Chapter 4

INVESTIGATION OF THE COLOR STABILITY OF CURRENT COMPOSITES: NEW DEVELOPMENTS, NEW MATERIALS

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The increasing interest in aesthetics today and the fact that dental health is an indispensable part of aesthetics have caused patients to demand longer-lasting aesthetic restorations. For this reason, composite resins have become frequently preferred materials by physicians[1,7].

One of the essential factors in the aesthetic success of current restorative materials is its compatibility with natural teeth. Dentistry needs to ensure color harmony between teeth and restoration. Cosmetic fillers are asked to maintain their color in oral conditions because coloration is one of the most critical aesthetic failures. To prevent this, color stability, which is one of the main factors of renewals in composite restorations, cannot be maintained. The effects of chemical and physical components on restorative materials can be predicted to make these restorations more aesthetic and long lasting[1].

There are many internal and external factors such as insufficient polymerization, water absorption, chemical reaction, nu-

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tritional habits, oral hygiene, and surface smoothness of restoration that affect the degree of coloration. Color changes due to the composite material structure are classified as internal colorings, and color changes caused by physician errors that may occur during the application of the restoration[2].

Fillers also have an important effect on the coloring of composite materials. It is known that composite materials with low filler content have less color stability. Fillers may separate from the resin matrix due to the abrasion of the resin composite. For this reason, external coloration may occur in the restoration as the surface roughness increases[3].

CLASSIFICATION OF DISCOLORATION IN COMPOSITE RESINS

Color changes occurring in composite resins arise due to various reasons. In composite resins, there are two types of coloration, internal and external. Internal stainings are permanent colorings that occur depending on the composite's structure, filler content, water absorption, and polymerization method. External stainings occur due to factors such as finishing and polishing processes during the application of the restoration, staining materials, surface roughness and hardness, poor oral hygiene, water absorption[2].

INTERNAL STAINING:

The internal colorations observed in composite resins material are realized according to the material's content and structure. Factors affecting the color of the material used in restorative dental materials that are polymerized with light include many features such as polymerization, matrix content, and filler properties[2].

Structure of Composite Resin

In dentistry, composite resins consist of three primary phases structurally. These phases, the organic polymer matrix phase, is called the inorganic phase and the intermediate phase. Bis-GMA (bisphenol A glycyl-ether-methacrylate), Bis-EMA (ethoxylated bisphenol A dimethacrylate), TEGDMA (triethylene glycol dimethacrylate) and UDMA (urethane dimethacrylate) are the most commonly used oligomers in much composite resin organic matrixes[2,4-6]. It is said that the color stability of composite resins containing UDMA is better than composites containing other monomers[7].

In auto polymerizing composites, the initiator is dibenzole peroxide, while the accelerator is aromatic tertiary amines. In composites that are polymerized with light, 450-550 nm wavelengths are used as the initiators, which show their effect by absorbing light[8]. When the composites are chemically polymerized, colorations are observed due to the chemical change of the tertiary aromatic amines. Moisture, UV (Ultraviolet) light, and oxidation can be listed among the materials that accelerate this deterioration. The most commonly used initiator type in light-polymerized composite resins; The chromophore group, which is yellow and stable, is camforoquinone. It is reported that the use of camforoquinone at high levels in the resin structure causes discoloration[9,10]. Concerning resin storage form, color changes can be observed in composite resins kept in a hot environment for a long time[11].

Water Absorption of Composite

Water absorption plays an essential role in the clinical success of composite resins. Hydrophilic composite materials showing water absorption are thought to be more prone to coloration. Microcracks are seen in the composite resin due to excessive water absorption or cavities formed in the filling and matrix interface, causing dye penetration and coloration. Also, composites with the main monomer content of Bis-GMA, compared to composites containing UDMA and Bis-EMA (ethoxylated bisphenol A glycol dimethacrylate), show greater water absorption and thus increase the probability of coloration[8].

Water absorption in resins with necessary filler Bis-GMA is 0% - 1%. Due to the TEGDMA added to these resins' structures to regulate their viscosity, this ratio may increase to 3-6%. TEGDMA contains ethoxy groups that are hydrophilic in the center, and therefore the surface hydrophilicity of the composite material also increases. As a result, Bis-GMA and TEGDMA structures show high water absorption due to the affinity of water. Due to the hydrophobic group in the structure of Bis-EMA, water absorption is low. In addition to these, TEGDMA is reported to show a high rate of water absorption compared to Bis-EMA, Bis-GMA, and UDMA[12,13].

Polymerization Method of Composite

Insufficient polymerization in composite resins causes poor color stability of the material. In cases where it is not polymerized sufficiently, the failure of the camhoroquinone used as the initiator to completely change its color from yellow to colorless causes yellow colorings in the composite resin structure. Over time, it has been reported that yellow color marks turn brown as a result of oxidation of amines with photo-activation of the material[9].

Time and preferred light devices in polymerization are also very effective in stainings. With the decrease of dimensional stability and monomer-polymer conversion, an increase in color change is observed. However, additional polymerization was found to be ineffective on all composite resins. Composite resins are reported to change color when they interact with chemicals and food dyes if they are not polymerized adequately[14-16].

External Staining:

External discolorations are generally caused by consuming colored food and drinks and poor oral hygiene. Besides, faults in contact with the blood and moisture, finishing and polishing through external tools or insufficient insulation, cause external discoloration[2].

Discoloration of the Composite Resin with Water Absorption and Coloring Agent

Composite resins can absorb water as well as absorb liquids with other pigments that can cause discoloration[17]. Water is thought to be a means of transporting coloring agents into the resin matrix. Filling particles in the composite resin cannot absorb water. Therefore, the more organic matrix the composite resin contains, the more water it absorbs[18].

There are many in vitro studies on foods and beverages such as coffee, tea, red wine, juice, cola, and ketchup that we consume in daily life. The results of the studies determined that these substances cause discoloration on the restoration surfaces. Alcohol, which is known to cause deterioration on the surface of composite materials, causes more coloration, creating a rougher surface[19,20].

The Effect of Finishing and Polishing on the Coloring of Composite Resin

Composite resins formed by filler particles with the hard structure embedded in the soft organic matrix have a heterogeneous structure[21]. The surface may remain rough due to not completing the finishing and polishing processes of composite resin restorations. As a result, it has been reported that increased plaque accumulation, gingival inflammations, secondary caries formation, and coloration can be observed[22].

The filler particles in the composite resins are hard from the resin matrix. During the finishing-polishing process, the resin matrix is easily separated and remains in the form of protrusions on the surface of the harder filler particles. Therefore, they cause the surface to become rough[23]. Organic matrix and inorganic fillers with different hardness in the composite resin are desired to be abraded in the final stage of the restoration, so it aims to minimize the coloration of the restoration by obtaining smooth surfaces [24].

Also, composite resins with large filling particles can increase surface roughness and increase coloration. As the filler particle sizes in the composite resin decrease in size, the surface roughness decreases, and resistance to coloration increases[25].

Effect of Mouthwashes and Toothpastes on Discoloration

It has been reported that mouthwashes used as a therapeutic antimicrobial agent or applied for whitening also cause color changes in teeth and restorations[26]. Elhejazi et al. evaluated the effect of 2 mouthwashes (Listerine, Orasept, Emuflor) on the color stability of 2 composite resins and one compomer material, one of which is ormoser based. They found that the Ormoser-based composite resin had the highest color change, and the gargle named Emuflor caused the most staining in all restorations. The researchers reported that the color factors and fluoride added to the mouthwashes are responsible for the staining[27].

In a study conducted by Öngöl et al., They found higher color change, especially in the Listerine and Chlorhexidine groups. In a study they did, Lee et al. concluded that the ΔE value of compomer samples kept in various mouthwashes (Listerine, Peridex, Rembrandt Age Defying, and Distilled water) for 24 hours and seven days was lower than 3.3. Toothpastes can also change the color properties, surface roughness, and hardness of restorative materials. Roopa et al. As a result of their application of whitening toothpastes to compomers and composite samples, they achieved a significant color change in both materials[29].

EVALUATION OF COLOR

Color Concept

Color is the physicochemical and psychophysical perception of light energy reflected from objects by an observer's vision system[30,31]. Color perception may vary depending on factors such as light source, observed object, and observer[32].

Color Analysis Systems

Color systems are used to define the color parameters of objects. In dentistry, mostly Munsell and CIE Lab (Commission International de I'Eclairage) and CIEDE 2000 color systems are used[33].

CIE L * a * b * Color System

Today, the CIE Lab color system is one of the most preferred color measurement systems in dentistry. In the CIE L * a * b * system developed in 1976 by the Commission Internationale de L'Eclairage (International Enlightenment Commission), three different variables are used: L *, a *, and b *. In this way, a material, restoration, or color change of the natural tooth can be expressed numerically (ΔE). The L * value and the 'Value' in the Munsell color system are proportional to each other and relate to the lightness-darkness, brightness, or light reflection rate of the color. Pure black 0 means pure white 100 L *. L * value of lighter colored objects is higher, and the L * value of dark-colored objects is lower. The a * coordinate is related to the locations of the red and green colors in the Munsell color system. The positive value of a * defines red and negative value represents green.

Similarly, b * coordinate is related to the places of yellow and blue colors. The positive value of b * indicates yellow, and the negative value indicates the amount of blue[34]. The most important advantage of the system is that color differences of the same or different objects can be calculated over time.

The amount of color change is expressed as ΔE and calculated as follows;

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

In this formula, ΔL *, Δa *, and Δb * represent the difference between the CIE L * a * b * color variables of the two objects[35].

The human eye is limited in perceiving these color differences and cannot detect ΔE values below 1. ΔE values between 1 and 3.3 are clinically perceptible but acceptable color differences. The most considerable clinically acceptable ΔE value is 3.7[36].

Current Composite Resin Restorative Materials

Composite resins are versatile materials that allow dentists to make direct aesthetic restorations. These materials have high fracture resistance and surface hardness, low abrasion, water absorption and solubility, low polymerization shrinkage, good biocompatibility, maintain tooth structural integrity, prevent fracture or crack formation, have anti-carious properties, color compatibility and stability. To provide these properties, composite resins have undergone many changes over the years. For this, many composite resin types are presented to the market by making changes in both the monomers that make up the organic polymer matrix phase of the composite resins and the inorganic filler particles[37,38].

Nanocomposite Resins

Microfill-filled composite resins are preferred in anterior tooth restorations because of their polishability. However, they are insufficient in posterior restorations because they are not robust against the masticatory forces. However, hybrid composites are more resistant to chewing forces if they cannot be polished as well as microfill composite resins. In dentistry today, composite resins containing micrometer and nanometer-sized filler particles are frequently used to restore both anterior and posterior teeth. These two properties are combined in nanocomposite resins[2].

Inorganic fillers on the surface of composite materials cause surface roughness due to the material moving away from the resin matrix during the clinical life of the material and creating a gap in that area. Since nano-filled composite resins contain small filler particle sizes, they are expected to undergo a lower degree of superficial coloring when they leave the surface compared to other materials. According to some researchers, increasing filler ratio in this type of composites caused less coloration due to decreasing the rate of organic matrix[39].

The composition and size of the filler particles is an important factor affecting the surface roughness of composite resins and is therefore associated with external coloring.

Therefore, it is expected that nanocomposites with a small particle size will obtain a smoother surface and less surface discolorations[2].

Ormosers

Structural changes have been made in the organic matrix of composites in the ormoser material (consisting of the first syllables of the words "organic modified ceramics") produced to improve the physical properties of traditional composites. In ormosers, inorganic-organic copolymers of urethane and thioether oligo methacrylate alkoxysilane are formed. The abrasion resistance of these materials is much higher than conventional composite resins. Unlike traditional composites, ormosers reduce dimethacrylate monomers using methacrylate polysiloxane as the main component in the organic matrix, thereby reducing the likelihood of an allergic reaction. In addition to the silaned inorganic filler particles, the ormosers contain an inorganic-organic copolymer. The advantages of the ormoser are low polymerization shrinkage, high abrasion resistance, biocompatible material, and protective against caries[40-42]. Awliya et al. In their studies comparing the color stability of ormoser-based and dimethacrylate-based composite resins, they found that ormoser samples were more resistant to discoloration[43].Ayad has shown that ormocer composites are significantly lower in color sensitivity than nanophil composite resins. Ren et al. Evaluated the color change of Ceram X Universal, which is an ormoser composite, which is kept in dyeing beverages after the thermal cycle, and reported that Ceram X Universal showed a lower color change compared to nanophil composite resin materials[44].

Bulk-fill Composite Resins

Bulk-fill composite resins, a new generation nanohybrid composite type, contain ytterbium trifluoride, barium glass, cocoxide, proacrylate, zirconium/silica particles. It is stated that these composites can be polymerized with a thickness of 4 mm. The material type of the composite also constitutes the name of the technique. It is known that the clinical study time decreases, and patient-physician comfort increases by applying this material as a single layer (bulk). The barium and ytterbium particles in the inorganic structure of this material increase the radioopacity and allow the effect of the light device to reach deep[45]. The contents of ytterbium trifluoride, barium aluminum silicate glass, and zirconium silica particles in these composite resins increase their transparency, allowing the light device to reach deeper [46].

Barutcigil et al. evaluated nanohybrid, bulk-fill posterior composite, and ormoser-based bulk-fill composite restorative materials in distilled water, coffee, and red wine. They evaluated the color change after 24 hours, one week, and three weeks. They found that Admira Fusion Xtra, which is an Ormoser based composite restorative material, changed more colors than other bulk-fill composite resins. The color change of Bulk-fill composite resins increased over time in red wine and coffee, while the color change of nanohybrid composite resin remained constant in red wine and coffee one week later[47].

Fiber-reinforced Composite Resins

These materials, which contain fiber in their structure, mimic the dentin tissue's stress-absorbing feature, allowing direct restoration of large class II restorations. It is stated that the fibers prevent the formation of cracks or stop the crack progression, which is one of the critical causes of failure[48].

Its contents; There are different fiber types such as glass fiber, polyester fiber, carbon fiber, aramid fiber, and ultra-high molecular weight polyethylene fiber, which are used to improve the mechanical properties of composite resin[49]. Tunçdemir et al. found that fiber reinforcement led to color and translucency parameter change in both anterior and bulk-fill resin composites. These changes were below the visual perceptibility threshold. The chemical composition of composite resins, such as the composition and quality of the resin matrix, the type and amount of initiator, inhibitor, and filler, are essential factors in the color change of composites. Composite resins containing fillers with a larger filler particle size may be more sensitive to water-induced discoloration. Therefore, they detected more total color changes in the posterior composite material, which has a filler particle size larger than the anterior composite. Ribbond (polyethylene fiber) reinforced posterior composite showed the most significant total color change, while EverStick (glass fiber) reinforced composite showed the lowest value. These color change results are associated with chemical structures[50,51].

Nanoceramic Composite Resins

Today, nanoceramic composites, which have nano-fillers in their structure and ceramic particles in addition to traditional glass particles, can be preferred. The particles in the structure of nanoceramic composites are homogeneously dispersed in the organic matrix. Ceramic nanoparticles are organically modified and consist of a polysiloxane backbone. Although used in the dentistry sector, these modified ceramics are preferred in various industrial areas as coatings due to their high resistance to abrasion, corrosion, and scratch resistance[52].

Self-adhesive Composite Resins

It is used in self-adhesive composite resins, small class I and V cavities, cervical lesions, and porcelain repairs that minimize technical precision. Self-adhesive fluid composite resins include the functional monomer GPDM (glycerophosphatdimetacrylate), which serves to roughen enamel and dentin. HEMA (hydroxyethyl methacrylate), another functional monomer that enhances the wettability and resin penetration of most adhesives[53,54]. These composites also contain acidic monomers such as 4-methacryloxyethyl trimellitate (4-META) and 2- (methacryloyloxyethyl dihydrogen phosphate (10-MDP) and pentaerythritol penta acrylate monophosphate (PENTA)55.

An ideal composite resin should exhibit a high degree of conversion and minimal polymerization shrinkage. Monteiro et al.

stated that different monomer contents and photoinitiator systems significantly affect the color stability of self-adhesive composite resins. The 2MP (2-methacryloyloxyethyl phosphate) based group showed the weakest color stability, while the use of BAPO (phenyl bis 2,4,6-trimethyl benzoyl phosphine oxide produced) provided the best color stability for acidic monomer based groups. This monomer has a large linear and reticulated molecular structure with many hydroxyl groups, making it susceptible to degradation and water absorption. Besides, the hydrophilicity of 2MP can disrupt molecular stability, creating pores in the polymer and causing discoloration[56].

Silorans

A monomer called siloran has been developed to reduce polymerization shrinkage in composite resins. Silorane; is a hybrid monomer system containing siloxane and oxirane, in which ring-opening polymerization of silorans is performed instead of polymerization of free radicals of dimethacrylate monomers[57]. The hydrophobic properties of siloxane to the material are useful in the long-term mechanical durability of composite resin in the mouth. Due to this hydrophobic property, the water absorption of the material is low, showing less coloration[58]. Studies show that less shrinkage occurs when compared to methacrylate-based composites, and siloran based systems are superior to edge compatibility and microleakage aspects[59].

The low polymerization shrinkage is the main advantage of the silo. In the most commonly used methacrylate-based composite resins, shrinkage occurs during polymerization, which causes stress on the cavity walls. This stress causes leakage, secondary caries development, post-op sensitivity, and marginal coloration[60-62].

Perez et al. reported that these systems' optical properties are different compared to the dimethacrylate based composites in their studies in which the optical properties of the silos are evaluated[63]. They reported that color changes for siloran-based composites were due to changes in the Δa * and Δb * coordinates. They specifically stated that the color difference in dimethacrylate-based composites generally results from ΔL * and Δb *. When they look at the translucency values, they report that siloran based composites show the lowest value[64].

Giomers

Giomers are called hybrid composite materials. It has fluoride release and storage properties and is reported in studies of remineralization in dentin tissue[65,66].

The PRG (pre-reacted glass ionomer) particles in its structure are formed as a result of the acid-base reaction occurring in an aqueous medium between the fluoroaluminacilicate glass particles and polyalkenoic acid. The name "Giomer" is derived from the words "Glass ionomer + polymer"[67]. PRG particles responsible for fluoride release are available in two different forms: surfactant (S-PRG) and all particle active (F-PRG)[63]. Because they contain resin, show more positive aesthetic properties than traditional glass ionomers, and resin-modified glass ionomers[68].

The ability of giomers to inhibit demineralization is similar to that of glass ionomer cements[69]. An in-vitro study investigating the long-term fluoride release of this material found that fluoride release was deficient in the first few days, but fluoride release increased significantly after 21 days[70]. The absorption and coloration of giomers are considerably higher compared to nanohybrid resin composites, which negatively affect their aesthetic properties[71].

Resin Modified Glass Ionomer Cement

RMGIC have polymerization similar to composite resins. In their structure, they also contain an acid-base reaction as in the glass ionomer. Also, most of these materials have substantially dark polymerization or autopolymerization resin properties. As a result, they provide a complete polymerization of the places that light cannot reach due to undesired reasons[72].

Thanks to their resin content, they are more aesthetic and durable compared to traditional glass ionomer cements. Adhesion to dental tissue is slightly less than conventional glass ionomers. Still, they are more advantageous because they form smoother surface properties and are easier to apply thanks to the capsule-gun system. Bonding before use is not recommended as it will reduce fluoride release[73].

Savas et al. reported that the restorative materials they tested showed significant color changes after 28 days of immersion in four types of solution. After immersion in different solutions, they observed the least effect on Glasiosite, a composite resin modified with a polyacid.GCP Glass Fill, a traditional high-viscosity glass ionomer cement with nanofluoride / hydroxyapatite, was more prone to color changes. Equia, a high viscosity conventional glass ionomer cement, and Ketac N100, a resin-modified glass ionomer cement with nanoparticles, follow this. They attribute this result to high staining sensitivity due to the high water absorption rate or surface texture. According to the water absorption results, there is the lowest water absorption level in Glasiosite among the materials tested. With Ketac N100, they observed that the highest values are available in GCP Glass Fill100[74].

Smart Monochromatic Composite Resins

Today, there is no single material that will meet all the requirements to reach the ideal material, but the studies on this subject are ongoing. These materials, called "smart" developed for this purpose, support the remaining tooth structure to the extent possible and can be changed by factors such as temperature, humidity, pH, stress[75].

Smart materials have features such as the ability to return to their original state even after removing the stimulus, piezoelectric property, thermotherapeutic properties like shape memory alloys or shape memory polymers, thermochromic property, photochromic property, magnetorheological property, sensitivity to biofilm formation. Today, burs, adhesives, and composites are produced with smart technology. Structurally colored, universally produced composites containing only one composite color tone and classic VITA tones have smart chromatic technology that gives the color "physical" dimension [76-78].

Today, a composite resin named "Omnichroma"(Tokuyama, Tokyo, Japan), which contains 260 nm spherical supra nano spherical fillers in the same size, produced with smart chromatic technology, has been put on the market. Thanks to this technology, it offers a wide variety of color matching features that cover a single color tone. It is stated that Omnichroma provides a successful color matching by creating a structural color similar to natural teeth from yellow to red. Structural color is expressed only by the physical properties of light (refraction, refraction, scattering, etc.). While creating a structural color from yellow to red, it combines the color of the adjacent tooth and its reflected light during the additive color mixing process, increasing the success of Omnichroma to adapt to natural teeth. Using the structural color with this system, the use of pigments and dyes becomes unnecessary in this system. In traditional composites, color selection increases the time spent in the seat and makes the color selection process subjective. Elimination of this situation in smart technology is also a critical advantage75-78.

Although smart monochromatic composite resin provides convenience for the physician by reducing the time spent in the clinic's shade selection, in vitro and in vivo studies are needed to evaluate the color stability.

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