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Cross-link density evaluation through softening tests: Effect of ethanol concentration

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ABSTRACT

Objectives. The aim of this study was to investigate whether the ethanol concentration used would influence the outcomes obtained through softening tests when comparing light-activation modes.

Methods. Disc specimens ($n = 20$) of Filtek Z250 and Filtek Z100 (3M ESPE) were light activated by standard (S) and pulse-delay (PD) modes. Initial Knoop hardness (KHN) measurements were performed 24 h after dry storage at 37 °C. Half of the specimens ($n = 10$) of each resin-composite were stored in absolute ethanol (100%) and the other half in 75% ethanol solution, for 24 h at room temperature, and KHN was determined anew. Initial hardness data were submitted to Student's *t*-test ($p = 0.05$). Percentages of hardness decrease were analyzed by two-way ANOVA followed by pairwise Tukey's test ($p = 0.05$). The statistical analyses were performed separately for each resin-composite.

Results. No statistically significant differences were observed between standard and pulse-delay modes for initial Knoop hardness values. After storage in 75% ethanol solution, KHN was decreased in all cases but no significant differences were detected between light-activation modes (Filtek Z250: PD = 12.6%, S = 13.5%; Filtek Z100: PD = 13.5%, S = 11.8%) regardless of the resin-composite tested. After absolute ethanol storage, higher decrease in KHN were observed. Samples light-activated by the PD mode (Filtek Z250 = 20.4% and Filtek Z100 = 16.9%) exhibited significantly higher percentage decrease of KHN than specimens light-activated by the standard mode (Filtek Z250 = 14.1% and Filtek Z100 = 8.8%), regardless of the resin-composite tested.

Conclusion. The ethanol concentration affected the outcomes of the softening test.

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1. Introduction

Several light-activation modes have been introduced in an attempt to attenuate the shrinkage stress resulting from the resin-composite polymerization process. These modes can allow more time for the composite to flow before reaching the gelation phase [1]. Despite conflicting results, some studies have described reduced shrinkage stress and gap formation while maintaining a similar degree of conversion (DC) [2–5]. However, polymers with similar DC may display distinct cross-link density (CLD) due to differences in the linearity of the chains.

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The CLD of a polymer network can be indirectly assessed by measuring its glass transition temperature (Tg) [6,7]. However, such evaluation requires complex tests and special equipment. On the other hand, some studies have used the softening test as an alternative method of evaluation [8–14]. The softening test is based on repeated hardness measurements before and after the immersion of the samples in organic solvents. It is generally accepted that highly cross-linked polymers are more resistant to degradation and solvent uptake, whereas linear polymers present more space and pathways for solvent molecules to diffuse within their structure [15]. This could result in increased softening, which can be assessed by a hardness test [9].

Studies investigating the influence of light-activation modes on the CLD of polymeric networks revealed different experimental designs, especially, variable storage media used. Yap et al. [14] used a 75% ethanol solution bath for 24 h and found no difference among light-activation modes when LED lights were used. In another study [6] that evaluated CLD by measuring the Tg through differential scanning calorimetry (DSC) and softening by using a hardness test after storage in a 75% ethanol solution, both tests showed differences among different light-activation modes evaluated (pulse-delay, soft-start and pulse-cure). Other studies using absolute ethanol have also found different effects on the polymer structures by using the softening test through hardness indentations [8,9,11,12,16].

Therefore, the aim of this study was to investigate whether the ethanol concentration is related to the decrease in Knoop hardness among materials cured using different light-activation modes. The null hypothesis tested was that the ethanol concentration would not affect the outcomes of polymer softening obtained through hardness tests.

2. Materials and methods

Two resin-composites were used in this study: Filtek Z250 and Filtek Z100 (3M/ESPE Dental Products, St Paul, MN, USA). Their composition is shown in Table 1. A quartz-halogen-tungsten unit XL2500 (3M/ESPE) was used for light-activation procedures. The output power (mW) was measured with a calibrated power meter (Ophir Optronics Inc., Danvers, MA, USA) and the diameter of the tip with a digital caliper (Mitutoyo, Tokyo, Japan) in order to determine the area of the light guide. Irradiance (700 mW/cm^2) was calculated by the ratio of the output power by the area of the light guide.

The resin-composite was packed into cylindrical brass molds (2 mm height, 5 mm inner diameter) and covered with a Mylar strip. The specimens were photo-activated according to the following modes:

1. Standard: 40 s of exposure at 700 mW/cm^2 with the light guide positioned directly onto the Mylar strip;
2. Pulse-delay: 5 s of initial activation at 100 mW/cm^2, followed by a waiting time of 3 min before the final activation of 39 s at 700 mW/cm^2.

The light radiant exposure was kept constant in at 28 J/cm^2. For the pulse-delay mode, the light guide tip was positioned 20 mm from the samples to obtain 100 mW/cm^2. Twenty specimens of each material were made for each light-activation mode. Samples were dry stored for 24 h in lightproof containers at 37 °C. Thereafter, they were ground with #1200 SiC in order to obtain a flat surface and to remove a possible oxygen inhibited layer. Knoop hardness was measured for the irradiated surface with an indenter (HMV-2, Shimadzu, Tokyo, Japan) under a load of 50 g for 15 s. Measurements were performed at five locations, and the average value was recorded as the initial Knoop Hardness Number (KHN, kg/mm^2) for each specimen. The data were analyzed by the Student's *t*-test ($p = 0.05$), in order to evaluate differences between the two light-activation modes. The statistical analyses were performed separately for each resin-composite.

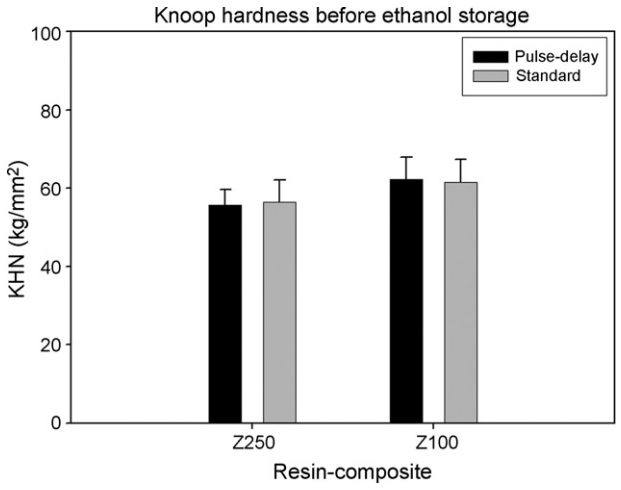
Half of the specimens per resin-composite ($n = 10$) were then stored in absolute ethanol and the other half in 75% ethanol solution for 24 h at room temperature, and Knoop hardness was then determined anew. The percentage of Knoop hardness decrease was statistically analyzed. The comparisons were performed by two-way ANOVA, in order to verify whether the distinct light-activation modes and ethanol concentrations had affected the hardness decrease. The interaction between light-activation mode and ethanol concentration was evaluated, and individual differences among the groups were determined by use of pairwise Tukey's test ($p = 0.05$). The statistical analyses were performed separately for each resin-composite.

3. Results

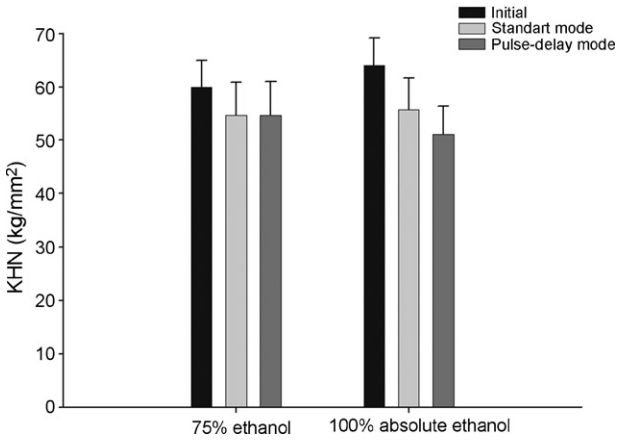
Graph 1 shows the mean values for Knoop hardness before ethanol storage for standard and pulse-delay modes. No significant differences were observed between both light-activation modes, regardless of the resin-composite tested (Filtek Z250: PD = 55.58 kg/mm^2 and S = 56.39 kg/mm^2/Filtek Z100: PD = 62.19 kg/mm^2 and S = 61.39 kg/mm^2).

Table 1 – Resin-composites tested

Resin-composite	Batch number	Organic matrix	Filler
Filtek Z250	3CR	BisEMA (34.5 wt%) UDMA (34.5 wt%) BisGMA (25 wt%) TEGDMA (6 wt%)	Silica/Zirconia (60 vol%)
Filtek Z100	5XR	BisGMA (50 wt%) TEGDMA (50 wt%)	Silica/Zirconia (66 vol%)



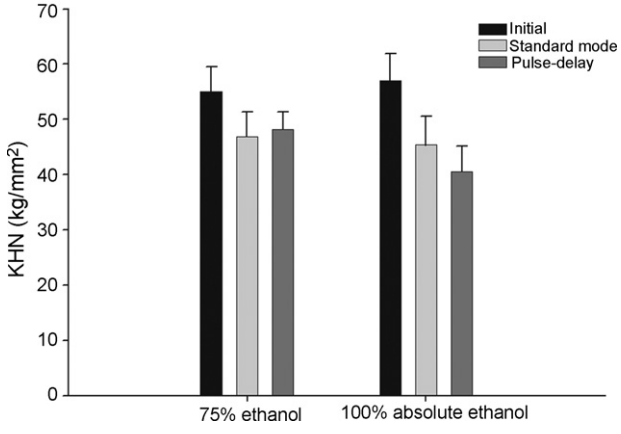
Graph 1 – Knoop hardness mean values before ethanol storage.



Graph 3 – KHN for Filtek Z100 before and after storage in different ethanol concentrations.

The two-way ANOVA data for the percentages of Knoop hardness decrease showed a significant interaction between light-activation mode and ethanol concentration ($p < 0.05$) for both analyses.

Graphs 2 and 3 show the KHN before and after storage in different ethanol concentrations for Filtek Z250 and Filtek Z100, respectively. Table 2 shows the mean values for Knoop hardness decrease after ethanol storage for both resin-composites. For the resin-composite Filtek Z250, no significant differences between the light-activation modes were detected for samples stored in 75% ethanol solution (PD = 12.6% and S = 13.5%). On the other hand, there was a significant difference between standard (14.1%) and pulse-delay (20.4%) modes when samples were stored in absolute ethanol, with significantly higher softening for the pulse-delay mode ($p < 0.05$). The results for the resin-composite Z100 followed the same pattern, i.e., a significantly higher softening for pulse-delay mode was verified on specimens stored in absolute ethanol (PD = 16.9% and S = 8.8%) whereas no difference was found on specimens stored in 75% ethanol solution (PD = 11.8% and S = 13.5%).



Graph 2 – KHN for Filtek Z250 before and after storage in different ethanol concentrations.

Table 2 – Mean values for the percentage of hardness decrease for Filtek Z250 and Filtek Z100 after ethanol storage

Ethanol concentration	Light-activation mode	% KHN decrease (s.d.) Filtek Z250	Filtek Z100
100%	Standard	14.1 (3.5)	8.8 (3.9)
100%	Pulse-delay	20.4 (4.0)	16.9 (3.1)
75%	Standard	13.5 (3.4)	11.8 (3.9)
75%	Pulse-delay	12.6 (4.9)	13.5 (3.6)

Values joined with bars indicate no statistical significant difference. The two columns are not inter-related.

4. Discussion

The hardness assessment before ethanol storage was conducted to estimate the DC resultant from different light-activation modes [17]. According to the results, both modes produced similar initial Knoop hardness values, regardless of the resin-composite tested. The percentage of Knoop hardness decrease after ethanol storage was analyzed to provide an estimation of the polymer CLD, an important factor that can be related to the resultant mechanical properties [18,19]. The outcomes show that comparisons between the standard and the pulse-delay light-activation modes were dependent on the ethanol concentration used as storage medium. Therefore, the null hypothesis that the ethanol concentration would not affect the outcomes of polymer softening obtained through hardness tests was rejected.

The pulse-delay mode is initiated by a short and low irradiance flash of light followed by a waiting time before the final cure with higher irradiance [20]. However, questions remain about the final polymer structure produced by this light-activation mode, such as the CLD. In the present study, no significant differences in the percentage of hardness decrease

were detected for samples polymerized by pulse-delay and standard light-curing modes after storage in the 75% ethanol solution, regardless of the resin-composite tested. This might suggest that a similar CLD was obtained for standard and pulse-delay light-activation modes [9]. These outcomes concur with a recent study [7] that investigated the Tg of Z250 and Z100 after light activation using different irradiances and reported that the light-activation mode did not affect the Tg.

On the other hand, for specimens stored in absolute ethanol, the pulse-delay mode resulted in significantly higher softening than the standard mode, irrespective of the resin-composite tested. Although the radiant exposure was kept constant for both light-activation modes (28 J/cm^2), this result might suggest a different CLD for the distinct light-activation modes. This is in agreement with previous statements that an initially slow cure may be associated with relatively few centres of polymer growth that favor the formation of a relatively linear polymer structure [8,9,12]. The different outcomes obtained by storing the samples in the absolute ethanol concentration and the aforementioned study regarding Tg measures [7] can be related to the different light-activation modes tested. While the present study used an initial irradiance of 100 mW/cm^2 followed by a 3 min delay until final curing, the aforementioned work [7] used continuous irradiances of at least 250 mW/cm^2. According to Asmussen and Peutzfeldt [9], the longer the delay time before the final cure, the more the formation of a relatively linear polymer will prevail.

It has been observed that cross-linked dimethacrylate networks swell when exposed to solvents. This occurs because the forces of attraction between the polymer chains are exceeded by the forces of attraction between solvent molecules and components of the chains [15]. Therefore, the solvent penetrates the resin matrix and expands the openings among chains. This solvent penetration ability is related to the solubility parameter, which describes the ability of a molecule to penetrate and dissolve another substance [15,21]. The differences in the solubility parameter between the polymer and the solvent will determine the extent of solvent uptake. Subsequently, when there is a small difference between the solubility parameter of the solvent and the polymer itself, higher solvent uptake will occur [15,22]. The solubility parameter of resin-composites is directly dependent upon the organic matrix formulation. Therefore, it might be speculated that the solubility parameter of absolute ethanol is closer to the solubility parameter of the resin-composites tested here when compared to the 75% ethanol solution.

The use of 75% ethanol solution as a storage medium is based on a study [23] which relates a maximum softening of BisGMA-based resin-composites using this concentration. However, the material tested in the aforementioned study [23] was an experimental, unfilled resin, containing 69.4 wt% of BisGMA and 29.5 wt% of TEGDMA, which is different from the formulations of the resin-composites used in the present study (Table 1). This might have accounted for the differences in the solubility parameters between the resin-composites and each solvent concentration tested, therefore significantly influencing the outcomes.

The aim of the present study was not focused on showing the best treatment to be applied in softening analyses, but to test whether considerations about CLD are dependent on the solvent concentration used as the storage media. The results of the current study present a significant influence on the outcomes of softening tests. Therefore, it is a factor that should be considered in future CLD studies.

5. Conclusions

Ethanol concentration significantly influenced the outcomes of the softening analyses. The storage of specimens in absolute ethanol exposed differences in the cross-link density between standard and pulse-delay light-activation modes, whereas the use of 75% ethanol solution did not.

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