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Flexural properties of glass fiber reinforced composite with multiphase biopolymer matrix

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The aim of this study was to evaluate flexural properties of glass fiber-reinforced composites with a multiphase biopolymer matrix. Continuous unidirectional E-glass fibers were preimpregnated with a novel biopolymer of poly(hydroxyproline) amide and ester. The preimpregnated fibers were then further impregnated in a co-monomer system of Bis-GMA–TEGDMA, which formed semi-interpenetrating polymer networks (semi-IPN) with the preimpregnated polymer. After light initiated polymerization of the monomer system, rectangular shaped bar specimens ($n = 4$) were tested by the three-point bending test. The control material was a fiber-reinforced composite with a Bis-GMA–TEDGMA-matrix only. The mean flexural strength of poly(hydroxyproline) amide preimpregnated fiber composite was higher than that of the control (FS = 888 vs. 805 MPa). The poly(hydroxyproline) ester preimpregnated fibers resulted in lower strength (FS = 541 MPa). The results of this study suggest that preimpregnation of glass fibers with poly(hydroxyproline) amide and the use of such fibers in fiber-reinforced composites with IPN polymer matrices, can reach relatively high mechanical properties.

1. Introduction

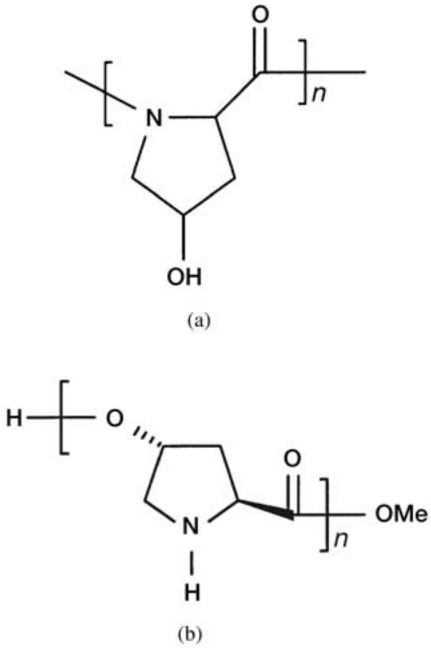
Bioresorbable and non-resorbable biopolymers have specific applications in the medical field. Bioresorbable polymers, such as polylactide and ε-caprolactone are used, for example, as bone substitutes or as a matrix for composites intended to be replaced by bone [1, 2]. Non-resorbable polymers are used as orthopedic bone cements or as a part of an implant [3, 4]. Typical polymers in bone cements contain poly(methyl methacrylate) (PMMA) and poly(butylmethacrylate) [4]. Attempts have been made to reinforce non-resorbable polymers with whiskers or short fibers [5–7]. In dentistry, non-resorbable polymers have been used for decades as prosthetic materials. In these applications, PMMA powder is mixed with, for example, methylmethacrylate–ethylene glycol dimethacrylate monomers [8]. By free radical polymerization, semi-interpenetrating polymer network (semi-IPN) structure, for the multiphase polymer, is formed. By definition, the IPN is formed from a linear polymer, which is partially or totally dissolved by bi- or multifunctional monomers [9]. Completion of polymerization forms a cross-linked interphase, called an IPN, between the linear phase and matrix. Polymer structures of this kind have successfully been used as polymer matrices for dental fiber-reinforced composites (FRC) [10, 11]. Recent developments in bioresorbable polymers have produced new types of polymers like biodegradable poly(hydroxyproline) (P) [12]. The linear polymer structure of P allows the use of P as a component for an IPN polymer structure. An IPN-structure is formed by the swelling and dissolving of the linear polymer. A requirement for dissolving this hydrophilic polymer component with a reactive monomer is hydrophilicity of the monomer or co-monomer system. One suitable co-monomer system, of relatively hydrophilic nature, is the bis-phenyl glycidyl dimethacrylate (Bis-GMA)–triethylene glycol dimethacrylate (TEGDMA) system [13].

The aim of the study was to investigate the preimpregnation of glass fibers with the novel biopolymer, P and to use these preimpregnated fibers with Bis-GMA–TEGDMA co-monomers in the fabrication of a semi-IPN polymer matrix for FRC. The flexural properties of the FRC were determined.

2. Materials and methods

2.1. Polymers

The experimental linear biopolymers of poly(4-hydroxy-L-proline) ester (PE) and poly(4-hydroxy-L-proline) amide (PA), (Fig. 1), were synthesized as described by Puska and Hormi [14]. The molecular weight of the polymer was controlled by the polymerization process. In this study the molecular weight (M_{vis}) of the PE was 10 000 g/mol and PA 2200 g/mol, respectively. PE and



(a)

(b)

Figure 1 (a) The structure of poly(4-hydroxy-L-proline) amide; (b) The structure of poly(4-hydroxy-L-proline) ester.

PA were in solid form after polymerization. For use in test specimen fabrication, a solution of PE and PA was made by adding the solvent, trifluoroethanol (TFE), so that the polymer concentration was 50 mg/ml.

The bifunctional monomer resin system was prepared by mixing Bis-GMA and TEGDMA in a ratio of 70 : 30 w/w (mole ratio 1.3 : 1). 0.14 g of a catalyst, dimethyl amino ethyl methacrylate (DMAEMA) (0.35 wt %) was mixed with 0.15 g of a light polymerizating initiator, camphorquinone (0.35 wt %). 11.72 g of TEGDMA (29.3 wt %) was added to this mixture and stirred. Finally, 28.00 g of Bis-GMA (70 wt %) was added. The mixture was heated at a temperature of 40 °C and stirred in darkness until a transparent mixture was obtained.

2.2. FRC test specimen fabrication

Six different test groups (Table I) were investigated in this study. There were four specimens (size 2 × 2 × 25 mm) in each group ($n = 4$). Continuous unidirectional bundle of E-glass fibers (containing about 4000 fibers) (composition: SiO_2 55%, CaO 22%, Al_2O_3 15%, B_2O_3 6%, MgO 0.5% and Fe^+ Na^+ K less than 1.0%), which were silanized (process R332, Ahlström, Karhula, Finland), were preimpregnated with PE or PA in TFE solution. After evaporation of the solvent, the bundle of fibers, called ''prepregs'', were further impregnated with the Bis-GMA–TEGDMA co-monomer system. Further-impregnation time was 24 h and it was carried out in a dark chamber. One prepreg or two prepregs were placed parallel to each other into stainless steel molds (size 2 mm × 2 mm × 25 mm) with an excess of the co-monomer resin system. The molds were covered with Mylar film™ and glass plates. The test specimens were initially polymerized with an Elipar™ Highlight (Espe, Seefeld, Germany) light-polymerization unit (wavelength 480 nm, light intensity ca. 600 mW/cm^2 for 40 s on both sides. After initial polymerization, the test specimens were post-cured with a light-curing device (LicuLite, Dentsply DeTrey GmbH, Dreieich, Germany), for 15 min. During post-curing, the temperature rose up to 80 °C. The test specimens were stored at room temperature in a desiccator for one week, before flexural testing.

TABLE I Description and classification of test groups

Group	Description
1FR	One bundle of fibers with Bis-GMA[a]–TEGDMA[b]-matrix
1FRPA	One bundle of fibers with PA[c] preimpregnation + Bis-GMA–TEGDMA-matrix
1FRPE	One bundle of fibers with PE[d] preimpregnation + Bis-GMA–TEGDMA-matrix
2FR	Two bundles of fibers with Bis-GMA–TEGDMA-matrix
2FRPA	Two bundles of fibers with PA preimpregnation + Bis-GMA–TEGDMA-matrix
2FRPE	Two bundles of fibers with PE preimpregnation + Bis-GMA–TEGDMA-matrix

[a] bis-phenyl glycidyl dimethacrylate.

[b] triethylene glycol dimethacrylate.

[c] poly(trans-4-hydroxyl-L-proline) amide.

[d] poly(trans-4-hydroxyl-L-proline) ester.

2.3. Flexural testing

Three-point bending tests (span 20 mm) were used to measure the flexural strength and flexural modulus (Young's modulus) of the specimens. Tests were done according to the ISO 10477 : 92 standard using a Lloyd Instruments LRX Material testing machine (Lloyd Instruments Ltd, Fareham, England), at a cross-head speed of 1 mm/min, and the stress–strain curves were drawn with a PC-computer program (Nexygen, Lloyd Instruments Ltd, Fareham, England). Test specimens were tested at room temperature (24 ± 2) °C in humidity of (31 ± 7)%. The ultimate flexural strength (FS (MPa)) was calculated from the formula:

$$\mathrm{FS} = 3Fl/2bh^2$$

where F is the applied load (N) at the highest point of the load-deflection curve, l is the span length (20 mm), b is the width (2.0 ± 0.1) mm and h is the height (2.0 ± 0.1) mm of the test specimen. Young's modulus (Y (GPa)) of the test specimens was calculated from the following formula:

$$Y = Fl^3/4bh^3d$$

where d is the deflection (mm) corresponding to the load F, at a point on the straight-line portion of the trace.

The mean values of flexural strengths and flexural moduli between PA and PE groups were compared by two-way ANOVA followed by Tukey's post hoc test.

2.4. Fiber quantity

The quantity of fibers in the test specimens was determined by combustion of the polymer matrix of the test specimens for one hour at 700 °C. The test specimens were weighed before and after combustion. The fiber content of the test specimens were calculated by the following formula:

$$m_f\% = (m_f/m_t) * 100\%$$

where $m_f\,\%$ is the mass percentage of fiber, m_f is the mass of fiber after combustion and m_t is the mass of test specimen. Volume fraction (V/vol %) of the fibers was calculated by using the following formula [15]:

$$V = (W_f/\rho_f)/(W_f/\rho_f + W_r/\rho_r)$$

where W_r is the weight proportion of reinforcement, ρ_r is the density of reinforcement (2.54 g/cm^3), is the weight proportion of resin and is density of resin (1.19 g/cm^3).

2.5. SEM analysis

Scanning electron microscopic (SEM) examination was made on bundle of fibers, with and without preimpregnation, to demonstrate the structure of PA and PE polymers on the surface of the fiber. To evaluate the final degree of impregnation of fibers with the resin, the test specimens were cut perpendicular to the fiber direction, into cubic specimens (2 mm × 2 mm × 1.5 mm^3) for SEM examination. The specimens were embedded into the urethane dimethacrylate resin, which was light polymerized for 40 s. Samples for SEM examination were made by wet grinding the surface of the specimen with silicone carbide grinding paper (FEPA #800, #2400 and #4000) using a grinding device LaboPol-21 (Stuers A/S, Rodovre, Denmark). Fibers and specimens were sputtered with carbon and examined with SEM (SEM-EDX Stereoscan 360, Cambridge Instruments, Cambridge, UK).

3. Results

3.1. Flexural properties

The flexural strength of the specimen with one prepreg and Bis-GMA–TEGDMA matrix (group 1FR) was 481 MPa (Fig. 2). The test specimens, which were preimpregnated with PA polymer and further impregnated with the Bis-GMA–TEGDMA system (1FRPA) had flexural strengths of 537 MPa, and PE impregnated (1FRPE) of 588 MPa. Using two prepregs (2FR), the flexural strength was increased to 805 MPa. In the group 2FRPA the strength was 888 MPa and 541 MPa for group 2FRPE. The ANOVA revealed that fiber content had a significant effect on the flexural strength ($p < 0.001$) whereas it had less of an effect on the strength of the type of preimpregnated polymer (PE or PA). However, the post hoc test (Tukey) revealed that specimens with a

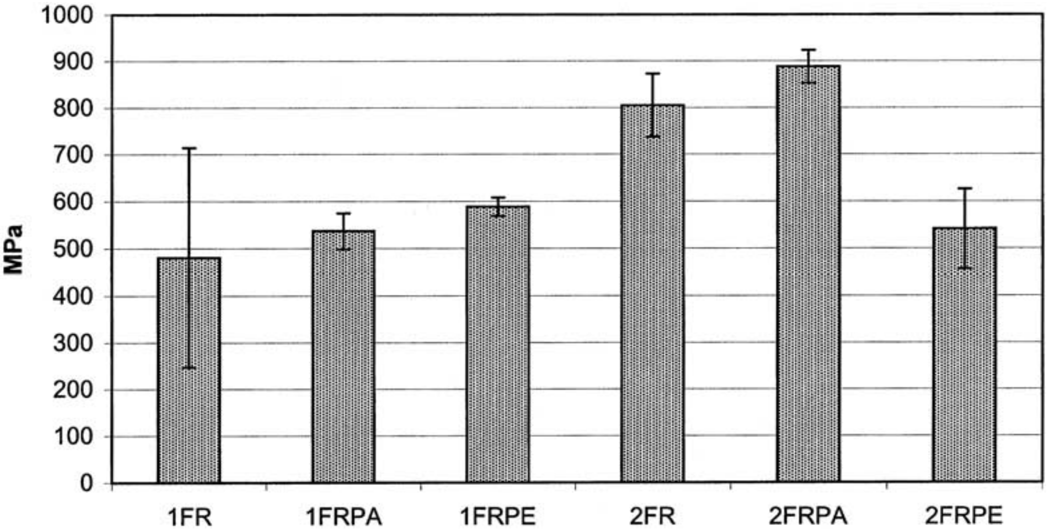


Figure 2 Ultimate flexural strength of the test species. A vertical line represents standard deviations. For group names, see Table I.

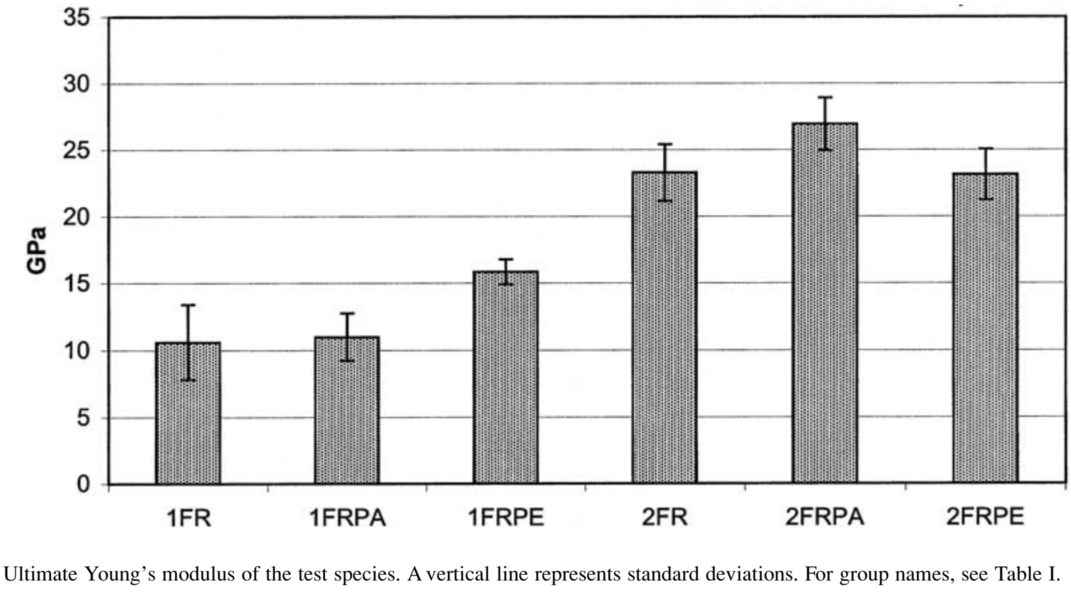
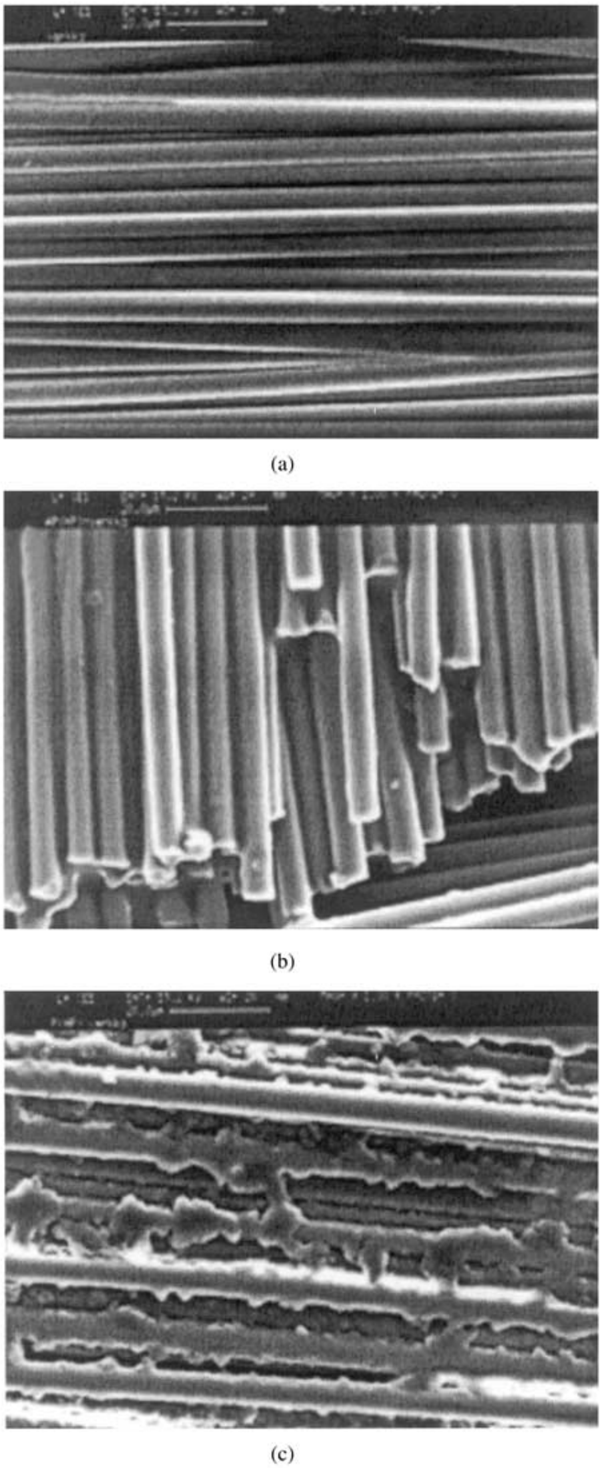


Figure 3 Ultimate Young's modulus of the test species. A vertical line represents standard deviations. For group names, see Table I.



(a)

(b)

(c)

Figure 4 SEM photomicrographs: longitudinal section of glass fibers (original magnification × 1000, bar = 20 mm). (a) E-glass fibers without impregnation; (b) E-glass fibers impregnated with poly-(hydroxyproline) amide and (c) E-glass fibers impregnated with poly(hydroxyproline) ester.

higher fiber quantity, with the PA preimpregnation yielded significantly higher strength than the PE polymer ($p = 0.001$).

The Young's modulus of the specimens in the 1FR group was 10.6 GPa (Fig. 3). In the 1FRPA group the modulus remained at a similar level (11.0 GPa) compared to 1FRPE group, which increased considerably (15.9 GPa). By increasing the fiber quantity the Young's modulus also increased (Fig. 3). The ANOVA indicated that fiber content had a significant effect on Young's modulus ($p < 0.001$). Preimpregnated polymers had less effect on Young's modulus according to the post hoc test ($p = 0.050$).

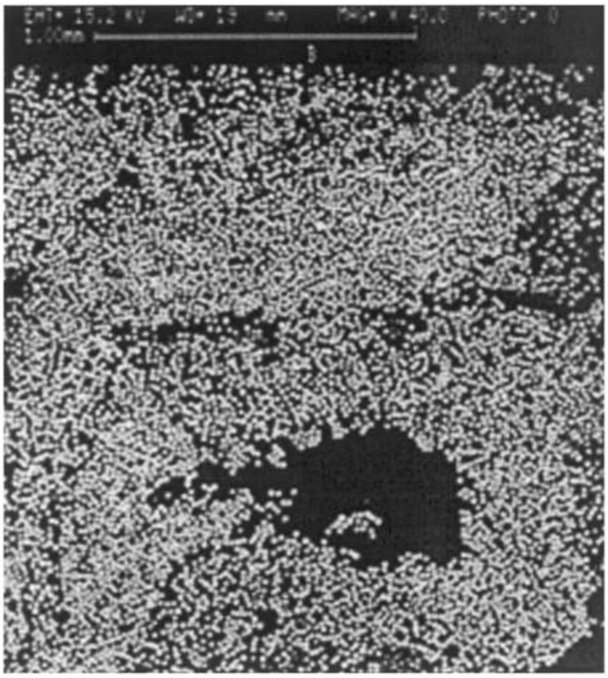


Figure 5 SEM photomicrographs: cross-section of E-glass fiber-reinforced composite with poly(hydroxyproline) amide (original magnification × 250, bar = 25 mm).

3.2. Fiber quantity

The quantity of glass fibers was 22.1 vol % (37.8 wt %) for one prepreg and 39.3 vol % (58.0 wt %) for two prepregs.

3.3. SEM analysis

SEM photomicrographs of non-preimpregnated fibers and fibers preimpregnated with PE and PA are shown in Fig. 4. Non-impregnated fibers had smooth surfaces (Fig. 4(a)), whereas PA preimpregnated fibers were evenly coated with a layer of PA polymer (Fig. 4(b)). PE polymer preimpregnation produced clusters of PE polymer on the surface of the fiber (Fig. 4(c)). The distribution of fibers in cross section of a test specimen with two prepregs was relatively even, and the fibers filled the whole cross-section of the specimen (Fig. 5). Good impregnation of fibers by the resin was obtained.

4. Discussion

This study investigated the flexural properties of FRC in a multiphase biopolymer matrix made by the preimpregnation of fibers with two novel biopolymers. The flexural strength of FRC was the highest in the group with two prepregs and preimpregnated with PA polymer. It has been shown by several studies that by increasing the quantity of fibers, the strength of a composite increases [16]. The results of the present study supported this, although group 2FRPE had a lower strength, which would have been expected. On the other hand, the distribution of fibers in cross-sectional view of test specimen, in groups 1FRPE and 1FRPA was not even, which should be taken into consideration in interpreting the results. Recently, it was shown that the position of the fibers greatly influenced the mechanical properties and this could also have influenced the results of the present study [17]. To optimize the reinforcing effect by fibers, the fibers should be placed at the tension side of the specimen during the loading process. Unfortunately, no attention was taken to ensure the location of one fiber prepreg to be at the tension side of the test specimen during loading, of the present study. The quantity of reinforcing fibers also influenced the flexural modulus (Young's modulus). This phenomenon has also been well established in the literature [16].

The differences between the mechanical properties of FRC with Bis-GMA–TEGDMA matrix and those having a PA–Bis-GMA–TEGDMA matrix, could be explained by plasticization of the highly cross-linked Bis-GMA–TEGDMA matrix by the linear polymer chains of PA. The influence of linear polymer chain plasticization of the cross-linked matrix on the flexural strength of the composite has also been suggested previously [18]. It could be possible that the plasticization by the linear polymer chains eliminates internal crack formation of the polymer matrix. In addition, there could be less stress concentrations at the fiber-polymer matrix interface with the plasticized polymer matrix than with the highly cross-linked matrix only.

An interesting finding was that the preimpregnated PA polymer produced FRC with higher strength and modulus than obtained with PE polymer preimpregnation. This could be due to the fact that the PA polymer swells and dissolves more easily with Bis-GMA and TEGDMA monomers with further-impregnation than the PE polymer. The swelling allowed the reactive Bis-GMA and TEGDMA monomers to diffuse and to come into contact with the surface of the silane coupling agent treated glass fibers. After polymerization, the reactive Bis-GMA and TEGDMA monomers form attachment between fibers and the polymer matrix. In the case of PE preimpregation, the Bis-GMA–TEGDMA monomers did not necessarily reach the surface of the glass fibers due to the PE polymer forming clusters. Thus, no chemical reaction between the methacrylate functionalized group of the polysiloxane network and the Bis-GMA–TEGDMA molecules was able to occur. This lead to the situation, where the PE polymer was only weakly bonded the surface of the glass fiber during the preimpregnation process and that the interface could be considered as a ''weak link'' of the composite, which resulted in lower flexural properties.

The clinical applications of the FRC material with a multiphase biopolymer matrix could be in orthopaedic and maxillofacial surgical applications. The present findings suggest that the initial strength of FRC could be tailor-made to fulfill the strength requirement for some applications. However, further *in vitro* studies are needed to show the behavior of FRC with a multiphase biopolymer matrix, in an environment simulating the conditions of the body. Also, it is of great importance to emphasize the anisotropic nature of unidirectional FRC which put demands on the design of the FRC appliance in the living tissue.

5. Conclusions

Within the limitations of the study, the following conclusions can be made:

1. Glass fibers could be preimpregnated with novel biopolymers and further impregnated with Bis-GMA–TEGDMA monomers.
2. Preimpregnation of glass fibers with poly(hydroxyproline) amide combined with Bis-GMA–TEGDMA monomers resulted in higher flexural strength and modulus than with Bis-GMA–TEGDMA matrix only.

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