Scientific Research Publishing

Journal of Materials Science and Chemical Engineering, 2018, 6, 57-64
http://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Nanoindentation Study on Mechanical Properties of Nano-SiO_2/Dental Resin Composites

Chao Zha[1,2], Jianhua Hu[1], Ainong Li[1], Shangyu Huang[1], Hanxing Liu[2,3], Gang Chen[1,2], Anqi Lei[1,2], Zuoqi Zhang[4], Bei Li[1,2,5*], Zhengzhi Wang[4*]

[1]School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, China
[2]Research Center for Materials Genome Engineering, Wuhan University of Technology, Wuhan, China
[3]International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, China
[4]Department of Engineering Mechanics, School of Civil Engineering, Wuhan University, Wuhan, China
[5]State Key Laboratory of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan, China
Email: *libei@whut.edu.cn, *zhengzhi.wang@whu.edu.cn

How to cite this paper: Zha, C., Hu, J.H., Li, A.N., Huang, S.Y., Liu, H.X., Chen, G., Lei, A.Q., Zhang, Z.Q., Li, B. and Wang, Z.Z. (2018) Nanoindentation Study on Mechanical Properties of Nano-SiO_2/Dental Resin Composites. *Journal of Materials Science and Chemical Engineering*, **6**, 57-64.
https://doi.org/10.4236/msce.2018.64008

Received: January 5, 2018
Accepted: April 5, 2018
Published: April 12, 2018

Abstract

The micro/nano-scale indentation tests were performed to explore the performance of bisphenol-*a*-glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) dental resin composites. The effect of the filling content of nano-SiO_2 particles on the mechanical properties of the dental composites was studied as well. The experimental results showed that the incorporation of the nano-SiO_2 particles at low concentrations (up to 10 wt.%) can apparently increase the hardness and elastic modulus of the dental rein composites. The plasticity index indicates a best elastic recovery capability at a proper amount (4 wt.%) of the nanoparticles. Combined with the infrared spectrum, the mechanical enhancement mechanisms of the dental resin composites were analyzed.

Keywords

Indentation, SiO_2 Nanoparticles, Dental Resin Composites, Mechanical Properties

1. Introduction

Dental resin composites have been widely used for restoring dental defects and caries instead of conventional metallic dental amalgam due to their sufficient strength, superior biocompatibility, and excellent esthetics [1] [2]. Resin compo-

sites generally consist of a polymeric matrix involving visible-light-cured bisphenol-*α*-glycidyl methacrylate (Bis-GMA), diluted with agent triethylene glycol dimethacrylate (TEGDMA). Meanwhile, inorganic macro/micro-fillers (e.g., barium glass powder (BG), SiO_2, Al_2O_3, ZrO_2) are incorporated with organic matrix by light curable technique to increase mechanical properties of the matrix [3] [4] [5] [6] [7]. Although inorganic fillers have been mixed into composite resin matrix to enhance the strength, toughness and wear resistance of the dental resins, there are still some issues in dental restorations, processing and biocompatibility. Recent research has led to the development of nano-fillers to reinforce the mechanical properties of the composites by regulating filler size, shape and compositions [8] [9] [10]. Promising consequences of applying nano-fillers include reducing polymerization shrinkage, improving mechanical properties such as toughness and flexure strength, and ensuring good biocompatibility and comfort level at the same time [11] [12].

In recent years, indentation at ultra-microscopic level has drawn broad attention in characterizing mechanical properties of metals, ceramics, polymers and biomolecules [13] [14]. Micro/nano-indentaion allows accurate determination and control of the indentation force and accurate measurement of the indentation depth. The mechanical properties (e.g., hardness and modulus) can be obtained directly from simultaneous indentation load-displacement curves. However, the studies of nano-filled dental resin composites using indentation at micro/nano-scale were still limited. The present paper aims to examine the mechanical properties of the dental resin composites with various nano-SiO_2 particle content using nano-mechanics testing system. The detailed analysis in this work is believed to provide an experimental insight into Bis-GMA/TEGDMA dental resin composites at micro/nano-scale.

2. Materials and Methods

2.1. Materials

The dental restoration matrix consisted of 70 wt.% Bis-GMA and 30 wt.% viscosity-modifying TEGDMA obtained from BOC sciences, USA. The photoinitiator camphorquinone (CQ) (0.2 wt.%) and the amine reducing agent ethyl 4-dimethylaminoben-zoate (EDAB) (0.8 wt.%) were added to help trigger the photo-polymerization process when exposed to radiation. The silanized nano-SiO_2 particles were then incorporated into the matrix with an average diameter of 20 nm and varying SiO_2 contents: 0 wt.%, 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.%, and 10 wt.%. All the samples were stirred for about 3 minutes using the high speed centrifuge to ensure the spherical nanoparticles were dispersed homogenously in the composite matrix. After that, they were irradiated for 180 s under the visible blue light with an irradiation flux of 1000 mV/cm^3. According to the content of the nanoparticle filler, the samples were designated as S0, S2, S4, S6, S8, and S10, respectively.

2.2. Indentation Tests

The mechanical properties of the dental resin composites were investigated by micro/nano-scale indentation tests. All the tests were performed using the commercially available Triboindenter system (Hysitron USA T-950) with a diamond equilateral triangular indenter (Berkovich). This instrument provides accurate automated testing for the mechanical properties at micro/nano-scale and high resolution real-time imaging of surfaces. The load resolutionis 1 nN and displacement resolution is 0.0002 nm.

The indentation tests were carried out in quasi-static force-control mode, in which the applied force is controlled in a pre-programmed manner and the displacement continuously monitored. The loading function of all the indentations in this work consisted of a 5^{-s} linear loading and 5^{-s} unloading segment together with a 10^{-s} holding at the peak load of 8 mN. This kind of loading could reduce the influence of the creeping effect [15] and its schematics is presented in **Figure 1**. The hardness and modulus could be obtained according to the load-displacement curve based on the Oliver and Pharr's method [14]. The final values of hardness and modulus data were calculated as the average of 6 distinct regions on each sample surface. Each region was again marked by and calculated as a mean of 12 spots with a spacing of 40 μm either in parallel or perpendicular direction to eliminate mutual influences.

3. Results and Discussions

3.1. Hardness and Moduus

Figure 2 shows the typical load-displacement curves of the S0, S2, S8, and S10, from which we can clearly see that the hmax (maximum indentation depth) decreases gradually with the increasing filler content. At the peak load, the hmax of S0 is about 300 nm more than that of S10, which implies that the dental resins reinforced with nano-silica particles exhibits much larger hardness than the free

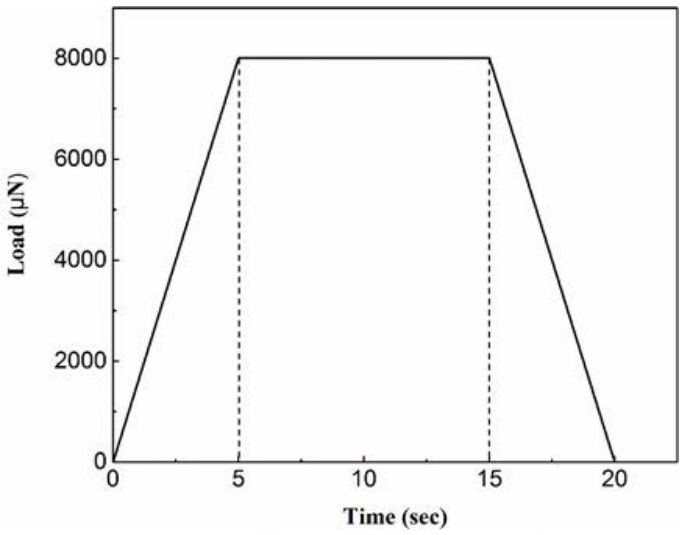


Figure 1. Schematics of the loading functionduring the indentation test.

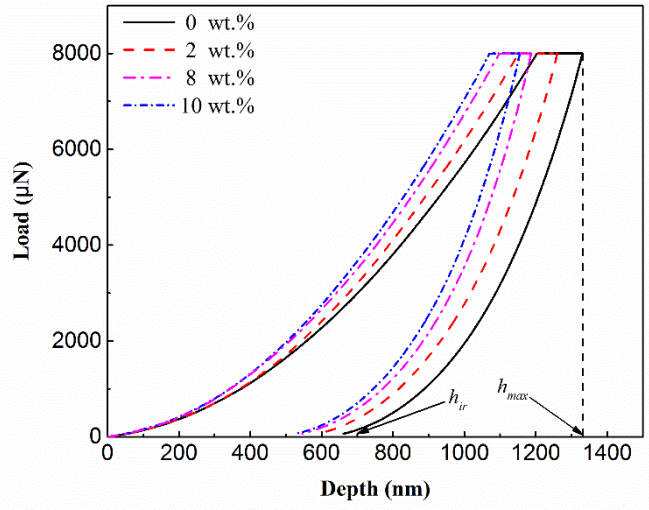


Figure 2. Load-displacement curves of S0, S2, S8, and S10 during the indentation.

one. However, the loading and unloading segments of the image possess steeper slopes with the increasing filler content. During the unloading process, the samples underwent elastic recovery and presented a decreasing hir (irreversible indentation depth) as the concentration of the nanoparticles increases. Especially for each increment (2 wt.%) in the filler content, hirhas the largest decrease of 71 nm from S0 to S2, which shows that the nano-SiO_2 particles can greatly improve the mechanical properties of dental resin composites even at low filler contents.

Figure 3 shows the results of hardness H and modulus E for different filler content. It can be seen that both H and E increase monotonously with the nanoparticle content. Hardness and modulusrise from 0.126 and 3.15 GPa of S0 to 0.208 and 4.09 GPa of S10, with an increment of 65% and 30%, respectively. The apparent increase in H and E is mainly due to two reasons. Firstly, the nano-SiO_2 particles have much higher H and E, and the resulting mixing effect of the dental resin matrix and the particles can lead to improvement of H and E of dental resin/SiO_2 composites. Secondly, the incorporation of nanoparticles can enhance the load-carrying capacity and inhibit the formation of internal micro-cracks based on the strong particle-matrix bonding, thereby improving the mechanical properties [3].

3.2. Plasticity Index

The plasticity index, which describes the relative plastic/elastic behavior of the material effectively when it undergoes external stresses and strains. The results of the plasticity index φ as a function of the filler particle content is shown in **Figure 4(a)**. **Figure 4(b)** shows the schematics of the calculation of plasticity index and it is defined as [16]

$$\varphi = W_{ir} / (W_{ir} + W_r) \tag{1}$$

where W_{ir} and W_r represent the irreversible work done during indentation and the reversible work recovered by viscoelastic processes during unloading,

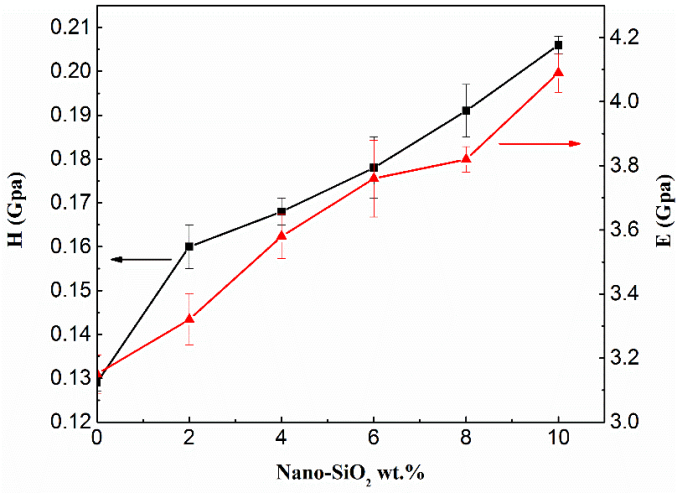
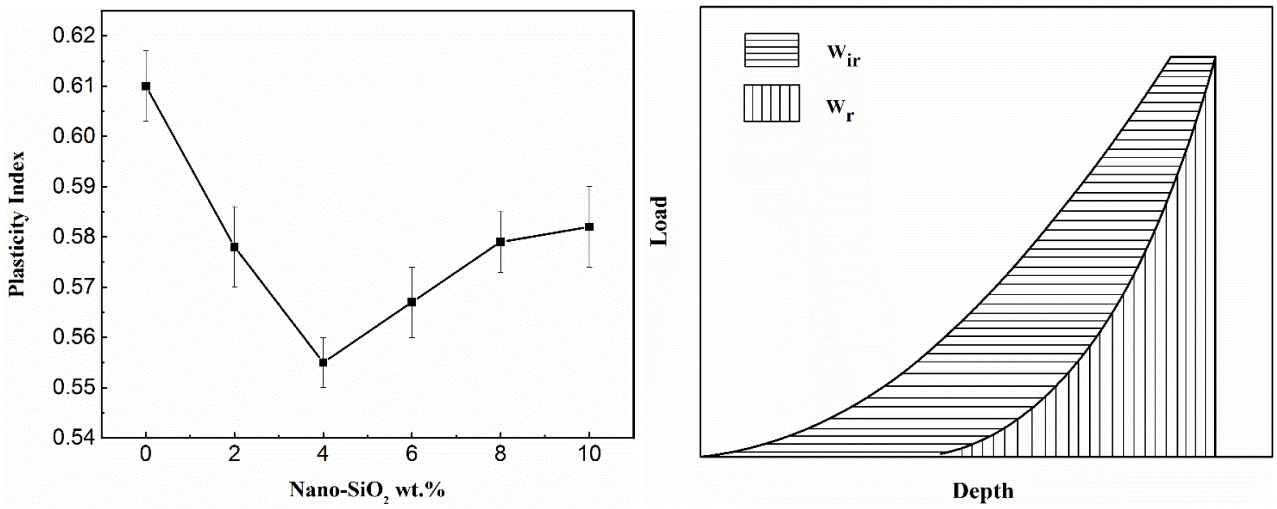


Figure 3. Hardness *H* and Elastic modulus *Eversus* particle filler content for dental resin composites.



(a) (b)

Figure 4. (a) Plasticity index *versus* particle filler content and (b) The schematics of calculation of plasticity index.

respectively. From **Figure 4(a)**, we can find that the plasticity index decrease initiallywith the nano-SiO_2 particle content from 0 wt.% to 4 wt.%, and then increases afterward when the filler mass ratio increases from 4 wt.% to 10 wt.%. A larger plasticity index meansmore plastic deformation proportion, therefore the dental resin composite with 4 wt.% nano-SiO_2 particles exhibits the best elastic recovery in the indentation process.

3.3. Infrared Test

The Fourier transform infrared spectroscopy (FTIR) profiles of the samples S0, S2 and S6 are shown in **Figure 5**. Through the spectrogram, we can see that the characteristicabsorption peak for the carbonyl C=O is located at the wavenumber of 1726 cm^{-1}, and those for the aliphatic C=C and aromatic C=C

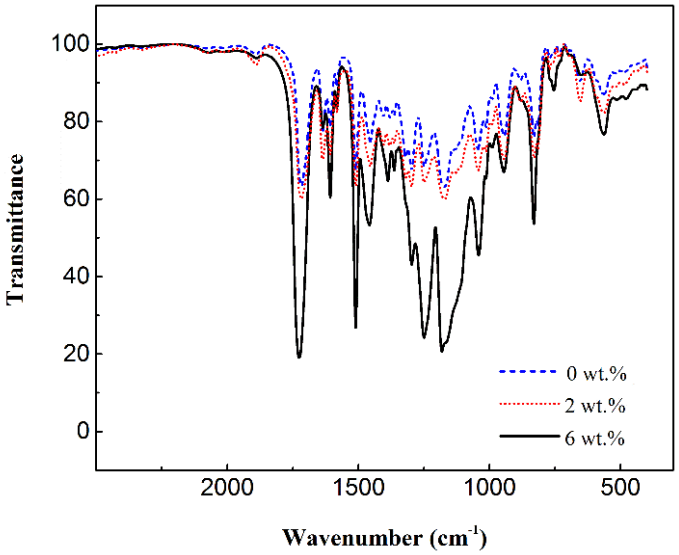


Figure 5. Fourier transform infrared spectrogram of the dental resin composites.

are at around 1638 cm^{-1} and 1582 cm^{-1}, and the stretch vibration absorption for the esteryl C-O is found at around 1182 cm^{-1}, 1249 cm^{-1} and 1297 cm^{-1}, respectively. It is also shown that the transmittance of the S6 sample is much lower than S0 at the whole frequency range, indicating that the dental resin composite with nano-SiO_2 particles possesses a higher crystallinity than the standalone one. More importantly, the crystallinity increases with the filler content. For polymer-based composites, the incorporated nanoparticles play roles as the nucleating agents during crystallization. With the nuclei, compact and fine spherulite particles can be formed in the polymeric matrix, and the hybrid composite exhibits microcrystalline structure, causing increased crystallinity [17]. For the dental resin composites, the nano-SiO_2 particles are used as the crystal nuclei and have a positive effect on the crystallization process of the resin matrix. This leads to improved filler-matrix coupling and thus contributes to increased mechanical performance, *i.e.*, the hardness and modulus, of the resin/nano-SiO_2 composites as the filler content increases.

4. Summary

In this work, the mechanical performance of the dental resin composites incorporated with nano-SiO_2 particles (20 nm) were investigated via micro/nano-scale indentation tests. The incoprorationof nano-SiO_2 particles (10 wt.%) can greatly enhance the hardness and elastic modulus of the Bis-GMA/TEGDMA dental composites, with an increment of 65% and 30%, respectively. Moreover, the elastic recovery was characterized by the plasticity index and it revealed that the dental resin composites with 4 wt.% nano-SiO_2 particles exhibit the best elastic recovery behavior. Finally, the reinforcement mechanism of the nano-SiO_2/resin composites was evaluated. The nano-SiO_2 particles act as the nucleating agents during the crystallization process of the dental composite

matrix, causing increased crystallinity and improved mechanical properties. It is believed that the findings in this study provide micro/nano-scale insights into the mechanical performance of dental resin composites.

Acknowledgements

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (11602177 and 51603160), the Fundamental Research Funds for the Central Universities (WUT: 173201001), the Natural Science Foundation of Hubei Province (2016CFB248), and the Open Fund Project of State Key Laboratory of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology (P2017-011).

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