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ORIGINAL ARTICLE

Color stability of white mineral trioxide aggregate

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Abstract
Objective This study aims to evaluate the color stability of white mineral trioxide aggregate (WMTA) after irradiation with three different curing lights and with a fluorescent lamp in an oxygen-free environment.
Material and methods Thirty samples of WMTA were divided into four experimental groups (three curing light and one fluorescent lamp) and one negative control group. The samples in the curing light groups were immersed in glycerine and were irradiated for 20, 60, and 120 s with a curing light. The samples in the fluorescent lamp group were immersed in glycerine and left on a laboratory shelf below a fluorescent lamp, whereas the negative control group was irradiated with a curing light without immersion in glycerine. A spectrophotometer was used to determine the color of each specimen before and after each light exposure and after 5 days. Data were analyzed using analysis of variance and Fisher's least significant difference test.
Results All the groups showed discoloration except for the negative control group. At 20, 60, and 120 s, there were no significant differences between the Optilux and Bluephase groups (which were the darkest). The Demi group was the curing light experimental group that showed the lowest degree of discoloration (P=0.0001). No differences were observed between the fluorescent lamp and the negative control groups. After 5 days, the fluorescent lamp group also showed darkening of the sample surface and there were no significant differences between this group and the other three experimental groups (P>0.05).
Conclusions WMTA showed dark discoloration after irradiation with a curing light or fluorescent lamp in an oxygen-free environment.
Clinical relevance WMTA may cause tooth discoloration when it is used in a coronal position.

Keywords Color stability · Curing light · Spectrophotometer · White mineral trioxide aggregate

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Introduction

The characteristics of mineral trioxide aggregate (MTA) make it a versatile material with several treatment options [1]. In some clinical situations, MTA is used in a coronal position; namely, to treat cervical resorption [2], and for pulp capping [3–5], pulpotomy [6, 7], and revascularization [8, 9], as well as a cervical base before internal bleaching treatment [10]. In these situations, the color of MTA is key to the final esthetic result; hence, white MTA (WMTA) is the MTA of choice [11]. WMTA is manufactured by both Dentsply (ProRoot MTA Tooth-colored Formula; Dentsply, Tulsa, OK, USA) and Angelus (MTA Branco; Angelus Soluções em Odontologia, Londrina, PR, Brazil).

In evaluating the effects of pH and mixing agents on the temporal setting of tooth-colored MTA, Watts et al [12] noted that all specimens of WMTA (regardless of mixing agent, pH, or time) were gray when removed from the molds 3 days after placement. In a different in vitro study that evaluated the efficiency of removal of WMTA when used as a root canal filling material [13], dark discoloration was observed in most of the WMTA specimens. In both these studies, the material was discolored at the points where it was deepest. Tsujimoto et al [10] covered samples of WMTA with two bleaching agents that were activated with a light-emitting diode, and observed a change in surface color from white to

gray in both groups. In addition, the discoloration occurred immediately after the bleaching agent was applied to the surface of the samples. In two case reports, Jacobovitz and Lima [14] and Belobrov and Parashos [15] described tooth discoloration after placement of WMTA. WMTA was developed for application in esthetically sensitive areas; thus, if its color changes to gray, it may cause tooth discoloration.

Despite the fact that unexpected findings have been reported in relation to the color of WMTA [10, 12–15], to date, no studies have been performed to evaluate the color stability of WMTA.

Given that Tsujimoto et al [10] observed discoloration of WMTA after treatment with light-activated bleaching agents, and that in clinical situations, a light-cured composite restoration is usually placed over WMTA, we considered it necessary to study the influence of curing light on the color stability of WMTA.

The aim of the present study was to evaluate the color stability of WMTA after irradiation with three different curing lights and with a fluorescent lamp in an oxygen-free environment.

Materials and methods

Sample preparation

Thirty samples of WMTA (Dentsply; Tulsa Dental, Tulsa, OK, USA) were prepared using silicon tubes (2 mm long× 2 mm diameter). Fifteen samples were prepared from WMTA batch number 10003598 and 15 from batch number 9001766. The WMTA was mixed in accordance with the manufacturer's instructions. The blocks of WMTA were stored in an incubator at 37 °C at 100 % humidity for 48 h to encourage setting. After removal of the silicon molds, the specimens were divided into four experimental groups (n= 6) and a control group (n=6). Table 1 shows the specifications for the lights used in the experimental groups. The light intensity of the curing units was measured using a radiometer (Bluephase® Meter; Ivoclar-Vivadent, Schaan, Liechtenstein).

Experimental groups

Curing light groups

The samples from all the curing light experimental groups (group 1, Optilux 501; group 2, Bluephase 20i; group 3, Demi) were immersed initially in pure glycerine for 15 min, and then irradiated with a curing light for 20, 60, and 120 s.

Fluorescent lamp group

The samples in this experimental group were immersed in pure glycerine for 15 min but were not irradiated with a curing light. They were left on a laboratory shelf at 22 °C and 30 % humidity and at 1 m below an 18 W lamp (Philips Master TL-D Super 80; Amsterdam, Netherlands).

Negative control group

The samples in this control group were not immersed in pure glycerine. Each sample was irradiated with one of the curing lights for 20, 60, and 120 s. The samples from all the groups were kept in the laboratory for 5 days. All procedures were performed by a single operator.

Spectrophotometric measurements

Color values were recorded using a reflectance spectrophotometer (SpectroShade, Handy Dental Type 713000; MHT, Arbizzano di Negar, Verona, Italy) by a single operator. The measurements were performed by positioning the spectrophotometer at 2 mm from the samples under constant laboratory light conditions. The instrument was calibrated before the measurements for each group, in accordance with the manufacturer's recommendations. Color was measured at five time points: at 0, 20, 60, and 120 s and after 5 days. Using the SpectroShade software, differences in color (ΔE) and color coordinates (ΔL^*, Δa^*, and Δb^*) were calculated, where ΔL is the change in luminosity [from 0 (black) to 100 (white)], Δa^* is the change in the red–green parameter, and Δb^* is the change in the yellow–blue parameter. ΔE was determined as follows [16]:

$$\Delta E = \left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\right]^{1/2}$$

Subsequently, 4 ΔE time intervals were calculated for each group.

Statistical analysis

Commission Internationale de l'Eclairage (CIE) L^* a^* b^* and ΔE values were analyzed statistically using analysis of variance and Fisher's least significant difference test. The level of significance was set at $P \leq 0.05$.

Results

No significant differences were observed between WMTA batches (P=0.09). Figure 1 shows a spectrophotometric image of a sample from each group at different time

Table 1 Light specifications

Group	Light source	Light type	Manufacturer	Wavelength (nm)	Light intensity
1	Optilux 501	Halogen	Kerr, Danbury, CT, USA	400–505	1,086.67 mW/cm^2
2	Bluephase 20i	Poliwave (halogen+LED)	Ivoclar- Vivadent	380–515	1,496.67 mW/cm^2
3	Demi	LED	Kerr, Danbury, CT, USA	450–470	1,340 mW/cm^2
4	Master TL-D Super 80	Fluorescent lamp	Philips, Amsterdam, Netherlands	320–800	18 W[a]

[a] Light intensity product information

intervals. The negative control group showed no discoloration over time.

MTA discoloration according to light

Table 2 shows the results of the ΔE evaluation for the different groups at different time points. At 20, 60, and 120 s, there were no significant differences in ΔE values between the Optilux and Bluephase groups, which were the darkest. The Demi group showed some discoloration, but it was significantly less than that of the Optilux and Bluephase groups (P=0.0001). No significant differences were observed between the fluorescent lamp group and the negative control group for the first three time points; these two groups corresponded to the lightest samples. At the 5-day time point, the negative control group had the lowest ΔE values, and differences were observed between the negative control group and the experimental groups. However, at this time point, no significant differences were observed among the experimental groups (P>0.05).

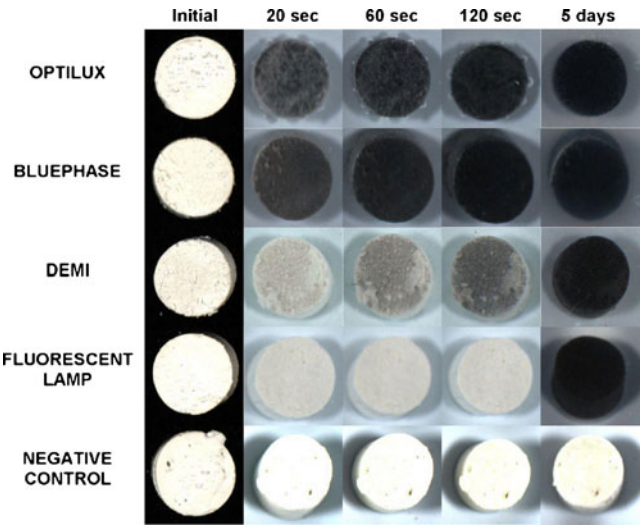

Fig. 1 Spectrophotometric images of one sample from each group taken at different time points

MTA discoloration according to exposure time

The 3 experimental groups that were exposed to curing light showed discoloration of the WMTA surface, which increased with exposure time (P=0.0001). The experimental group that was exposed to fluorescent light showed darkening of the sample surface at 5 days but not at the other time points. The color of the samples in the negative control group remained stable over time.

Figure 2 shows the mean L values for the different groups. At 5 days, all the groups had a similar degree of darkening, except the negative control group, which remained stable throughout.

Discussion

Color change can be assessed both visually and with specific instruments. The spectrophotometric and the CIE $L^*a^*b^*$ system were chosen to evaluate color variation (ΔE) because they are well suited to the detection of small changes in color and have advantages such as repeatability, sensitivity, and objectivity [17].

Watts et al [12] reported that, under their conditions, all specimens of WMTA were gray when removed from the molds. The surfaces of the samples that were exposed directly to phosphate-buffered saline (PBS) remained light in color. Once the samples had been removed from the molds and transferred to PBS, the dark discoloration faded over the course of the 28-day trial, but it remained visible in the internal portion of the specimens upon fracture. Similarly, Boutsioukis et al [13] observed dark discoloration of WMTA in most specimens that had been sealed previously with intermediate restorative material. With these findings in mind, we hypothesized that the presence or absence of oxygen plays an important role in the discoloration of WMTA. To corroborate this hypothesis, we conducted a pilot study in which WMTA samples were sealed in test tubes; half were saturated with pure oxygen and half with pure nitrogen. The surface color of the nitrogen-saturated samples changed from white to gray after exposure to curing light irradiation. However, the color of the oxygen-saturated

Table 2 ΔE values (mean ± SD) for the different groups at the different time points

Groups	20 s		60 s		120 s		5 days	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Optilux 501	35.27 aA	11.18	47.36 aB	8.8	55.19 aBC	6.56	62.22 aC	4.07
Bluephase 20i	38.80 aA	9.71	49.83 aB	8.28	57.46 aBC	7.06	61.30 aC	4.18
DEMI	20.88 bA	8.54	31.04 bB	9.27	40.82 bC	9.1	60.63 aD	3.68
Fluorescent lamp	8.85 cA	0.98	9.38 cA	1.42	9.11 cA	1.02	61.65 aB	3.03
Negative control	3.73 cA	1.59	3.12 cA	1.77	3.72 cA	1.68	3.34 bA	1.69

Different lower case letters indicate statistically significant differences between the groups ($P \leq 0.05$). Different upper case letters indicate statistically significant differences between time intervals ($P \leq 0.05$)

samples remained stable. The main drawback to this pilot study was that it was only possible to ensure optimum experimental conditions for a few minutes. In the present study, we used glycerine gel to reduce exposure to oxygen during irradiation with the curing light, as in restorative dentistry [18]. The samples that were coated with glycerine gel had low oxygen diffusion and might behave like those under a nitrogen atmosphere.

According to the information supplied in the material safety datasheet, ProRoot MTA consists of 75 % Portland cement, 20 % bismuth oxide (Bi_2O_3), and 5 % calcium sulfate dehydrate. Bi_2O_3 is added to WMTA as a radiopacifier [19]. It has been reported that Bi_2O_3 undergoes a thermal dissociation under high temperature, which yields metallic bismuth and oxygen [20]. The reduced black crystals of bismuth atoms are responsible for the darkening of the sample and the presence of these crystals has been identified by X-ray diffraction [21]. Increasing the partial pressure of oxygen at high temperature avoids the formation of metallic bismuth and the sample remains transparent. Our results suggest parallel behavior under irradiation. It is known that Bi_2O_3 can be excited by visible and UV light [22]. The irradiated Bi_2O_3 behaves in the same way as heated Bi_2O_3. It turns dark when heated or irradiated under a nitrogen atmosphere (or coated with glycerin), whereas it remains stable when heated or irradiated under an oxygen atmosphere.

The role of oxygen could also be explained in another way. It is known that some compounds that absorb light (as chromophores) reach an excited state that can interact with molecular oxygen [23]. This interaction may progress in different ways; one of which is the transfer of energy from the excited chromophore to oxygen. Once the energy transfer ends, the chromophore recovers its starting properties whereas the oxygen dissipates the excess energy to the surroundings as heat. Therefore, oxygen might act as a quencher that quickly deactivates the excited state of WMTA, thus preventing a light-induced decomposition of WMTA that eventually could produce dark or gray byproducts. In contrast, irradiation of oxygen-free samples (coated with glycerine) might create an excited WMTA state that persists longer, due to the absence of the quenching effect of oxygen. In this excited state, WMTA might have enough time to decompose and yield dark byproducts. In this way, the presence of oxygen would prevent photochemically induced darkening, whereas the absence of oxygen would promote it. The results of the present study showed that the color of WMTA remained stable over time in an oxygen environment (negative control group).

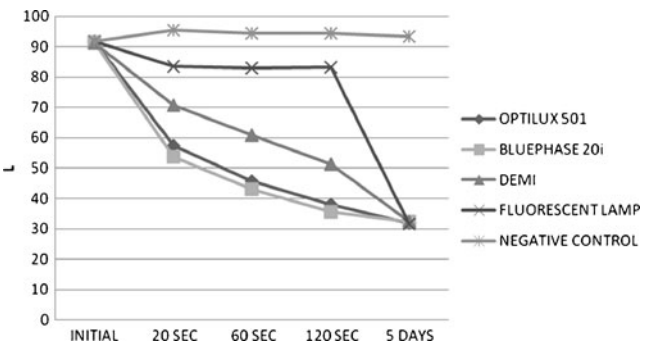

Fig. 2 Mean L values for the different groups at the different time points (*black* 0 and *white* 100)

We speculate that the formation of metallic bismuth under light irradiation could be the main reason for the darkening of the WMTA samples, but further investigations are required to confirm this.

In addition to the effects of the presence or absence of oxygen, we observed that light is key to starting or accelerating the darkening process for WMTA. We showed that the samples that were irradiated with the Bluephase 20i or Optilux 501 curing light discolored significantly faster than those irradiated with the Demi light. The Optilux 501 halogen and the Bluephase 20i poliwave lights have broad emission bands (400–505 and 380–515 nm, respectively). These bands overlap partially with the UV-visible diffuse reflectance spectrum for nanocrystallite Bi_2O_3 [22], which spans from wavelengths shorter than 300 to 500 nm, with a maximum at 400 nm. Thus, both the Optilux 501 and Bluephase 20i curing lights can excite Bi_2O_3, initiating the photochemical process. In contrast, although the Demi LED light has a higher intensity, its light spectrum is narrower (450–470 nm), and the overlap with the reflectance spectrum of Bi_2O_3 is small, which results in a less efficient excitation and a slower darkening of WMTA. The

discoloration in the fluorescent lamp experimental group was significantly slower than that in the other groups (except the negative control group). However, at 5 days, there were no significant differences in terms of the surface darkness of the samples among all the glycerine-coated groups. Given that the fluorescent lamp has a broad bandwidth (with three main narrow peaks at 436, 556, and 628 nm), in theory, it should have darkened the samples more quickly. Perhaps the distance of 1 m between the WMTA samples and the fluorescent lamp prevented them from receiving a high intensity of light. Hence, the intensity and wavelength of light seem to play a crucial part in the speed at which WMTA darkens. More research is needed to evaluate the color stability of WMTA under clinical conditions.

Conclusion

WMTA showed dark discoloration after irradiation with a curing light (Demi, Optilux 501, or Bluephase 20i) or with a fluorescent lamp in an oxygen-free environment.

Conflict of interest The authors declare that they have no conflict of interest.

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