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

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The use of non-metal clasp denture (NMCD) materials may seriously affect the remaining tissues because of the low rigidity of NMCD materials such as polyamides. The purpose of this study was to develop a high-rigidity glass fiber-reinforced thermoplastic (GFRTP) composed of E-glass fiber and polyamide-6 for NMCDs using an injection molding. The reinforcing effects of fiber on the flexural properties of GFRTPs were investigated using glass fiber content ranging from 0 to 50 mass%. Three-point bending tests indicated that the flexural strength and elastic modulus of a GFRTP with a fiber content of 50 mass% were 5.4 and 4.7 times higher than those of unreinforced polyamide-6, respectively. The result showed that the physical characteristics of GFRTPs were greatly improved by increasing the fiber content, and the beneficial effects of fiber reinforcement were evident. The findings suggest that the injection-molded GFRTPs are adaptable to NMCDs because of their excellent mechanical properties.

Keywords: Non-metal clasp dentures, Glass fiber-reinforced thermoplastics, Flexural properties, Fiber content

INTRODUCTION

Patients today demand excellent esthetics as well as good function in prosthodontic restorations[1,2]. Removable partial dentures (RPDs) using resin-clasp retentive parts are defined as non-metal clasp dentures (NMCDs), and are often much more esthetically pleasing than conventional RPDs with metal clasps[3,4]. Generally, thermoplastic resins such as polyamide, polyester and polycarbonate have been used as NMCDs that can be injection-molded in one piece including clasps, minor and major connectors, and denture bases[5,6]. Several types of polyamides are most commonly used, having the longest history among the thermoplastic resins used for NMCDs[2]. Several studies have evaluated the properties of polyamide denture base materials, such as their flexural properties[1,2,3], water sorption[1,2,7,8], color stability[1,4,7], bond strength to acrylic resins[9,10], dimensional accuracy[11], and surface roughness[4,12]. According to the results of these studies, polyamides were thought to be an alternative to the conventional acrylic resins due to their esthetic and functional characteristics and physical properties such as thermo-injectability, high impact strength and flexibility. Polyamide dentures provide an excellent fit, and there is a low risk of the denture breaking during chewing or if it is dropped[12,13]. However, the high degree of flexibility is often a disadvantage from a clinical standpoint because polyamides do not have sufficient rigidity to evenly distribute the applied forces on the denture[14]. Accordingly, the use of NMCDs can seriously affect the remaining tissues because of their low rigidity, and such NMCDs do not conform to the standard principles of RPD design[2,13]. Therefore, there is a need for esthetic NMCD materials with improved strength and flexibility to be developed. It is expected that reinforcement of NMCD materials using glass fiber may fulfill this requirement.

In the previous study, a laboratory glass fiber-reinforced thermoplastic (GFRTP) composed of E-glass fiber and polypropylene for NMCDs was developed using a pultrusion and hot press method[16]. The results indicated that this GFRTP had superior flexural properties to commercially available NMCD materials. However, it was speculated that the multi-filament glass fibers did not fully infiltrate into the polypropylene matrix in the laboratory pultrusion and hot press system, because the density and elastic modulus of the GFRTP experimentally obtained by laboratory testing were lower than those of the GFRTP estimated by using a rule of mixture.

The purpose of this study was to develop the GFRTPs composed of E-glass and polyamide-6 using pellets consisting of polyamide-6 reinforced with E-glass fiber by an injection molding method. Moreover, the effects of fiber content on the flexural properties of GFRTPs were investigated.

MATERIALS AND METHODS

Material preparation

Polyamide-6 pellets (Daicel Polymer, Tokyo, Japan) were used as a thermoplastic matrix. The structural formula of polyamide-6 is shown in Fig. 1. Polyamide-6 is produced by ring-opening polymerization; it is not a condensation polymer. GFRTP pellets (Plastron, PA6-GF50-01, Daicel Polymer) consisting of polyamide-6 reinforced with E-glass fibers were used (Fig. 2a). To enhance the chemical bonding between the glass fiber and polyamide-6 matrix, the glass fiber is treated with a silane coupling agent. The fiber content of the GFRTP pellets was 50 mass%, with the fibers having a diameter of 17 µm and a length of 10 mm (Fig. 2b). Unreinforced polyamide pellets (without fiber-reinforcement) for dilution were added to GFRTP pellets with fiber content...
in gypsum molds with cavities (65 mm long, 32 mm wide, 3.0 mm high) using an injection molding machine (MH-01, Unival, Tokyo, Japan). The GFRTTP plates were carefully removed from the molds, and cooled to room temperature in an ambient atmosphere. The GFRTTPs were denoted as GF-0 (unreinforced polyamide), GF-5 (glass fiber content of 5 mass%), GF-10, GF-20, GF-30, GF-40, and GF-50.

Measurement of density
The apparent density of GFRTTPs with varying fiber content and the controls was determined according to Archimedes’ principle in distilled water. The density was taken to be the average of six measurements \( n=6 \). The theoretical density \( \rho_c \) of GFRTTPs with varying fiber content was calculated using the following equations:

\[
V_f = (W_f/\rho_f)/[(W_f/\rho_f) + ((1-W_f)/\rho_m)] \tag{1}
\]
\[
\rho_c = V_f\rho_f + (1-V_f)\rho_m \tag{2}
\]

where \( V_f \) is the fiber volume content, \( W_f \) is the fiber weight content, \( \rho_f \) is the E-glass fiber density (2.6 g/cm\(^3\)), and \( \rho_m \) is the polyamide-6 matrix density (1.13 g/cm\(^3\)).

Three-point bending tests
The flexural strength of the prepared GFRTTP specimens was investigated using a three-point bending test. According to Japanese Industrial Standards (JIS) T6501\(^1\), rectangular bar-shaped specimens (length 65 mm, width 10 mm, and thickness 3.0 mm) were prepared by cutting an injection-molded GFRTTP plate as described in material preparation. The specimens were then polished with 600-grit SiC paper under running water. The accuracy of the dimensions of all specimens was 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 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 elastic modulus \( E \) were calculated using the following equations:

\[
F = (3/2)(PL/bh^2) \tag{3}
\]
\[
E = (1/4)(L^3/bh^5)k \tag{4}
\]

where \( P \) is the maximum load, \( L \) is the span length, \( d \) is the specimen width, \( h \) is the specimen thickness, and \( k \) is the initial stage of the load-deflection curve. The experimental value was taken as the average of six measurements \( n=6 \). In addition, the fracture surface of the GFRTTPs was observed after the bending test under a field-emission scanning electron microscope (FE-SEM; JSM-6340F, JEOL, Tokyo, Japan) at an acceleration voltage of 5 kV. The sample was vacuum-dried and platinum-sputtered for FE-SEM observation.
Statistical analysis
The experimental results were analyzed using analysis of variance and Scheffe’s multiple comparison test among the means at \( p=0.05 \).

RESULTS
Figure 3 shows the apparent density of GFRTPs with varying fiber content. GF-0, GF-5, GF-10, GF-20, GF-30, GF-40, and GF-50 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/cm³, respectively; the apparent density increased with increasing fiber content. GF-0, GF-5, GF-10, GF-20, GF-30, GF-40, and GF-50 had theoretical densities of 1.13, 1.16, 1.20, 1.27, 1.36, 1.46, and 1.58 g/cm³, respectively. The measured density, obtained based on Archimedes’ principle, mostly agreed with the theoretical density obtained using the rule of mixtures.

Figure 4 (a) shows plots of the flexural strength in relation to fiber content. The flexural strength of GF-0, GF-5, GF-10, GF-20, GF-30, GF-40, and GF-50 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 GF-0, GF-5, GF-10, and GF-20 (\( p>0.05 \)). There were also no significant differences among the flexural strength values for GF-10, GF-20, GF-30, and GF-40 (\( p>0.05 \)). The flexural strength of GF-50 was significantly higher than the other GFRTPs (\( p<0.05 \)). Figure 4 (b) shows plots of the elastic modulus against fiber content. The elastic modulus of GF-0, GF-5, GF-10, GF-20, GF-30, GF-40, and GF-50 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 GF-50 was significantly higher than the other GFRTPs \( (p<0.05) \).

Figure 5 shows stress-strain curves obtained from the three-point bending tests. The stress-strain curves of GF-0, GF-5, and GF-10 increased linearly from the early stages to the fracture point. The stress-strain curves of GF-20, GF-30, and GF-40 increased linearly from the early to middle stages, and then showed nonlinear behavior up to maximum stress. In contrast, the stress-strain curve of GF-50 exhibited remarkably high rigidity compared with other GFRTPs.

Table 1 shows both load and deflection at the proportional limit of GFRTPs obtained by the bending tests. The loads at the proportional limit tended to increase with increasing fiber content. The load at the proportional limit of GF-50 was significantly higher than the other GFRTPs \( (p<0.05) \); however, there were no significant differences in the load at the proportional limit among all the other GFRTPs \( (p>0.05) \). The deflection at the proportional limit of GF-40 was significantly smaller than those of GF-0, GF-5, and GF-20 \( (p<0.05) \).

Table 2 shows the fracture scores for GFRTPs

### Table 1  Load and deflection at the proportional limit obtained from the three-point bending test of GFRTPs with varying fiber content

<table>
<thead>
<tr>
<th>ID</th>
<th>Proportional limit</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load (N)</td>
<td>Deflection (mm)</td>
</tr>
<tr>
<td>GF-0</td>
<td>43.2±8.8(^a)</td>
<td>1.65±0.44(^a)</td>
</tr>
<tr>
<td>GF-5</td>
<td>39.8±8.1(^a)</td>
<td>1.60±0.21(^b)</td>
</tr>
<tr>
<td>GF-10</td>
<td>43.7±8.4(^a)</td>
<td>1.46±0.31(^h)</td>
</tr>
<tr>
<td>GF-20</td>
<td>66.8±9.5(^c)</td>
<td>1.59±0.33(^b)</td>
</tr>
<tr>
<td>GF-30</td>
<td>67.2±13.0(^a)</td>
<td>1.19±0.17(^b)</td>
</tr>
<tr>
<td>GF-40</td>
<td>57.2±11.9(^a)</td>
<td>0.97±0.08(^c)</td>
</tr>
<tr>
<td>GF-50</td>
<td>97.3±23.8</td>
<td>1.18±0.14(^b)</td>
</tr>
</tbody>
</table>

Values with the same superscript are not significantly different from each other (Scheffe’s test, \( p>0.05 \)).

### Table 2  Fracture type after the three-point bending test for GFRTPs with varying fiber content

<table>
<thead>
<tr>
<th>ID</th>
<th>Complete fracture into two pieces</th>
<th>Partial fracture on tensile side</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF-0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>GF-5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>GF-10</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>GF-20</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>GF-30</td>
<td>0</td>
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<tr>
<td>GF-40</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>GF-50</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>
Fig. 6 Typical GFRTP specimen with fiber content of 30 mass% (GF-30) after the three-point bending test. (a) Photographic image of the tensile side of the specimen. (b) FE-SEM image of partial fracture on the tensile side (original magnification: 1,500×).

DISCUSSION

With increased patient awareness about esthetic restorations, NMCDs made from thermoplastics such as polyamide, polyester, and polycarbonate have been increasing use recently. They are considered to be superior to conventional RPDs with metal clasps in terms of esthetics; however, the use of NMCDs made from thermoplastics, especially polyamide, may seriously affect some tissues because of the low rigidity of thermoplastics. Several types of polyamide are commercially available. Polyamides are semi-crystalline polymers whose repeating units are characterized by the amide group. A distinction is made between two types: polyamides made from hydrolytic polymerization of ε-caprolactam (e.g. polyamide-6,6 and polyamide-12) and polyamides made from polycondensation of hexamethylenediamine and adipic acid (e.g. polyamide-6,6). Polyamide-12 is proposed as a denture base material in dentistry because of its high impact strength, toughness, and resistance to fracture. However, the flexural strength, elastic modulus and rigidity are inferior to other NMCD materials such as polyester and polycarbonate. In contrast, polyamide-6 is a particularly attractive class of polymer because of its competitive price, excellent strength and rigidity, low friction coefficient, and high dimensional stability and chemical and wear resistance, making it mostly used type of polyamide worldwide. Therefore, this study demonstrated the development of GFRTPs composed of E-glass fiber and polyamide-6 as an NMCD material, and investigated the effect of varying fiber content (0 to 50 mass%) on its physical properties.

The apparent density increased with increasing glass fiber content after the bending tests. The GF-0 specimens all completely fractured into two pieces. However, the GF-20, GF-30, GF-40, and GF-50 specimens all had partial fractures on the tensile side without complete fracture.

Figure 6 (a) shows a typical photograph of GF-30 with a partial fracture on the tensile side after the bending test. Figure 6 (b) shows an FE-SEM photograph of the fractured section of a GF-30 specimen. Tight binding between the glass fiber and the polyamide can be observed in the GFRTP, because the lengths of pulled-out fibers are relatively short.

The results obtained from the three-point bending tests showed that both the flexural strength and elastic modulus tended to increase with increasing glass fiber content (Fig. 4). The flexural strength increased from 50.5 to 274.8 MPa as the glass fiber content increased from 0 to 50 mass%. The elastic modulus also increased from 1.85 to 8.69 GPa as the glass fiber content increased from 0 to 50 mass%. The flexural strength and elastic modulus of polyamide are reported to be 27–98 MPa and 0.54–1.77 GPa, respectively. Thus, it was confirmed that the GFRTPs prepared in this study had superior flexural properties when compared with unreinforced conventional polyamide. 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. Besides, the effect of fiber reinforcement appeared remarkably in GFRTP with fiber content of 50 mass%. Although the effect of fiber content on flexural properties is summarized above, more investigation might be needed to examine a large difference between fiber contents of 40 and 50 mass%.

Some basic investigations regarding glass fiber reinforcement of polyamide denture base resins with low rigidity have been reported. Sasaki et al. investigated the effect of reinforcement on the flexural properties of NMCDs made of thermoplastics such as polyamide, polyester, and polycarbonate. In their study, commercially available unidirectional glass fiber-reinforced composite (FRC) was used for reinforcement. The authors reported that the elastic modulus of polyamide with FRC was 1.74 times higher than that of unreinforced polyamide. However, the application
of continuous unidirectional FRC to RPDs in the oral environment has limitations. It is known that RPDs must withstand the multi-directional forces that are exerted within the mouth during mastication. Continuous unidirectional FRC is anisotropic with high strength and rigidity in one direction; there are large differences in properties between the longitudinal and transverse axis in relation to the fiber direction. The GFRTPs in this study were injection-molded using pellets consisting of polyamide reinforced with glass fibers 10 mm in length (see Fig. 2) that were homogeneously dispersed through the polyamide matrix through injection molding. Generally, such GFRTPs are defined as quasi-isotropic materials at the macro scale, and are expected to have a reinforcing effect on the RPDs in the oral environment because they have the same properties in all directions.

The typical stress-strain curves of the GFRTPs with fiber content above 20 mass% (GF-20, GF-30, GF-40, and GF-50) clearly indicated non-linear behavior, while those with fiber content below 10 mass% (GF-0, GF-5, and GF-10) exhibited linear behavior (Fig. 5). These data support the argument that GFRTPs have greater rigidity and toughness with a higher fiber content. The fractured specimens of GFRTPs with fiber content above 20 mass% after the bending tests exhibited partial fractures on the tensile side (Table 2; Fig. 6 (a)). This is because the bending load applied by three-point bending test produces the maximum compressive or tensile stress at outermost position (i.e., upper or bottom) within the cross-section of the specimen. However, none of the GFRT specimens with fiber content above 20 mass% fractured into two pieces (Table 2). It is thought that the fiber contents above 20 mass% could contribute to intercept transverse crack propagation within specimen. Meanwhile, the composite materials such as GFRTP can produce an excellent function by the good bonding between the reinforcement fiber and the matrix resin. The surface of glass-fiber is generally treated with an aminosilane coupling agent, in order to enhance the bonding between glass-fiber and polyamide-6 matrix. FE-SEM observation of fractured GFRTP specimens showed no void formation around the fibers in addition to short pulled-out fibers of ~20 µm (Fig. 6 (b)). As an evidence data, it indicates the good bonding between the fibers and the matrix.

Load and deflection at the proportional limit of GFRTPs are related to permanent deformation of dentures (Table 1). Generally, the retentive force of a prosthesis must be at least 20 N; in a prosthesis with two or four retentive clasps, approximately 5 to 10 N would be required for each clasp. The retentive force is influenced by the amount of undercut for each clasp. Therefore, it is important to select the optimal amount of undercut for each clasp material in prosthodontic treatment. For example, for cobalt-chromium clasps, a 0.25 mm undercut is commonly chosen. A 0.50 mm undercut is the optimal choice for thermoplastic resin clasps, which need to engage a deeper undercut to gain clinically acceptable retention. The deflection at the proportional limit of GFRTPs with varying fiber content (0.97–1.65 mm) is within the elastic deformation that occurs during insertion or removal of the denture. It is expected that the GFRTP prevents any loss of retention caused by permanent deformation.

The occlusal force exerted on polyamide denture (48 N) has been reported to be significantly lower than that on polymethyl methacrylate (PMMA) denture (100 N). The use of denture materials with a lower elastic modulus may result in pain due to greater mobility of an unstable denture, leading to a decrease in chewing efficiency. According to JIS T6501, heat-polymerizing PMMA requires a flexural strength of greater than 65 MPa and an elastic modulus of greater than 2.0 GPa as standard values for safe prosthodontic treatment. In this study, the GFRTPs with a fiber content greater than 10 mass% surpassed the JIS T6501 specification on both flexural strength and elastic modulus, although unreinforced polyamide-6 did not satisfy the standards. It is interesting to note that the load at the proportional limit (97.3 N) of the GFRTP with a fiber content of 50 mass% was similar to the occlusal force exerted on denture (100 N) in PMMA denture wearers. This finding may suggest that GFRTPs with a fiber content of 50 mass% do not undergo permanent deformation of clasps during mastication. However, the mechanical properties of GFRTPs were obtained from bar-shaped specimen for three-point testing due to their bulk characterization from the viewpoint of materials development. In fact, the nature of denture bases, where different shapes and thickness ratios are used in a clinical setting, cannot be easily simulated from the experimental results in this preliminary study. Clinical application of the GFRTPs to denture components having a complicated three-dimensional shape such as clasp and denture base should be investigated further.

Finally, several studies have focused on the color stability of NMCDs. It has been reported that clinically noticeable staining may occur on NMCDs made from polyamide; and color stability has a long-term effect on the esthetics of NMCDs. Further investigation of the color stability of GFRTPs and water sorption after immersion in solution is required.

CONCLUSION

In the present study, the NMCD materials made from E-glass fiber-reinforced polyamide-6 were developed. Such GFRTPs composed of glass fiber and polyamide-6 could be used with commercially available injection machines. As expected, the density and flexural properties of GFRTPs were greatly improved by changing the fiber content of the GFRTP. In other words, it is speculated that the mechanical properties of GFRTPs can be tailored by varying the fiber content for different clinical situations. Within the limitations of this study, the injection-molded GFRTPs have such excellent properties of GFRTPs in the three-point bending tests with bar-shaped specimens. For the clinical application, further research is needed in the shape of practical NMCD conditions.
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