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Flexible fiber-reinforced composites with improved interfacial adhesion by mussel-inspired polydopamine and poly(methyl methacrylate) coating

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ABSTRACT

To obtain a kind of light-curable fiber-reinforced composite for dental restoration, an excellent interfacial adhesion between the fiber and the acrylate resin matrix is quite essential. Herein, surface modification on glass fibers were carried out by coating them with poly(methyl methacrylate) (PMMA), polydopamine (PDA), or both. The PMMA or PDA coating was performed by soaking fibers in PMMA/acetone solution or dopamine aqueous solution. PDA/PMMA co-coated glass fibers were obtained by further soaking PDA-coated fibers in PMMA/acetone solution. These modified fibers were impregnated with bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) (5:5, w/w) dental resin at a volume fraction of 75%, using unmodified fibers as reference. Light-cured specimens were submitted to evaluations including flexural properties, morphological observation, dynamic mechanical thermal analysis (DMTA) and pull-out test. In comparison with unmodified glass fibers, all the modified glass fibers showed enhancements in flexural strength and modulus of Bis-GMA/TEGDMA resin composites. Results of DMTA and pull-out tests confirmed that surface modification had significantly improved the interfacial adhesion between the glass fiber and the resin matrix. Particularly, the PDA/PMMA co-coated glass fibers displayed the most efficient reinforcement and the strongest interfacial adhesion due to the synergetic effects of PDA and PMMA. It indicated that co-coating method was a promising approach in modifying the interfacial compatibility between inorganic glass fiber and organic resin matrix.

1. Introduction

Most endodontically treated teeth require a post-and-core build-up for restoring the teeth to optimum health and function [1]. Prefabricated fiber posts are the most popularly used materials for these endodontical treatments due to their advantages in biocompatibility, mechanical properties and aesthetic features [2,3]. Many prefabricated fiber posts (e.g. RTD, 3 M and DMG) are now easily obtained worldwide [4,5]. However, each tooth in the arch exhibits anatomic characteristics such as root curvature, mesio-distal width and labio-lingual dimension. In other words, root anatomy dictates post selection for endodontical treatments. In the case of abnormal curved root canal, prefabricated fiber posts cannot fit into the canal well, and thus fail to achieve satisfactory endodontical treatment [6]. Flexible prepreg, i.e. pre-impregnated composite fibers, can be a good solution for this situation because of its chairside operability [7].

The bonding of a post to the tooth structure should improve the prognosis of the post-core restored tooth by increasing post retention and by reinforcing the tooth structure [8]. Prepregs composed of glass fibers and light-curable acrylate resin are preferred for dental restoration because they can form strong bonding to acrylate cements, which are so essentially required to fix posts in root canals firmly [9].

In the case of fiber-reinforced dental composites, a primary issue is the interfacial adhesion between the fiber and the resin matrix, especially in a moist environment [10,11]. Perfect adhesion is absolutely necessary to transfer load from the matrix to the fiber, i.e. the strong fiber carries the load, while the matrix distributes it and transfers it from one fiber to the other. Glass fibers are generally treated with silane coupling agent to enhance chemical bonds between the fiber and the resin matrix [12]. The Si group in the silane coupling agent is able to interact with inorganic surface of glass fiber, while another group in silane coupling agent is able to form covalent bonds with the organic resin matrix. Apparently, organic resin matrices with different chemical structures dictate silane coupling agent selection. The bonding between glass fiber and silane coupling agent via the formation of Si-O-Si is reportedly not so stable in aqueous environments [13]. Plasma treatment is also applied to improve fiber-matrix adhesion, in which newly activated components or surface roughness are introduced onto the fiber's surface.

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The adhesion between the fiber and the matrix was thus enhanced [14]. Due to its relatively high cost and low treating efficiency, however, plasma treatment is not popularly used in scaled-up production. For dental composites, an ideal modification method is low-cost, effective, nontoxic and causes no adverse effect on mechanical properties of glass fibers. In addition, it is welcomed if the modified fibers can remain acceptable interfacial adhesion when the composites are used in aqueous environments.

To achieve this goal, surface modification with mussel-inspired dopamine (DA) seems one of the simplest and most effective strategies in enhancing interfacial adhesion for various composites [15]. The amino acid dihydroxyphenylalanine (DOPA), has been identified to be largely responsible for the cohesive and adhesive strengths of mussel adhesive proteins in aqueous environments [16]. As an analogue of DOPA, DA resembles the strong adhesion ability of DOPA, and it is able to attach onto different substrates (e.g. metal, ceramic, polymer) by virtue of the strong anchoring force of its catechol functionality [17]. The DA coating process is easy and mild. Briefly, substrates are simply soaked in a DA aqueous solution at room temperature, and a polydopamine (PDA) layer on the substrate surface is readily formed via the oxidative polymerization of DA [18]. Various substrates including hydroxyapatite, carbon nanotube, glass, polytetraethylene (PTFE), polyester, silicon rubber, etc., have all been surface-coated with PDA in a similar manner [19–27]. The method would not ruin any structure of the original substrate, and it is extremely useful for biomedical applications because it does not require the time-consuming synthesis of complex linkers and the process is solvent-free and nontoxic.

In the aspect of using PDA modifications to improve interfacial adhesion in composites, some achievements were reported in recent years. To improve the dispersibility and interfacial interaction of nanofillers in polymer nanocomposites, a layer of PDA was constructed onto the surface of clay. It was found able to benefit not only the dispersion of clay in epoxy resin matrix but also to enhance the effective interfacial stress transfer [27]. PDA coating was also used to coat aramid fibers. In comparison with silane coupling modifications, the adhesion between the PDA-modified fibers and rubber matrix was remarkably improved [28]. The surface free energy of both carbon and glass fibers was found to increase after PDA coating; therefore, the fibers displayed quite good wettability to epoxy resin [29].

With these approaches, in this study, PDA coating on glass fibers was proposed to achieve good infiltration with light-curable acrylate resin, and thus their interfacial adhesion could be improved. In view of the structure similarity and excellent compatibility between poly(methyl methacrylate) (PMMA) and acrylate resins [30–32], PMMA coating or PDA/PMMA co-coating on glass fibers was also investigated. As illustrated in Fig. 1, prepregs consisting of glass fibers and bisphenol A glycidyl methacrylate (Bis-GMA) dental resin were prepared, light-cured and submitted to characterizations including flexural properties, dynamic mechanical thermal analysis (DMTA) and pull-out test. In comparison with unmodified glass fibers, the null hypothesis of the present study was that the aforementioned modifications on glass fibers could not significantly improve the interfacial adhesion between the fiber and the resin matrix.

2. Experimental

2.1. Materials

The glass fibers used in this study were SE8400LS from Owens Corning Co., Ltd. (USA). The fibers were cleaned in distilled water under ultrasonication for 10 min before they were used in the following modifications. Dental resins as Bis-GMA, triethylene glycol dimethacrylate (TEGDMA), 2-(dimethylamino) ethyl methacrylate (DMAEMA), camphorquinone (CQ) and PMMA ($M_w = 35{,}000$) were purchased from Sigma-Aldrich (USA). Dopamine hydrochloride (DA · HCl) was also purchased from Sigma-Aldrich and used directly. Tris(hydroxymethyl aminomethane) (Tris) was purchased from Alfa Aesar Company (USA). Other chemicals used in the study were from Beijing Chemical Plant (China).

2.2. Coating modifications on glass fibers

2.2.1. PDA coating process

A certain amount of DA · HCl was dissolved in distilled water to get a transparent solution with concentrations of 1.0, 2.0 or 4.0 mg/mL, and the solution pH was adjusted to 8.5 by adding Tris. Pre-cleaned glass fibers were then immersed into the solution at room temperature for different times (2, 10 or 24 h). After the reaction, glass fibers were

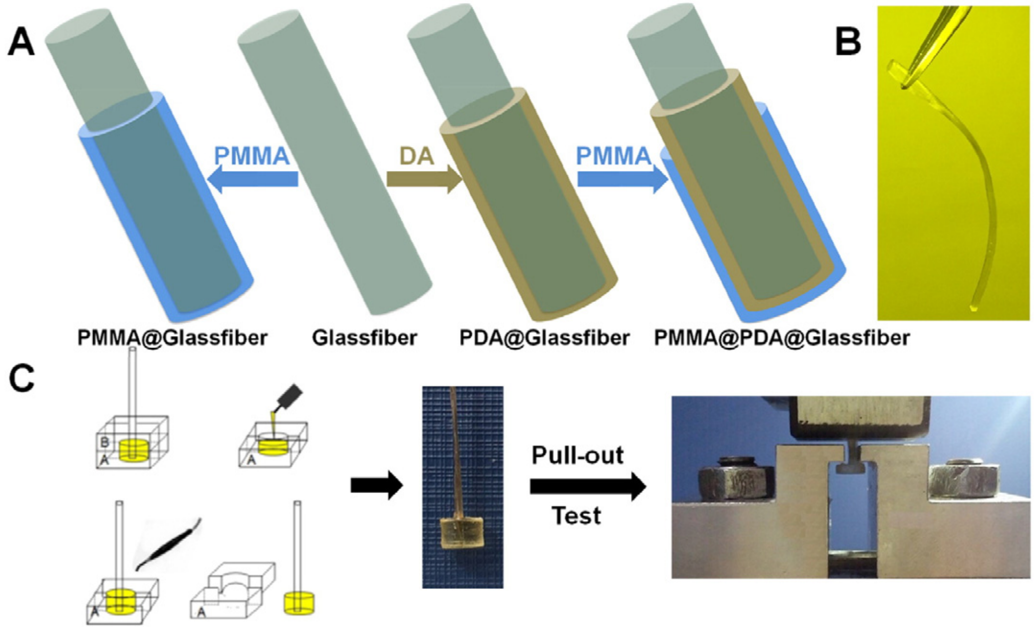

Fig. 1. Schematic description of glass fibers with different surface modifications (A), the prepared prepreg (B) and the following composite samples for pull-out test (C).

retrieved, washed with distilled water three times, and freeze-dried. The untreated glass fibers were referred to as Glassfiber and the PDA-coated glass fibers were referred as PDA@Glassfiber.

2.2.2. PMMA coating process

PMMA was added to acetone, and the system was continuously stirred overnight to get a PMMA/acetone solution (5 wt.%). Subsequently, glass fibers were immersed into the solution for some time until the fibers were impregnated completely. The glass fibers were retrieved from the solution, and acetone evaporated naturally to leave a PMMA coating on glass fibers. The PMMA-coated glass fibers were referred as PMMA@Glassfiber.

2.2.3. PDA/PMMA co-coating process

The aforementioned PDA@Glassfiber was immersed into the 5 wt.% PMMA solution in acetone for 5–10 s and taken out. After acetone evaporated, PDA and PMMA co-coated glass fibers were obtained, and referred as PMMA@PDA@Glassfiber.

2.3. Preparation of prepregs

The light-curable resin mixture was prepared by mixing equal amounts of Bis-GMA and TEGDMA (50:50 in weight), with DMAEMA and CQ being added at the 0.5 wt.% of total resin. The system was uniformly mixed with continuous stirring. Then, bunched glass fibers were soaked into the resin mixture until a kind of transparent state was achieved with no obvious tiny bubbles between fibers. Then, the glass fiber bunch was taken out from the resin mixture vertically to drip off excess resin. Thus, prepregs were obtained and stored in dark environment to prevent premature solidification. At this stage, the volume fraction of glass fibers in the prepregs was ~75%. The unmodified and the three modified glass fibers were all used in preparing the prepregs.

2.4. Flexural properties evaluation

To prepare specimens for flexural properties evaluation, according to ISO 10477 standard, a Teflon mold with the size of 25 mm × 2 mm × 2 mm (l × w × h) was applied. Bunches of prepregs were put parallel into the mold along the long axis until the mold was fully filled. In order to prevent pre-mature curing, these operations were conducted in a yellow-light room. After being degassed in vacuum, the prepregs were photo-cured for 120 s for each side by using curing light (300 mW/cm^2; Coltolux LED), followed by post-treatment at 37 °C for 48 h. The specimens were carefully polished before being subjected to three-point bending tests. The final dimensions of the specimens were measured by a Vernier caliper.

The three-point bending test was performed on a universal testing machine (Instron 1121, UK), with a span of 20 mm and a crosshead speed of 1.0 mm/min being set. The flexural strength (*Fs*) and flexural modulus (*Ey*) of composite specimens were calculated as follow:

$$Fs = 3Fl/2bh^2 \tag{1}$$

$$Ey = l^3 F_1/4fbh^3 \tag{2}$$

where F is the applied load (N) at the highest point of–load-deflection curve, l is the span length (20 mm), b is the width of the specimen, h is the thickness, F_1 is the load (N) at a convenient point in the straight line portion of the trace and f is the deflection 9 (mm) of the specimen at load F_1. Ten specimens for each group were tested.

2.5. Dynamic mechanical properties

Dynamic mechanical properties of all the samples were determined by a dynamic mechanical thermal analyzer (DMTA V, Rheometric Scientific Inc., USA) in a three-point bending mode at a frequency of 5 Hz and a scan rate of 5 °C/min within a temperature range of 25 °C–250 °C. The sizes of the specimens were the same as those for flexural properties evaluation.

2.6. Pull-out test

A pull-out test was designed as shown in Fig. 1C for the purpose of quantitatively identifying the interfacial properties between glass fibers and Bis-GMA/TEGDMA (50:50 in weight) resin matrix. Briefly, unmodified and modified glass fibers were cut into strands of 40 mm in length, and a Bis-GMA/TEGDMA resin core of 6 mm in diameter and 2 mm in height was built around the end of glass fibers. After being light-cured, the specimens were submitted to a pull-out test and the interfacial adhesion between glass fiber and resin matrix was characterized by the maximum failure load (N). In preparing the pull-out specimens, a specially designed mold made of PTFE was used. The mold was composed of two halves which were convenient for taking out the specimens. The specimens were built through the following steps: (1) injecting the light-cured resin into the mold; (2) inserting glass fiber strand into the resin; (3) light-curing for 60 s (300 mW/cm^2, Coltolux LED); (4) splitting the mold, taking out the specimens and light-curing for an additional 60 s to ensure polymerization. Ten specimens for each kind of glass fibers were tested. Instron 1121 was used to apply a tensile force along the long axis of the glass fibers at the crosshead speed of 0.5 mm/min until failure occurred. The maximum failure load of each specimen was recorded, at which point the specimen was damaged by fiber dislodgement.

2.7. Characterizations

Surface elemental compositions of modified glass fibers were determined by X-ray photoelectron spectroscope (XPS, Thermo ESCALAB 250, USA) with an Al Kα X-ray source (1486.6 eV photons) under vacuum (8–10 Torr) using an incidence angle of 45° at a power of 150 W. The chemical structure of the PDA coating was analyzed using Raman spectroscopy (Renishaw in Via, UK). Morphological observations were conducted by scanning electron microscope (SEM, S-4700, Hitachi) at an accelerating voltage of 20 kV after being sputter-coated with platinum (30 mA, 20 s) using a sputter coater (Polaron E5600, USA).

2.8. Statistical analysis

The results of the three-point bending test and the pull-out test were represented as mean ± standard deviation for $n = 10$. Statistical analyses were made based on t-test and differences between groups were considered significant at $p \le 0.05$.

3. Results

3.1. PDA coating on glass fibers

PDA coating on glass fibers was carried out by applying several DA solutions of different concentrations for various reaction times. As shown in Fig. 2, the pristine glass fiber displayed a very smooth surface (Fig. 2a), while all the modified glass fibers demonstrated rough surfaces depending on the treating parameters. When the concentration of DA solution was fixed at 2 mg/ml, the fiber surface could be seen becoming rougher as the reaction time increased from 2 h to 10 h (Fig. 2b and c). A distinguishable coating layer was apparently observed and covered the glass fiber completely as the reaction time was extended to 24 h (Fig. 2d). When the reaction time was set to 24 h and the concentration of DA solution was adjusted to 1 mg/ml (Fig. 2e) or 4 mg/ml (Fig. 2f), the surface coating that was observed was not as intact as that obtained from DA solution of 2 mg/ml (Fig. 2d). Blank domains with no coating material could be found when DA solution of low

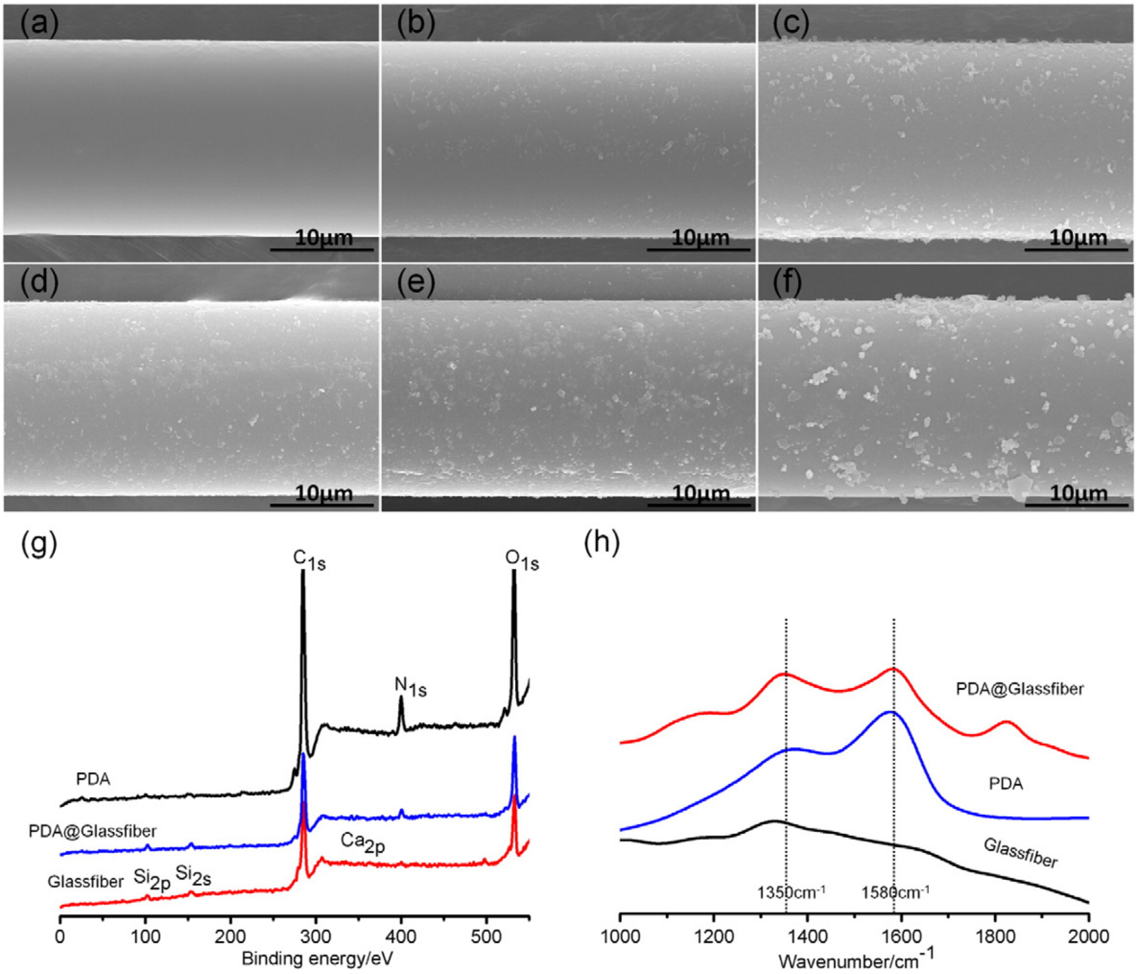

Fig. 2. PDA coating on glass fibers by applying different modification parameters and characterized using SEM observation (a–f), XPS (g) and Raman spectra (h). The DA solution concentration and reaction time for modification: (a) pristine glass fiber; (b) 2 mg/ml, 2 h; (c) 2 mg/ml, 10 h; (d) 2 mg/ml, 24 h; (e) 1 mg/ml, 24 h; (f) 4 mg/ml, 24 h.

concentration was used, whereas excess patches could be found if the DA solution had a relatively high concentration. In previous studies, it was found that a DA solution of 2 mg/ml was quite efficient in obtaining a homogenous PDA surface layer by coating PDA on fiber post [33] or polymeric nanofibers [34]. Therefore, with all the morphological comparisons on PDA-modified glass fibers in Fig. 2, the following PDA@Glassfiber were also preferably prepared by soaking glass fibers in DA solution of 2 mg/ml for 24 h at room temperature, for the purpose of obtaining a homogeneous coating layer of PDA on glass fibers.

The surface chemical composition and structure of the PDA@Glassfiber were identified by XPS (Fig. 2g) and Raman spectra (Fig. 2h). In comparison with pure PDA and pristine glass fibers, the XPS spectrum of PDA@Glassfiber clearly displayed characteristic signals of both PDA and glass components. The N_{1s} peak at 400 eV indicated the presence of PDA. Those Si (100 eV and 153 eV) and Ca (343 eV) signals originated from the glass fibers. In Raman spectroscopical analysis, inorganic glass fibers did not show an obvious peak in wavenumbers of 1200–1700 cm^{-1}. While the organic PDA presented two peaks at 1350 and 1580 cm^{-1}, which contributed to the aromatic component of PDA. Accordingly, the Raman spectrum of PDA@Glassfiber resembled these two peaks, indicating the successful coating of PDA on glass fibers.

3.2. PMMA coating and PDA/PMMA co-coating on glass fibers

In preliminary studies, PMMA solutions in acetone of different concentrations (2 wt.%, 5 wt.%, 10 wt.% and 15 wt.%) were ever used to coat glass fibers [35]. It was found that the viscosity of 2 wt.% PMMA/acetone solution was thin and PMMA coating on glass fibers was not satisfactory. However, the solutions were too thick to get a homogeneous PMMA coating on glass fibers, when the concentration of PMMA/acetone solution was higher than 10 wt.%. The mechanical properties of Bis-GMA/TEGDMA composites reinforced with PMMA/acetone solution of 5 wt.% treatment were found to be the highest among all the designs [35]. Therefore, PMMA/acetone solution of 5 wt.% was chosen as a proper solution to perform the coating modification in this study. The resulting PMMA@Glassfiber was observed using SEM, and the morphology is shown in Fig. 3a. The PMMA coating on the fiber could be seen quite smooth without any hint of adhesion between fibers.

In Fig. 3b, the glass fiber was firstly coated with PDA as aforementioned, followed by being soaked into PMMA/acetone solution (5 wt.%). The surface coating on the fiber could be seen a little thicker than that on PMMA@Glassfiber. And the surface roughness increased slightly. However, the PMMA@PDA@Glassfiber still displayed relative smooth surface without any hint of adhesion between fibers.

3.3. Flexural properties and fractural morphology

The prepreg made from PMMA@PDA@Glassfiber and Bis-GMA/TEGDMA is shown in Fig. 1B as an example to show the physical appearance. It could be seen the prepreg was flexible, quite transparent and homogeneous without visible bubbles. Composites made from prepregs containing different kinds of glass fibers were submitted to three-point bending test, and the flexural strength and modulus were obtained (Fig. 4). As shown in Fig. 4a and b, the light-cured pure Bis-GMA/

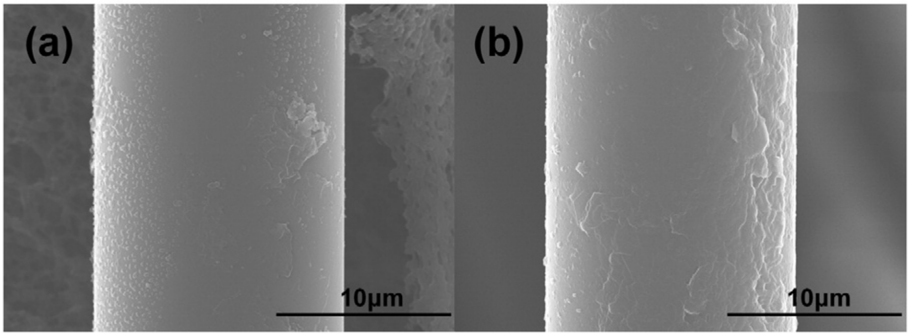

Fig. 3. SEM images show the PMMA coating (a) and PDA/PMMA co-coating (b) glass fiber.

TEGDMA resin specimens only demonstrated flexural strength and modulus at 113.7 ± 5.2 MPa and 1316.8 ± 48.1 MPa, respectively. When it was reinforced with glass fibers, without regarding the surface coating, all the composites displayed significant increases in the flexural strength and modulus, which went up to more than 800 MPa and 28 GPa, respectively. In comparison with the pristine glass fiber reinforced composites, the other three composites containing surface-modified glass fibers achieved further higher flexural strength and modulus, showing dependence on the type of surface coating. It could be seen that the PMMA@Glassfiber reinforced composites had better flexural properties than PDA@Glassfiber reinforced composites, but the PMMA@PDA@Glassfiber reinforced composites displayed the highest flexural strength (1025 ± 51.8 MPa) and flexural modulus (32.2 ± 1.2 GPa) among all the groups.

Composite fractures resulting from the bending test were observed under SEM, and images are presented as Fig. 5a–d. In the case of pristine glass fibers being used, many caves could be seen on the fractured surface due to the pulled-out glass fibers (Fig. 5a). Little resin was detected on the exposed fiber surface. Besides, distinguishable gaps were found between the fibers and the resin matrix. On the contrary, the other three fractural surfaces displayed trim cross-section, showing no hint of fibers pulling out. The glass fibers, either modified by PDA and PMMA or PDA/PMMA, could be seen adhering to the resin matrix tightly without a distinguishable gap (Fig. 5b–d). With a closer look at Fig. 5b, however, the adhesion of cured Bis-GMA resin to PDA@Glassfiber seemed a little inferior to those glass fibers with surface PMMA coating.

3.4. Dynamical properties

The tanδ curves of various glass fiber–reinforced Bis-GMA/TEGDMA composites are shown in Fig. 6 as a function of temperature. All the specimens demonstrated a broad damping peak in the range of 50 °C–250 °C. The pure Bis-GMA/TEGDMA resin matrix demonstrated its peak temperature around 100 °C, which was the glass transition temperature (T_g) of the pure resin. As the resin was reinforced with pristine glass fibers, the tanδ peak could be seen shifting to higher temperatures (114 °C). If the glass fibers had been surface modified, the resulting tanδ peak could be seen further shifting to higher temperatures. Among them, the highest peak temperature was detected at ~139 °C, when the PMMA@PDA@Glassfiber was used as the reinforcement for Bis-GMA/TEGDMA resin.

3.5. Pull-out test

By building a Bis-GMA/TEGDMA core around the ends of different glass fibers, the interfacial adhesion between fibers and the resin matrix was quantitatively evaluated via pull-out test. To avoid discrete data, only those maximum failure loads obtained at the failure mode of fiber dislodgement were reasonable and valid (Fig. 7a). As shown in Fig. 7b, those maximum failure loads of samples containing modified glass fibers were generally higher than that of the group prepared from pristine glass fibers. However, the increase in the maximum failure load was not so significant when the glass fibers were only surface-coated with PDA (increasing 10.2%) or PMMA (increasing 19.7%). A significant increase in the maximum failure load was achieved in the case of PMMA@PDA@Glassfiber reinforced composite being tested, in which, the maximum failure load increased 43.3% over that of the pristine glass fiber group. Noticeably, the modification with PMMA displayed higher contribution to the interfacial adhesion between glass fiber and resin matrix in comparison with the case of PDA modification.

4. Discussion

To obtain high-performance fiber-reinforced composites for dental restoration, the perfect interfacial adhesion between fiber and resin matrix was essential for effective stress transfer between different phases

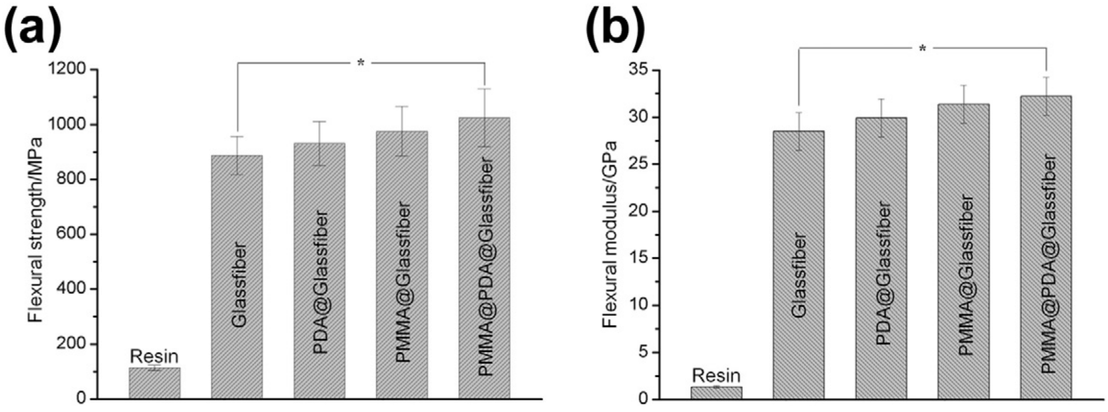

Fig. 4. Flexural strengths (a) and flexural modulus (b) of fiber reinforced Bis-GMA/TEGDMA composites containing different glass fibers obtained from three-point bending test (* $p < 0.05$).

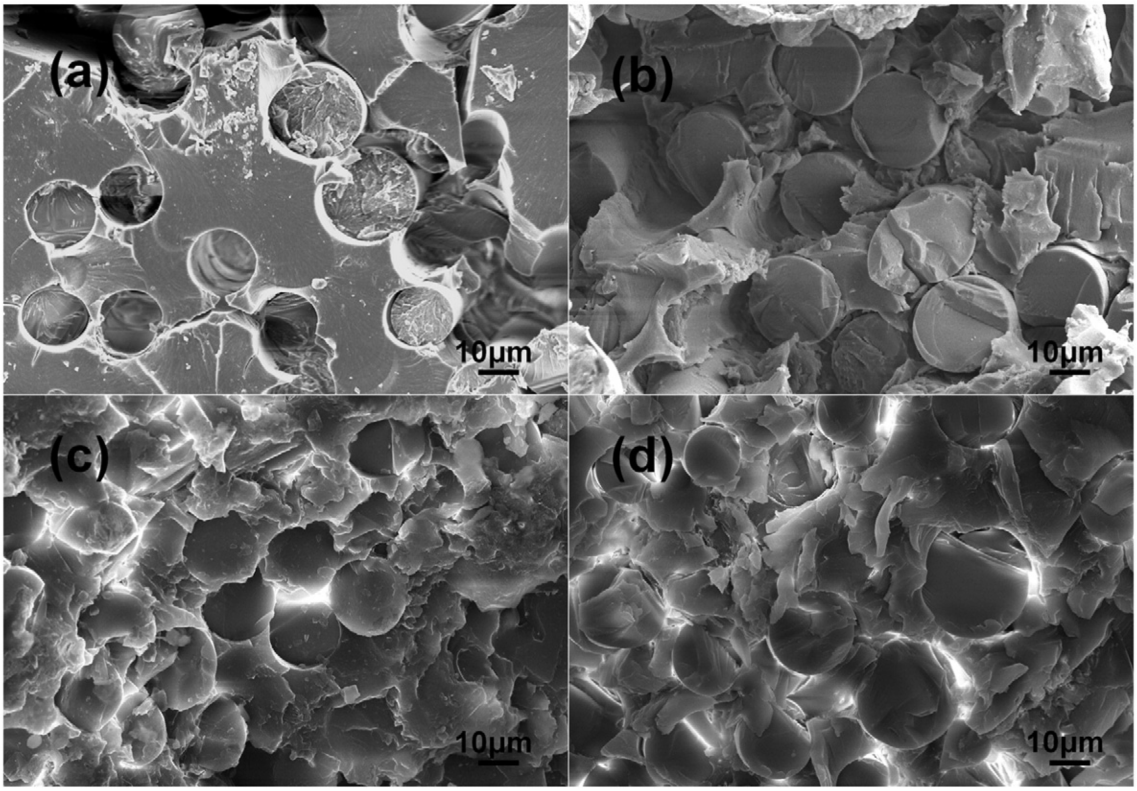

Fig. 5. SEM observations on the fractural morphologies of fiber-reinforced Bis-GMA/TEGDMA composites containing different glass fibers after the three-point bending test: (a) pristine Glassfiber; (b) PDA@Glassfiber; (c) PMMA@Glassfiber; (d) PMMA@PDA@Glassfiber.

[36]. In the present study, with the aim of developing a kind of light-curable prepreg for endodontical treatment, great attention has been paid to improving the interfacial adhesion between glass fibers and Bis-GMA/TEGDMA resin matrix.

In previous works [30–32], we reported the preparation of core-shell nanofibers with PMMA shell and their excellent adhesion to Bis-GMA/TEGDMA resin, which resulted in a significant increase in flexural properties by using the core-shell nanofibers as reinforcement. It was suggested that the shell polymer PMMA was able to form a kind of semi-interpenetrating network (IPN) structure with acrylate type resin after light-curing. The similarity in chemical structure of PMMA and Bis-GMA/TEGDMA was believed able to make PMMA partly dissolve into acrylate monomers via the interaction between methacryloyl groups on both components. Therefore, PMMA chains were entangled with the crosslinked resin network after light-curing [30,31]. Accordingly, in the present study, glass fibers coated with PMMA surely demonstrated better interfacial adhesion to Bis-GMA/TEGDMA resin matrix in comparison with untreated glass fibers, as confirmed by the data of flexural properties (Fig. 4) and pull-out test (Fig. 7). Also, the damp peak in tanδ curve of PMMA@Glassfiber reinforced composites shifted to higher temperature than the untreated glass fiber reinforced composites (Fig. 6). This indicated that the T_g of Bis-GMA/TEGDMA resin matrix increased due to the formation of semi-IPN structures between PMMA on glass fiber surface and the resin, in which the interaction limited the motion of polymer segments in resin matrix.

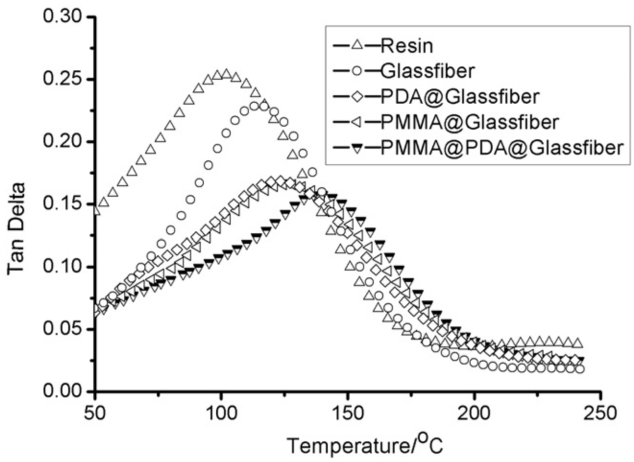

Fig. 6. The tanδ curves of various glass fibers reinforced by Bis-GMA/TEGDMA composites as a function of temperature.

On the other hand, mussel-inspired PDA surface modification was highlighted in recent years to improve the interfacial adhesion between different phases in composites [27–29,37–40]. The approach was identified to be effective and efficient. We even used PDA coating on prefabricated fiber posts to improve their interfacial adhesion with dental acrylate adhesives [33]. In this study, PDA coating was applied on glass fibers and the modified fibers demonstrated good attachment to Bis-GMA/TEGDMA resin matrix. Similar to those results obtained in using PMMA@Glassfiber, the PDA@Glassfiber-reinforced composites also displayed higher flexural properties, higher T_g and higher maximum failure load, than those of composites reinforced with untreated glass fibers (Figs. 4–7). The explanation for this amelioration apparently originated from the universal excellent adhesive ability of PDA to various substrates by virtue of the strong anchoring force of the catechol functionality via interactions such as hydrogen bond, chelation and π–π stacking [41].

However, the effect of PMMA and PDA coating on improving the interfacial adhesion between glass fiber and Bis-GMA/TEGDMA resin matrix displayed a slight difference, in which both the flexural properties and the maximum failure load were a little higher in the case of PMMA coating than in the case of PDA coating. Besides, the T_g of PMMA@Glassfiber reinforced composite was also a little higher than that of PDA@Glassfiber reinforced composite. This point was suggested

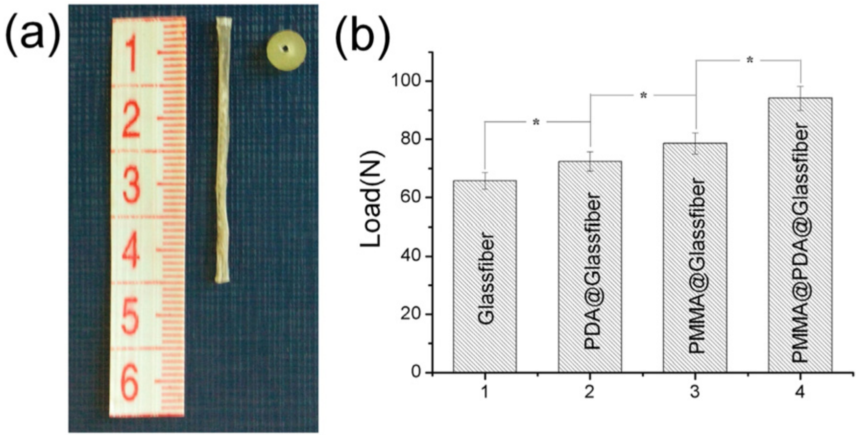

Fig. 7. The failure mode of pull-out test (a) and the maximum failure load (b) in different groups: (1) pristine glass fibers; (2) PDA@Glassfiber; (3) PMMA@Glassfiber; (4) PMMA@PDA@Glassfiber. (* $p < 0.05$).

due to their different mechanisms in improving interfacial adhesion. In the case of PMMA@Glassfiber, a semi-IPN structure was supposed to form in the interfacial phase. While in the case of PDA@Glassfiber, the glass fiber and the resin could be deemed as sticking together by the 'PDA glue'. Apparently, the semi-IPN structure in the case of PMMA@Glassfiber would limit the motion of chain segments in the resin matrix more significantly, and thus further increase the T_g in comparison with the case of PDA@Glassfiber.

In view of the adhesive ability of PDA and the semi-IPN formation ability of PMMA, the modification strategy that co-coating glass fibers subsequently with both PDA and PMMA was proposed. It was expected that the thin PDA layer was able to hold PMMA tightly onto glass fibers, and then the PMMA formed a semi-IPN structure with Bis-GMA/TEGDMA resin matrix. Thus, a perfect interfacial adhesion would be obtained. Delightfully, the outcomes confirmed this strategy as being feasible and effective. As shown in Figs. 4–7, the highest flexural strength and modulus, the highest T_g value, and the highest maximum failure load in pull-out test, were all found in the case of PMMA@PDA@Glassfiber reinforced Bis-GMA/TEGDMA composites among all the designs. The catechol groups in PDA and the semi-IPN structure in the interfacial inter-phases between the glass fibers and the resin matrix played a kind of synergetic strengthening effect on interfacial adhesion.

5. Conclusion

The vital function of interfacial adhesion in preparing dental composites urged researchers to find efficient and effective modification methods for reinforcements. Glass fibers coated with mussel-inspired PDA adhesive component or Bis-GMA compatible PMMA demonstrated good wettability to light-curable acrylate resins. A tight interfacial adhesion was achieved between the fiber and the resin matrix and, subsequently, the mechanical properties of the resulting composites increased, which benefited from the efficient interfacial stress transfer between the two phases. The successive co-coating of PDA and PMMA on glass fibers could further strengthen the interfacial adhesion in comparison with either case of only PDA or PMMA modification being applied. These findings suggested a new universal strategy for the surface modification of chemically inert high-performance fibers in developing novel dental composites.

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