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Original

The effect of amine-free initiator system and the polymerization type on color stability of resin cements

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Abstract: We investigated the short-term (4 weeks) color stability of light-cure and dual-cure resin cements. Sixty disk-shaped test specimens of adhesive resin cement (10 × 1 mm) were prepared. One feldspathic porcelain test specimen (12 × 14 × 0.8 mm) was prepared from a prefabricated ceramic block. The feldspathic sample was placed on the resin cement disk and all the measurements were performed without cementation. Specific color coordinate differences (ΔL, Δa, and Δb), and the total color differences (ΔE) were calculated after immersion in distilled water for different periods. Data were compared using one-way analysis of variance (ANOVA) ($\alpha = 0.05$). The test results revealed that different chemical structures and curing modes affected the ΔE values ($P < 0.05$). The highest ΔE values were obtained for RelyX Unicem dual-cure cement (2.14 ± 0.40), and the lowest for NX3 light-cure cement (0.78 ± 0.34). Third generation adhesive resin cement free of tertiary amines and benzoyl peroxide showed relatively slight color change in both test groups (light-cure and dual-cure resin cement). (J Oral Sci 58, 157-161, 2016)

Keywords: color stability; polymerization; resin cement.

Introduction

Tooth-colored restorative materials have been widely used in dental practice to meet esthetic demands of patients (1-3). Ceramic restorations, including laminate veneers, inlays, onlays, and crowns are among the most popular choices; however, these restorations must be bound to the natural tooth surface using adhesive cement. Cements are categorized according to their polymerization type or bonding procedure, and include total etch, one-step etch bond, self-adhesive resins, chemically cured resins, dual-cure resins, and light-cured resins (3-5). Different cements and cementing processes are necessary for different types of restorations.

Laminate veneer is a unique case of dental restoration method. In general, the laminate veneer restorations are relatively thin and reflect the color of cement, which is often a light-cured resin. Dual-cure resin cements are also used for restorations in places of difficult access; they can be polymerized in areas where the curing light cannot penetrate (5).

Discoloration of resin cements is a common problem, particularly in translucent restorations. In fact, color changes in the restorations and the surrounding tissue are the primary reasons for the replacement of esthetic restorations (3).

Discoloration can be due to either extrinsic or intrinsic factors. The extrinsic factors include stains caused by food, smoking, and beverages (6). The intrinsic factors are directly related to the restorative material, such as the chemical composition of the material, filler type, composition of the resin matrix, photoinitiator type, polymerization type, and the ratio of the carbon-carbon

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Table 1 Tested adhesive resin materials

Product	Group	Shade	Polymerization type	Initiator system	Content	Manufacturer
NX3	NXLC	Clear	Light cure	Free tertiary amines and benzoyl peroxide	Uncured methacrylate ester monomers, inert mineral fillers, activators and stabilizers, and radiopaque agent glycerine, water, fumed silica and inert glass powder, gelatin	Kerr, Canada
Rely X Veneer	RXV	Translucent	Light cure	Distinct amines react with camphoroquinone	BISGMA and TEGDMA polymer	3M Espe, USA
Variolink Veneer	VRV	Value 0	Light cure	Distinct amines react with camphoroquinone	Dimethacrylates, inorganic fillers, ytterbium trifluoride, catalysts and stabilizers, pigments	Ivoclar-Vivadent, Liechstein
NX3 Dual Cure	NXDC	Clear	Dual cure	Free tertiary amines and benzoyl peroxide	HEMA, PTU, CHPO, uncured methacrylate ester monomers, titanium dioxide, and pigments	Kerr, Canada
Variolink II	VRDC	Transparent	Dual cure	Distinct amines react with benzoyl peroxide (redox polymerization system)	Barium glass, ytterbium trifluoride, Ba-Al-F silicate glass, spheroid mixed oxide (%46 v, %70 w) BISGMA, UDMA, TEGDMA	Ivoclar-Vivadent, Liechstein
Rely X Ultimate	RXU	Translucent	Dual cure	Distinct amines react with benzoyl peroxide (redox polymerization system)	Methacrylate monomers, radiopaque silanated fillers, initiator, stabilizer, rheological additives. Catalyst paste: methacrylate monomers, radiopaque alkaline (basic) fillers, initiator, stabilizer, pigments, rheological additives	3M Espe, USA

BISGMA: Bisphenol-A-diglycidyl ether dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; HEMA: hydroxyethyl methacrylate; PTU: pyridyl thiourea; CHPO: cumene hydroperoxide.

double bonds (7-10). The discoloration caused by intrinsic factors is accelerated by UV irradiation and temperature changes (11). Dual-cure resins contain tertiary amines and benzoyl peroxide and tend to darken over time. In contrast, the color of the photo-initiator camphoroquinone, commonly used in light-cured cements, is more stable. Insufficiently polymerized camphoroquinone however, gradually yellows (3,8,12). To prevent discoloration, some resin cements have been made without a tertiary amine photoinitiator. Recently, new resin cements without a benzoyl peroxide/amine redox initiator system have been shown to be more color-stable (13). In clinical practice, a discoloration of fully polymerized resin cements has also been observed, even after a short time. However, most of the discolorations depend on the intrinsic factors and the chemical structure of the cement. Many studies have examined the color stability of resin cements (14-16). However, most of them have investigated just the extrinsic factors. Only a few studies have focused on the resin cement material itself (17-19), despite the known effect of the resin color on the final restoration (20).

The objective of this study was to compare the short-term color stability of light-cured and dual-cured resin cements, using an amine-free initiator system. The null hypothesis for this research was that the chemical structure and polymerization type of the resin cements would not affect color stability.

Materials and Methods

The composition and the polymerization type (given by the manufacturers) of the test specimens used in this study are listed in Table 1. The table also contains the names and definitions of the experimental groups. The specimens were of 10 mm diameter, corresponding to the spectrophotometer sample compartment size, and of 1 mm in thickness as required by ISO 7491:2000 (21) ($n = 10$). An acrylic mold was used. The specimens were light-cured directly using an LED curing unit (Elipar S10; 3M ESPE AG, Seefeld, Germany) for 40 s, at four equidistant points on the disk. The light irradiance was measured with a radiometer (LED Demetron, Demetron Research Corp., Danbury, CT, USA), and confirmed for all groups as 850 mW/cm^2. The specimens were ground using a series of silicon carbide papers (#200, 400, and 600). The grinding and polishing procedures were performed on one side of the specimens to obtain 1.0 mm thickness. The thickness was checked using a digital micrometer (MDC-25 M, Mitsutoyo, Tokyo, Japan). One feldspathic porcelain test specimen (12 × 14 × 0.8 mm) was prepared from a prefabricated ceramic block (CEREC Blocks, Sirona Dental Systems GmbH, Bensheim, Germany). Each specimen was immersed in 100 mL of distilled water at 37 ± 2°C for 24 h and 4 weeks. Before the colorimetric measurements, the resin specimens were cleaned using an ultrasonic cleaner in distilled water for 10 min and dried with oil-free

Table 2 Mean and standard deviation of the color difference (ΔE) values after immersion in distilled water for 4 weeks

Polymerization type	Test groups		Distilled water immersion Start (1 day)	4 weeks	ΔE values*
Light cure	NXLC	L	84.64	84.27	0.78 ± 0.34[a]
		a	−0.27	−0.09	
		b	6.76	6.62	
Light cure	VRV	L	83.87	83.02	0.97 ± 0.24[a]
		a	2.19	2.17	
		b	7.97	8.29	
Light cure	RXV	L	86.7	85.95	1.01 ± 0.33[a]
		a	−0.6	−0.65	
		b	4.72	5.24	
Dual cure	NXDC	L	85.9	85.15	1.08 ± 0.34[a]
		a	−1.06	−1.04	
		b	6.84	7.17	
Dual cure	VRDC	L	85.57	83.18	1.21 ± 0.53[a]
		a	-0.16	−0.01	
		b	5.77	5.57	
Dual cure	RXU	L	84.71	82.29	2.14 ± 0.40[b]
		a	−0.33	−0.37	
		b	7.47	7.36	

*In "ΔE values" column, different letters indicate a significant difference.

Table 3 One-way ANOVA test results

	Sum of squares	df	Mean square	F	Sig.
Between groups	7,016	5	1,403	9,911	0.000
Within groups	4,248	30	142		
Total	11,264	35			

compressed air for 30 s. The CIE L*a*b* values of the polished surfaces of each specimen were measured on a white surface. To simulate the clinical conditions, the feldspathic porcelain specimen was placed on the resin cement disc and all the measurements were performed on the specimen without cementation. Before each measurement, the spectrophotometer (Vita Easyshade, Vident, Brea, CA, USA) was calibrated according to the manufacturer's recommendations. Specific color coordinate differences (ΔL, Δa, and Δb) were calculated on the first day and after 4 weeks of immersion in distilled water. The total color differences (ΔE) were calculated using the following formula; $\Delta E = ((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)^{1/2}$, where L refers to the brightness, a stands for the redness to greenness, and b for yellowness to blueness. High ΔE value indicates a large color difference. Three measurements were taken for each specimen, and the average values were calculated.

Statistical analyses were performed using SPSS software program (SPSS 21.0, IBM SPSS Statistics, Armonk, NY, USA). According to Kolmogorov-Smirnov test results, all the data showed a normal distribution ($P >$ 0.05). The data were statistically analyzed using one-way ANOVA. Homogeneity of variance was examined using Levene's test ($P > 0.05$). For multiple comparison of mean values, the Tukey's honestly significant difference test was used ($\alpha = 0.05$).

Results

All the mean L*a*b* values and ΔE values are listed in Table 2. One-way ANOVA test results (Table 3) revealed that different resin cements with different chemical structures and curing modes affected the ΔE values ($P < 0.05$).

The highest ΔE values (total color difference) were obtained in the Rely X Ultimate RXU (2.14 ± 0.40) group (see Table 1 for group characteristics), and the lowest in the NX3 NXLC (0.78 ± 0.34) group. All the light-cure resin cements showed lower ΔE values than the dual-cure resin cements. The resin cements with the amine-free initiator system (NXLC and NXDC) had relatively low ΔE values in both light-cure and dual-cure resin cement groups. However, only the RXU group showed a significant difference in comparison with other test groups ($P <$ 0.05). Although there was no significant difference ($P >$

0.05), most of the dual-cure resin cements showed higher ΔE values when compared with light-cure resin cements.

Discussion

The findings of this *in vitro* study demonstrated that our null hypothesis (the chemical structure and polymerization type of the adhesive-resin cements do not affect color stability) should be rejected. In practice, the short-term color stability of the resin cement is important because the discoloration of restorations, after cementation, is esthetically unappealing. This study evaluated the effect of different light- and dual-cure resin cements on the internal color stability.

Color changes are generally determined using a spectrophotometer. The CIE L*a*b* system, one of the most common color measurement systems in use, was employed in this study to evaluate three different color parameters (10): the changes in shade ΔL, the changes in hue on the red/green scale Δa, and the changes in hue on the yellow/blue scale, Δb (22). The spectrophotometry data were translated into quantitative values (23). There are different opinions on what constitutes a noticeable color change (24).

In recent years, the ΔE values of 1.028 and 2.629 were used for the interpretation of visual thresholds (24) for the direct restorative dental materials and dentures, respectively (25), because these values reflect a 50% drop in perceptibility. For other materials, the reported 50% acceptability thresholds were set at the ΔE value of 2.7 for resin disks, 3.3 for direct restorative dental materials, and 5.5 for dentures (25,26).

The resin cement thickness used in this study (1 mm) was larger than the thickness used in clinical settings. However, it was chosen according to the ISO standards (21) and spectrophotometry requirements. Our aim was to measure the color changes of light- and dual-cure resin cements, simulating the clinical conditions for the feldspathic porcelain, which has a thickness of 0.8 mm. Only one ceramic material, color, and thickness were selected for standardization; however, the porcelain test samples were not cemented because the surface treatments can alter the light transmission and color stability.

Previous reports have suggested that the resin cement is the primary cause of color changes in veneers, while the ceramics cause only minimal discoloration (27). The incubation time in this study was 4 weeks, consistent with the periods used in previous colorimetric studies (10). Some investigations have shown that the resin cements produce color changes in specific combinations with ceramic restorations. Moreover, the final color of the restoration may be altered depending on the ΔL, Δa, or Δb of the resin cement (27). The color changes in the present study ranged from 0.78 to 2.14; the values were below the clinically acceptable limit of 2.7 for the composite disks. These findings are consistent with the study of Shiozawa et al. (3), where ΔE values are in the range of 0.5 to 1.3 for dual-cure resin cements.

As expected, the light-cured resin cements had lower ΔE values in comparison with the dual-cure resin cements. The higher values for the latter can be attributed to their chemical composition; the degradation of residual amines or oxidation of unreacted carbon-carbon double bonds might have caused some discoloration (27). We expected that the dualcure resin cements would be less color stable than the light-polymerized materials; however, our data revealed no statistically significant differences between color changes in these two types.

Most self-cure or dual-cure resin cements use benzoyl peroxide and tertiary amines to initiate the polymerization and curing, and this chemical combination tends to discolor with time (3,8,28). Among the dual-cure cements, the NXDC group had lower ΔE values than the others. This third-generation adhesive resin cement uses an amine-free redox initiator system and optimized resin matrix, lower ΔE values may attributed to this point. In the light-cured resin cement group, the NXLC group had the lowest ΔE test values. Our findings are in accordance with the results of Smith et al. (13), who have shown that resin cements lacking benzoyl peroxide and an amine redox initiator system are more color stable.

Clinicians should feel confident using the dual-cure adhesive resin cements for the laminate veneers. Previous reports have shown that the difference between the color stability of light- and dual-cure resin cements is not acceptable. (22,27). This might be related to the oxygen-inhibited layer that forms on the surface of the tooth. The color changewould increase in the presence of the oxygen-inhibited layer. However, in our study, the tooth surfaces were polished and there was no oxygen-inhibited layer (3). In a clinical setting, the oxygen-inhibited layer may be present and cause some discoloration of the restorations.

Here, we evaluated the color stability of light- and dual-cure adhesive resin cements after 4 weeks of water immersion. The effect of long-term water immersion or thermal cycling was not assessed. Therefore, additional studies are required to evaluate the effect of such treatment on the color stability of resin cements.

Considering the limitations of this study, the following conclusions were drawn: 1) the color changes of both light- and dual-cure resin cements were within clinically acceptable limits; 2) although the light-cured resin cements had lower ΔE values than the dual-cure cements, the difference was not significant; 3) third-generation adhesive resin cements with free tertiary amines and benzoyl peroxide underwent smaller color changes than the light- and dual-cure resin materials.

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