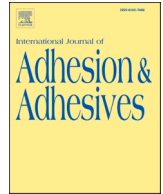




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Silver nanoparticles added to a commercial adhesive primer: Colour change and resin colour stability with ageing

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ABSTRACT

This study evaluated the influence of silver nanoparticles (NAg) incorporated into the primer of a three-step adhesive system (Scotch-Bond Multi-purpose) over the composite-resin colour (CIELab and CIEDE 2000) as a function of the concentration and ageing methods. Ninety specimens were prepared and distributed into 6 groups (n = 15), according to the NAg concentration: NAg 0 (0 wt%); NAg 50 (0.005 wt%); NAg 100 (0.010 wt%); NAg 150 (0.015 wt%); NAg 200 (0.020 wt%); NAg 250 (0.025 wt%). Initial colour readings were performed to evaluate colour change (CC) after NAg addition to primers. Readings after 30 days of storage in water (30D), thermocycling (TC), and accelerated artificial ageing (AAA) were performed to verify the influence of each method over CC. Data was calculated according to CIELab and CIEDE 2000 systems and analysed with one-way and two-way ANOVA ($p \leq 0.05$), complemented with post-hoc Tukey test. Data presented normality, homoscedasticity, and statistical difference. ΔE_s gradually increased according to the percentage of added NAg into the primer. Thermocycling and UV light exposure induced a higher colour change when compared to water ageing (D30). Significant statistical difference was found for all ageing methods. CIEDE 2000 and CIELab are similar methods of colour evaluation. Besides, primers with up to 0.025 wt% applied in cavities deeper than 1 mm were colour-safe and did not jeopardise the aesthetic perception of the simulated restoration.

1. Introduction

The antimicrobial property of silver is well known since ancient Greece [1], and the use of silver nanoparticles (NAg) applied to Dentistry started its spreading in 19th century [2]. These nanoparticles' biological, chemical, and mechanical properties have been widely investigated with concern to their use to inhibit biofilm formation [3], to achieve an antimicrobial effect [4–8], and to avoid hard dental tissue demineralisation whilst preserving their properties [9]. Its small size and associated large superficial area make NAg effective against many microorganisms [2] and suitable for use with different dental materials [3,8,9].

Evidence that the addition of 0.05–0.1 wt% of NAg to adhesives did not interfere in the adhesive bond strength have been shown [6]. Besides

presenting an antimicrobial effect against *S. mutans* [2,3,8], such nanoparticles did not exhibit significant cytotoxicity and have been safely used over fibroblasts [6] and human dental pulp stem cells [3]. However, consensus still lacks regarding the maximum concentration of NAg that can be safely applied, as it is known that higher concentrations may interfere on material's mechanical and biological properties whilst inducing undesirable colour changes [6,10].

The incorporation of metallic nanoparticles might interfere on light absorption and refraction [11], jeopardizing the visual properties of restorative materials. The colour of nanoparticles depends on which material the core is made of. It also depends on the production and incorporation process, since their size and shape, as well as aggregation state, are strongly influenced by those parameters regardless of origin [11]. Depending on the heating time and temperature used in the silver

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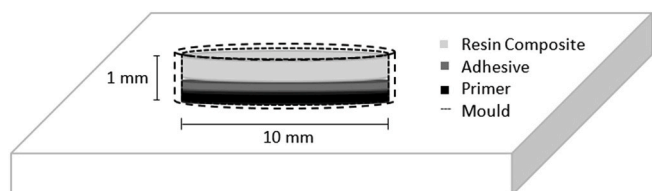


Fig. 1. Scheme of mould and specimens preparation over a flat glass plate.

nanoparticles obtention, their shape might change and so does their colour. Rounded corners or spherical shaped nanoparticles have a light yellow-orangish colour [11], whilst cubic- and tetrahedron-shaped nanoparticles present a brighter yellow colour and darkish red hues [12]. Some authors report colour alterations during the NAg synthesis [9], or when applied to thermally activated acrylic resins [13].

However, literature lacks information concerning colour change related to NAg-modified adhesive systems.

In vitro ageing methods are used to evidence colour change on resin-based materials. Seven-to thirty-day water ageing promotes water saturation, but it does not always induce colour change [10]. Thermocycling (T) may cause superficial microcracks and silane deterioration [14–16], as the matrix and inorganic fillers of resin-composites have different linear thermal expansion coefficients. Furthermore, upon exposure to 300 h of accelerated artificial ageing (AAA), the ultraviolet light can be absorbed by non-polymerized amines [10,17,18], and that process can be used to simulate one year of clinical service [19].

After a cavity preparation, the primer is usually the first agent to get in contact with the dental tissue. The eventually remaining bacteria can compromise the restoration durability, and for that reason, a primer with antimicrobial properties is highly desirable. To assure that the addition of NAg into the primer of a three-step adhesive system will not

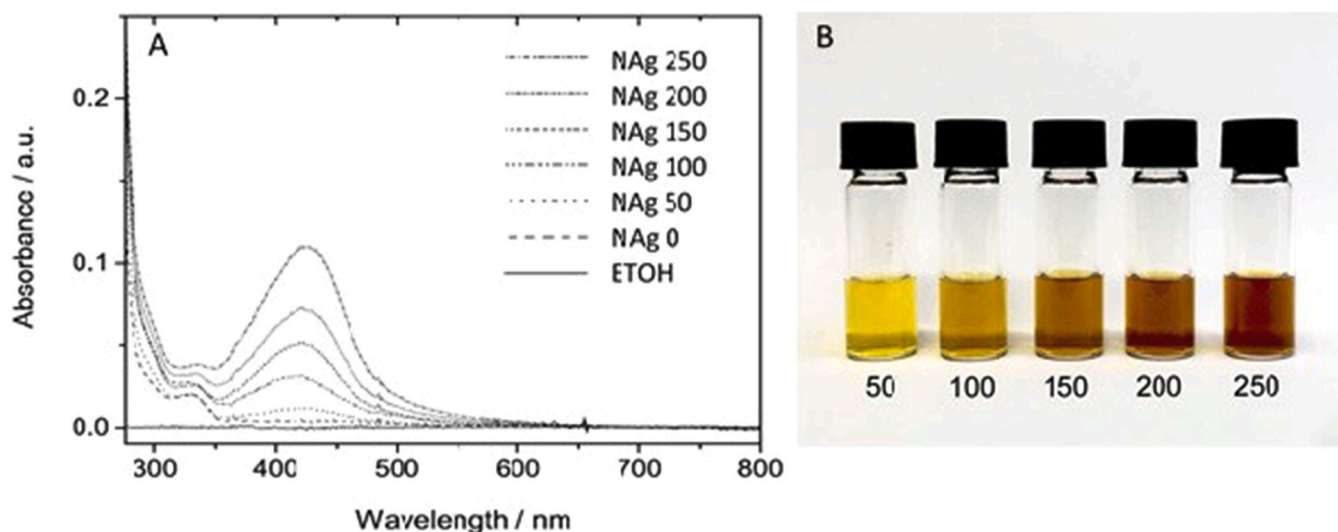


Fig. 2. A-B - UV-vis spectra of the experimental primers (A) obtained using a 1-mm path quartz cuvette and experimental primers containing different NAg concentrations (B).

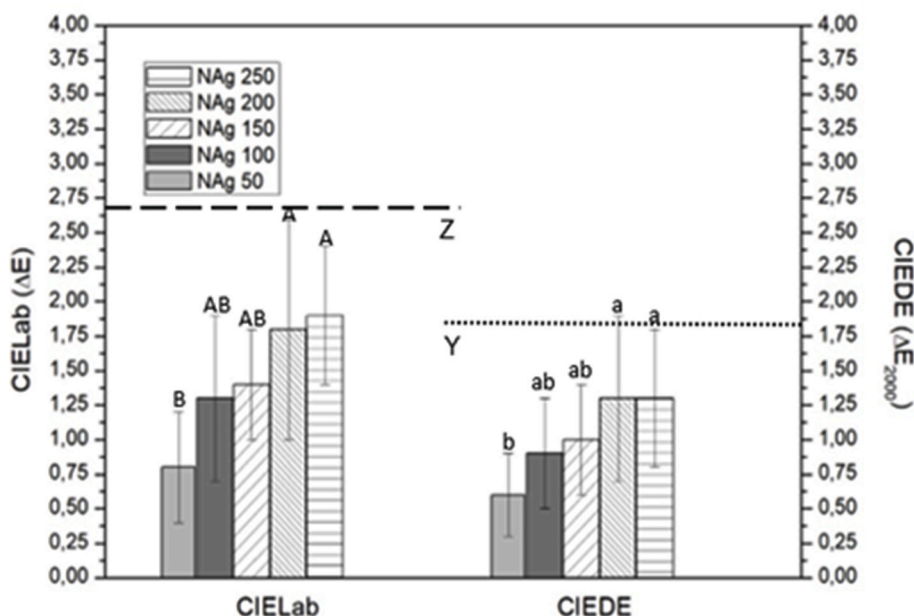


Fig. 3. Influence of the addition of different NAg concentrations on ΔEs. Z represents CIELab acceptability limit (2.7) and Y, CIEDE threshold (1.8).

Table 1
Mean and standard deviations of a* and b* according to % NAg – Water ageing.

% NAg	Before ageing		After ageing	
	a*	b*	a*	b*
0	-0.8 ± 0.1	14.0 ± 0.4	-0.6 ± 0.1	13.6 ± 0.3
0.005	-0.5 ± 0.2	14.8 ± 0.4	-0.4 ± 0.1	14.2 ± 0.5
0.001	-0.3 ± 0.2	15.6 ± 0.4	-0.6 ± 0.3	14.4 ± 0.4
0.0015	-0.6 ± 0.2	15.1 ± 0.6	-0.7 ± 0.2	14.2 ± 0.4
0.002	-0.5 ± 0.1	15.7 ± 0.8	-0.9 ± 0.4	14.6 ± 0.6
0.0025	-0.6 ± 0.2	15.6 ± 0.5	-0.8 ± 0.3	15.0 ± 0.4

Table 2
Mean and standard deviations of a* and b* according to % NAg – Thermocycling.

% NAg	Before ageing		After ageing	
	a*	b*	a*	b*
0	-1.0 ± 0.3	17.5 ± 0.5	0.4 ± 0.5	11.8 ± 0.7
0.005	-1.1 ± 0.2	17.3 ± 0.5	0.5 ± 0.2	12.0 ± 0.7
0.001	-1.0 ± 0.2	18.0 ± 0.3	0.6 ± 0.1	12.7 ± 0.3
0.0015	-0.8 ± 0.2	17.7 ± 0.3	0.6 ± 0.2	12.7 ± 0.9
0.002	-0.8 ± 0.2	18.5 ± 0.9	0.8 ± 0.1	12.8 ± 1.1
0.0025	-0.7 ± 0.3	18.1 ± 0.2	0.8 ± 0.2	13.2 ± 0.6

Table 3
Mean and standard deviation of a* and b* according to % NAg – Accelerated Artificial Ageing.

% NAg	Before ageing		After ageing	
	a*	b*	a*	b*
0	-0.4 ± 0.1	15.7 ± 0.2	2.4 ± 0.2	22.4 ± 0.9
0.005	-0.6 ± 0.2	15.7 ± 0.3	2.7 ± 0.2	23.4 ± 0.2
0.001	-0.6 ± 0.2	16.7 ± 0.4	2.9 ± 0.2	23.7 ± 0.1
0.0015	-0.5 ± 0.2	16.4 ± 0.8	2.5 ± 0.1	22.6 ± 0.4
0.002	-0.5 ± 0.2	16.6 ± 0.6	2.7 ± 0.1	23.0 ± 0.8
0.0025	-0.6 ± 0.1	17.0 ± 0.4	2.6 ± 0.2	23.5 ± 0.6

interfere in the colour of the restoration, the interaction between these nanoparticles and this type of materials needs to be investigated.

Thus, this study aims to evaluate the influence of different concentrations of NAg (0.005 wt% - 0.025 wt%) incorporated into a primer of a three-step adhesive system on the colour of the resin composite (simulating a bonded restoration), before and after ageing.

2. Materials and methods

2.1. NAg synthesis and experimental primers preparation

Monodisperse and fully dispersible 20 nm NAg were prepared according to the previously described method [3]. Briefly, 11.7 mL of an ethanolic solution containing 5 wt% of polyvinyl alcohol (MM 100,000) were heated at reflux, for 5 min. Then, 1.5 mL of an aqueous AgNO₃ (0.171 g) solution was added and the mixture was kept under reflux for 10 min, leading to a yellowish-brown hue solution. After that, the reaction medium was immediately cooled to room temperature, filtered through a 0.22 µm PVDF membrane syringe filter for the removal of eventual aggregates and stored at 4 °C, protected from direct light incidence. The primers modified with different concentrations of NAg were prepared by diluting a 1 wt% NAg stock dispersion in ethanol and incorporating a suitable volume directly into the SBMP primer (Scotchbond™ Multi-Purpose, 3 M ESPE, St. Paul, MN, USA) under vigorous stirring, whilst keeping the primer concentration constant at 97.5 wt% in the samples. The NAg concentrations in the primer were

adjusted to 0.005, 0.01, 0.015, 0.02, and 0.025 wt%.

2.2. Primer samples colour analysis

Direct readings were performed using a 1.0-mm optical path quartz cuvette, in an Agilent UV–vis spectrophotometer (model HP8453A, Santa Clara, CA, USA) equipped with tungsten and deuterium lamps, and a diode array photodetector for prompt reading in the 190- to 1100-nm range, and 1-nm resolution.

2.3. Sample preparation

Ninety resin composite (Filtek™ Z350 XT 3 M ESPE, St. Paul, MN, USA) disk-shaped specimens (see Fig. 1), shade A2B, were prepared (n = 15) on a flat glass plate. To simulate the steps of a clinical restoration the following sequence was performed:

- 1 Ten (10) µL of a NAg-primer mixture was put into a Teflon™ mould (inner diameter:10 mm; height: 1 mm);
- 2 Air-sprayed for 5 s;
- 3 Ten (10) µL of SBMP bonding agent was put into the mould;
- 4 Photo polymerisation for 10 s;
- 5 Resin composite was applied;
- 6 A microscope slide was pressed over the resin to obtain a flat surface;
- 7 Final 20-s photopolymerisation [20].

After that, specimens were stored for 24h in distilled water, at 37 °C, for post-polymerisation. The control group was prepared with the commercial SBMP primer and bond.

The groups were divided according to their NAg concentration (wt%) and named according to the corresponding value in ppm: NAg 0 (0 wt%); NAg 50 (0.005 wt%); NAg 100 (0.010 wt%); NAg 150 (0.015 wt%); NAg 200 (0.020 wt%); NAg 250 (0.025 wt%).

2.4. Colour analysis

Colour changes can be calculated according to differences on lightness, chroma and hue, as represented by the CIELab coordinates: +L* (lightness); -L* (darkness); +a* (red); -a* (green); +b* (yellow); and -b* (blue). Another formula used to evaluate colour is the CIEDE2000, a CIELab-based formula with corrections: lightness, chroma, and hue weighting functions (K_LS_L, K_CS_C, K_HS_H), the so-called rotation function - an interactive term between chroma and hue for greater blue colour performance - and a rescaling factor (R_T) to improve performance for grey colours.

The colour measurements were performed on a white plate (ISO 7491) with a spectrophotometer (CM-3700d, Konica Minolta Inc, Tokyo, Japan), with 2nd standard observer and D65 illuminant. The CIELab scale (a) was chosen to allow the comparison with previous CIELab findings, and the CIEDE 2000 scale (b) was selected due to its more complex CIELab-based formulas, and for being considered clinically superior as far as colour change detection is concerned [21]. Initial readings were performed after sample preparation to evaluate if the addition of NAg to primers could jeopardise material colour, whilst final readings were performed after ageing to assess its influence on NAg-modified resin samples.

$$(a)\Delta E = [(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2]^{\frac{1}{2}}$$

$$(b)\Delta E_{00} = \left\{ \left[\frac{\Delta L^*}{(K_L S_L)} \right]^2 + \left[\frac{\Delta C^*}{(K_C S_C)} \right]^2 + \left[\frac{\Delta H^*}{(K_H S_H)} \right]^2 + R_T \left[\frac{\Delta C^*}{(K_C S_C)} \right] \times \left[\frac{\Delta H^*}{(K_C S_C)} \right] \right\}^{\frac{1}{2}}$$

2.5. Ageing

The samples were submitted to three different *in vitro* ageing methods. Water ageing was used to allow water saturation, and thermocycling was used to simulate the buccal temperature variation and its humidity conditions. Accelerated artificial ageing (AAA) has been used as a weatherproof challenge to induce a colour change in resin-based materials, as it combines the possible degradation caused by light, water, and temperature. For D30 water ageing assays, samples were individually immersed for 30 days in 3 mL of distilled water at 37 °C. The water was changed every seven days to avoid biological contamination. The thermocycling (TC) experiments were performed by cycling the samples 10,000 times at temperatures ranging from 5 °C to 55 °C, fixing the immersion bath time to 30 s to verify the possible colour change induction [22]. The AAA assay was carried out by immersing the samples in 3 mL of deionized water, subjecting to a weathering machine (Suntest CPS+, Atlas Material Testing Technology, Gelnhausen, Germany) for 300 h with 2-h UV light cycles (765 W/m²) exposure at 55 °C, and 1 h without exposure at 37 °C (ISO 7491) [23].

The results of the ΔE related to the addition of NAg to primers were evaluated with one-way ANOVA, whilst the interaction between ageing and concentration was assessed with two-way ANOVA. The Tukey pairwise comparison test was performed (α = 0.05).

3. Results

The colour analysis of the primers incorporated with different concentrations of NAg is presented in Fig. 2. The UV–vis electronic spectra were obtained directly from experimental primers, without dilution, in a 1-mm path quartz cuvette. The experimental primers' UV–vis spectra showed a characteristic band, centred at 421 nm that was proportional to the concentration of NAg. This band is missing in the SBMP primer alone and can be attributed to the confined Surface Plasmon Resonance Band (SPB) of Silver Nanoparticles.

The SPB is known as a broad and robust band observed in UV–visible

absorption spectrum of gold, silver, and other metallic nanoparticles. The SPB band shape, position, and intensity are strongly dependent on the surrounding medium, size, shape, electronic interactions of the stabilising ligands with the nanoparticle, and the state of agglomeration [24,25]. Therefore, a careful control on the incorporation process is necessary to avoid any possible aggregation responsible for the appearance of absorption bands at the lower energy regions of the spectrum. For the 20-nm monodisperse and spherical NAg used in this study, the SPB band was responsible for the yellowish-brown colour in the experimental primers (Fig. 2 B).

ΔEs of the influence of NAg addition to primers are shown in Fig. 3. Means and standard deviations for a* and b*, for each NAg wt%, before and after ageing are given in Tables 1–3. As expected, the colour analysis of the modified primers showed high absorbances for high NAg wt% (Fig. 2 A). Data presented normality (CIELab: p > 0.150; CIEDE 2000: p > 0.150) and homoscedasticity (CIELab: p = 0.263; CIEDE 2000: p = 0.187). ΔEs gradually increased according to NAg concentration. One-way analysis of variance and Tukey tests showed statistical significance between NAg 50, NAg 200 and NAg 250 for both mathematical systems (Fig. 3).

The two-way ANOVA results demonstrated that the main factors are statistically significant, and there is an interaction of primers and ageing parameters. The Tukey interaction test (Fig. 4) evidenced that the exposure to UV light and thermocycling induced a higher colour change than the one verified with D30 water ageing (Fig. 4). Significant statistical difference was found between all ageing methods whilst similar behaviour was observed for CIELab and CIEDE 2000.

The a* and b*, before and after D30, T, and AAA tests are listed in Tables 1–3, respectively. Water ageing (D30) did not influence results of a*, whilst b* showed a slight decrease. Thermocycling increased a* and decreased b*, which means that specimens became more reddish and less yellowish, respectively. After AAA, the yellow and red hues of the samples are enhanced due to the simultaneous increase of a* and b*.

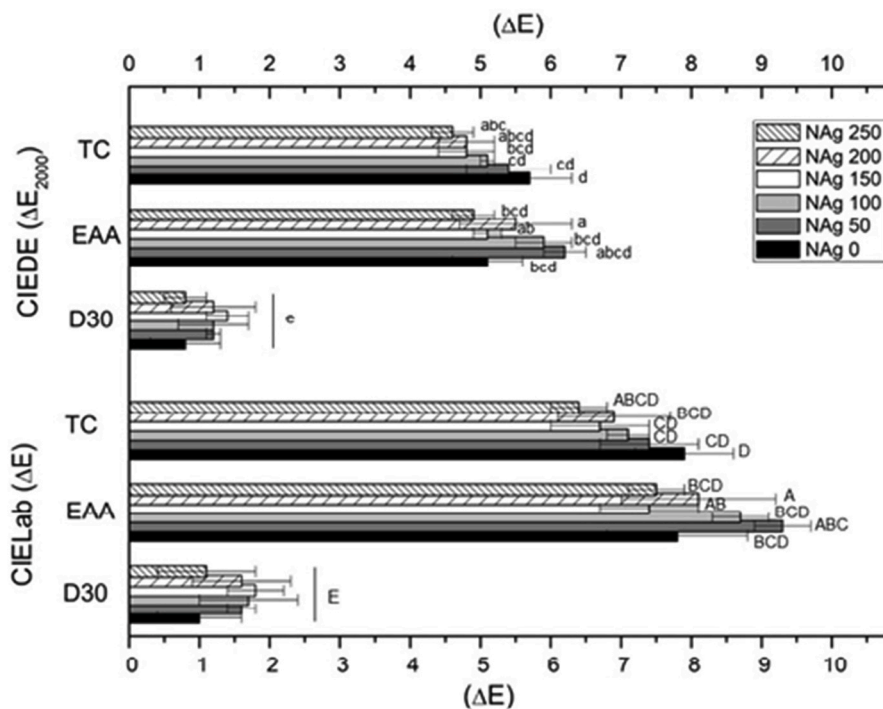


Fig. 4. ΔEs for both mathematical systems according to NAg concentration and ageing method.

4. Discussion

The present study investigated the effect of NAg-primers and different ageing in the colour of resin composite simulated restorations. The ΔE variation was clinically acceptable (CIELab $\Delta E \geq 3.3$; CIEDE $\Delta E \geq 1.8$) when adding up to 0.025 wt% of NAg. The colour after ageing was different according to each ageing method. Although three different ageing methods were chosen in this study, there is still no method that could faithfully represent the clinical ageing condition. Also, the methodology of NAg incorporation states that it must be incorporated into the primer, limiting their usage in one-step adhesives.

The aesthetic perception is a subjective topic, as the individual concept of beauty is personal. Therefore, the ideal colour of an aesthetic restoration may depend on the patient and clinician perspectives, mood, age, gender, room lighting conditions, and evaluator bias [26]. For matching the visual aspects of materials and dental tissues, the colour might be explored by ΔE measurements. An acceptable ΔE has been already reported for CIELab and CIEDE 2000: $\Delta E \geq 3.3$ are considered clinically unacceptable [27–29], whilst others suggest that the acceptable limit is 2.7 for CIELab and 1.8 for CIEDE 2000 [30].

Pearson's correlation test of the NAg wt% added to the primers for CIELab and CIEDE 2000 was positive ($p = 0.99$) and ΔE_{00} were lower than ΔE_{ab} (Figs. 3 and 4). This seems to corroborate the assumption that CIEDE 2000 is more accurate and clinically superior to detect colour change [21,30]. However, very similar results were achieved using both CIELab and CIEDE 2000, suggesting that both methods will similarly evaluate colour change. Moreover, the colour values of both mathematical systems remained under the respective limits.

The gradual incorporation of conservatory NAg into primers performed in the present study was directly associated to primer's chroma, as higher absorbance peaks were observed following the increase in NAg concentration (Fig. 2A and B). The same response was noticed with ΔE values (Fig. 3); however, for both mathematical systems, they remained under the acceptable reported limit [26–29].

Nevertheless, it was reported in literature [6] that the addition of 0.2 wt% of NAg to SBMP reduced the adhesive resistance and changed the colour of the material, though NAg concentration reduction to 0.05–0.15 wt% NAg was biologically safe to fibroblasts and did not compromise either adhesive or visual aspects. A previous study [3] with conservative NAg concentrations (0.005 wt% - 0.025 wt%) considered 250 ppm NAg an optimal concentration for best bactericide and bacteriostatic effects without jeopardizing human dental pulp stem cells viability and bonding strength. Therefore, conservative concentrations should be a viable alternative when the colour is a relevant parameter to be considered, whilst concentrations higher than 0.025 wt% should be further investigated.

The D30 had the lowest ΔE , which might be due to the constant temperature of the water-saturated sample, which was probably not enough to induce a colour change. The AAA method provided the most significant colour change, possibly due to the combination of temperature cycling and UV light exposure. According to literature [19], 300h of exposure to UV light, as performed in the AAA, is capable to simulate one year of clinical service. However, the high ΔE found to AAA (Fig. 4) might not correspond to a real one-year clinical situation as a patients' restoration might not be exposed to the same amount of UV irradiation as inside the ageing machine. On the other hand, the temperature variation of the oral cavity is present in a patient's daily basis routine and thus, the authors suggest that thermocycling might be the ageing method that best simulates the physical conditions (temperature and humidity) of the oral environment.

The yellowness of the restoration is the most patient-perceived aspect [26]. After thermocycling and artificial accelerated ageing, all groups, including control, presented a positive change both on a^* (redness) and b^* (yellowness) after been submitted to TC and AAA (Tables 2 and 3). Water may degrade the silane [15] whilst temperature cycling may cause internal tensions and microcracks [14,16] on the

structure of the material as consequences of the different linear thermal expansion coefficients. Also, non-polymerized amines may react with oxygen and aromatic groups upon UV light irradiation, and the material tends to get more yellowish or reddish [27,31]. Therefore, the colour stability of an adhesive material will probably depend on its composition and the way monomers and fillers react under chemical, physical, and thermal changes. The camphorquinone + tertiary amine system is a traditional photoinitiator that requires a co-initiator for polymerisation reaction optimisation [32]. Over time, this co-initiator undergoes oxidation, leading to colour instability [33].

Additionally, the interface between fillers and organic matrix might undergo hydrolysis and degrade the silane, also leading to colour change. All experimental groups, including the control group (NAg 0), presented significant ΔE after ageing. Accordingly, the colour change seems to be primarily associated with the material composition itself. The presence of NAg in the matrix was not significant to promote any additional colour change, demonstrating the high stability and potential of spherical silver nanoparticles as antimicrobial agents of the SBMP primer.

This is important to notice that future studies are needed to incorporate the nanoparticles within adhesives that present different primer chemistry compositions and different adhesive strategies.

5. Conclusions

The addition of NAg into the primer of SBMP increased the ΔE ; however, it remained under the acceptable limit reported in the literature of 2.7 - CIELab and 1.8 - CIEDE 2000, as far as colour change is concerned. Therefore, within the limitations of an *in vitro* set-up, the present study demonstrated that the use of primers with NAg up to 0.025 wt% in cavities more than 1 -mm deep does not change the colour perception significantly and is colour safe. CIEDE 2000 and CIELab methods presented similar results, and both might be used for colour evaluation of resin-based materials. Even though the same material was applied in the deepest layer of the simulated restoration, they presented different ΔE s after each ageing assay. This difference indicates that ageing studies should be carried out with at least two different methods to ensure robust results supporting the colour change investigations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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