Development and characterization of glass fiber-reinforced thermoplastics for non-metal clasp dentures

（グラスファイバーで強化したノンメタルクラスプデンチャー材料の開発と特性評価）

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Abstract

Recently, non-metal clasp dentures (NMCDs) made from thermoplastic resins such as polyamide, polyester, polycarbonate, and polypropylene have been used as removable partial dentures (RPDs). However, the use of such RPDs can affect various tissues because of their low rigidity. In this study, high-rigidity glass fiber-reinforced thermoplastics (GFRTPs) were fabricated for use in RPDs, and their physical properties such as apparent density, flexural properties, and color stability were examined. GFRTPs made from E-glass fibers and thermoplastics such as polypropylene and polyamide-6 were fabricated using an injection molding. The effects of the fiber content on the GFRTP properties were examined using glass-fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass%. Commercially available denture base materials and NMCD materials were used as controls.

The experimental densities of GFRTPs with various fiber contents agreed with the theoretical densities. The flexural strength and modulus of GFRTPs increased with increasing glass-fiber content. However, polyamide-6 GFRTPs were more brittle than ductile polypropylene GFRTPs. Moreover, the polypropylene GFRTPs with fiber contents of 10 and 20 mass% had good properties for use in NMCDs, because they had sufficient rigidity, similar to those of conventional denture base materials, and their flexibility was similar to those of available NMCD materials.

The color changes of polypropylene GFRTPs with fiber contents of 0, 10, and 20 mass% after 4 weeks of coffee immersion were measured by colorimetry. The results indicate that the GFRTPs showed clinically acceptable color stability and might be satisfactory for clinical use. Therefore, GFRTPs are expected to become applicable

materials for esthetic dentures.

It is therefore thought that a fiber content of 10 or 20 mass% is beneficial for preparing GFRTPs for NMCDs. In conclusion, GFRTPs composed of glass fiber and polypropylene are appreciable for NMCDs, because their rigidities can be controlled by varying the fiber content.

Key words: Non-metal clasp dentures, Mechanical properties, Color stability, Glass fiber-reinforced thermoplastics, Fiber content

Introduction

In response to the demands for esthetic and metal-free restoration, removable partial dentures (RPDs) without metal clasps, made from thermoplastic resins such as polyamide, polyester, polycarbonate, and polypropylene, are now frequently used in prosthodontic treatment [1-3]. RPDs using resin-clasp retentive parts are defined as non-metal clasp dentures (NMCDs) [1,2]. Such NMCDs made using thermoplastic resins are often much more esthetically pleasing than conventional RPDs with metal clasps.

Several studies of the mechanical properties of thermoplastic resin NMCDs, such as flexural strength [3-6], tensile strength [3], shear bond strength [5,7], impact strength [4-6], and micro-hardness [8], have been reported. Takabayashi [3] reported that thermoplastic resins have high resistance to fracture although they have poor flexural properties. Hamanaka et al. [4] concluded that thermoplastic resins have significantly poorer flexural properties and higher or similar impact strengths compared with conventional heat-polymerized polymethyl methacrylate (PMMA). They reported that NMCDs made from injection-molded thermoplastic resins have substantial advantages over those made from conventional PMMA, including higher toughness, higher impact resistance, and higher flexibility. The mechanical properties of thermoplastic resins, such as flexural properties and micro-hardness, are inferior to those of PMMA [4,8]. Wadachi et al. [9] investigated whether thermoplastic resins used for NMCDs have sufficient stiffness compared with conventional PMMA for denture bases. The authors suggested that when a thermoplastic resin with a low degree of elasticity is used as a denture base, reinforcement with a metal frame is needed to prevent deformations

caused by occlusal force. The use of such NMCDs without metal frameworks can affect remaining tissues because of their low rigidity, and such NMCDs do not conform to the standard principles of RPD design [1,10].

Reinforcement using glass fiber is considered a possible remedy for the defects of NMCDs made from thermoplastic resins. Several basic research and clinical studies have been conducted on the fiber reinforcement of prosthodontic appliances such as crowns, fixed partial dentures, complete dentures, and dental dowels (posts) [11-13]. Dental prostheses made from fiber-reinforced composites are often much more esthetically pleasing than those made from metal alloys. Another advantage of dental prostheses made from fiber-reinforced composites is that their properties can be tuned by changing the fiber properties, for example, the type of fiber [14], fiber diameter [15], volume fraction of fiber [16], and insertion position of fiber [17]. In current prosthodontics, fiber-reinforced composites have seen particular use as fiber dowels, because control of the fiber properties can be used to achieve an elastic modulus similar to that of dentin, resulting in less damage to the remaining tooth structure [18]. Also, there have been several studies on the fiber reinforcement of denture base resins [12,19]. The results from these studies suggest that glass fiber-reinforced PMMA has higher mechanical properties than conventional PMMA. Although the effect of fiber reinforcement on PMMA as denture base resins is well known, its effect on NMCD materials is poorly understood. Generally, NMCDs have been fabricated using an injection-molding method [9]. In this method, it is difficult to thoroughly infiltrate the long glass-fibers into the matrix, and to precisely control the fiber content [20].

Therefore, the fabrication and characterization of glass-fiber-reinforced thermoplastics (GFRTPs) for NMCDs have not been performed in detail.

In the present study, GFRTPs composed of glass fiber and thermoplastic for NMCDs were developed, using injection molding technique. The effects of the fiber content on the physical properties of the GFRTPs, such as apparent density, flexural properties, and color stability, were investigated. From these characterizations, the author evaluated the validities of GFRTPs which were fabricated as a novel NMCD material for use in RPDs.

Materials and Methods

Material preparation

Two types of GFRTP pellets consisting of polypropylene (Plastron®, PP-GF50-02; 50 mass% fiber content) or polyamide-6 (PA6-GF50-01; 50 mass% fiber content) reinforced with E-glass fibers of diameter of 17 μm and length 10 mm were supplied by Daicel Polymer (Tokyo, Japan), respectively (Fig. 1). Unreinforced polypropylene or polyamide-6 pellets (Daicel Polymer) were prepared for production of GFRTPs with controlled fiber contents, respectively. The effects of fiber content on the GFRTP properties were investigated using various glass-fiber contents, that is, 0, 5, 10, 20, 30, 40, and 50 mass%. Mixtures of the GFRTP and unreinforced pellets were prepared by melt-mixing in a conventional melt-mixer. Polypropylene and polyamide-6 were melted at 250 °C for 12 min, and at 260 °C for 11 min, respectively. GFRTP plates were prepared in gypsum molds with cavities (65-mm long, 32-mm wide, 3.0-mm high) by injection molding system (MH-01, Unival, Tokyo, Japan). The GFRTP plates were

carefully removed from the molds, and cooled to room temperature in an ambient atmosphere. The GFRTPs prepared with fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass% are denoted by GF0, GF5, GF10, GF20, GF30, GF40, and GF50, respectively. Two commercially available denture base materials (Polybase, PB; Ivocap, IC) and two commercially available NMCD materials (Valplast, VA; EstheShot Bright, EB) were used as controls (Table 1).

Measurement of density

The apparent densities of GFRTPs with various fiber contents and the controls were determined according to Archimedes' principle in distilled water. Each density was the average of six measurements ($n = 6$). The theoretical density ρ_c of GFRTPs with various fiber contents was calculated using the following equations:

$$V_f = (W_f/\rho_f)/[(W_f/\rho_f) + ((1 - W_f)/\rho_m)] \quad (1)$$

$$\rho_c = V_f \rho_f + (1 - V_f) \rho_m \quad (2)$$

where V_f is the fiber volume content, W_f is the fiber weight content, ρ_f is the fiber density (2.6 g/cm^3), and ρ_m is the polypropylene matrix density (0.9 g/cm^3) or the polyemide-6 matrix density (1.13 g/cm^3).

Three-point bending test

The flexural properties of the prepared denture base specimens were investigated using a three-point bending load. The three-point bending test, which produces tensile or compressive stress, is one of the commonest methods used to predict failure in bending of denture bases. The specimens used for the three-point bending tests were prepared

using a cutting–grinding technique, to give rectangular bars of length 65 mm, width 10 mm, and thickness 3.0 mm. Each specimen was polished with 600-grit SiC paper under running water to prepare specimens of appropriate size for the three-point bending tests. The accuracies of the dimensions of all specimens were verified with a micrometer (CD-20CP, Mitutoyo, Kanagawa, Japan) at three locations for each dimension to a tolerance of 0.05 mm. Three-point bending tests were performed on denture base specimens at a constant loading speed of 5 mm/min, with a span length of 50 mm, using a computer-controlled Instron testing machine (TG-5kN, Minebea, Tokyo, Japan). The flexural strength (F) and flexural modulus (E) were calculated using the following equations:

$$F = (3/2)\ (PL/bh^2) \quad (3)$$

$$E = (1/4)\ (L^3/bh^3)\ k \quad (4)$$

where P is the maximum load, L is the span length, b is the specimen width, h is the specimen thickness, and k is the slope at the initial stage in the load–deflection curve. Experimental values are reported as averages of six measurements ($n = 6$).

Color stability evaluation

From the above-mentioned flexural tests on the optimum fiber content for GFRTPs, GFRTPs made from polypropylene were prepared with fiber contents of 0, 10, and 20 mass%. To match the denture base to the gingival color, 2 mass% of pigments (Aesthetic Intensive-Color: Purpur Red, Candulor, Glattpark, Switzerland) were added to the pellets before injection molding. Each specimen had a length of 10 mm, width of 7 mm, and thickness of 3.0 mm. The specimens were polished with 600-grit SiC paper

under running water. The baseline colors of the GFRTP specimens were measured before immersion. The GFRTP specimens were immersed for 4 weeks in 20 mL of black coffee without sugar (NESCAFE Excella®, Nestlé Japan., Hyogo, Japan) [21], the staining solution, in a Teflon-sealed polystyrene bottle at 37 °C, with the coffee refreshed weekly. After staining, the specimens were washed with distilled water and then dried with paper towels. Color changes after 24 h and after 1, 2, 4 weeks of immersion were measured by a colorimeter (ShadeEye NCC; Shofu, Kyoto, Japan) against a white background, as shown in Fig. 2. This device used a pulsed xenon lamp as an optical light source and a three-component silicon photocell as the optical sensor [22]. The colorimetric measurements were performed by contacting the measurement tip of the optical sensor to the GFRTP specimen. The measurements are averages of six specimens (n = 6), with each specimen measured three times.

The color parameters are expressed using the Commission Internationale de l'Eclairage (CIE) Lab color system [23,24], relative to the D65 illuminant standard. In this three-dimensional color space, the three axes are L^*, a^*, and b^*. The axis of L^* is a measure of lightness, with 100 for white and 0 for black. The axes of a^* and b^* are measures of the red–green and yellow–blue chromatic coordinates, respectively. A positive a^* or b^* represents a red or yellow shade, respectively, and a negative a^* or b^* represents a green or blue shade, respectively.

The color difference (ΔE^*), comparing the color before and after immersion, was calculated using the following equation [24]:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (5)$$

Moreover, the ΔE^* values were converted into National Bureau of Standards (NBS)

units by the following equation [21,25]:

$$\text{NBS units} = \Delta E^{*} \times 0.92 \quad (6)$$

These values are shown in Table 2 [21]. A threshold value of 3.0 was set in NBS units for clinically acceptable color change [25,26].

Statistical analysis

The experimental results were analyzed using analysis of variance and the Scheffe multiple comparison test among the means at $p = 0.05$.

Results

Fabrication and physical properties of glass-fiber-reinforced thermoplastics for non-metal-clasp dentures

Figure 3 shows the apparent densities of polypropylene GFRTPs with various fiber contents. The GFRTPs prepared with fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass% had measured densities of 0.90 ± 0.00, 0.95 ± 0.04, 0.99 ± 0.03, 1.05 ± 0.04, 1.19 ± 0.04, 1.25 ± 0.01, and 1.33 ± 0.03 g/cm^3, respectively; the apparent density increased with increasing fiber content. The GFRTPs prepared with fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass% had theoretical densities of 0.90, 0.93, 0.96, 1.04, 1.12, 1.22, and 1.34 g/cm^3, respectively. The measured densities of the GFRTPs, obtained based on Archimedes' principle, agreed with the theoretical densities obtained using the rule of mixtures. The apparent densities of the control group, that is., PB, IC, VA, and EB, ranged from 1.01 to 1.18 g/cm^3 and increased in the order VA < IC < EB < PB.

Figure 4(a) shows plots of the flexural strengths of polypropylene GFRTPs against

fiber contents. The flexural strengths of the GFRTPs with fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass% were 55.8 ± 2.3, 61.2 ± 4.5, 73.2 ± 7.8, 83.0 ± 22.4, 148.5 ± 18.2, 183.0 ± 35.7, and 217.6 ± 22.7 MPa, respectively; the flexural strength increased with increasing fiber content. The flexural strengths of GF30, GF40, and GF50 were significantly higher than those of GF0, GF5, GF10, and GF20 ($p < 0.05$). However, there were no significant differences among the flexural strengths of GF0, GF5, GF10, and GF20 ($p > 0.05$). The flexural strengths of the control group, that is, PB, IC, VA, and EB, ranged from 50.9 to 89.1 MPa and increased in the order VA < EB < IC < PB. Figure 4(b) shows plots of the flexural moduli of polypropylene GFRTPs against fiber contents. The flexural moduli of the GFRTPs with fiber contents of 0, 5, 10, 20, 30, 40, and 50 mass% were 1.75 ± 0.14, 1.93 ± 0.12, 2.30 ± 0.49, 2.86 ± 0.77, 4.78 ± 0.49, 6.13 ± 1.26, and 7.42 ± 1.26 GPa, respectively; the flexural modulus increased with increasing fiber content. The flexural moduli of GF30, GF40, and GF50 were higher than those of GF0, GF5, GF10, and GF20 ($p < 0.05$). The flexural moduli of the control group, that is, PB, IC, EB, and VA, ranged from 1.24 to 2.81 GPa and increased in the order VA < EB < IC < PB.

Figure 5 shows stress–strain curves of polypropylene GFRTPs obtained from the flexural tests. The stress–strain curves of GF30, GF40, and GF50 increased linearly from the early to middle stages, and then showed nonlinear behavior up to maximum stress; they showed sudden reductions in strength and had several failure points. In contrast, the stress–strain curves of GF0, GF5, GF10, and GF20 indicated ductile behaviors. The control groups, apart from PB, also showed ductile behaviors. These samples did not fracture after maximum stress. The stress–strain curves confirmed that

the GFRTPs had high rigidities, which were improved by fiber reinforcement of the thermoplastic using an injection-molding method.

Effect of fiber content on flexural properties of glass fiber-reinforced polyamide-6 prepared by injection molding

Figure 6 shows the apparent density of polyamide-6 GFRTPs with varying fiber content. GF0, GF5, GF10, GF20, GF30, GF40, and GF50 recorded densities of 1.12±0.01, 1.18±0.05, 1.20±0.06, 1.25±0.01, 1.42±0.06, 1.52±0.04, and 1.58±0.03 g/cm^3, respectively; the apparent density increased with increasing fiber content. GF0, GF5, GF10, GF20, GF30, GF40, and GF50 had theoretical densities of 1.13, 1.16, 1.20, 1.27, 1.36, 1.46, and 1.58 g/cm^3, respectively. The measured density, obtained based on Archimedes' principle, mostly agreed with the theoretical density obtained using the rule of mixtures.

Figure 7(a) shows plots of the flexural strength of polyamide-6 GFRTPs in relation to fiber content. The flexural strength of GF0, GF5, GF10, GF20, GF30, GF40, and GF50 measured 50.5±9.4, 57.4±15.1, 81.7±23.4, 116.9±17.7, 151.7±40.4, 149.5±39.5, and 274.8±56.9 MPa, respectively; the flexural strength tended to increase with increasing fiber content. There were no significant differences among the flexural strength values for GF0, GF5, GF10, and GF20 ($p > 0.05$). There were also no significant differences among the flexural strength values for GF10, GF20, GF30, and GF40 ($p > 0.05$). The flexural strength of GF50 was significantly higher than the other GFRTPs ($p < 0.05$). Figure 7(b) shows plots of the elastic modulus of polyamide-6 GFRTPs against fiber content. The elastic modulus of GF0, GF5, GF10, GF20, GF30, GF40, and GF50 were

1.85±0.13, 1.97±0.21, 2.25±0.49, 3.32±0.55, 4.73±0.69, 5.50±1.21, and 8.69±1.93 GPa, respectively; the elastic modulus increased with increasing fiber content in the same way as for flexural strength. Likewise, the elastic modulus of GF50 was significantly higher than the other GFRTPs ($p < 0.05$).

Figure 8 shows stress–strain curves of polyamide-6 GFRTPs obtained from the three-point bending tests. The stress–strain curves of GF0, GF5, and GF10 increased linearly from the early stages to the fracture point. The stress–strain curves of GF20, GF30, and GF40 increased linearly from the early to middle stages, and then showed nonlinear behavior up to maximum stress. In contrast, the stress–strain curve of GF50 exhibited remarkably high rigidity compared with other GFRTPs.

Color stability of glass-fiber-reinforced polypropylene for non-metal clasp dentures

Figure 9 shows a photograph of each specimen before and after 4 weeks of immersion in the coffee. Visual inspection of polypropylene GFRTPs revealed almost no color change before and after immersion. In contrast, the VA seemed to change color, but this change was not visibly certain.

Figure 10 shows the color differences (ΔE^*) for each specimen after immersion in the coffee. For polypropylene GFRTPs, the ΔE^* values at 24 h and 1, 2, and 4 weeks after immersion for GF0, GF10, and GF20 ranged from 0.65 to 0.77, from 1.39 to 2.09, and from 1.03 to 2.45, respectively. For controls, the ΔE^* values at 24 h and 1, 2, and 4 weeks after immersion for VA, EB, PB, and IC ranged from 2.48 to 3.87, from 0.52 to 1.07, from 0.39 to 1.59, and from 0.36 to 0.61, respectively. The ΔE^* value of VA was the largest among all specimens and immersion periods.

Table 3 shows the color differences in NBS units, along with critical remarks for each specimen after immersion in the coffee. For polypropylene GFRTPs, the NBS unit at 24 h and at 1, 2, and 4 weeks after immersion for GF0, GF10, and GF20 ranged from 0.60 to 0.71, from 1.28 to 1.93, and from 0.95 to 2.25, respectively. For controls, the NBS unit at 24 h and at 1, 2, and 4 weeks after immersion for VA, EB, PB, and IC ranged from 2.28 to 3.56, from 0.48 to 0.99, from 0.36 to 1.47, and from 0.33 to 0.56, respectively. As shown in Table 2, after immersion for 4 weeks the color differences according to the critical levels were only "slight" for GF0 and "noticeable" for GF10 and GF20. The color change values between GF10 and GF20 showed no significant differences across all immersion periods ($p > 0.05$). All GFRTP specimens exhibited clinically acceptable color change in NBS units. On the other hand, as with the ΔE^* units, color change in NBS units of VA was the largest among all specimens in any immersion period. The color change of VA after 4 weeks of immersion was "appreciable."

Discussion

In the present study, GFRTPs for NMCDs were prepared. The effects of the fiber content on the physical properties of the GFRTPs were investigated.

The apparent density increased with increasing glass-fiber content (Figs. 3 and 6). This is because the density of glass fiber (2.6 g/cm^3) is larger than those of polypropylene (0.9 g/cm^3) and polyamide-6 (1.13 g/cm^3). The experimental densities of the GFRTPs with various fiber contents agreed with the theoretical densities obtained from the densities of glass fiber and thermoplastic such as polypropylene or

polyamide-6. These results indicate that injection molding produced GFRTPs with good uniformity, which did not contain voids, and with properties closely resembling those of the original pellets.

The results obtained using flexural tests showed that both the flexural strength and modulus tended to increase with increasing glass-fiber content (Figs. 4 and 7). The three-point bending test determines the maximum stress and a composite's stiffness when a flexural load is applied to the bulk material. This method was used to evaluate the bulk parameters such as flexural strengths and flexural moduli of GFRTPs with various fiber contents. The GFRTPs derive their strength from the flexural modulus and strength of the fibers embedded in the matrix, which are significantly greater than those of the matrix alone [17]. In the present study, the flexural strengths of polypropylene GFRTPs and polyamide-6 GFRTPs increased from 55.8 to 217.6 MPa, and from 50.5 to 274.8 MPa, respectively, with increasing glass-fiber content from 0 to 50 mass%. The flexural moduli of polypropylene GFRTPs and polyamide-6 GFRTPs increased from 1.75 to 7.42 GPa, and from 1.85 to 8.69 GPa, respectively, with increasing glass-fiber content from 0 to 50 mass%. Thus, it was confirmed that the GFRTPs prepared in this study had superior flexural properties when compared with unreinforced polypropylene or polyamide-6. Additionally, the flexural properties of GFRTPs can be tailored by varying the glass-fiber content. In other words, the GFRTPs might be expected as tailor-made materials that can be designed for different clinical situations and/or requirements.

The stress–strain curves of the polypropylene GFRTPs with fiber contents >30 mass% (GF30, GF40, and GF50) clearly indicate high rigidity, whereas those with fiber

contents <20 mass% (GF0, GF5, GF10, and GF20) indicate ductile properties (Fig. 5). Generally, thermoplastics such as polypropylene show a nonlinear relationship between stress and strain because of their ductility. However, the stress–strain curves of the polypropylene GFRTPs with fiber contents >30 mass% showed linear behavior, with high rigidity, in the early stage. The stress–strain curves of the polyamide-6 GFRTPs with fiber contents >20 mass% (GF20, GF30, GF40, and GF50) clearly indicated non-linear behavior, while those with fiber contents <10 mass% (GF0, GF5, and GF10) exhibited linear behavior (Fig. 8). These results show that the GFRTP rigidity was improved by fiber reinforcement of the thermoplastic using injection molding. However, GFRTPs made with a polyamide-6 matrix were more brittle than those with a ductile polypropylene matrix, so the polypropylene GFRTPs had better properties for use in NMCDs than the polyamide-6 GFRTPs. Moreover, the polypropylene GFRTPs with fiber contents of 10 and 20 mass% had good properties for use in NMCDs, because they had sufficient rigidity, similar to those of conventional PMMA denture base materials such as PB and IC, and their flexibility was similar to those of available NMCD materials such as VA and EB (Figs. 4 and 5).

The color stability of GFRTPs is a critical factor in maintaining their appearance; however, it is difficult to discern small color changes caused by penetration of colored solutions, using the human eye (Fig. 9). For colored solutions, coffee, tea, and coke are identified to be staining substances [27]. Among these solutions, coffee is the most chromogenic agent. Moreover, in most in vitro studies, the final period is typically 4 weeks in order to achieve a cumulative staining effect and obtain distinct results [27-29]. Therefore, applying the same method as used by other researchers [3,30], the color

stability of the polypropylene GFRTPs with fiber contents of 0, 10, and 20 mass% was assessed during the 4 weeks of immersion in coffee solution, by evaluating their ΔE^* and NBS values.

First, color differences were assessed by determining the ΔE^* values, using the CIE Lab system, of the GFRTPs after immersion in coffee. The Lab system makes it possible to evaluate the degree of color change based on the human visual perception of color difference [29]. The CIE Lab system is recommended for testing differences in material color because it is the most common color system [30]. Wieckiewicz et al. [25] evaluated the color stability of polyamide after exposure to air, water, coffee, and red wine for 36 days. They set a ΔE^* threshold level of 3.3, which was considered visible by the human eye and thus clinically unacceptable. They reported that polyamides immersed in coffee and wine for 36 days had clinically unacceptable color stability. In the present study, all of the experimental ΔE^* values for the GFRTPs, which ranged from 0.65 to 2.45, were lower than the threshold of 3.3 ΔE^* units used by Wieckiewicz et al. [25] (Fig. 10). These results demonstrate that the present GFRTPs will not discolor during exposure to the oral environment.

The color differences in the GFRTPs were also assessed using NBS units. Several studies have quantified the color difference of denture base materials by using NBS units [25,31]. According to the critical levels for color differences (Table 3), GF0 exhibited “slight” color change after 4 weeks of immersion in the coffee, with the NBS unit ranging from 0.60 to 0.71. Both GF10 and GF20 exhibited “noticeable” color changes after immersion for 4 weeks, with NBS unit ranging from 0.95 to 2.25. All of the GFRTPs were lower than the threshold level of 3.0 for NBS unit, which were

clinically acceptable color changes.

From the results obtained in both ΔE^* and NBS units, the present, novel GFRTPs showed clinically acceptable color stability. Conversely, polyamide-type thermoplastic (VA) exhibited "appreciable" color change though EB, PB, and IC showed "slight" color change, as measured in NBS units, after immersion in coffee for 4 weeks at 37 °C. This result agrees with reports by other researchers [3,25].

Finally, a novel NMCD made from the GFRTP designed in the present study is esthetically pleasing and has sufficient rigidity, and its properties can be controlled based on the fiber loading. The tailored mechanical characteristics of GFRTPs are a great advantage in selection of materials in different clinical situations. Therefore, it is expected that the GFRTPs designed in the present study will provide useful alternatives to current RPDs, satisfying both esthetics and function for clinical use in prosthodontic treatment.

Conclusions

In this study, novel NMCD materials made from E-glass fiber-reinforced thermoplastic were prepared by injection molding for use in esthetic prosthodontic appliances. The results and conclusions are summarized as follows.

1) The measured densities of GFRTPs with various fiber contents agreed with the theoretical densities obtained using the rule of mixtures. The GFRTPs with various fiber contents produced by injection molding had good uniformity and did not contain voids.
2) The flexural properties of GFRTPs could be greatly improved by increasing the

fiber content, and can be tailored by varying the fiber content for different clinical situations. In particular, the polypropylene GFRTPs with fiber contents of 10 and 20 mass% can be used in NMCDs because their excellent mechanical properties give both sufficient rigidity and elasticity.

3) The polypropylene GFRTPs after 4 weeks of immersion in the coffee showed clinically acceptable color stability. This result demonstrated that the present GFRTPs will not discolor during insertion of the denture.
4) The GFRTPs composed of glass fibers and polypropylene may be satisfactory for clinical use, making these materials attractive for prosthodontic NMCDs.

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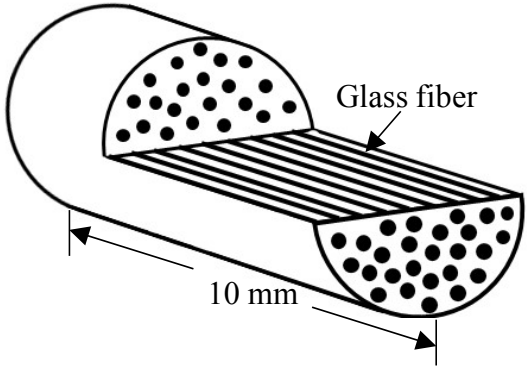
(a)

(b)



(c)

Figure 1. GFRTP pellets composed of glass fiber and thermoplastic. (a) Polypropylene GFRTP pellets . (b) Polyamide-6 GFRTP pellets. (c) Illustration of cross-sectional appearance of GFRTP pellet.

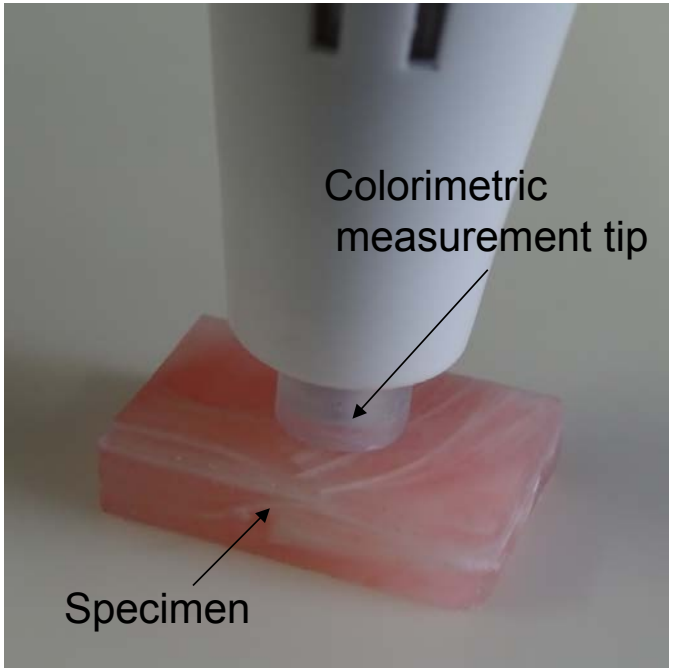


Figure 2. Photograph of the specimen and device setup during measurement. The elastic tip of the instrument was in contact with the middle of the specimen.

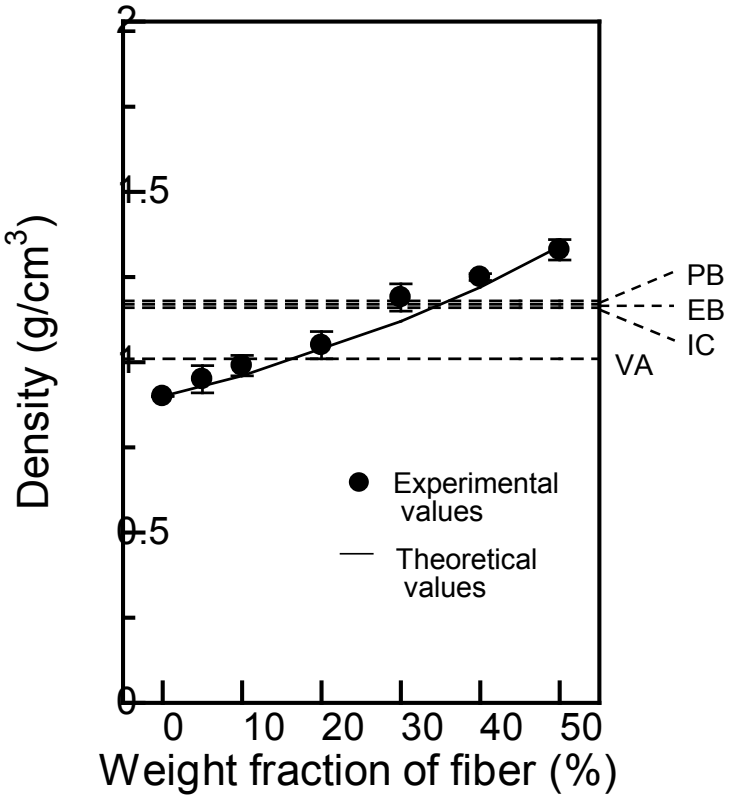


Figure 3. Relationship between apparent densities and fiber contents of polypropylene GFRTPs.

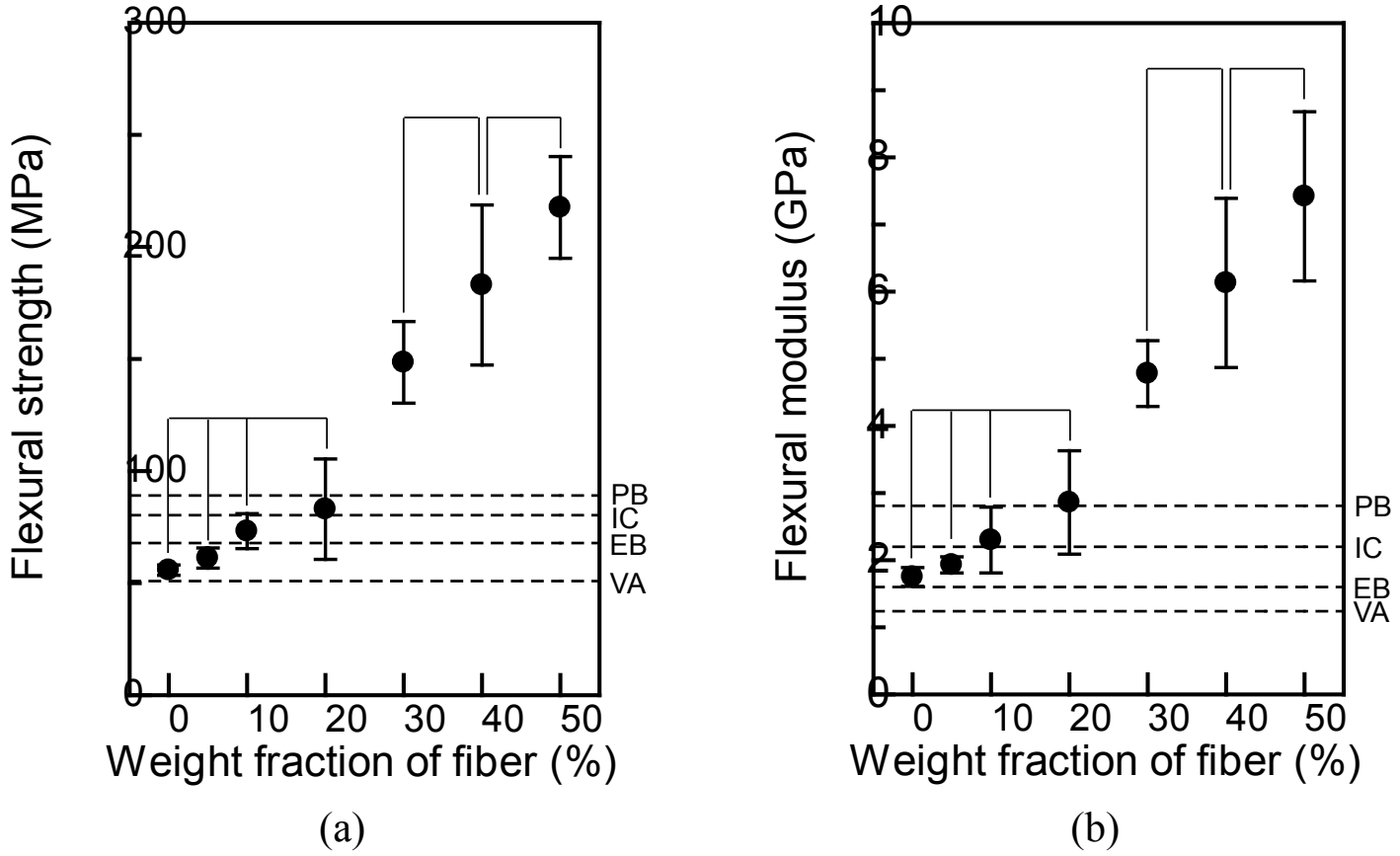


Figure 4. Flexural properties of polypropylene GFRTPs obtained using three-point bending tests. (a) Relationship between flexural strengths and fiber contents of GFRTPs. (b) Relationship between flexural moduli and fiber contents of GFRTPs. Values connected by horizontal bars are not significantly different from each other ($p > 0.05$).

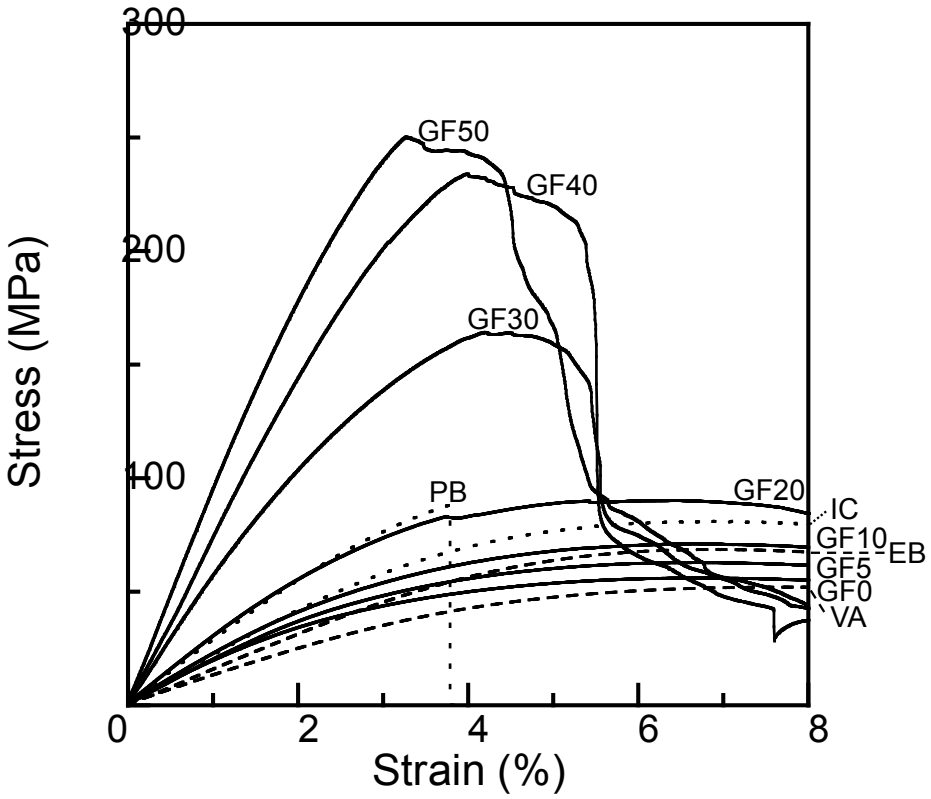


Figure 5. Typical stress–strain curves for polypropylene GFRTPs with various fiber contents and controls, obtained from flexural test.

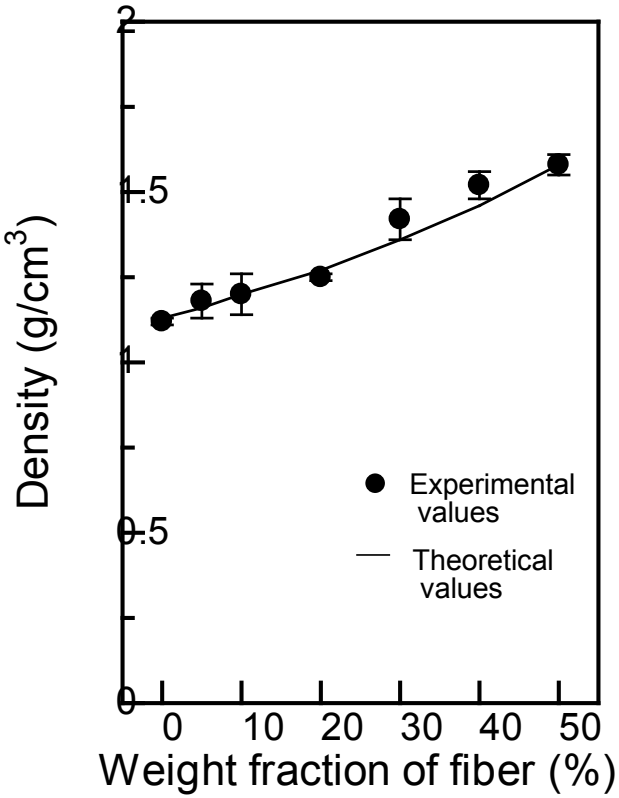


Figure 6. Relationship between apparent density and fiber content of polyamide-6 GFRTPs.

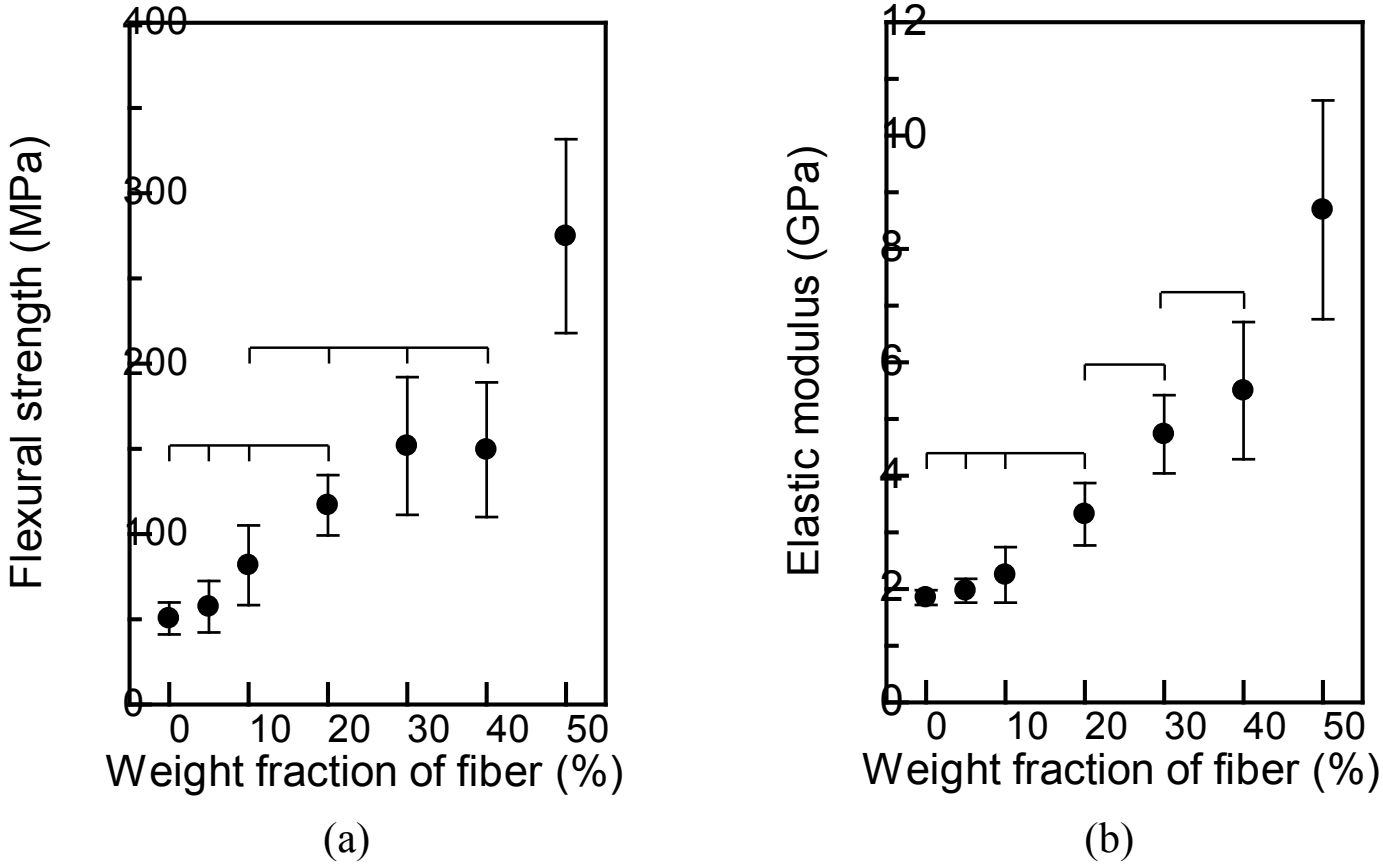


Figure 7. Flexural properties of polyamide-6 GFRTPs obtained using three-point bending tests. (a) Relationship between flexural strength and fiber content of GFRTPs. (b) Relationship between elastic modulus and fiber content of GFRTPs. Values connected by horizontal bars are not significantly different from each other (p>0.05).

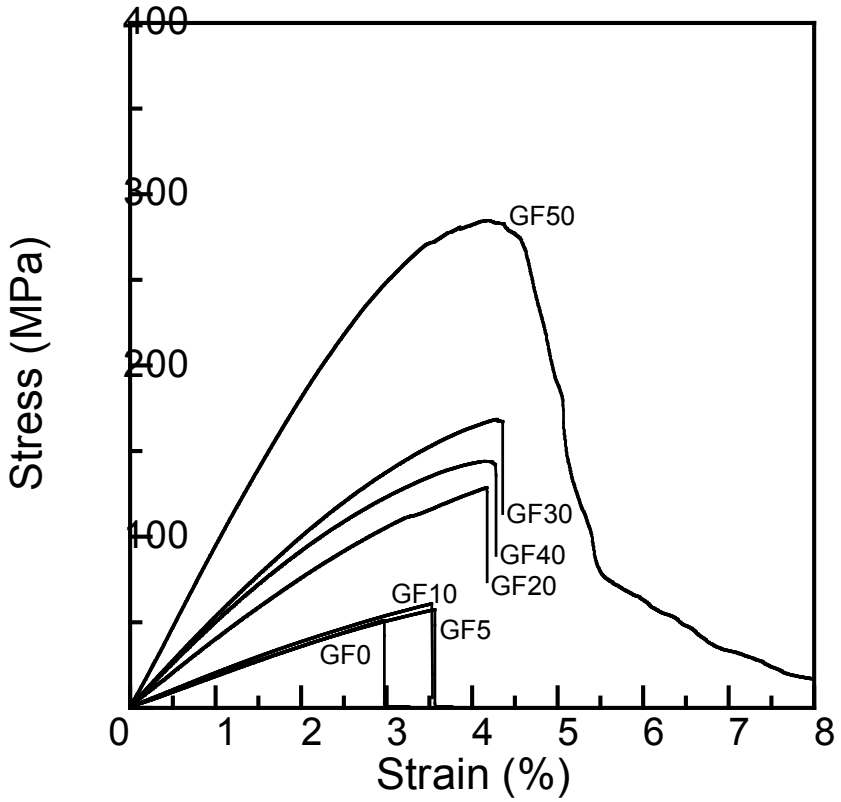


Figure 8. Typical stress–strain curves for polyamide-6 GFRTPs with varying fiber content obtained from the three-point bending test.

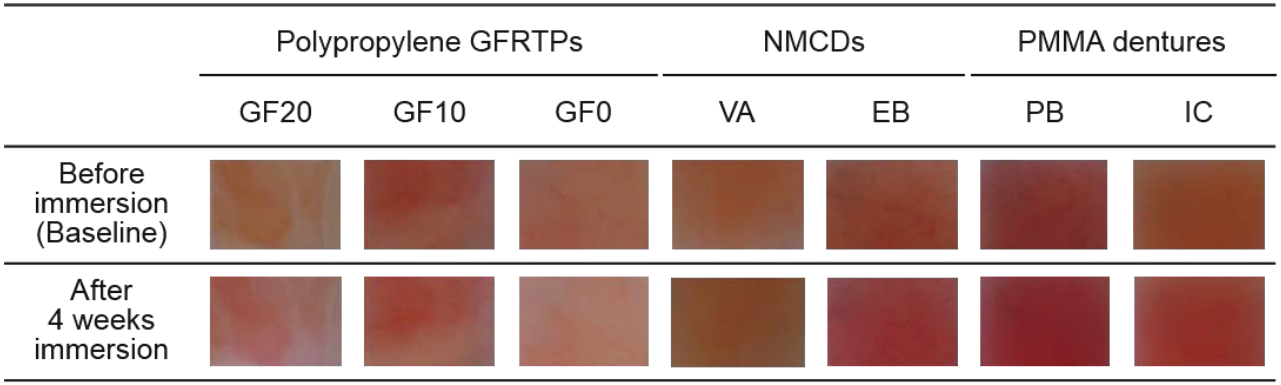


Figure 9. Photographs of each specimen before and after 4 weeks of immersion in coffee.

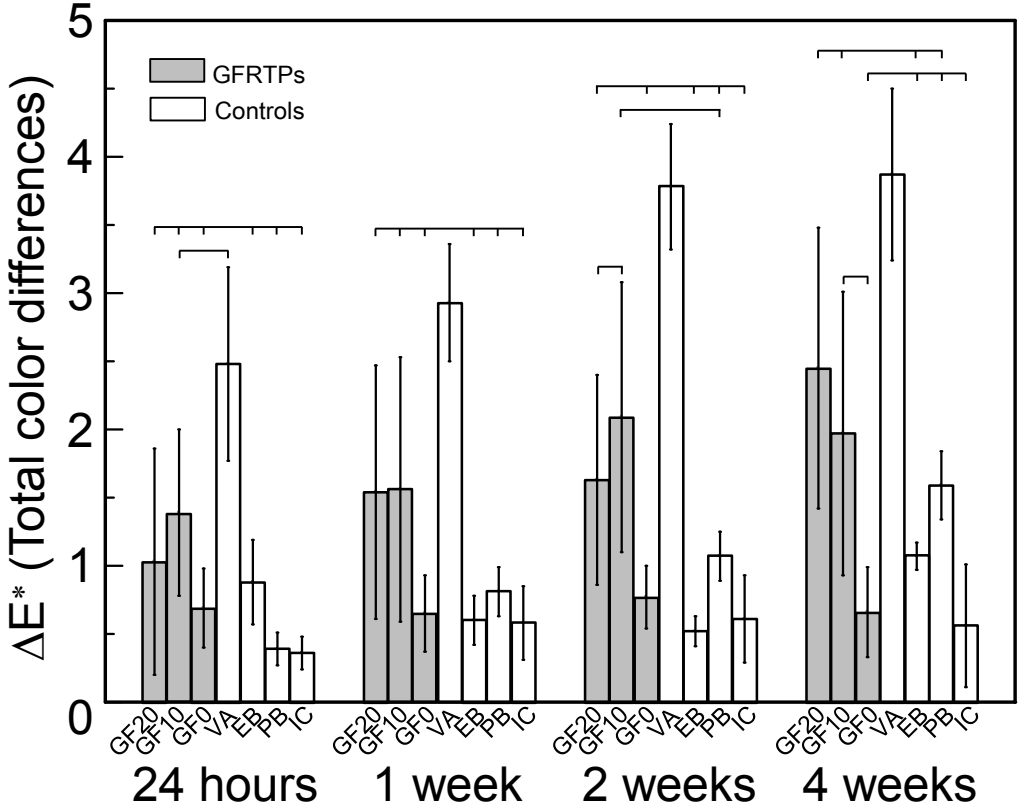


Figure 10. Color differences measured in ΔE^* at 24 h and at 1, 2, and 4 weeks after immersion in coffee. Values connected by horizontal bars are not significantly different from each other ($p > 0.05$).

Table 1. Materials used as controls.

Material Type	Brand Name	Code	Composition	Processing Method	Manufacturer	Lot Number
Denture base materials	Polybase	PB	Polymethyl methacrylate	Auto-polymerization	NISSIN, Kyoto, Japan	Powder: 5D2816100 Liquid: 5B3553170
	Ivocap	IC	Polymethyl methacrylate	Heat-polymerization	Ivoclar Vivadent, Tokyo, Japan	S05474
Non-metal clasp denture materials	Valplast	VA	Polyamide	Injection molding	UNIVAL, Tokyo, Japan	140444
	EstheShot Bright	EB	Polyester copolymer	Injection molding	i-CAST, Kyoto, Japan	4L8368070

Table 2. National Bureau of Standards (NBS) ratings.

NBS unit	**Critical remarks of color differences**	
0.0– 0.5	Trace	Extremely slight change
0.5– 1.5	Slight	Slight change
1.5– 3.0	Noticeable	Perceivable
3.0– 6.0	Appreciable	Marked change
6.0– 12.0	Much	Extremely marked change
12.0 or more	Very much	Change to other color

Table 3. Color differences measured in NBS units and critical remarks at 24h and 1, 2, and 4 weeks after immersion in the coffee solution.

	24 h		1 week		2 weeks		4 weeks	
	NBS units	**Critical remarks**	**NBS units**	**Critical remarks**	**NBS units**	**Critical remarks**	**NBS units**	**Critical remarks**
GF0	0.63 ± 0.27	Slight	0.60 ± 0.26	Slight	0.71 ± 0.21	Slight	0.61 ± 0.30	Slight
GF10	1.28 ± 0.56	Slight	1.44 ± 0.89	Slight	1.93 ± 0.91	Noticeable	1.82 ± 0.96	Noticeable
GF20	0.95 ± 0.76	Slight	1.42 ± 0.86	Slight	1.50 ± 0.71	Noticeable	2.25 ± 0.95	Noticeable
VA	2.28 ± 0.66	Noticeable	2.70 ± 0.39	Noticeable	3.48 ± 0.42	Appreciable	3.56 ± 0.58	Appreciable
EB	0.81 ± 0.28	Slight	0.55 ± 0.16	Slight	0.48 ± 0.10	Trace	0.99 ± 0.09	Slight
PB	0.36 ± 0.11	Trace	0.74 ± 0.17	Slight	0.98 ± 0.17	Slight	1.47 ± 0.23	Slight
IC	0.33 ± 0.11	Trace	0.53 ± 0.25	Slight	0.56 ± 0.29	Slight	0.52 ± 0.41	Slight

ΔE^* values were converted to NBS units by the equation: NBS units = $\Delta E^* \times 0.92$.