INFLUENCE OF PULSE-DELAY CURING ON SORPTION AND SOLUBILITY OF A COMPOSITE RESIN

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ABSTRACT

*T*he purpose of this study was to evaluate the sorption and solubility of a composite resin (TPH[3]; Dentsply) cured with halogen light due to different storage media and curing modes. The methodology was based on the ISO 4049 standard. Two independent groups were established according to the storage time (7 days-G1; 60 days-G2). A stainless steel mould (2 mm x 8 mm Ø) was used. The selected curing modes were: I (Conventional - C): 40s - 600 mW/cm^2; II (Pulse I - PD): 3 s - 200 mW/cm² + 2 min (delay) + 39 s - 600 mW/cm²; III (Pulse II): 10 s - 200 mW/cm² + 2 min (delay) + 37 s - 600 mW/cm²; IV (Pulse III): 3 s- 600 mW/cm² + 2 min (delay) + 37 s -600 mW/cm². The media used were: distilled water, 75% ethanol and 100% chloroform. Five repetitions were made for each group. The specimens were placed in a desiccator at 37ºC for 24 h and, after that, at 23ºC for 1 h to be weighed until a constant mass (m_1) was obtained. The discs were immersed separately into the 3 media for 7 days (G1) and 60 days (G2), and thereafter reweighed (m_2). The reconditioning in the desiccator was done until a constant mass (m_3) was obtained. Sorption and solubility were calculated and the data of G1 and the sorption data of G2 were subjected to two-way ANOVA and Tukey's tests (p=0.05). The solubility data of G2 were analyzed by Kruskal-Wallis test (p=0.05). For G1 and G2, no statistically significant differences were found in sorption among curing techniques (p>0.05). The solubility values were negative, which means that there was mass gain. Regarding the storage media, in G2 chlorophorm had the highest sorption values. It may be concluded that the curing modes (C and PD I, II and III) did not affect the sorption of the tested composite resin. However, different storage media influenced sorption behavior. The solubility test demonstrated negative data, masking the real solubility.

Key words: Composite resins. Solubility. Solvents.

INTRODUCTION

An increasing demand for esthetic restorative materials has occurred greatly in recent years[20]. Visible light-cured composite resins are widely used in restorative dentistry. Polymerization of the methacrylate monomers in these composite resins leads to a highly crosslinked structure[5]. Traditionally, the manufacture's have recommended high light intensity or power density (PD) to provide a higher degree of monomer conversion to polymer, improving the mechanical properties of composite resins. Unfortunately, the degree of conversion of these materials is always proportionally associated with shrinkage and a high rate of polymerization[2,3,10]. In order to reduce the contraction stresses, a slow cure of composite resins can be used, which results from a more extended period of viscous flow in the pre-gel phase of light-activated resins[3,8]. A slow cure may be achieved by the so-called soft-start curing technique, where a reduced intensity of curing light is used during the first part of the polymerization period[5,26]. Another method is the pulse-delay cure, where the polymerization is initiated by a short flash of light followed by a waiting time of some minutes before the final cure is performed[17,21]. Such method does not seem to modify the polymerization mechanisms and the degree of conversion of the monomer[11]. However, it is important to consider that the different irradiation procedures will lead to different structures of the resulting polymer, even though the degree of conversion of the double bonds is the same[5].

Ideally, dental polymer should remain stable[12]. However, due to their hydrophilic nature, it usually does not occur[12,16]. Water sorption may deteriorate polymer mechanical

properties[16]. This effect is a product of the separation of the polymer chains by a molecule that does not form primary chemical bonds with the chain. The phenomena of sorption and solubility may serve as precursors to a variety of chemical and physical processes that can create biological concerns[14]. Thus, the polymer structure quality resulting by photo-activated mode may lead to differences in sorption and solubility. Additionally, as the degree of conversion and crosslink can influence the chemical degradation that is usually caused by oxidation processes and\or hydrolysis[23], the evaluation of composite resin in solvents plays an important role to create scientific evidence for its application in dentistry.

The aim of this study was to investigate the effect of different pulse-delay curing protocols on water sorption and solubility of a composite resin using three solvents. The tested null hypotheses were: (1) there is no difference among curing techniques with respect to sorption and solubility; (2) there is no difference among solvents tested on the sorption and solubility.

MATERIAL AND METHODS

A nanohybrid composite resin (TPH[3]; Dentsply Ind. e Com. Ltda, Rio de Janeiro, RJ, Brazil; shade A2), which contains BisGMA and BisEMA resins and 75.2% in weight of silanized barium, boro-silicate-aluminium/barium, fluor-aluminium-boro-silicate/silica fillers, and a commercial light-curing unit that allows independent command over time and intensity (VIP; Bisco Inc., Schaumburg, IL, USA) were selected for this study. The 4 light-curing modes evaluated were listed in Table 1. The light energy density, which is critical for polymerization, was kept constant for all curing modes. The light irradiance for each cure mode was checked with the in-built radiometer prior to use to ensure consistency of light output. Three solvents were used: distilled water, 75% ethanol, 100% chloroform. The sorption and solubility test was performed in compliance with ISO 4049:1988[15] standard specifications, except for the specimen dimensions and types of solvent. The specimen dimensions were changed to approximate to the light guide diameter of the light-curing unit. Two independent groups were established according to the storage time (7 days-G1; 60 days-G2). Five disc-shaped composite resin specimens were prepared for each group. The composite material was placed in a stainless steel mould (2 mm thick x 8 mm diameter) and confined between two opposing acetate strips. A 1-mm-thick glass slide was placed on the mould and excess material was extruded by pressure. The composite was irradiated using the different light curing modes. The polymerized specimens were removed from the mould and excesses were eliminated with a scalpel blade.

Specimens were stored in desiccators at 37°C containing silica gel. After 24 h, the discs were removed, stored in desiccators at 23°C for 1 h and were then weighed in an analytical balance (Bioprecisa, Electronic Balance, Curitiba, PR, Brazil) accurate to 0.01 mg. This cycle was repeated until a constant mass (m1) was obtained, i.e. until the mass loss of each specimen was not more than 0.2 mg within a 24-h period. Thereafter, the specimens were stored separately in 5 mL of each solvent (distilled water, 75% ethanol and 100% chlorophorm) at 37°C. G1 was stored for 7 days and G2 for 60 days. After completing the storage periods, the specimens were weighed again, after being carefully wiped with an absorbent paper until reaching a constant weight (m_2). Thereafter, the specimens were reconditioned in the desiccators until they reached a constant weight (m_3) using the cycle describe for m_1. The thickness and diameter of each specimen were measured at 4 points and at the center of the specimen using a digital electronic caliper (Mitutoyo Corporation, Tokyo, Japan).

The values for sorption and solubility, in micrograms *per* cubic millimeter, were calculated using the following equations:

$$W_{sp} = \frac{m_2 - m_3}{V}$$

$$W_{sl} = \frac{m_1 - m_3}{V}$$

where :

m_1 is the conditioned mass prior to immersion in the solvent;

m_2 is the mass of the specimen after immersion in the solvent;

m_3 is the reconditioned mass;

V is the volume of the specimen.

Sorption and solubility were calculated and the data of G1 (7 days) and the sorption data of G2 (60 days) were subjected to two-way ANOVA and Tukey's tests (p=0.05). The solubility data of G2 were analyzed by Kruskal-Wallis test (p=0.05), since a non-normal data distribution was observed.

TABLE 1- Description of the different light curing modes evaluated in this study

Curing modes	Curing profiles	Density energy (J/cm²)
Conventional (C)	600 mW/cm² (40 s)	24
Pulse delay I (PD I)	200 mW/cm² (3s) - delay (2 min) - 600 mW/cm² (39 s)	24
Pulse delay II (PD II)	200 mW/cm² (10s) - delay (2 min) - 600 mW/cm² (37 s)	24.2
Pulse delay III (PD III)	600 mW/cm² (3s) - delay (2 min) - 600 mW/cm² (37 s)	24

TABLE 2- Means and standard deviations (±SD) of solvent sorption and solubility in µg/m³ for G1 (7 days of storage)

Curing modes	Water		Ethanol		Chloroform	
	Sorption	Solubility	Sorption	Solubility	Sorption	Solubility
Conventional	18.76±1.52[a,A]	-2.86±0.71[α,β]	20.32±1.72[a,A]	-1.1±1.49[¥,β]	18.36±1.43[a,A]	-0.38±0.85[¥,β]
Pulse Delay I	24.02±4.88[a,A]	-1.68±0.8[α,γ]	22.66±3.04[a,A]	0.38±1.06[¥,β]	19.30±1.46[a,A]	-2.42±1.08[α,β]
Pulse Delay II	22.16±4.94[a,A]	-1.46±1.40[α,γ]	21.32±3.02[a,A]	-1.46±0.84[α,β]	18.02±1.48[a,A]	-0.96±2.75[α,β]
Pulse Delay III	20.48±1.27[a,A]	-3.36±0.47[α,β]	21.48±1.68[a,A]	-2.38±1.78[α,β]	16.52±2.11[b,A]	-1.12±2.2[α,β]

For sorption data, same superscript lowercase letters (a or b) in rows indicate no statistically significant difference among the solvents for each curing mode (p=0.05). In columns, same superscript uppercase letter (A) indicate no statistically significant difference among the curing modes for each solvent (p=0.05).
For solubility data, same superscript Greek letters (α or ¥) in rows indicate no statistically significant difference among the solvents for each curing mode (p=0.05). In columns, same superscript Greek letters (β or γ) indicate no statistically significant difference among the curing modes for each solvent (p=0.05).

TABLE 3- Means and standard deviations (±SD) of solvent sorption and solubility in µg/m³ for G2 (60 days of storage)

Curing modes	Water		Ethanol		Chloroform	
	Sorption	Solubility	Sorption	Solubility	Sorption	Solubility
Conventional	11.02±4.55[a,A]	-4.66±1.49[α,β]	20.60±5.11[b,A]	-3.06±5.23[α,β]	41.92±5.44[c,A]	-24.1±10.2[¥,β]
Pulse Delay I	9.16±0.62[a,A]	-1.48±0.86[α,γ]	23.42±3.44[b,A]	-5.84±1.49[α,β]	44.04±3.28[c,A]	-25.0±0.70[¥,β]
Pulse Delay II	9.40±1.66[a,A]	-0.92±0.67[α,γ]	21.92±1.74[b,A]	-5.32±3.65[¥,β]	38.44±2.15[c,A]	-24.8±1.14[£,β]
Pulse Delay III	10.10±1.10 [a,A]	-1.68±0.44[α,γ]	18.32±3.19[b,A]	-2.66±3.42[α,β]	41.18±3.61[c,A]	-26.5±0.43[¥,β]

For sorption data, same superscript lowercase letters (a, b or c) in rows indicate no statistically significant difference among the solvents for each curing mode (p=0.05). In columns, same superscript uppercase letter (A) indicate no statistically significant difference among the curing modes for each solvent (p=0.05).
For solubility data, same superscript Greek letters (α, ¥ or £) in rows indicate no statistically significant difference among the solvents for each curing mode (p=0.05). In columns, same superscript Greek letters (β or γ) indicate no statistically significant difference among the curing modes for each solvent (p=0.05).

RESULTS

Sorption and solubility mean for G1 and G2 are shown in Tables 2 and 3, respectively. Regarding sorption data for 7 days (G1) and 60 days (G2), there were no statistically significant differences (p>0.05) among the curing modes when immersed in the 3 solvents (distilled water, p=0.162; p=0.652, respectively; 75% ethanol, p=0.531; p=0.182, respectively; 100% chloroform, p=0.102; p=0.179). Therefore for sorption data, the first anticipated null hypothesis was accepted. The effect of different solvents showed statistically significant differences (p<0.05) for both evaluation periods. Hence, the second null hypothesis was rejected. For G1, chloroform provided the lowest mean sorption value when PD III curing mode was used (p=0.002). In other experimental variables, there were no statistically significant differences among solvents. For G2, in all curing modes, chloroform provided the highest sorption mean values (p<0.001), while distilled water provided the lowest ones (p<0.001). Ethanol showed intermediate mean values, being statistically different from water and chloroform (p<0.001).

Regarding solubility data in G1 and G2, the two null hypotheses were partially rejected. For G1 when evaluated in water solvent, the conventional mode was significant different from PD I and II (p=0.030), however similar to PD III (p>0.05). Analyzing the other solvents (ethanol and chloroform), there were no significant differences among curing modes (p>0.05). For G2, there were no significant differences among curing modes in ethanol (p=0.414) and chloroform (p=0.07). In water solvent, the pulse modes (PD I, II and III) were statistically similar (p>0.05), however significantly different from conventional mode (p=0.007).

DISCUSSION

The clinical performance of BisGMA-based materials is to a great extent dependent on their mechanical properties and resistance to chemical degradation by acids and other organic substances found in the oral cavity[20,27]. A given degree of conversion may be associated with polymers of structures differing in crosslink density[5] that can be influenced by photoactivation methods[1,5,6].

The curing modes tested in the present study did not affect the sorption values obtained with 3 solvents and 2

evaluation periods (7 days and 60 days). These findings are in accordance with the results of previous studies that used different curing protocols with similar energy density[19,27]. The pulse curing modes used in present study simulated three different conditions with the same energy density. Pulse delay I and II techniques were based on Kanca and Suh[17] (1999) investigations, which introduced this photoactivation mode to reduce the contraction stress of composite resins. Pulse delay III technique with higher initial light energy was tested because PD curing modes with short flash of initial light (PD I and II) can activate only a minor part of the camphoroquinone molecules resulting in few growth centers and a relatively linear polymer structure that can be more susceptible to ethanol degradation[5,24]. The susceptibility of the more linear or less crosslink polymer to softening in solvents may be explained by the solvent-polymer interaction and, consequently, by Hoy's solubility parameter for polar forces[16,24]. Some studies have shown a significant reduction in mechanical properties, such as flexural modulus and hardness, when composites are photo-cured by PD mode and submitted to solvent action[5,18,24]. However, based on the methodology used in the present study and the obtained results, the curing modes had similar behaviors, which can be explained by the energy density used (24 J/cm^2). Witzel, et al.[27] (2005) described that studies reporting the influence of curing mode in composite properties after ethanol storage used energy densities that were lower than 24 J/cm^2. Another explanation would be the use of filled composite resins for the test, since studies[4-6] that have reported that the PD mode provides polymers with a linear structure, used unfilled resins for their tests. Water sorption in composite materials is a diffusion-controlled process and occurs mainly in the resin matrix[9]. As most composites have the filler content between 80 and 85% and only 20-25% of organic matrix, this can influence on the different results found in previous studies about curing modes. A lower crosslinking degree will result in a higher degree of swelling[24], and hence a larger sorption effect. Therefore, it may be speculated that the absence of influence of solvents sorption due to different curing modes observed in the present study may be the result of the formation of a densely crosslinked polymer network due to the use of a sufficient energy density, compensating for the potentially negative effects of a low curing rate[27].

The effect of different solvents was clearly observed in G2 (60 days of storage) where 100% chloroform generated the highest sorption values, followed by 75% ethanol and distilled water, independently of the curing mode. Distilled water is a ISO-recommended solvent for resin-based filling material[15] and simulates the wet intraoral environment provided by saliva and water. 75% ethanol has been the solvent of choice to simulate accelerated ageing of restorations as it has a solubility parameter that matches the one of BisGMA[16,28]. The extent of solvent uptake by the polymer is a function of the differences in solubility parameter between the polymer and the solvent, being greatest when this difference is small[14]. When ethanol penetrates the polymer network, it causes an expansion of the structure, allowing the release of uncured monomers and

causing dissolution of linear polymer chains[13,27]. This expansion is facilitated when crosslink density is low, since the solvent can disrupt secondary inter-chain bonds, but not primary crosslink bonds[24,27]. Although chloroform is not found in oral environment and has degradation and dissolution effects[7,25] unlike water and ethanol, this solvent was used in the present study to evaluate the composite behavior, when photo-cured by different curing modes. It was observed that the chloroform sorption data in G2 were higher than those of the other solvents. Thus, this solvent allowed for assessing the different curing modes under a more aggressive condition. Even though, the sorption values were also similar for all curing modes tested.

Both groups evaluated in this study (G1-7 days and G2-60 days) were analyzed independently because their specimens were prepared separately. G1's storage period was established based on the ISO 4049:1988 standard[15] specifications, while G2 was designed for an evaluation time longer than 1 week. The specimens were submitted to a longer storage time in order to reach saturation, in accordance with Ortengren, et al.[23] (2001), who reported that most composites evaluated in their study reached saturation within 7 to 60 days. Negative values were detected in solubility data for all tested solvents and periods. This may indicate that the composite resin was more susceptible to water sorption leading to mass gain, which could mask the real solubility. It does not mean that no solubility occurred, but rather that water sorption was greater than solubility[12]. This result may be attributed to composite's higher hydrophilicity[12]. Some studies[12,22] have also found negative values.

The use of slow-cure methods (pulse curing modes) combined with the interval between two irradiations seem not to interfere with solvent sorption and could be useful for adhesive composite restorations.

CONCLUSION

Under the conditions of this *in vitro* study, it may be concluded that: 1. The curing modes (C and PD I, II and III) did not influence the sorption of the tested composite resin in the 3 solvents and in the 2 storage periods; 2. For 60 days of evaluation (G2), the storage media influenced sorption behavior; 3. The solubility test demonstrated negative data, masking the real solubility.

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