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Influence of Ethanol Concentration on Softening Tests for Cross-link Density Evaluation of Dental Composites

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This study investigated the influence of ethanol concentration on softening tests for cross-link density evaluation (microhardness) of dental composites. Specimens of Filtek Z100 (3M ESPE) were light-activated by standard or pulse-delay methods. After initial Knoop hardness readings (KHN_1), half of specimens (n = 10) for each irradiation method was stored in 100% ethanol, and half in 75% ethanol, during 24 hours, and hardness was determined anew. Hardness deterioration (ΔKHN) was recorded as the difference between pre and post-storage values. KHN_1 data were submitted to one-way ANOVA and Tukey's test ($\alpha = 0.05$), and hardness deterioration was analyzed by two-way ANOVA and Tukey's test ($\alpha = 0.05$). For KHN_1, no significant differences were detected between the activation modes ($p = 0.697$). Samples light-activated by the pulse-delay method presented significantly higher softening compared to the standard mode when samples were immersed in 100% ethanol. Conversely, no significant differences between curing modes were detected for samples stored in 75% ethanol.

Keywords: *dental composite, cross-link density, ethanol, softening*

1. Introduction

Resin-based composites are increasingly popular in restorative dentistry. One of the inherent shortcomings of these materials is, however, the shrinkage stress developed during constrained polymerization, which can strongly interfere with the clinical performance of restorations. Thereby, in the last few years, numerous light-curing approaches have been proposed in order to attenuate the resulting stress at the tooth-filling interface[1,2]. The primary aim of these strategies is to allow more time for the composite to flow during setting[1] and to facilitate a certain degree of polymer chain relaxation[2] before reaching the gelation phase. In fact, some investigators have reported reduced shrinkage stress and improved marginal integrity without compromising the final double-bond conversion of the material[3,4].

Besides shrinkage stress, studies concerning the dental polymer structure resulting from different curing strategies usually concentrate on degree of conversion (DC). The DC, despite being an important factor, does not give a complete characterization of the network structure, as polymers with similar degree of cure may present distinct cross-link density (CLD) due to differences in the linearity of the chains[5]. The CLD plays a major role on the properties of the polymer, and highly cross-linked materials generally present increased fracture strength and wear resistance[6].

The degree of cross-linking of a polymer can be assessed by measurement of its glass transition temperature. However, this evaluation demands more complex tests and special equipments. Thereby, some investigators have conducted softening tests as an indirect method of evaluation[5,7-9]. These tests rely on hardness assessments prior to and after the immersion of samples in organic solvents, which are able to penetrate the resin matrix and expand the openings among chains[10]. It is well-recognized that highly cross-linked polymers are more resistant to degradation reactions and to solvent uptake, as more limited space and pathways are available for solvent molecules to diffuse within the structure[10]. Therefore, a more linear polymer would be softened to a higher degree than a polymer with more cross-links[5,10].

Two distinct ethanol concentrations are usually selected for softening analyses, namely 75 and 100%. Different solvent concentrations, however, present distinct softening abilities, and therefore could differently interfere with the swelling process. Nonetheless, literature is lacking of studies comparing the softening ability of these two ethanol concentrations with regard to current dental composite formulations. Thereby, the aim of this study was to investigate whether these different ethanol concentrations could interfere with the results of microhardness of dental resin composites light-activated by different methods.

2. Experimental

The hybrid dental composite Filtek Z100, shade A2, (3M ESPE, St. Paul, MN, USA) and the light-curing unit XL2500 (3M ESPE) were selected. The output power was measured with a calibrated power meter (Ophir Optronics, Danvers, MA, USA) and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). Light irradiance (700 mW/cm^2) was computed as the ratio of the output power by the area of the unit tip.

The composite was placed into a cylindrical brass mold (5 mm inner diameter x 2 mm thickness) and covered with a transparent polyester strip. Two different curing protocols were investigated:

- *Standard*: irradiation at a continuous light-intensity of 700 mW/cm^2 for 40 seconds, with the light tip positioned directly onto the polyester strip; and
- *Pulse-delay*: starting at 100 mW/cm^2 for 5 seconds, followed by a waiting time of 3 minutes, and final cure for 39 seconds at 700 mW/cm^2.

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The total radiant exposure was kept constant at approximately 28 J/cm^2. For producing 100 mW/cm^2, a standard separator was used for positioning the curing guide tip 2 cm away from the composite surface. Twenty specimens were made for each activation mode. Samples were dry-stored for 24 hours in light-proof containers, at 37 °C, and then wet-polished with 1200-grit silicon-carbide abrasive paper in order to obtain a smooth, planar surface. Knoop hardness measurements were conducted on the irradiated surface through an indenter (HMV-2, Shimadzu, Tokyo, Japan), under a load of 50 g for 15 seconds. Readings were performed at five locations, and the mean value between them was recorded as the initial Knoop Hardness Number (KHN_1, Kg/mm^2) for each specimen. Half of specimens per composite was then stored in 100% ethanol, and half in 75-25% ethanol-distilled water solution, during 24 hours at room temperature, and hardness was determined anew.

Hardness deterioration (ΔKHN) was calculated by the difference between pre and post-storage values. Initial hardness data were submitted to one-way ANOVA and Tukey's test, and hardness deterioration was analyzed by two-way ANOVA and Tukey's test. The statistical analysis was conducted at a significance level of 0.05.

3. Results and Discussion

Table 1 summarizes KHN_1 data. The initial hardness assessment was carried out in order to estimate the DC resultant from the different curing strategies, and both activation modes yielded similar values. Although recent findings indicate that calculations based on the total energy delivered to guide irradiation protocols are controversial[11], the present results are in line with previous investigations which show that similar DC can be obtained by different combinations of irradiance vs. exposure time[3,5,7].

On the other hand, hardness deterioration due to ethanol storage (Table 2) was assessed to provide an estimation of the polymers CLD, and a significant difference between standard and pulse-delay methods was detected for samples immersed in 100% ethanol, as specimens light-activated by the pulse-delay mode disclosed significantly higher softening ($p < 0.05$). Although the total radiant exposure was the same for both modes, this outcome suggests that different curing procedures resulted in different polymer structures. This is probably related to the fact that the pulse-delay mode is initiated by a short flash of light followed by a waiting time before the final cure is performed[12], and slow polymerization start is generally associated with relatively few centers of polymer growth, which may result in a more linear final polymer structure[5,7]. On the other hand, a high initial irradiance generally initiate a multitude of growth centers and favor the formation of a polymer with more cross-links[5,7]. Since solvent uptake and swelling are directly related to the CLD[10], a polymer with fewer cross-links is generally more sensitive to the plasticizing action of solvents[6,10,13].

Table 1. Means for KHN_1.

Light-curing mode	Ethanol concentration (%)	KHN_1
Standard	100	65.12 (4.93)^a
	75	59.41 (5.13)^a
Pulse-delay	100	64.11 (3.44)^a
	75	62.35 (5.68)^a

Means followed by the same letter were similar at $p < 0.05$.

Table 2. Means for ΔKHN (standard deviation).

Light-curing mode	ΔKHN	
	75% ethanol	100% ethanol
Standard	6.79 (2.03)^{A,a}	5.60 (2.46)^{A,b}
Pulse-delay	8.16 (2.03)^{A,a}	10.72 (1.79)^{A,a}

Means followed by different capital letters in the same line, and different small letters in the same column, were significantly different at $p < 0.05$.

Conversely, no significant differences between curing modes were verified for samples stored in 75% ethanol. Studies conducting softening tests with 75% ethanol are based on an investigation which relates a maximum softening of BisGMA-based composites at this concentration[13]. The main reason for the present results is probably related to the formulation of the tested material. The aforementioned study evaluated an experimental resin containing approximately 70 wt. (%) of BisGMA and 30 wt. (%) of TEGDMA, while the present composite contains a 50/50 wt/wt. (%) BisGMA/TEGDMA blend. In fact, Asmussen[14] reported that the softening effect of solvents decreases with the increasing content of TEGDMA up to 50 mol%, what it is probably related to its ability in promoting cross-link reactions.

In addition, alteration in the organic matrix components may result in changes in the magnitude of composites' solubility parameter. The solubility parameter describes the ease with which a molecule can penetrate and dissolve another substance, and a maximum softening is expected when there is minimal magnitude mismatch between the solvent and the polymer itself[6]. The solubility parameter of 75% ethanol [3.15×10^{-4} ($J^{1/2}m^{-3/2}$)] is higher than that of 100% ethanol [2.6×10^{-4} ($J^{1/2}m^{-3/2}$)[6], and the solubility parameter of TEGDMA is approximately 15% lower than that of BisGMA[15]. Thereby, it can be speculated that increasing the TEGDMA content in the resin matrix may alter the solubility parameter of the composite to a magnitude that could interfere with the softening effect promoted by 75% ethanol. Furthermore, the resin tested by Wu and McKinney[13] was an unfilled composite, and the presence of fillers in a polymer network can strongly influence solvent uptake and softening effect, as it reduces the overall volume of the absorbing material[10]. Although in a further study[6] the authors have assessed softening on particulate materials, and similar findings for 75% ethanol were observed, the composites tested also strongly differentiate from the current available dental resin formulations with respect to organic and inorganic components.

Several softening studies which evaluate the polymer network structure promoted by different curing modes present conflicting outcomes[5,8,9]. These differences may be attributed to distinct curing strategies, storage periods or hardness tests. However, the results of the present study show that the ethanol concentration is another factor that should be regarded as of significant importance, and 100% ethanol seems to be a more suitable solvent to predict differences related to polymer CLD in 24 hours softening tests with current dental resin formulations. Notwithstanding, further studies are required to investigate the influence of additional resin formulations on the outcomes of softening tests.

4. Summary and Conclusion

The present investigation show that the outcomes of softening tests for cross-link density evaluation of dental composites can be influenced by the ethanol concentration. 100% ethanol seems to be a more suitable solvent for 24 hours softening tests with current resin composite formulations.

References

1. Bouschlicher MR, Rueggeberg FA, Boyer DB. Effect of stepped light intensity on polymerization force and conversion in a photoactivated composite. *Journal of Esthetic Dentistry.* 2000; 12(1):23-32.
2. Lu H, Stansbury JW, Bowman CN. Impact of curing protocol on conversion and shrinkage stress. *Journal of Dental Research.* 2005; 84(9):822-826.

3. Sakaguchi RL, Berge HX. Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites. *Journal of Dentistry.* 1998; 26(8):695-700.
4. Uno S, Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. *Scandinavian Journal of Dental Research.* 1991; 99(5):440-444.
5. Asmussen E, Peutzfeldt A. Influence of pulse-delay curing on softening of polymer structures. *Journal of Dental Research.* 2001; 80(6):1570-1573.
6. McKinney JE, Wu W. Chemical softening and wear of dental composites. *Journal of Dental Research.* 1985; 64(11):1326-1331.
7. Asmussen E, Peutzfeldt A. Two-step curing: influence on conversion and softening of a dental polymer. *Dental Materials.* 2003; 19(6):466-470.
8. Soh MS, Yap AU. Influence of curing modes on crosslink density in polymer structures. *Journal of Dentistry.* 2004; 32(4):321-326.
9. Yap AU, Soh MS, Han TT, Siow KS. Influence of curing lights and modes on cross-link density of dental composites. *Operative Dentistry.* 2004; 29(4):410-415.
10. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. *Dental Materials.* 2006; 22(3):211-222.
11. Musanje L, Darvell BW. Polymerization of resin composite restorative materials: exposure reciprocity. *Dental Materials.* 2003; 19(6):531-541.
12. Sahafi A, Peutzfeldt A, Asmussen E. Effect of pulse-delay curing on in vitro wall-to-wall contraction of composite in dentin cavity preparations. *American Journal of Dentistry.* 2001; 14(5):295-296.
13. Wu W, McKinney JE. Influence of chemicals on wear of dental composites. *Journal of Dental Research.* 1982; 61(10):1180-1183.
14. Asmussen E. Softening of BISGMA-based polymers by ethanol and by organic acids of plaque. *Scandinavian Journal of Dental Research.* 1984; 92(3):257-261.
15. Asmussen E, Uno S. Solubility parameters, fractional polarities, and bond strengths of some intermediary resins used in dentin bonding. *Journal of Dental Research.* 1993; 72(3):558-565.