

And the voltage change on the sensor is:

$$\Delta V(t)=I\cdot\Delta R(t)=I\cdot A\cdot\Delta T(x=0,t) \qquad (6)$$

Table 1

THERMAL EFFUSIVITY AND THERMAL CONDUCTIVITY OF FILTEK SUPREME XT

Sample No.	Effusivity (e) [Ws$^{1/2}$/m^{2}K]	Thermal conductivity (k) [W/m·K]	Thermal diffusivity ($\alpha \cdot 10^7$) [m^2/s]	R^2	Ambient temperature [°C]
1	1550.367	1.163611	5.6331	0.99867	24.86761
2	1564.435	1.18872	5.7736	0.998651	25.17308
3	1569.752	1.198227	5.8266	0.998874	25.14298
4	1559.042	1.179087	5.7197	0.998831	25.05404
5	1558.916	1.178861	5.7185	0.998819	25.00991
6	1567.366	1.193959	5.8028	0.998843	24.90626
7	1563.857	1.187688	5.7678	0.998821	24.84845
8	1559.927	1.180667	5.7286	0.998801	24.844
9	1556.343	1.17427	5.6928	0.998753	24.6928
10	1557.56	1.176441	5.7049	0.998709	24.63362

Averaged values: $\bar{e}$ =1560.8 Ws$^{1/2}$/m^{2}K; $\bar{k}$ =1.182 W/m·K; $\bar{\alpha} = 5.737 \cdot 10^{-7}$ m^2/s

Table 2

THERMAL EFFUSIVITY AND THERMAL CONDUCTIVITY OF FILTEK Z250

Sample No.	Effusivity (e) [Ws$^{1/2}$/m^{2}K]	Thermal conductivity (k) [W/m·K]	Thermal diffusivity ($\alpha \cdot 10^7$) [m^2/s]	R^2	Ambient temperature [°C]
1	1599.044	1.250764	6.1183	0.998801	24.10101
2	1596.241	1.245726	6.0904	0.998858	24.83032
3	1604.015	1.259707	6.1677	0.998708	24.88163
4	1599.168	1.250988	6.1195	0.998956	24.96818
5	1598.001	1.248889	6.1079	0.998775	24.89771
6	1601.3	1.254822	6.1407	0.998885	25.07319
7	1609.238	1.269114	6.2196	0.998868	25.13203
8	1601.049	1.254371	6.1382	0.998947	25.14537
9	1611.144	1.272549	6.2385	0.998844	25.19224
10	1603.031	1.257936	6.1579	0.998761	25.25381

Averaged values: $\bar{e}$ =1602.8 Ws$^{1/2}$/m^{2}K; $\bar{k}$ =1.256 W/m·K; $\bar{\alpha} = 6.150 \cdot 10^{-7}$ m^2/s

Table 3

THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF TEETH [22]

	Thermal conductivity (k) [W/m·K]	Thermal diffusivity (α) [m^2/s]
Enamel (longitudinal)	0.933	$4.69 \cdot 10^{-7}$
Dentin (perpendicular to tubules)	0.582	$1.87 \cdot 10^{-7}$
Dentin (parallel to tubules)	0.569	$1.83 \cdot 10^{-7}$

Using equation (4) we can write:

$$\Delta V(t) = \frac{1.1284 I \cdot A \cdot G\sqrt{t}}{e_1 + e_2} \qquad (7)$$

By neglecting the sensor effusivity, e_2, and calibrating the system (to measure A and G which depend on sensor characteristics and supplied power), the slope of the linear dependence $\Delta V(t) = f(\sqrt{t})$, gives the effusivity of the measured sample.

Results and discussion

In tables 1 and 2 the experimental values of the thermal constants for Filtek Supreme XT and Filtek Z250, respectively, are given. Effusivity and thermal conductivity are directly measured, while the thermal diffusivity is calculated by equation,

$$\alpha = k^2 / e^2 \qquad (8)$$

The Pearson product-moment correlation coefficient that is calculated for 20 measurements of each sample shows a good accuracy of the results (tables 1 and 2). Also the ambient temperature is given.

Our results show slightly decreased values of the thermal constants of Filtek Supreme XT with respect of Filtek Z250, probably due to the smaller filler particle size.

For comparison, in table 3 the thermal constants of enamel and dentin are given as reported in [22].

It results that both analyzed composite materials have the values of the thermal conductivity and diffusivity very close to the ones of enamel, with the better fitting in the case of Filtek Supreme XT. Comparing with the values for dentin, the thermal conductivity is about two times higher, while the thermal diffusivity is three times higher. Having the same orders of magnitude, and taking into account their excellent handling, mechanical and rheological properties, the analyzed composites are an excellent choice as restorative materials.

Given the viscoelastic or hysteretic type behavior of these composites materials, Kevin-Voight or Maxwell rheological model with imaginary structure coefficients can be applied [23-30]. Then, a non-differentiable mechanical model (scale relativity (SR) model) was built [31-35]. We note that the SR model is based both on the fractal space-time concept and on a generalization of Einstein's principle of relativity to scale transformations. In other words, the SR model is built by completing the standard laws of classical physics (motion in space-time) by new scale laws (the space-time resolution are used as intrinsic variables, playing for the scale transformations the same role as played by velocities for motion transformations) [36-41]. In a future work this model will be used to explain some thermal properties of nano-structured restorative composites.

Conclusions

Our results show slightly decreased values of to thermal constants of Filtek Supreme XT with respect to Filtek Z250. Both analyzed composite materials have the values of the thermal conductivity and diffusivity very close to the one of enamel, but comparing with the values for dentin, the thermal conductivity is about two times higher, while the thermal diffusivity is three times higher.

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