

## Research Article



# The influence of nanofillers on the properties of ethanol-solvated and non-solvated dental adhesives

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### Conflict of Interest

No potential conflict of interest relevant to this article was reported.

### Author Contributions

Conceptualization: Lima AF; Data curation: Saraceni CHC; Lima AF; Formal analysis: Lima AF; Funding acquisition: Lima AF; Investigation: Cruz LBT; Oliveira MT; Saraceni CHC; Lima AF; Methodology: Oliveira MT; Lima AF; Project administration: Lima AF; Resources: Saraceni CHC, Lima AF; Supervision: Lima AF; Validation: Saraceni CHC; Oliveira MT; Lima AF; Writing - original draft: Cruz LBT; Writing - review & editing: Saraceni CHC; Oliveira MT; Lima AF.

## ABSTRACT

**Objectives:** The aim of this study was to evaluate the influence of different concentrations of nanofillers on the chemical and physical properties of ethanol-solvated and non-solvated dental adhesives.

**Materials and Methods:** Eight experimental adhesives were prepared with different nanofiller concentrations (0, 1, 2, and 4 wt%) and 2 solvent concentrations (0% and 10% ethanol). Several properties of the experimental adhesives were evaluated, such as water sorption and solubility ( $n = 5$ , 20 seconds light activation), real-time degree of conversion (DC;  $n = 3$ , 20 and 40 seconds light activation), and stability of cohesive strength at 6 months (CS;  $n = 20$ , 20 seconds light activation) using the microtensile test. A light-emitting diode (Bluephase 20i, Ivoclar Vivadent) with an average light emittance of 1,200 mW/cm<sup>2</sup> was used.

**Results:** The presence of solvent reduced the DC after 20 seconds of curing, but increased the final DC, water sorption, and solubility of the adhesives. Storage in water reduced the strength of the adhesives. The addition of 1 wt% and 2 wt% nanofillers increased the polymerization rate of the adhesives.

**Conclusions:** The presence of nanofillers and ethanol improved the final DC, although the DC of the solvated adhesives at 20 seconds was lower than that of the non-solvated adhesives. The presence of ethanol reduced the strength of the adhesives and increased their water sorption and solubility. However, nanofillers did not affect the water sorption and strength of the tested adhesives.

**Keywords:** Adhesives; Longevity; Polymerization; Solvents; Storage

## INTRODUCTION

Dental adhesive agents are used in direct and indirect restorations [1-3]. The properties of adhesive systems are extremely important for the reliability and longevity of adhesive procedures. The chemical and physical properties of resin materials are directly related to their composition [4,5], since the monomer type may have some influence on the conversion and on the type of polymer that is formed, which may increase or decrease cross-link density [6].

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Enhanced mechanical properties of the adhesive may improve hybrid layer resistance to tension caused by masticatory forces, and may also increase the resistance to stress promoted by shrinkage resulting from resin composite polymerization [7]. Systems with low water sorption and solubility may have low rates of hydrolytic degradation due to the reduced interaction between water and the formed polymer, which is a relevant factor for the properties of dental adhesives [8].

One alternative for improving the properties of resin systems is the addition of fillers [9-11]. Filler particles may increase the cohesive strength (CS) of adhesive agents without affecting polymerization [10]; however, such results were obtained through the evaluation of non-solvated experimental dental adhesives. The solvents of different concentrations that are present in some dental adhesives [12] can modulate their properties and bonding performance [13]. They allow the adhesive agent to diffuse on the demineralized dentin, and facilitate the removal of excess water found among collagen fibrils [14,15]. In adhesion, the removal of excess solvent through air-blowing can promote a significant increase in the strength of the bond to dentin [16]. The absence of solvent in an adhesive can improve its mechanical properties, as well as reducing the water sorption and solubility of the system [17]. Usually, solvent-free adhesives are presented as the 'bond' or 'adhesive' in two-bottle systems. Initially, the primer agent, which contains solvent and hydrophilic monomers, promotes diffusion through the demineralized dentin and facilitates the removal of excess water [12]. After primer application, a hydrophobic resin without solvent is applied, increasing the strength and reducing the water degradation of the hybrid layer over time [12,18].

Considering that single-bottle adhesives are widely used in dental procedures, it is important to evaluate the influence of nanofillers on the properties of solvated adhesives in order to predict the behaviour of these agents in clinical practice. These fillers, at an optimal concentration, can improve some characteristics of systems, such as cohesive and flexural strength, as well as increasing the bond strength of adhesive formulations [10,19-22]. In addition, these fillers can influence the agents' polymer conversion, a property with great importance for the durability of bonding procedures.

As previously described, non-solvated adhesives are found as the hydrophobic layer and the last step of two-bottled systems, which is important to reduce degradation over the years. Comparisons between ethanol-solvated and non-solvated adhesives are of interest, not only as a way to simulate hydrophobic agent performance under different tested conditions, but also as a comparison of the effects of solvent presence on adhesive composition, especially for single-step adhesives. Therefore, the objective of this study was to evaluate the influence of nanofiller concentrations on the chemical and physical properties (degree of conversion [DC], rate of polymerization [RP], water sorption and solubility, and CS) of experimental ethanol-solvated and non-solvated adhesives. The null hypothesis was that the addition of nanofiller and the presence of solvent would not influence the properties of the experimental adhesives.

## **MATERIALS AND METHODS**

### **Adhesive preparation**

Two formulations were prepared: one by mixing the monomers, 40 wt% bisphenol glycidyl methacrylate (Bis-GMA; Esstech Inc., Essington, PA, USA) and 60 wt% 2-hydroxyethyl

methacrylate (HEMA; Esstech Inc.), and the other containing solvated adhesives with 35 wt% Bis-GMA, 55 wt% HEMA, and 10 wt% ethanol (Merck KGaA, Darmstadt, Germany). For all formulations, the initiator system was composed of 0.5 mol% camphorquinone (CQ; Esstech Inc.), 1 mol% dimethylaminoethyl amine benzoate (EDAB; Sigma-Aldrich Inc., St. Louis, MO, USA), and 0.5 mol% diphenyliodonium hexafluorophosphate (DPI; Sigma-Aldrich Inc.).

The experimental groups were formed with various concentrations of silanized nanofiller (silica, 7 nm average particle size, Aerosil 380, Degussa, Frankfurt, Germany), establishing 8 groups according to their respective concentration (0, 1, 2, and 4 wt%), for non-solvated (G1, G2, G3, and G4) and ethanol-solvated (G5, G6, G7, and G8) adhesives.

### Light-curing unit

A polywave light-emitting diode (Bluephase G2, Ivoclar Vivadent AG, Schaan, Liechtenstein) with an average tip light emittance of 1,200 mW/cm<sup>2</sup> was used for all light-curing procedures. This light-curing unit provides a spectral output that covers both the 380–420 nm (with a 400 nm peak) and the 420–500 nm ranges (with a 460 nm peak), thereby providing effective activation of photoinitiator molecules. The light energy supplied for all evaluations was 24 J/cm<sup>2</sup> (20 seconds activation) for water sorption, solubility, and CS evaluation, and 40 seconds for real-time polymerization.

### Real-time polymerization

Real-time polymerization was analysed using Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Scientific, Hemel Hemstead, UK) with rapid scan monitoring of the peaks at 1,638 and 1,608 cm<sup>-1</sup>, at a high acquisition rate (0.2 per second), through a liquid nitrogen-cooled MCT detector (Thermo Scientific). A polyvinylsiloxane mold (5 mm in diameter × 1 mm in thickness) was fixed around the diamond surface of the attenuated total reflectance reader. The experimental dental adhesive from each group was dispensed onto the mold (*n* = 3) and covered with a Mylar strip. The resin was light-cured for 40 seconds and closely monitored for 80 seconds. To obtain the polymerization rate, the changes between the first measurements obtained at each second ( $\cong$  9 measurements/sec) were divided by the time of evaluation. Then, the RP was obtained by taking the first derivative of conversion (%) with regard to time (seconds). The DC was calculated using the formula below:

$$DC (\%) = \left\{ 1 - \left( \frac{\frac{1,638 \text{ cm}^{-1}}{1,608 \text{ cm}^{-1}} \text{ polymerized}}{\frac{1,638 \text{ cm}^{-1}}{1,608 \text{ cm}^{-1}} \text{ unpolymerized}} \right) \right\} \times 100$$

### Sorption and solubility

The water sorption and solubility measurements were performed according to ISO 4049 [23], with the exception of the sample dimensions, which were reduced to allow single-step light curing. Silicone molds were used to prepare the discs (5 mm in diameter × 1 mm in thickness). The specimens were randomly prepared using silicon molds, filled with the experimental adhesive agent from each group, covered with a Mylar strip to avoid oxygen-inhibited layer formation, and then light-cured.

Polymerized specimens (*n* = 5) were stored in plastic tubes in a desiccator at 37°C. The samples were weighed daily during the drying period using an analytical scale until a constant weight was obtained (*m*<sub>1</sub>); that is, the variation between 3 weight measurements was no more than  $\pm$  0.001 g. The diameter and thickness were measured, and the dimensions

were used to calculate the sample volume ( $\text{mm}^3$ ). The samples were then immersed in distilled water (1.5 mL) and stored at  $37^\circ\text{C}$  for 7 days.

After this period, specimens were lightly dried with absorbent paper and weighed for mass measurement after immersion in water ( $m_2$ ). Next, the samples were placed in a desiccator at  $37^\circ\text{C}$  for the final mass measurement. The specimens were weighed daily until they reached a constant weight ( $m_3$ ). Water sorption and solubility were calculated as  $\mu\text{g}/\text{mm}^3$ , using the following formulae:

$$\text{Sorption} = \frac{(m_2 - m_3)}{V}$$

$$\text{Solubility} = \frac{(m_1 - m_3)}{V}$$

$m_1$ : initial weight before immersion in distilled water ( $\mu\text{g}$ );

$m_2$ : mass after immersion in distilled water ( $\mu\text{g}$ );

$m_3$ : mass after the second drying cycle ( $\mu\text{g}$ );

V: volume of the  $m_1$  sample ( $\text{mm}^3$ ).

### Cohesive strength

For the CS evaluation ( $n = 20$ ), hourglass-shaped samples (1 mm in width  $\times$  1 mm in thickness at constriction, for a  $1 \text{ mm}^2$  cross-sectional area) were prepared using silicone molds. The specimens were randomly prepared using silicon molds, filled with the experimental adhesive agent from each group, covered with a Mylar strip to avoid oxygen-inhibited layer formation, and then light-cured. Ten specimens from each group were stored at  $37^\circ\text{C}$  for 24 hours for evaluation, and the other 10 were stored at  $37^\circ\text{C}$  for 6 months. For testing, the samples were fixed to the device used for microtensile strength testing with cyanoacrylate glue (Super Bonder, Loctite Ltd., São Paulo, Brazil), and loaded using a universal testing machine (2000RK, Kratos, São Paulo, Brazil) at a crosshead speed of  $0.5 \text{ mm}/\text{min}$ . The rupture area was measured with a digital calliper (Mitutoyo, Tokyo, Japan). The microtensile values (F, kgf) corresponding to the CS, were converted into MPa, using the following formula:

$$CS = \frac{F \times 9.8}{\text{Rupture Area}}$$

### Statistical analysis

All obtained measurement data were analysed for normality and homogeneity of variance (Shapiro-Wilk and Levene tests, respectively). For DC, the maximum RP and the water sorption were analyzed using 2-way analysis of variance (ANOVA), with 'filler content' and 'solvent' as the main factors. For comparisons among groups in all evaluations, the Tukey test was performed, at a 5% significance level. The statistical analysis was performed using the SAS software (SAS Institute, Cary, NC, USA).

Considering the solubility of adhesives, as the ANOVA prerequisites were not satisfied, 2 non-parametric analyses were performed using the Kruskal-Wallis test for group comparison and the Dunn test to establish the statistical significance of differences among the groups.

## RESULTS

### Real-time polymerization

After 20 seconds, the experimental adhesives containing ethanol presented less conversion than the non-solvated ones (Table 1). For the non-solvated adhesives, the nanoparticles did not influence the conversion ( $p = 0.613$ ). Comparing the solvated adhesives alone, those containing 1 wt% and 2 wt% of nanoparticles showed greater conversion at 20 seconds. The least conversion was observed for the adhesive with no filler. However, the final conversion (obtained after 80 seconds of real-time evaluation) of the ethanol-solvated adhesives was higher than that of the non-solvated adhesives ( $p < 0.001$ , Table 1 and Figure 1). The adhesives containing filler had higher DC ( $p < 0.001$ ; Table 1 and Figure 1).

Non-solvated adhesives presented higher RP ( $p < 0.001$ ; Table 1 and Figure 2). The addition of filler promoted an increase in the RP for both adhesives with and without solvent, ( $p = 0.017$ , Figure 2).

### Water sorption and solubility

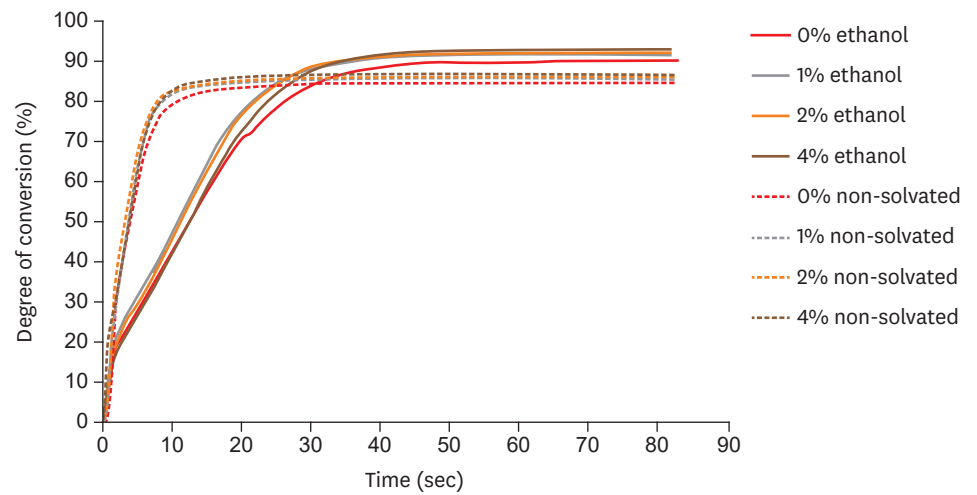
Water sorption was not influenced by the fillers ( $p = 0.192$ ). The solvated adhesives showed higher water sorption than the non-solvated adhesives ( $p = 0.017$ , Table 1).

**Table 1.** Degree of conversion (DC; %), rate of polymerization (RP; %/sec), water sorption ( $\mu\text{g}/\text{mm}^3$ ), and solubility ( $\mu\text{g}/\text{mm}^3$ ) of ethanol-solvated and non-solvated experimental dental adhesives, according to the nanofiller content and the presence or absence of solvent

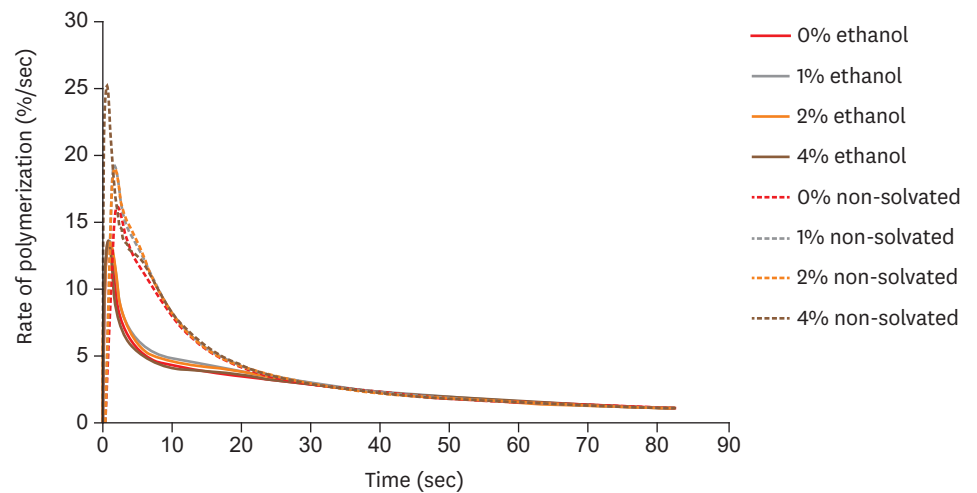
Property	Concentration (%) of nanofiller	Without solvent	With solvent (10% ethanol)	
DC at 20 sec	0	83.6 $\pm$ 0.2 <sup>Aa</sup>	70.7 $\pm$ 3.6 <sup>Bc</sup>	
	1	85.0 $\pm$ 0.8 <sup>Aa</sup>	78.1 $\pm$ 0.7 <sup>Ba</sup>	
	2	85.7 $\pm$ 0.3 <sup>Aa</sup>	77.2 $\pm$ 0.3 <sup>Ba</sup>	
	4	86.0 $\pm$ 0.2 <sup>Aa</sup>	73.1 $\pm$ 2.2 <sup>Bb</sup>	
DC (final) at 40 sec	0	84.6 $\pm$ 0.2	90.1 $\pm$ 1.2	b
	1	85.7 $\pm$ 0.8	91.7 $\pm$ 0.6	ab
	2	86.3 $\pm$ 0.3	92.3 $\pm$ 0.3	a
	4	86.6 $\pm$ 0.3	92.9 $\pm$ 0.6	a
		B	A	
Maximum RP	0	29.9 $\pm$ 0.9	15.5 $\pm$ 0.3	b
	1	33.1 $\pm$ 0.8	17.2 $\pm$ 0.9	a
	2	32.6 $\pm$ 1.2	17.4 $\pm$ 0.6	a
	4	31.0 $\pm$ 2.7	17.1 $\pm$ 0.9	ab
		A	B	
Water sorption	0	62.26 $\pm$ 8.00	76.20 $\pm$ 10.82	
	1	54.85 $\pm$ 11.31	68.28 $\pm$ 15.31	
	2	58.70 $\pm$ 11.53	65.62 $\pm$ 13.45	
	4	53.46 $\pm$ 5.26	58.51 $\pm$ 13.84	
		B	A	
Solubility	0	13.66 (4.53; 19.13) <sup>a</sup>	35.43 (29.42; 40.31) <sup>b</sup>	
	1	3.49 (1.76; 12.64) <sup>b</sup>	27.50 (22.68; 33.42) <sup>b</sup>	
	2	1.59 (-0.73; 10.14) <sup>b</sup>	31.25 (18.86; 37.4) <sup>b</sup>	
	4	-0.08 (-3.45; 14.13) <sup>b</sup>	21.23 (15.89; 24.42) <sup>b</sup>	
		B	A	

Data are presented as means  $\pm$  standard deviation. Data were analyzed using 2-way analysis of variance and the *post hoc* Tukey test, except for data from the solubility test, which were analyzed using the non-parametric Kruskal-Wallis test and the *post hoc* Dunn test. The data of the solubility test are shown as medians and (interquartile intervals, 25%; 75%).

Different letters indicate a statistically significant difference. Capital letters compare columns and lowercase letters compare lines at a significance level of  $\alpha = 0.05$ .



**Figure 1.** Graphical representation of the real-time conversion of ethanol-solvated and non-solvated experimental dental adhesives, according to the nanofiller content and the presence or absence of solvent.



**Figure 2.** Rate of polymerization (degree of conversion/sec) of ethanol-solvated and non-solvated experimental dental adhesives according to the nanofiller content and the presence or absence of solvent.

The solvated adhesives had higher solubility than the non-solvated adhesives ( $p < 0.001$ ; **Table 1**). The nanofillers reduced the solubility of non-solvated adhesives; nevertheless, this property did not show a significant difference among the adhesives containing ethanol.

### Cohesive strength

For adhesives containing ethanol, it was impossible to measure the CS, as the specimens presented bending characteristics or breaking during removal from the silicone matrix, which made the evaluation impossible. The CS of non-solvated agents was not influenced by the addition of filler ( $p = 0.608$ , **Table 2**). Storage in water (6 months) led to a significant reduction in the CS of the experimental adhesives ( $p < 0.0001$ ), regardless of their nanofiller concentration.

**Table 2.** Cohesive strength (MPa) of non-solvated experimental dental adhesives, according to the nanofiller content and the storage time

Concentration (%) of nanofiller	Storage time	
	24 hr	6 mon
0	47.7 ± 14.9	34.1 ± 11.6
1	47.6 ± 8.6	36.4 ± 11.1
2	54.5 ± 14.6	35.8 ± 14.8
4	52.5 ± 8.0	38.1 ± 12.1
	A	B

Data were analyzed using 2-way analysis of variance and the *post hoc* Tukey test. Different letters indicate a statistically significant difference at a significance level of  $\alpha = 0.05$ .

## DISCUSSION

The present study evaluated the effect of nanofillers on the properties of ethanol-solvated and non-solvated dental adhesive models. It was verified that nanofillers, at the tested concentrations, as well as in the presence of ethanol, could influence the properties of the evaluated formulae. In this sense, the null hypothesis of the present study was rejected.

The clinical procedure for adhesive application requires solvent evaporation by means of gentle air application. Unfortunately, this technique does not completely remove the solvent from the adhesive [14,15]. Mixing water and ethanol at the moment of bonding can reduce the vapor pressure of the mixture, inhibiting complete solvent evaporation. In addition, the complete evaporation of ethanol, despite the presence of water, cannot be performed within a viable clinical time frame [15]. For this reason, the evaluation of agents containing ethanol carried out in the present study, simulating the remaining solvent present at the moment of adhesive polymerization in dental procedures, is justified.

The RP and DC were both slightly affected by the presence of nanofillers, with higher values observed among adhesives containing filler particles. A possible explanation for these results may be the presence of functional silane added to the filler. Silane is a molecule that contains 2 functional groups at the end of its backbone, which promote suitable bonding between organic and inorganic substrates [24,25]. One of these functional groups is the hydrolysable alkoxy group, which is responsible for the promotion of surface bonding, in this case to the inorganic filler [25]. The other functional group present in functional silanes is the organofunctional group (methacrylate when used for methacrylate resins, as in this study), which is responsible for the promotion of bonding between the resin and the filler particles [24,25]. This bonding between the resin base and the filler materials promoted by the silane is important for the improvement of the resin's mechanical properties, maintaining a stable and reliable bond between the filler and the resin matrix. During light-curing, the uncured functional group of a resin monomer reacts with the organofunctional group of the silane agent to form a chemical bond, such as  $-C-C-$  [26]. After light activation, the free radicals formed by the initiator system react with the carbon double bonds and the silane organofunctional group, generating free radicals that, after the reaction, form a stable bond connecting the resin matrix and the filler particles [25]. Such interactions may be responsible for the better performance of filler-loaded materials than materials without filler regarding the DC and the RP.

The presence of ethanol reduced significantly the RP of adhesives. Ethanol decreased the viscosity of the system and increased intermacromolecular spacing [14,15], negatively impacting the RP. This RP reduction may explain the lower DC obtained for the solvated

resins at 20 seconds. Unlike non-solvated resins, the DC of the adhesives containing ethanol was influenced by the addition of filler, with better conversion after 20 seconds of activation for adhesives containing 1 wt% and 2 wt% filler. The presence of filler reduced system viscosity, thereby decreasing the intermolecular space, facilitating molecular interactions, and consequently promoting higher RP, as observed. This fact, associated with the interaction of the monomers and the silane on the filler particles [24,25], seemed to increase the DC for these filler concentrations (1 wt% and 2 wt%).

The final DC (after 80 seconds of real-time evaluation) was higher for ethanol-solvated adhesives than for non-solvated adhesives. The higher viscosity of non-solvated resins may have caused a premature reduction of chain mobility compared to solvated agents, in which the interaction of monomers is inhibited by the entrapment of the formed chains [27,28]. The higher fluidity of solvated adhesives allows higher chain mobility, increasing the final DC [14,15,28].

Although the nanofiller had no influence on water sorption, the presence of ethanol was crucial for increasing this property in the experimental adhesives. The solvent dilutes the concentration of monomers, increasing the space between the forming chains. Through this process, ethanol can be entrapped between the formed chains, and is dislocated by water, increasing water sorption [28]. For the same reason, the presence of ethanol increased the solubility of the model adhesives, lixiviating the ethanol present in the polymer, as well as the unreacted monomers. For the non-solvated adhesives, the addition of filler positively influenced the solubility of the agent. A possible explanation for this result is the higher DC obtained in the filled materials, probably promoted by the interaction between the monomers and the silane in the polymerization process [25].

One of the objectives of this study was to evaluate the influence of nanofillers on the CS of ethanol-solvated and non-solvated adhesives. However, after preparation, the specimens of ethanol-solvated resins broke upon removal from the silicone molds or became bent, which made the evaluation impossible. For non-solvated adhesives, the addition of filler neither influenced the CS nor avoided/reduced hydrolytic degradation after 6 months in water. These results disagree with those of a previous study that demonstrated some benefits of filler addition for the mechanical properties of model adhesives [11]. The difference between the results of the present study and those of the previous study can be explained in terms of differences in the monomeric composition, filler size, and the amount of filler used. In contrast, the results of this study corroborate those of a previous study that evaluated the influence of nanofillers on adhesive properties, in which the addition of similar concentrations of filler to those tested in the present study did not increase the CS of the materials compared to the unfilled adhesive model [10]. Another study demonstrated that the use of nano-clay as a filler reduced enamel microleakage; however, similar to the results observed in this study, dental adhesive stability was not observed after 6 months of storage in water [29]. Although the CS of the polymer was not maintained after 6 months of water immersion in this study, the addition of nanofiller had a positive influence on the materials' DC and solubility. Combining these results with those of previous studies [10,11], the addition of filler particles should be considered as an interesting approach to the improvement of dental adhesive properties.



## CONCLUSIONS

The addition of nanofillers positively influenced the analyzed chemical and physical properties of adhesive models. The addition of ethanol promoted changes in the evaluated properties, such as a reduction in RP, an increase in water sorption, and an increase in the final DC.

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