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## The Glass Transition Temperature in Dental Composites

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### 1. Introduction

In dentistry, two types of composites are used: light- and chemical-cured. Light-cured composites are preferred by dentists, mainly due to their longer working time before the curing process is initiated by exposure to visible light. Such materials have been indicated for various clinical procedures such as aesthetic and functional restorations of anterior and posterior teeth, preventive restorations, cementation of endodontic posts, indirect restorations with prostheses, and bonding of orthodontic appliances.

The importance of the curing efficiency to the performance of light-cured composites is well established. The physical and mechanical properties of these materials are influenced by the level of monomer to polymer conversion achieved during the polymerization process (Manfazzoli et al., 1994). Light intensity and irradiation time are important factors to achieve an appropriate degree of conversion (DC) of photoactivated composites (Rueggeberg et al., 1992). DC also depends on the medium in which the material is being cured. An important physical property of the cured matrix is indicated by the glass transition temperature ( $T_g$ ). The  $T_g$  of a dental composite is only of relevance if it lies within the range of intraoral temperatures (Knox et al., 2000; Moore et al., 1999). Inadequate polymerization determines a low final  $T_g$  in material. Intraoral temperatures that exceed the  $T_g$  may result in material softening and, consequently, in failure of the clinical procedure (Rueggeberg et al., 1992).

Glass transitions are one of the most important phenomena in polymeric materials because they determine the physical state and final mechanical properties of the material. The  $T_g$  represents a point at which dramatic changes take place in polymer properties.  $T_g$  is the temperature at which amorphous polymers undergo a transition from a glassy to a rubbery state. At temperatures lower than  $T_g$ , only localized molecular movements are observed (secondary relaxations); for  $T > T_g$ , the flow of chains occurs. Between both (i.e.,  $T = T_g$ ), a rather complicated behavior known as the primary (or  $\alpha$ ) relaxation is observed. Moreover, crystallization is possible for a great number of polymers so that such materials are formed by two phases differing highly in their rheological properties. In the case of totally amorphous polymers, the occurrence of localized molecular motion below  $T_g$  in a glassy polymer ( $\beta$  relaxation) is considered a precursor of the large-scale molecular motion ( $\alpha$  relaxation). In the case of amorphous polymers, the former is attributed to the availability of a set of configurational states through the faster, uncorrelated, rotational motions of the smallest unit of the chains within the randomly distributed sites of frozen-in density fluctuations (McCrum et al., 1991).

For composites with application in dentistry, the  $T_g$  is an especially important parameter to be taken into account. The dental composites must have a  $T_g$  higher than the maximum temperature in the oral cavity in order to preserve the material's physical and mechanical properties. Therefore, to illustrate the importance of the glass transition temperature of the material to be applied in dentistry, this chapter reports the results obtained from the authors' study that evaluated the influences of thermal shock and of factors related to photopolymerization (exposure time and power density of the light-curing unit) on the  $T_g$  of three light-cured orthodontic composites.

## 2. Dental composites

The composites are formed by combining two or more chemically different components, which in general, have better physical and mechanical properties than either of the original components individually. The dental composites are basically composed of an organic matrix, inorganic particles (fillers) and a coupling agent, usually an organo-silane. The resin matrix is comprised of a monomer system, an initiator system for free radical polymerization, and stabilizers for maximizing the storage stability of the uncured composite and the chemical stability of the cured composite (Peutzfeldt, 1997). The monomers are the most important components of the organic part because they become converted to solids during the process of polymerization. The bisphenol A glycol dimethacrylate (Bis-GMA) is the most common dimethacrylate monomer used in current commercial dental composites (Figure 1), which is described as an ester of an aromatic dimethacrylate. Other monomers, such as bisphenol A ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), and ethyleneglycol dimethacrylate (EGDMA) can also be found in the dental composites. The Bis-GMA is the reaction product of an epoxy resin (bisphenol A ethylene glycol) and glycidyl ester methacrylate (GMA). It is a long and rigid molecule with reactive carbon-to-carbon double bonds at both ends. Its high molecular weight, relatively high viscosity, and the presence of aromatic groups contribute to the rigidity of the molecular chain.

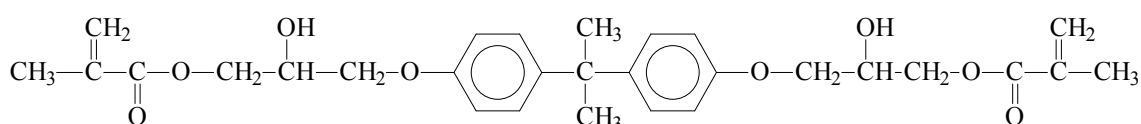


Fig. 1. Bis-GMA molecule.

The high viscosity of Bis-GMA is lowered by dilution with a monomer of lower molecular weight to facilitate the incorporation of inorganic particles and to improve the material homogenization. The most commonly used diluent is triethyleneglycol dimethacrylate (TEGDMA) (Figure 2), which is a relatively flexible linear molecule with carbon unsaturated bonds at both ends. All other components being equal, an increase of filler content will improve several physical and mechanical properties. However, the dilution of BisGMA also has negative effects such as increased polymerization shrinkage of the mixture.

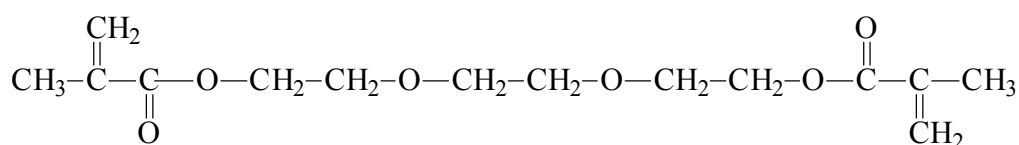


Fig. 2. TEGDMA molecule.

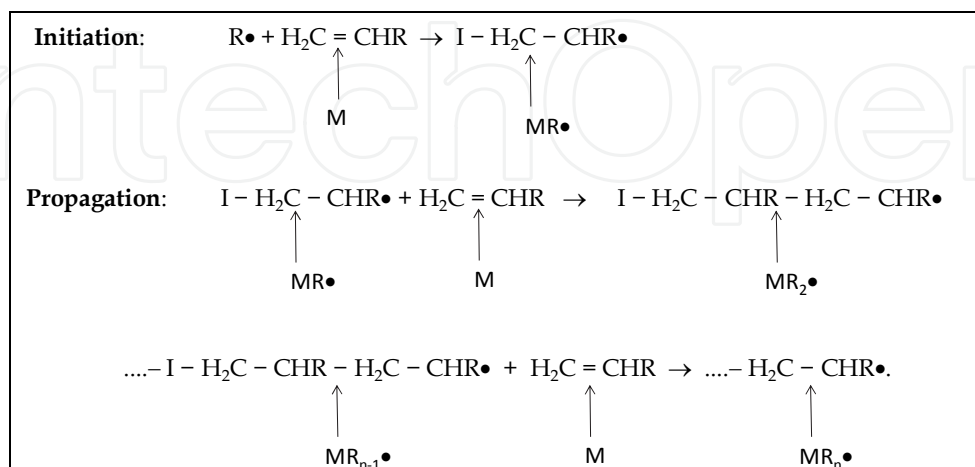
Different fillers have been used in formulating dental composites: barium glass, quartz, pyrolytic silica, silicate-lithium-aluminum, and colloidal silica. The incorporation of filler particles into the organic matrix improves the physical and mechanical properties of the cured material. The amount of filler added and the size and form of the particles are factors that determine the final properties of the composite such as fracture toughness, wear resistance, hardness, and thermal expansion. Furthermore, the filler particles tend to influence the stiffness of the polymer chain. The fillers are treated with silane coupling agents to reinforce the adhesion between the filler and the matrix polymer and also to increase the hydrolytic stability of the polymer (Halvorson et al., 2003).

The properties of composites are determined by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the nature of the interface between the phases (Nielsen & Landel, 1994). A great variety of properties can be obtained by changing one of the components. For example, the use of monomers that form a rigid polymer network with higher cross-linking density can lead to a composite with high  $T_g$ . Because the composition greatly influences the behavior of dental composites, better clinical results will be obtained as professionals gain more information about materials and their clinical implications.

## 2.1 Polymerization process

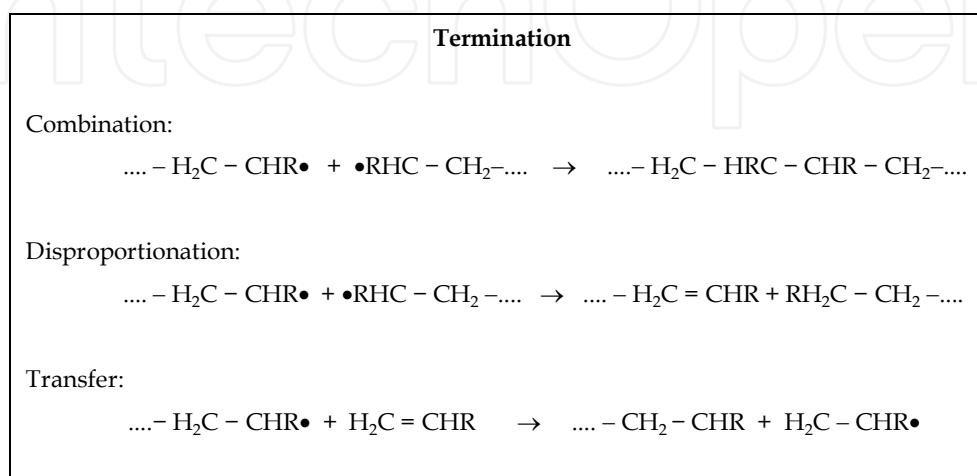
The cure reaction of the dental composite occurs through a chemical process of polymerization where the monomers join together through chemical bonds to form large-chain molecules called polymers.

The dimethacrylate undergoes a chain polymerization also called addition polymerization. This reaction begins when a reactive species and a monomer react to form an active center (Fraunhofer, 2010; Peacock & Calhoun, 1959; Tager, 1978). The chain polymerization process occurs in a sequence of three stages: initiation, propagation and termination. In initiation, the free radical ( $R\bullet$ ) reacts with the monomer molecule ( $M$ ), producing another active free radical species (excited monomer molecule,  $MR\bullet$ ), which is capable of further reaction. In propagation, this process is followed by successive additions of monomer units to the polymer resulting in a macroradical ( $MR_n\bullet$ ).



The resulting macroradical may change into an inactive polymer molecule (chain termination). The termination of polymerization occurs with the suspension of chain growth

due to the disappearance of the active center through combination, disproportionation, or transfer, depending on the type of monomer and polymerization conditions. In combination, two free radicals interact and form a covalent bond. Disproportionation occurs when two growing chains interact, while a transfer occurs when the growth of the original chain stops and another shorter chain starts the propagation process (Fraunhofer, 2010). These reactions produce dead polymer chains that are not capable of further additions (McCabe & Walles, 2008). The term dead polymer represents the cessation of growth for the propagation radical.



The polymerization of dimethacrylate results in a highly cross-linked structure. However, the monomer conversion is not complete and there will always be the presence of considerable amounts of residual monomer in the cured composite. The extent to which the monomer is converted to polymer is called the DC.  $T_g$  has been found to be well correlated to DC in polymers, based on a number of different dimethacrylates (Baran et al., 1994; Ferracane & Greener, 1986; as both cited in Peutzfeldt, 1997).

Free radicals ( $R\bullet$ ) can be generated by chemical activation or external activation energy (light or heat). The dental composites polymerized by chemical systems are named chemical-cured and those polymerized using external irradiation are named light-cured composites.

The first composites used in dentistry were chemical-cured composites. These materials are presented in the form of two pastes: one contains an initiator, generally benzoyl peroxide, and the other contains an activator, a tertiary amine (typically N, N - dimethyl-p-toluidine). When the two pastes are mixed, a reaction occurs between the initiator and the activator, resulting in the appearance of free radicals leading to the polymerization of Bis-GMA. The reaction is characterized by heat release and contraction of the polymer. In the chemical-activated system, a conversion is expected to occur uniformly throughout the volume of the material. However, the chemical-cured composites have some disadvantages: the possibility of the incorporation of air bubbles during mixing, the possibility of incomplete mixing of the pastes, and the possible difficulties resulting from the operator having to proportion the pastes. Moreover, there is a reduced working time due to rapid polymerization. These facts contributed to the replacement of the chemical-cured composites with light-cured materials. The visible light-cured composite is available in one-paste form, packaged in syringe. This system has a photoinitiator, typically camphorquinone, which has an absorption spectrum in the range between 400 and 500 nm, with an absorption peak around 467 nm. In the initiation stage, the camphorquinone and a reducing agent represented by a tertiary amine,

the dimetilaminoetilmetacrilato (DMAEMA), generate free radicals when irradiated by visible light, initiating the polymerization process (Figure 3). When light-cured composite are irradiated, the molecules of camphorquinone exhibit an excited triplet state that reacts with tertiary amines (DMAEMA), forming complex excitations (exciplex) that are converted in free radicals (Figure 3). The amounts of initiator and activator in the composite formulation may influence the DC of the material (Schneider, et al., 2008).

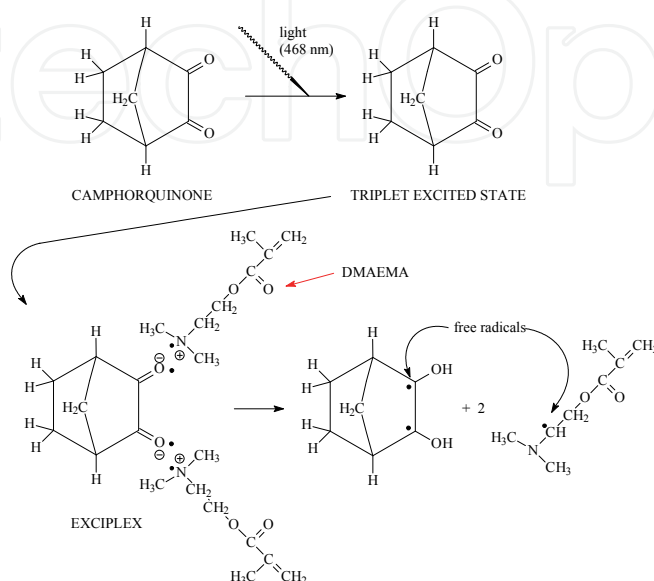


Fig. 3. Scheme shows the mechanism of the free radical formation of light-cured composites.

Halogen lamps and LEDs (Light-emitting diode) are light sources commonly used to activate the light-cured composites. In the lamp units, the light is produced when electrical energy heats a small tungsten filament to extremely high temperatures (Dunn et al, 2002). In this type of light source, a filter is used to select a particular range of wavelengths relevant to the activation of camphorquinone.

In the LED source, the light is generated through junctions of doped semiconductors, emitting light beams with wavelengths between 450 and 490nm, coinciding exactly with the absorption band of the spectrum of camphorquinone. This source presents a higher efficiency than the halogen source due to the greater coupling between its emission band and the camphorquinone absorption band (Stahl, et al., 2000). The halogen light unit has a broader emission spectrum when compared to the camphorquinone absorption spectrum.

Several concepts are relevant to the emission of light by light-curing units. The light intensity of the source is also called the power density or irradiance and it is expressed as  $\text{mW}/\text{cm}^2$ . The power density (PD) is the ratio of average power (P) and unit area (A) of the active tip, i.e.,  $(\text{PD} = \text{P}/\text{A})$ . Moreover, the energy density (ED) represents the amount of power supplied to a given irradiated surface, which is expressed as  $\text{J}/\text{cm}^2$ . The energy density (ED) is the product of the power density (PD) of the source and the exposure time (t) from surface to light, or  $(\text{ED} = \text{PD} \times t)$ .

In the process of the polymerization, it is necessary to expose the material to light; this process can significantly affect the number of free radicals formed, and consequently, the cure of material. A sub-polymerization can reduce the strength of the material and affect its biocompatibility. Thus, the amount of radiation energy used must be sufficient to promote the complete polymerization of the material. Factors such as light intensity, energy density,



and exposure time are relevant for evaluating the efficiency of the source used for the cure of the composite. The light has an influence on the DC of materials, affecting its mechanical and physical properties.

### 3. Glass transition and measurement techniques

Glass transition is the temperature where the polymer goes from a hard, glass-like state to a rubber like state and it provides a method to characterize a property of a polymeric material. The best way to envision this type of transition is to put a rubber band (rubber like state, very flexible) into a container of liquid nitrogen. When removed, the rubber band is solid and inflexible (glass state), and in fact, the rubber band can be shattered. Upon standing and warming to room temperature, the rubber band will again become flexible and rubbery (rubber like state).

Routinely, there are two primary ways to measure  $T_g$ : Differential Scanning Calorimetry (DSC, the "official" method), and Mechanical Analysis (MA). DSC defines  $T_g$  as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. This is a second order endothermic transition (requiring heat to go through the transition) so, in the DSC, the transition appears as a step transition and not as a peak, as might be seen with a melting transition. MA defines  $T_g$  in terms of the mobility of the chains as the polymer goes from glass to rubber state with the associated change in free molecular volume. Each of these techniques measures a different result of the change from glass to rubber. The DSC is measuring a heat effect, whereas the MA is measuring a physical (mechanical) effect. Both techniques assume that the effects are created over a narrow range of a few degrees in temperature. If the  $T_g$  is very broad, it may not be seen with either approach. The DSC and MA may also often give results that differ from one another by 5-10 °C when used to test a polymer. Moreover, some polymers are more amenable to DSC or to MA, because the transition is easier to observe using one technique over the other (McCrum, 1991).

Mechanical spectroscopy (MS) is a MA particularly well suited to the study of the behavior of dental composites because it studies the absorption spectra of mechanical energy under the conditions of applied periodic external stress.

In the elastic analysis of materials, it is assumed that elastic strain is a function of stress only. This is not strictly true since there is time dependence to the elasticity. In metals, the effect is very small and generally negligible, but in polymers, the effect is much more significant. The general name for this time dependence is anelasticity.

A solid is considered anelastic when there is a phase difference or delay of the effect (strain) in relation to the cause (stress), making Hooke's law with time as a variable. From a thermodynamic point of view this means that, in response to a change in the mechanical forces applied, it takes some time for the anelastic solid to achieve equilibrium. Then, the auto-adjust system, in response to a change in the external variable, is known as relaxation. When the external variable is mechanical (a strain or stress), the phenomenon is known as anelastic relaxation. One can, therefore, interpret anelastic behavior as a manifestation of internal relaxation processes.

The anelastic behavior of a material can be described in terms of a group of parameters considered to be intrinsic attributes of the material. The starting point for this approximation is a stress-strain relation in the form of a linear differential equation involving stress, strain, and their derivatives in time (Nowick & Berry, 1972). The simplest differential stress-strain equation capable of representing anelasticity involves three independent parameters and the mechanical model most appropriate to describe the behavior of an anelastic solid, where it is

present only as a relaxation process, is known as the Three Parameters Model; it consists of a Voigt unit composed of a spring connected in parallel with a damper, associated in series with another spring.

When a uniform stress is applied in  $t = 0$ , the spring deforms instantly, while the Voigt unit will take some time to deform completely, due to the damper. When the stress is eliminated, the spring will return immediately to the starting position while the Voigt takes some time to reach its initial position, also due to the damper. Whereas the damper consists of a viscous linear liquid, the stress-strain differential equation for the Three Parameters Model is:

$$J_R \sigma + \tau J_U \dot{\sigma} = \varepsilon + \tau \dot{\varepsilon} \quad (1)$$

where  $\sigma$  is the stress,  $\varepsilon$  is the strain,  $\tau$  is the relaxation time,  $J_R$  is the relaxed compliance, and  $J_U$  is the unrelaxed compliance.

When a dynamical stress is applied to the system, the real and imaginary parts of the complex compliance are (Schaller et al., 2001):

$$J_1 = J_U + \frac{\delta J}{1 + (\omega\tau)^2} \quad (2)$$

$$J_2 = \delta J \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (3)$$

where  $J_1 = \varepsilon_1/\sigma_0$ ,  $J_2 = \varepsilon_2/\sigma_0$ ,  $J^*(\omega) = J_1 - i J_2$ ,  $\delta J = J_R - J_U$ ,  $\sigma_0$  is the stress amplitude,  $\varepsilon_1$  and  $\varepsilon_2$  are, respectively, the components of the strain in phase and  $90^\circ$  out of phase with the stress,  $\omega$  is the vibration angular frequency, and in  $\omega = 2\pi f$ ,  $f$  is the vibration frequency.

Equations (2) and (3) are called the Debye equations and are shown in Figure 4. The quantity  $J_1$  will of  $J_U$  at high frequencies ( $\omega\tau \gg 1$ ) to  $J_R$  at low frequencies ( $\omega\tau \ll 1$ ). The quantity  $J_2$  shows a peak function, it has small values in high and low frequencies and goes to a maximum at  $\omega\tau = 1$ . Any function that varies with frequency  $\omega\tau/(1 + \omega^2\tau^2)$  can be called a Debye peak.

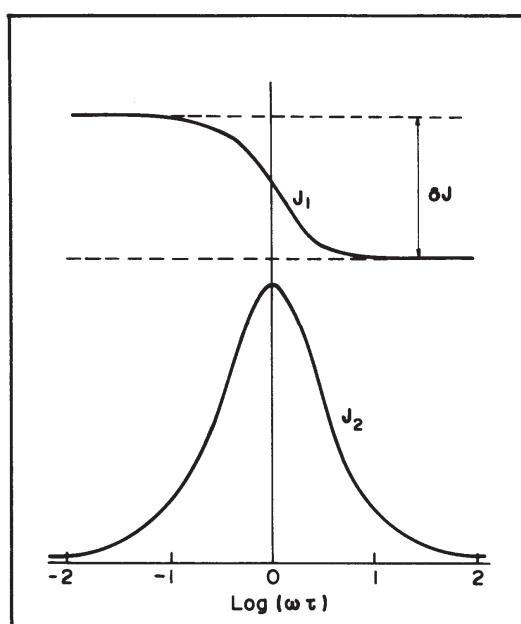


Fig. 4. Comparison of  $J_1(\omega)$  and  $J_2(\omega)$  as a function of  $\log(\omega\tau)$  for a single relaxation process.



Internal friction is related to the real and imaginary parts of the compliance by Nowick & Berry (1972). Then,

$$Q^{-1} = \Delta \left( \frac{\omega\tau}{1 + (\omega\tau)^2} \right) \quad \Delta \ll 1 \quad (4)$$

where the dimensionless quantity  $\Delta$  is called relaxation strength.

Using the Arrhenius equation for the relaxation time, the internal friction can be written as a function of temperature:

$$Q^{-1} = \frac{Q_m^{-1} T_m}{T} \operatorname{sech} \left[ \frac{E}{k} \left( \frac{1}{T_m} - \frac{1}{T} \right) \right] \quad (5)$$

where  $\Delta = (2Q_m^{-1} T_m)/T$  for  $\Delta \ll 1$ ,  $Q_m^{-1}$  is the maximum of internal friction at temperature  $T_m$ ,  $E$  is the activation enthalpy,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

The principle of internal friction measurement is very simple; the sample is put to vibrate on its fundamental mode (free or forced vibration), which causes the dissipation of energy in the heat form, due to internal friction. Internal friction can be measured statically or dynamically. Dynamic experiments are most suitable because of the relatively short time needed for their execution. Basically, dynamic experiments are divided into three groups: wave propagation, sub-resonant, and resonant.

In the case of wave propagation, high frequency short pulses (around  $10^6$ - $10^9$  Hz) propagate through the sample and the attenuation coefficient and the velocity of these waves are measured. The internal friction is related to the attenuation coefficient of the waves and the elasticity modulus is related to the velocity of the propagation of these waves. Sub-resonant experiments highlight the torsion pendulum with forced vibration and dynamic-mechanical analysis equipment (DMA). The main advantage of this equipment is the possibility of working in a large and continuous frequency range ( $10^{-5}$ - $10^2$  Hz), without the need to change the geometry of the sample, i.e. with the same sample. Resonant experiments constitute the largest and oldest group of methods for measuring mechanical spectroscopy. The most important techniques are the torsion pendulum, vibrant bars, and composed oscillators, with frequency from  $10^{-1}$  to around  $10^6$  Hz. Requiring different sample geometries for each technique is the major inconvenience of these techniques.

In general, a resonant system must have two elements: the elastic element (which, in fact, is anelastic), and inertia. The situation is considerably simplified when this system, for example, is a wire stretched with a weight placed at one end, possessing torsional vibrations. This is the case of the torsion pendulum, in which the deflection, at any point, can be expressed in terms of a single parameter, the angular displacement,  $\Theta$ , of the inertial component. The physical quantity that is responsible for this shift is the torque,  $\Gamma$ , which operates in the sample. In the case of an ideal elastic solid,  $\Gamma = G\Theta$ , where  $G$  is the rigidity modulus of the sample. For an anelastic solid  $\sigma = M^* \varepsilon$ , with  $\sigma \equiv \Gamma$ ,  $M^* \equiv G^*$  and  $\varepsilon \equiv \Theta$ , and they result in,

$$\omega^2 \approx G/I \quad (6)$$

$$\delta \approx \pi\phi \quad (7)$$

where  $I$  is the inertia momentum,  $\phi$  is the phase difference between  $\sigma$  and  $\epsilon$ , and  $\delta$  is a constant.

Considering two oscillations separated by  $N$  periods:

$$\delta = \frac{1}{N} \ln \left( \frac{A_1}{A_2} \right) \tag{8}$$

The dimensionless quantity  $\delta$  represents the natural logarithm of the ratio of amplitudes  $A_n$  on two successive vibrations, and is called the logarithmic decrement. Then, the internal friction is given by:

$$Q^{-1} = \tan \phi \approx \phi \approx (\delta / \pi) = \frac{1}{N\pi} \ln \left( \frac{A_1}{A_2} \right) \tag{9}$$

4. Evaluation of glass transition temperature by mechanical spectroscopy

The specifications, main ingredients and manufacturers of the orthodontic composites used are displayed in Table 1.

Composite	Manufacturer	Composite composition	Inorganic content (wt%)
Fill magic	Vigodent (Rio de Janeiro – RJ, Brazil)	BisGMA, Methacrylate acid ester, and fluorosilicate glass	38.1
Ortho Lite Cure	Orthosource (Hollywood – CA, USA)	BisGMA, TEGDMA, glass and silica	70.0
Transbond XT	3M Unitek (Monrovia – CA, USA)	BisGMA, N-dimethyl benzocaine, hexafluoride phosphate, silane and silica	74.6

Table 1. Orthodontic composites used in this study.

Beam-shaped specimens of each material were prepared in a brass mold with internal dimensions of 40 x 4 x 4 mm for  $T_g$  measurements. The samples were irradiated using two different LED light-curing units: Free Light II Elipar (3M ESPE, Seelfeld – Germany) with a power density 232 mW/cm<sup>2</sup> and LDIII (Gnatus, Ribeirão Preto – Brazil) with a power density of 52 mW/cm<sup>2</sup>, which will be named here for convenience as F1 and F2, respectively. The power output was measured with a power meter (Model 13PEM001; Melles Griot, Irvine, CA, USA). F1 was used for an exposure time of only 40 s; the exposure times for F2 were 40, 60, 90, and 120 s due to its lower power density. Two specimens were made for each exposure time and were irradiated on the opposite faces of the lateral surface. The samples were kept in the dark at room temperature until completely cured. Half of the specimens were submitted to thermo shock (or thermocycling) before  $T_g$  measurements. Thermal shock was performed in a humid environment in order to simulate daily meals. For this, the samples were immersed in tanks with distilled water at 5, 37, and 60 °C. The immersion time in each tank was 15 s. This process was carried out for an hour, with

approximately 42 cycles and a break of three hours at 37°C. The process was repeated four times a day for three days, totaling 504 cycles. The  $T_g$  was evaluated using the group of samples that was submitted (CT) to the thermocycling and the other group that was not (ST). Measurements of mechanical spectroscopy (internal friction) were performed in a torsion pendulum, operating at a 1.4 to 9.4 Hz frequency range.

A typical internal friction curve versus temperature is shown in Figure 5, where the maximum intensity occurs in the  $T_g$ . Table 2 shows the  $T_g$  value obtained for the investigated composites in the CT and ST conditions.

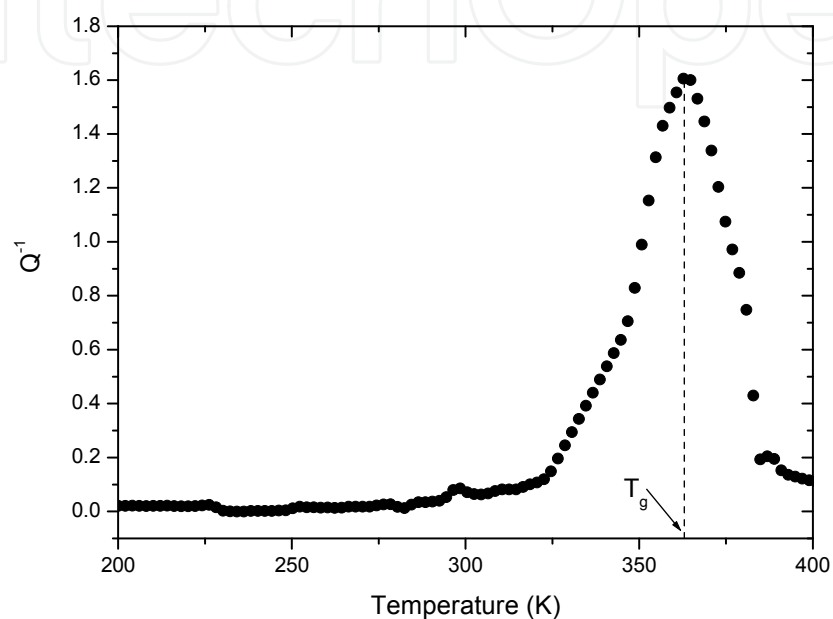


Fig. 5. Typical internal friction curve obtained by mechanical spectroscopy technique.

The higher  $T_g$  values were reached when the three composites were irradiated with the F1 source for both conditions (ST and CT). The Ortho Lite and Transbond composites presented higher  $T_g$  values in the ST condition and the lowest  $T_g$  values were observed for Fill Magic. The three composites showed  $T_g$  values within the range of oral temperature (273 to 340 K).

The effect of *exposure time* could be observed when the composites were irradiated with the source F2. For the ST condition, the  $T_g$  value of the Fill Magic and Ortho Lite composites increased when the exposure time was increased. In contrast, the  $T_g$  of the Transbond did not depend on the duration of the light exposure time. For the CT condition, when the exposure time was increased, the  $T_g$  of Fill Magic composite increased and the  $T_g$  of Ortho Lite decreased. For Transbond, there was an initial decrease between 40 and 90 s and the highest value was obtained at 120 s. For both conditions (ST and CT), the values of  $T_g$  obtained with an exposure time of 120 s reached values close to those obtained using 40 s with source F1, except for the Ortho Lite composite in the CT condition.

The thermal shock factor changed the  $T_g$  final reached by the three composites. The thermal shock prompted a rise in the  $T_g$  values of the Fill Magic composite and a reduction in  $T_g$  values for the other two composites.

The differences observed in the  $T_g$  of the studied composites can be attributed to the structural characteristics of each material. Factors such as monomer type, inorganic filler type, and content determine the physical and mechanical properties of the cured composite.

The  $T_g$  determines the physical state of a polymer and influences several properties.  $T_g$  variation has been attributed to various molecular parameters, such as molecular weight, stiffness of the cross-linked chains, and free volume entrapped in the network (Min et al., 1993). Other investigations have shown that  $T_g$  can be affected by cross-linked chains and filler content (Emami & Söderholm, 2005; Lu et al., 2001; Papadogiannis et al., 2003; Nielsen & Landel, 1994).

Composite	Source	Exposure time (s)	$T_g$ (K)	
			ST	CT
Fill Magic	F1	40	363	377
	F2	40	308	300
	F2	60	295	338
	F2	90	323	342
	F2	120	357	362
Ortho Lite Cure	F1	40	387	372
	F2	40	370	332
	F2	60	380	318
	F2	90	368	315
	F2	120	383	307
Transbond XT	F1	40	384	376
	F2	40	378	354
	F2	60	373	340
	F2	90	378	318
	F2	120	378	372

Table 2.  $T_g$  values obtained for investigated composites in function of light source, exposure time, and treatment condition (ST and CT).

Figure 6 compares the internal friction curve of the three composites, which have different compositions (Table 1). The Fill Magic composite has in its composition the Bis-GMA monomer and 38.1 wt% of inorganic content. The Ortho Lite contains the Bis-GMA and TEGDMA monomers, and 70 wt% of glass and silica as inorganic filler. The Transbond has the Bis-GMA as monomer and 74.6 wt% of silanized silica as filler. As can be seen in the figure, the curves of the Transbond and Ortho composites are very similar, with peaks around 370 K. These two composites have practically the same amount of filler in their composition and the Ortho Lite has TEGDMA beyond Bis-GMA. Although the composites possess different organic composition, no difference is observed in the loss tangent curves. On the other hand, the Fill Magic presents a loss tangent curve more intense, with a peak around 310 K. This composite also has the Bis-GMA monomer in its composition, but has half the amount of filler that the other two composites have. Studies indicate that the increase of filler particles in the composite’s composition introduces a broadening and reduction in the loss tangent value (Nielsen & Landel, 1994). The polymerization of multifunctional monomers produces network polymers with highly heterogeneous environments as they contain very highly cross-linked regions as well as less densely cross-

linked regions connecting them (Kannurpatti et al., 1997). This heterogeneity results in a broad distribution of mobilities or relaxation times [Kannurpatti et al., 1997]. Therefore, from comparing these three curves, one can conclude that the main cause of the observed difference in the peak position and curve form is the amount of filler. The Ortho and Transbond samples present broader curves and less intensity than the Fill Magic composite does because both have more filler particles in their compositions.

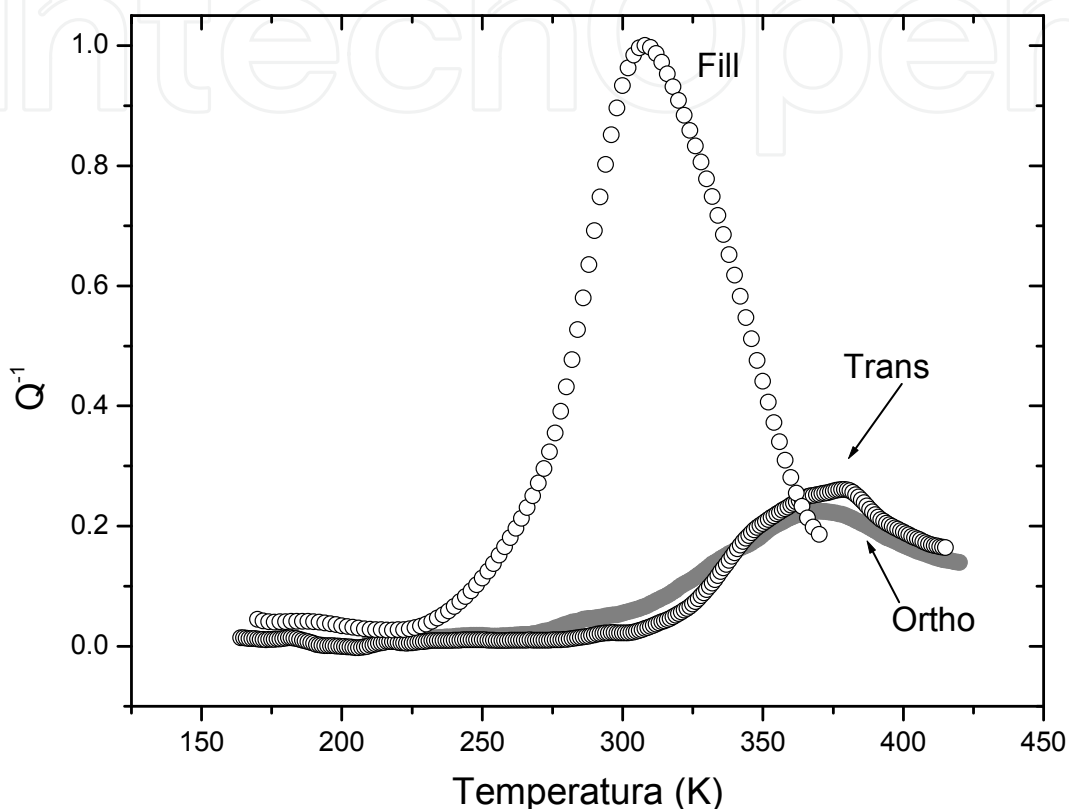


Fig. 6. Internal friction for three tested composites with the same exposure time (40 s) and thermal condition (ST).

The polymerization of dimethacrylates monomers produces densely cross-linked networks. The network is characterized by the heterogeneity caused by the formation of regions with higher and lower cross-linking. High heterogeneity is characteristic of a polymer structure with a larger number of cross-links. Hi Lu et al. attributed to broadening of the loss tangent peak to an increase in the heterogeneity of the network. Therefore, the characteristic of the relaxation peak of each composite points to differences in the final structure, suggesting that the Lite Cure and Transbond composites could have a higher cross-link density than Fill Magic, which would have a more homogeneous network.

The influence of the exposure time in the  $T_g$  is shown in Figure 7A. The light source used to cure has a power density of 52 mW/cm<sup>2</sup>, which is smaller than the minimum necessary to produce an adequate polymerization (233 mW/cm<sup>2</sup>) (Rueggeberg, 1994). Using this light-curing unit, it was possible to reach only an adequate polymerization and a  $T_g$  higher than the maximum oral temperature using an exposure time of 120 s. Better than power density, studies have shown that the properties of the light-cured composites are mainly influenced by the amount of energy delivered during irradiation (Dewaele et al., 2009). As mentioned

earlier, the energy density is the product between the power density of the light source and the duration of irradiation (exposure time).  $T_g$  values above the oral temperature range were obtained when the three composites were irradiated for 40 s with source F1 ( $ED = 232 \text{ mW/cm}^2 \times 40 \text{ s} = 9.28 \text{ J/cm}^2$ ) in both thermal conditions. On the other hand, in the Fill Magic/source F2 combination it was possible to obtain adequate  $T_g$  value only with exposure times of 90 s ( $4.68 \text{ J/cm}^2$ ) and 120 s ( $6.24 \text{ J/cm}^2$ ) in the CT and ST conditions, respectively.

Figure 7B shows how thermal shock in a humid environment can influence the  $T_g$  of the material. For the Fill Magic composite, the obtained loss tangent curves indicate that the thermal treatment improved the mechanical and thermal properties of the material. The thermal treatment promoted a broadening and a decrease of intensity, indicating the formation of a more heterogeneous network with reduced chain mobility and, consequently, an elevation of the  $T_g$ . This effect could have been caused by thermal treatment in a humid environment (thermocycling). The absorbed water and temperature rise during the thermocycling contribute to molecular mobility, increasing the probability of contact between the groups that have not reacted, and therefore, of creating chemical bonds (Mesquita et al., 2006). Higher mobility and the increase of chemical reactions contribute to an increase in cross-link density, causing an increase in  $T_g$ .

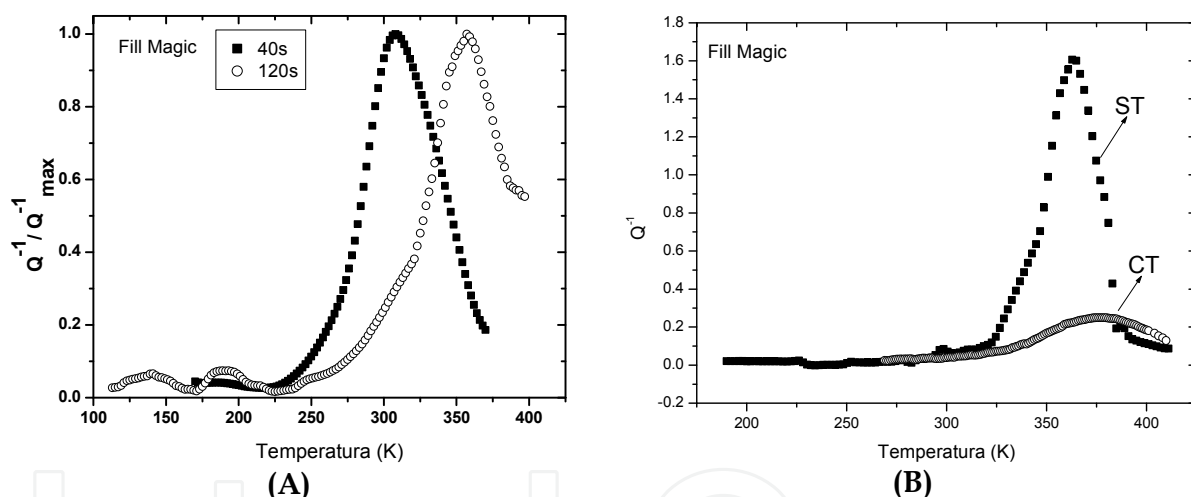


Fig. 7. Internal friction for the Fill Magic composite: (A) for 40 and 120 s exposure times in the same thermal conditions; (B) in different thermal conditions for the same exposure time

## 5. Conclusion

Within the limitations of in vitro study, the investigation with three orthodontic composites demonstrated the following:

To reach  $T_g$  above the oral temperature range, the energy density of light sources and the environment where the composite will be cured are relevant factors to be considered.

Each dental composite behaves differently when cured in a moist environment, subject to temperature variation.

The glass transition temperature reached by the composite depends on the amount of filler particles contained in its composition.



For application using composites with small amounts of filler in its composition and light sources with power density less than 232 mW/cm<sup>2</sup>, the exposure time is a relevant factor to reach a  $T_g$  above the oral temperature range. For Fill Magic orthodontic composite, it was necessary to use 6.24 J/cm<sup>2</sup> of energy density (source F2 – 120 s) in the ST condition and 4.68 J/cm<sup>2</sup> (source F2 – 90 s) in the CT condition to reach an adequate  $T_g$  value.

For light sources with power density higher than 232 W/cm<sup>2</sup>, an exposure time of 40 s is sufficient to reach satisfactory values of  $T_g$ , independent of temperature and humidity conditions.

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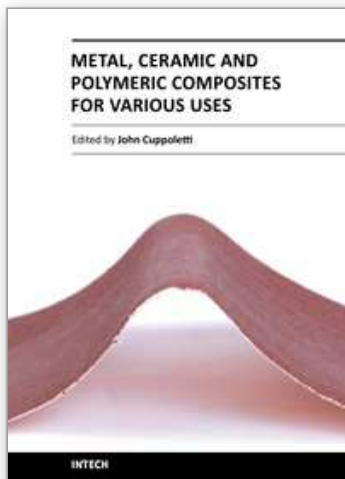
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