Materials Research Express

PAPER

Improving flexural properties of polymethyl methacrylate denture filled by carbon nanofibers under low filling content

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Keywords: denture resin, CNFs, flexural properties

Supplementary material for this article is available online

Abstract

In this article, we chose carbon nanofibers (CNFs) with high aspect ratio and excellent mechanical strength to investigate the evolution of the assemble behavior belong to the nanofillers and its effect on mechanical properties of CNFs enhanced polymethyl methacrylate (PMMA) base denture resins. Test specimens were manufactured by mixing 0.5%, 1% and 3% content of CNFs with PMMA powder and the flexural properties of the specimens were tested by three-points testing. Comparing with the low flexural strength of pure PMMA base denture resins, Statistical evaluation results revealed that CNFs fillers highly improved the flexural strength of the composite resins to 66.44 ± 1.40 MPa, 68.75 ± 6.82 MPa and 89.26 ± 1.97 MPa at content reached 0.5%, 1% and 3%, respectively. Flexural modulus of neat PMMA was 2.79 ± 0.48 GPa, and the flexural modulus of the sample contains 0.5%, 1% and 3% reached 6.42 ± 0.75 GPa, 5.95 ± 0.29 GPa and 6.27 ± 0.14 GPa, respectively. Scanning electron microscopy revealed the aggregation of CNFs fillers, which is considered a stereoscopic framework that played the role of a special enhancing reinforcement under low filler content, and this strategy is considered to be expanded and developed to a common strategy that guiding our design in composite denture resins.

1. Introduction

Polymethyl methacrylate (PMMA) base polymer materials are types of typical polymer resins that extensively applied in dental applications [1–6] for past decades due to its excellent performances, low cost, well processability and high dimensional stability under complicated intraoral conditions. But as the intrinsic disadvantages of polymer materials, limited mechanical strength and modulus always lead premature failure during the servicing in overdenture cases. Plenty of researches were reported towards higher mechanical strength and mechanical modulus of PMMA base denture resins based on different strategies, such as molecular design [7–11], filler bending [12–16], construction of interpenetrating networks [17, 18].

Incorporation of fillers is one of the fastest growing strategies that towards mechanical enhancement of PMMA base resins that inspired by many mature theories and practices in the research of polymer composites, such as inorganic nano fillers [19–21], natural fibers [22] and many other fillers in different shapes. It’s generally recognized that the role of fillers in the composite are designed to induce the deflection and termination of the cracks during the failure process of the composite [23, 24], which always redistributed stress and consuming higher energy. Therefore, to design fillers with higher enhancement effects of better interfacial properties started getting to an another research hotspots which focused more on the stress transfer mechanisms. Therefore, how the aggregation form and topology structure of the fillers inside PMMA base dental resin effect mechanical properties of the composite is still an interesting issue that needed to be researched.

To construct a stereoscopic frame work that assembled by fillers themselves may be an effective strategy to adjust stress distributions and enhance the overall mechanical properties of PMMA base denture resins. Comparing with independently distributed fillers, stress transferring between interfaces of self-assembled fillers...
would play out more mechanical advantages, and the mechanical strength conversion rate of independently
distributed fillers due to interfacial failure could be inhibited. Thus it could guide us to develop more novel
strategies to enhance PMMA base denture resins via adjusting interactions between fillers.

Carbon nanofibers (CNFs) are novel one-dimensional nanomaterials with high strength, high aspect ratio
and low density that be developed in past few decades, which were applied in various of conditions such as
composites, energies, biomaterials, sensors, shape memory materials and drug delivery et al. Herein, CNFs were
applied as nanofillers in polymer composites, special entangling behaviors from their unique high aspect ratio
features lead their aggregation in polymer matrix, which is different from traditionally designed uniformly
distribution strategy, and this special filler distribution would form unique stress transferring frame to highly
improve

2. Materials and tests

2.1. Materials
PMMA pre-polymerized powders were purchased from Shanghai New Century Dental Materials Co., Ltd. ,
liquid methyl methacrylate monomers were purchased from Damao Chemical Reagent Factory and carbon
nanofibers were purchased from Beijing Dk nano S&T Ltd. (with diameter of 150–200 nm and length of 5–10
μm, tensile strength higher than 7 GPa, degree of graphitization > 90%, digital photos and SEM images of the
nanofibers are illustrated in figure 1). All chemicals were used without any purification.

2.2. Fabrication of specimens
10 g PMMA pre-polymerized powders and 5 g of MMA liquid monomers were firstly measured and separately
stored, then 0.075, 0.15 g and 0.45 g of CNFs powders were respectively mixed with the PMMA pre-polymerized
powders, which were denoted as CNF-0.5, CNF-1 and CNF-3 respectively. Afterwards, above mentioned
quantitative liquid monomers were quickly poured to the mixed powders and stirred to a uniform slurry, and
the dilute slurry were rapidly poured into a rectangle shaped mold (80 mm × 10 mm × 4.5 mm) and kept in
water storage under room temperature for 24 h, then the cured specimens were demolded from the molds and
kept in 37 °C water storage for 24 h for testing. Besides, PMMA denture resins without any fillers were denoted
as CNF-0. Above fabrication procedures were designed as clinical treatments.

2.3. Mechanical properties test
Flexural properties of PMMA base denture resin was tested by three-points bending test that performed on a
universal force measuring machine (Shimadzu AG-XPLUS10KN, Japan) at a crosshead speed of 10 mm min−1
and a supporting span distance of 60 mm. Flexural strength (FS) of the specimens were calculated by the
equation as following:

$$FS = \frac{3Fl}{2bh^2}$$

Where F (N) is the recorded maximum stress during flexural failure, l (m) is the distance between the supporting
span, and b (m) and h (m) were the width and height of the specimen respectively.

Flexural modulus (FM) of the specimens were also calculated, which was guided by the following equation:

$$FM = \frac{F_1l^3}{4bh^4d}$$

Where $F_1$ (N) is the recorded load at a point which has the highest slope in the strain-stress curve, d (m) is the
deflection while the stress reached $F_1$. 

![Figure 1. (a) Digital photos of the CNFs; (b) SEM images of the CNFs.](image-url)
Impact toughness of the resin composites were operated on cantilever beam impact testing machine (XJU-5.5, Chengde Jinjian Testing Instrument Co., Ltd., China) and rockwell hardness of the specimens were tested on Rockwell Hardness (TH300, Beijing TIME High Technology Ltd. China).

2.4. Scanning electron microscopy
Topographies of the fracture surface of PMMA denture resins was observed by SEM (Hitachi S-4800, Japan) to analyze the distribution, aggregation forms of the fillers and their interactions with resin matrix. The fracture surface of resin was cut from the failure specimen and adhesive to a conductive tape. Due to the poor conductivity of PMMA matrix, Au was sputtered onto the sample surface to enhance the image.

2.5. IR spectrum of PMMA base denture resins
Reflective infrared spectroscopy was performed (VERTEX80, Bruker, Germany) to investigate any chemical changes that occurred to the PMMA base dental after the introducing CNFs fillers.

2.6. Data analyses
Data analyses was performed by used statistical software (SPSS 18.0).

3. Results and discussion

Figure 2 showed the IR spectrum analysis performed to verify if any chemical changes occurred in the sample after mixing with CNF fillers. We note from the figure that no signaling occurs in the IR spectrum after mixing with CNF fillers, which corresponds to the entire single C–C bonds without any dipole moment in the CNFs special structure. For the pure PMMA base denture resin, CNF-0, some characteristic peaks that represent structural features occurred as we predicted. Peaks located at 2900–3000 cm⁻¹ are corresponded to H bonds from −CH₃ and −CH₂- groups in PMMA chain, while the signals occurred in 1735–1750 cm⁻¹ and 1300–1400 cm⁻¹ should be attributed to C═O bonds and C–O bonds, respectively. Therefore, it should be noticed that no obvious changes happened to chemical structure of PMMA base denture resins after blending CNFs, which indicates there’s no further chemical reactions happened between them and the mechanical mechanism of the composite can be easily discussed as a simple stress transfer model.

SPSS analyzes results for flexural test results revealed that the content of CNFs fillers on sample’s flexural properties. As we predicted, CNFs an effective nanofiller enhanced the flexural properties of PMMA base denture resin a lot, and the sample denoted as CNF-3 demonstrated the highest flexural strength as 89.26 ± 1.97 MPa, followed by CNF-1 (68.75 ± 6.82 MPa) and CNF-0.5 (66.44 ± 1.40 MPa). Comparing with the control group (CNF-0, 48.85 ± 4.62 MPa), flexural strength of the specimens significantly increased by 36%, 40.73% and 82.72% as the increasing of CNFs filler content. Besides, flexural modulus of CNFs enhanced PMMA base denture resins also improved a lot, which increased by 129.98%, 113.11% and 124.71% as the increasing of CNFs filling content (flexural strength and modulus as illustrated in figure 3). In short, low filling content of CNFs filler influenced a lot on the flexural properties of PMMA base denture resins. Herein, detailed SPSS

![Figure 2. IR spectrum of CNFs and the blended specimens](image-url)
analyzes results and Kruskal-Wallis test results are illustrated as tables 1–1, 1–2 and 2–1, 2–2 in Supporting Information (available online at stacks.iop.org/MRX/8/015404/mmedia).

Intrinsic mechanisms of the mechanical enhancement should be considered as an interesting question due to the low filling content of CNFs. As we discussed in above passages, CNFs under low filling content would spontaneously assemble to a stereoscopic framework due to their large aspect ratio and play a special role in redistribute stress that applied on sample. Thus its necessary to verify how the CNFs fillers aggregate in the PMMA polymer matrix. Figure 4 illustrated the SEM topographies of the fracture surfaces of CNFs enhanced PMMA base denture resins. As we can see in figure 3(a), a smooth fracture with few folds occurred in the fracture plane of CNF-0 sample, which indicated few plastic deformation occurred during the failure of CNF-0, thus few energy were consumed. Therefore, it can be also inferred that the cracks fast grew and went through the failure surface due to the smooth failure surface, above mentioned failure features all led to the poor flexural properties of CNF-0 sample. After blending CNFs nanofillers, as the topography of the fracture surface of CNF-0.5, a ultra-low filling content valued at 0.5% drove the CNFs fillers aggregate to isolated aggregates, which are similar to the special ‘sea-island’ structure that occurred in other types of polymer blends. Obviously, more folds occurred around the aggregates, which demonstrated CNFs aggregated fillers would induce the deflection and termination of the cracks during flexural failure. Meanwhile, the CNFs themselves would also play their intrinsic high mechanical strength, thus the overall flexural properties would significantly improve though the filling content of CNFs is ultra-low. Then we tried to raise the content of CNFs. When the filling content of CNFs raised
to 1%, the isolated CNFs aggregates started to connect together as we observed in figure 4(c), which is within our design. Connected CNFs aggregates have better stress transferring abilities thus the intrinsic excellent mechanical properties of CNFs would play more, and that’s why the flexural strength and modulus of CNF-1 are higher than that of CNF-0.5. As the content of CNFs fillers increased to 3%, the nanofibers or the aggregates connected closer as figure 3(d) showed, thus the flexural properties of the PMMA base denture resin got stronger as we just analyzed.

The evolution of CNFs and their aggregates can be vividly depicted by figure 5(a). Firstly, ultra-low content of CNFs nanofillers were blended into PMMA polymer matrix, but the fillers just aggregate to isolated aggregates due to the limited filler content. As we adding more CNFs fillers, the isolated aggregates gradually connect together and form to a fully supporting stereoscopic framework. Reflected to the macro properties, we recorded strain-stress curves of PMMA base denture resin with different filler content. Obviously, flexural modulus reached to a similar level no matter how many fillers were blended into the polymer matrix, which indicated that the filler content effect few on the value of flexural modulus, and this feature indicated that we could obtain high modulus PMMA base denture resin composites with even lower filler content. Besides, flexural strength of the composites have positive correlation with the filler content, and it’s corresponded to the mixture law of composite materials due to the high strength of CNFs.

Considering some accidents occurring in user’s daily life, impact toughness and hardness of the dental resin were furtherly investigated. Similar to flexural properties, impact performance of the specimens were also improved after adding CNFs fillers, where the impact toughness of CNF-0, CNF-0.5, CNF-1 and CNF-3 were 5.50 ± 0.42 kJ m⁻², 31.25 ± 1.42 kJ m⁻², 29.11 ± 0.73 kJ m⁻² and 40.15 ± 1.58 kJ m⁻², respectively. Besides, rockwell hardness of the composite resins were also highly improved, compared with the hardness (65.8 ± 6.71) of neat resin, rockwell hardness of CNF-0, CNF-0.5, CNF-1 and CNF-3 were respectively improved to 79.4 ± 5.11, 83.1 ± 2.74 and 96.01 ± 5.92, which was improved by 45.92% at maximum (detailed SPSS analyzing results and Kruskal-Wallis test results are listed as tables 3–1, 3–2 and 4–1, 4–2 in Supporting Information). Anyway, the addition of CNFs fillers improved mechanical properties of the PMMA composite as a type of denture material.

4. Conclusions

a. Carbon nanofibers (CNFs) is an ideal nanofiller that highly improved both mechanical properties of PMMA base denture resins under low content.
b. Due to the high aspect ratio of fiber fillers, we can add low content fillers in the matrix to play significant effects, and it’s considered that it can be expanded and developed to a common strategy that guiding our design in composite denture resins.

Acknowledgments

This work has been financially supported by National Natural Science Foundation of China (Grant No. 81771041) and Science and Technology Project of Jilin Provincial Department of Finance (Grant No. jcsz2020304–26 and Grant No. jcsz2020304–8).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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