

The properties of dental resin composites reinforced with silica colloidal nanoparticle clusters: Effects of heat treatment and filler composition

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ABSTRACT

Resin composites have been frequently applied in dental restoration due to their distinguished overall performance. The size, structure and composition of inorganic fillers have significant effects on the properties of dental resin composites (DRCs). The aim of our research is to strengthen the structure of spray-dried silica colloidal nanoparticle clusters (SCNCs) by means of a calcination process, and achieve the excellent comprehensive performance of DRCs by the combined use with different fillers. The results indicate that the SCNCs calcined at 500 °C has a significant strengthening effect on the flexural properties and hardness of DRCs except the decrease of compressive strength in comparison to the uncalcined SCNCs. To overcome this problem, the SiO₂ nanoparticles (NPs) as building blocks for SCNCs and the SCNCs were further adopted as co-fillers of the calcined SCNCs (CSCNCs). It can be found that the strengthening effect of SCNCs is better than that of the NPs at the same filling ratio. The DRCs filled with 60 wt% CSCNCs and 10 wt% SCNCs have a greatly enhanced compressive strength, reaching the same level with the DRCs filled with 70 wt% SCNCs. More importantly, the corresponding flexural strength (143.5 ± 8.3 MPa), flexural modulus (8.91 ± 0.48 GPa) and hardness (70.7 ± 1.4 HV) still have an improvement of 14%, 23% and 48% in comparison with those of the counterpart, respectively.

1. Introduction

Dental caries, one of the most usual mouth diseases, negatively affects the general health status in recent years [1,2]. To cure the missing tissue, amalgam alloys have been used as a filling material for several decades due to their low costs, placement and durability [3,4]. However, several defects, including toxicity, imperfect bioactivity, environmental pollution, and inadequate aesthetic appearance, prevent them from being a popular restoration material [5,6]. Alternatively, the light curable dental resin composites (DRCs) are believed to be the most frequent option for patients and dentists because of their outstanding esthetics, operability, and biocompatibility [7,8]. However, the occurrence of fatigue and crack propagation under masticatory forces is one of the main reasons for the relatively low longevity of DRCs [9–11].

The DRCs are mainly based on methacrylate monomers and modified inorganic fillers of various types (silica, hydroxyapatite, zirconia, alumina, etc), morphologies and sizes [12–17]. The inorganic fillers are crucial for the design of DRCs since optimized filler types, compositions, structures, and contents may result in enhancements in the mechanical properties [18,19], antibacterial activity [20], radiopaque property [21], and biomineralization [22,23]. In particular, the filler structures have significant effects on mechanical and optical properties, which has been widely studied in previous work [8,24,25]. Samuel et al. [26] found out that the addition of mesoporous fillers enables the composites better mechanical properties owing to their capability of constructing micromechanical filler/resin matrix interface anchoring. Wang et al. [27] investigated the multimodal fillers for the DRCs and evidenced that the use of secondary particles in composite can further enhance the total

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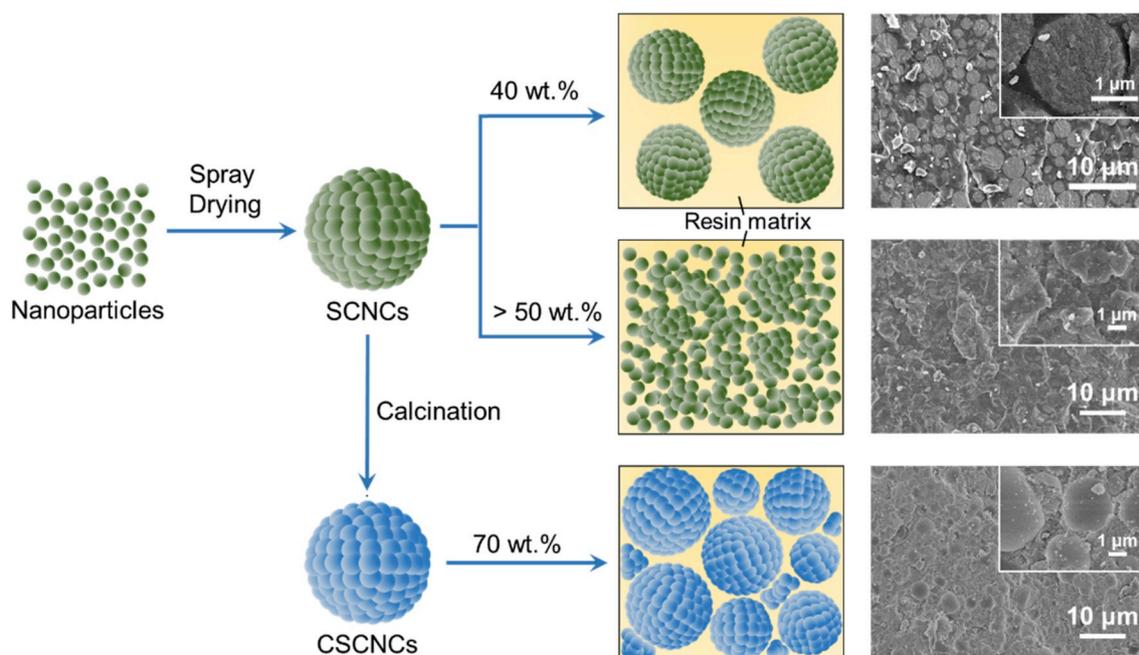


Fig. 1. Representative schematic diagram of the CSCNCs preparation and possible inner structures of DRCs with different type of fillers, and the corresponding SEM images of the cross-section surface.

loading amount of filler, especially with adding two discrepant secondary particles, which resulted in the obviously increased mechanical performances and decreased polymeric shrinkage of DRCs. These DRCs with hybrid fillers have been commonly used in clinical restoration due to their outstanding properties compared with individual micro-filler or nano-filler based composites [18,28].

Recently, 'nanoclusters (NCs)' are described as micron-scale aggregations of nanoparticles, which combine the advantages of both nanoparticles and microparticles. NCs have been applied to the commercial oral cavity repair materials, and demonstrate a remarkable strengthening mechanism compared with the hybrid filler system, which gives rise to extended longevity in any storage and test conditions [11,29]. The existing processes for preparing the NCs for DRCs include sintering at 1300 °C [30], coupling [18,31], and solvent evaporation [32], but these methods have intrinsic limitations, such as complexity, time-consuming process, high energy consumption, and low yield from the view of industrial applications. In our previous work [33], a spray-drying method was adopted to fabricate regular shape silica colloidal nanoparticle clusters (SCNCs) with 1–3 μm average sizes and close packing structures as novel dental fillers. This method is suitable for industries, which is practical, rapid, economical and efficient. The SCNCs composed of 60 nm SiO₂ particles creates the significant increase of flexural strength and compressive strength of the DRCs by comparison with the nanoparticle- and microparticle-based composites. Nevertheless, the adhesion among NPs in SCNCs prepared by merely spray drying was not enough strong due to a simple aggregation during the solvent evaporation process. This may cause the premature breakdown of SCNCs when they were filled into resin matrix with a high content (Fig. 1), resulting in restraining the improvement of the properties of DRCs. Therefore, a strategy of enhancing the inner structure of SCNCs is still a challenge.

In this study, the SCNCs were thermally treated in a relatively low temperature to enhance their structural stability to overcome the above issue. At the same time, the meritorious characteristics of the secondary structure of SCNCs are kept. The effects of calcination temperature and filler constitution of the calcined SCNCs (CSCNCs), SCNCs and NPs on the performances of DRCs were investigated, and the reinforcing mechanism was also explored. Furthermore, the DRCs with the presence

of a certain mass ratio of CSCNCs and SCNCs as fillers were compared with some commercial products and fillers.

2. Experimental section

2.1. Chemicals and materials

Ethanol, n-propylamine, ammonia water, cyclohexane and ethyl orthosilicate were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. 3-Methacryloyl trimethoxypropylsilane (γ -MPS) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Triethylene glycol dimethacrylate (TEGDMA), bisphenol A glycidyl methacrylate (Bis-GMA), ethyl 4-dimethylamino benzoate (4-EDMAB) and camphorquinone (CQ) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Four kinds of commercially available DRCs including Filtek™ Z350 XT (3M ESPE, USA), Charisma (Heraeus, Germany), Ceram.X (Dentsply, USA) and SDR (Dentsply, USA) were obtained, and the information of commercial DRCs and our products is shown in Table S1 for comparison. The dental Ba-glass powders (Schott, Germany) with sizes of 180 and 1000 nm were also purchased for comparative studies.

2.2. Preparation of CSCNCs

The 60 nm monodispersed silica dispersions were synthesized through a sol-gel method using a rotating packed bed reactor [34], which were further freeze dried to obtain SiO₂ nanopowders. The SCNCs were made from silica nanodispersions utilizing a commonly-used spray dryer (B-290, BÜCHI Labortechnik AG, Switzerland) with a 0.4 L/h feed rate, 3 wt.% solid content, 480 L/h compressed air flow rate, and 100 °C inlet temperature [33]. The CSCNCs-400, CSCNCs-500, CSCNCs-600 and CSCNCs-700 were obtained by calcining the SCNCs at different temperatures of 400–700 °C using a muffle furnace (LH 30/13, Nabertherm, China) for 3 h.

2.3. Modification of fillers

All the fillers were modified via silanization with γ -MPS [33]. Briefly, 10 g inorganic particles, 1.1 mL γ -MPS, 0.3 mL n-propylamine and 200

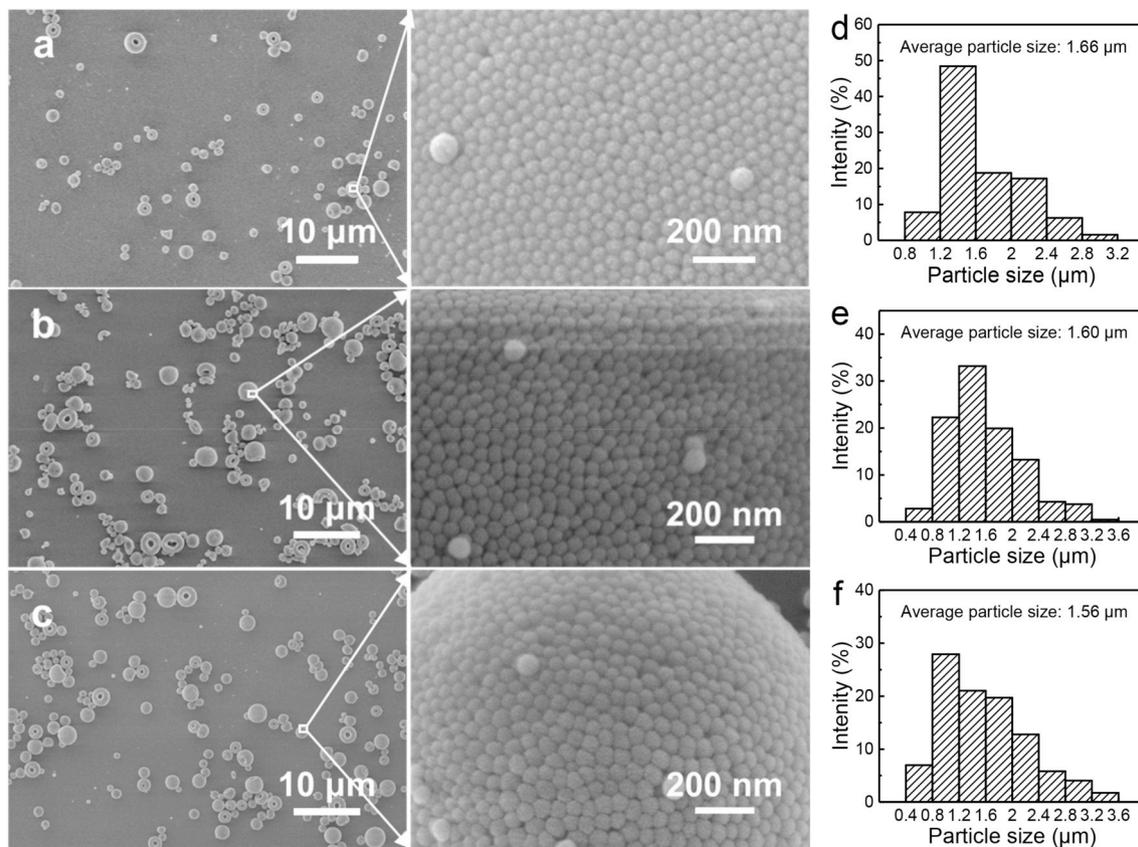


Fig. 2. SEM images (a, b, c) of the SCNCs (a, d) and CSNCs with 500 °C (b, e) and 700 °C (c, f) heat treatments and the corresponding average sizes with size distributions (d, e, f).

mL cyclohexane were mixed at 25 °C with relentless stir for half an hour and further mixed at 65 °C for another half an hour. Subsequently, the rotary evaporation method was adopted to remove the solvent. Finally, the powders were achieved under a condition of 90 °C vacuum drying for 16 h.

2.4. Fabrication of DRCs

The experimental DRCs were synthesized according to our previous work [34]. Briefly, silanized filler, photoinitiators (CQ/4-EDMAB = 0.02/0.08, wt./wt.) and the resin matrix (Bis-GMA/TEGDMA = 50/50, wt./wt.) were sufficiently mixed up using a three-roller machine (TR50M, Shanghai Renhe Scientific Instrument Co., Ltd., China). The uncured paste products were loaded into silicone rubber molds and photo-polymerized using a LED light curing unit (SLC-VIII B, 430–490 nm, Hangzhou Sifang Medical Apparatus Co., Ltd., China). For comparison, the dental Ba-glass powders with particle sizes of 180 and 1000 nm were loaded into the same resin base with same loading.

2.5. Characterization of the fillers

The scanning electron microscopy (SEM) (JSM-6701F, JEOL, Japan) was applied to observe the morphology and size of the CSCNCs and cross-section of DRCs. The structural stability of the CSCNCs was explored using an ultrasonic probe (SCIENTZ-IIID, Ningbo Scientz Biotechnology Co., Ltd., China) operated at a frequency of 22 kHz and power output of 500 W. The SCNCs and CSCNCs were suspended in ethyl alcohol with different durations of ultrasound, which were employed using the same ultrasonic processor. The pore size distribution of CSCNCs was measured using a BET surface area analyzer (Autosorb-iQ-MP, Quantachrome, USA), and calculated in accordance with the Barrett-Joyner-Halendard (BJH) cylindrical pore model.

Thermogravimetric (TG) analysis was measured using a thermogravimetric analyzer (STA-449C, NETZSCH, Germany) under the N₂ atmosphere with a heating rate of 10 °C/min from 50 to 900 °C. The fillers were tested using a FT-IR Spectrum (Nicolet 6700 spectrometer, Nicolet Instrument Co., USA) in a 4000–400 cm⁻¹ wave range.

2.6. Characterization of the DRCs

2.6.1. Mechanical properties

The 3-point bending test, which is stipulated in ISO 4049: 2009, was conducted to measure the flexural strength and modulus. The 25 mm × 2 mm × 2 mm bar specimens were fabricated for the three-point bending measurement, which were performed with 20 mm span and at 0.75 mm/min crosshead speed using a universal tester (CMT6503, MTS Industrial Systems Co., Ltd., China). The compressive strength was measured by this universal tester with Φ 4 mm × 6 mm cylindrical specimens. The microhardness tester (HXD-1000TMC/LCD, Shanghai Taiming Optical Instrument Co., Ltd., China) was adopted to determine the vickers microhardness under a load of 50 g for 10 s. For each test, six parallel samples were examined.

2.6.2. Depth of cure

Based on the ISO 4049: 2009, the depth of cure of DRCs was measured using a mold with a cylindrical cavity (Φ 4 mm × 10 mm). The composite pastes were filled into the split mold, and vertically irradiated for 20 s in contact with one end. After the irradiation, the uncured paste was immediately removed, and a digital caliper (E02-150, As One Corporation, Japan) was adopted to measure the height of cured resin. The height was then divided by 2, and this obtained result was recorded as the cure depth. The above test was repeated twice for each composite.

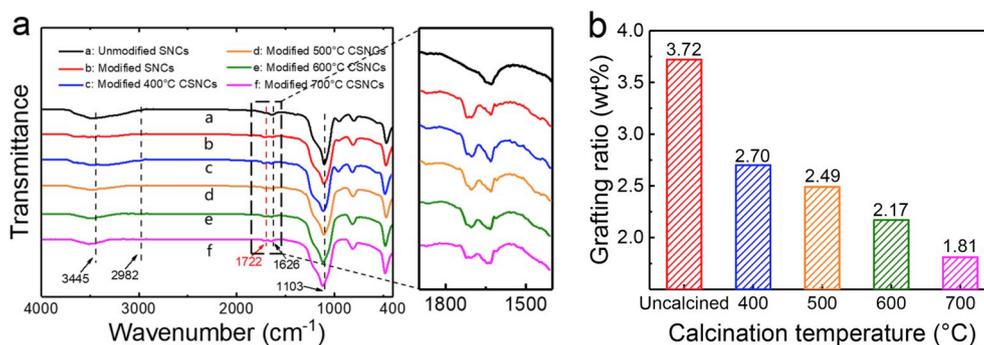


Fig. 3. FT-IR spectra (a) of SCNCs and CSCNCs before and after calcination and the corresponding grafting ratios (b).

2.6.3. Degree of conversion

An FT-IR spectrometer equipped with an attenuated total reflectance crystal (ATR) (Nicolet 8700, Bruker Optik GmbH, Ettlingen, Germany) was used to confirm the degree of conversion of DRCs with a 2000–500 cm^{-1} wave range. The FT-IR spectra of both cured and uncured DRCs were recorded before and after irradiating for 60 s. For each sample, it was confirmed by the ratio of peak absorption at 1637 cm^{-1} (aliphatic C=C) and 1608 cm^{-1} (aromatic C=C) [35,36]. The degree of conversion was calculated based on the following equation:

$$\text{Degree of conversion (\%)} = \left[1 - \frac{(A_{1637}/A_{1608})_{\text{polymer}}}{(A_{1637}/A_{1608})_{\text{monomer}}} \right] \times 100$$

2.7. Statistical analysis

The significant difference of the datasets was analyzed by Tukey's test with a one-way analysis of variance at a 0.05 p value using SPSS software.

3. Results and DISCUSSION

3.1. Characterizations of the CSCNCs

The SCNCs were heat treated in order to strengthen the SCNCs for better applications in the DRCs. Fig. 2 gives typical SEM images of SCNCs, CSCNCs-500, CSCNCs-700, and the corresponding average sizes with size distributions. The NPs with a primary size of 60 nm were closely gathered into the SCNCs which had an average secondary particle size of 1.66 μm . After heating at 500 and 700 $^{\circ}\text{C}$, the CSCNCs with average sizes of 1.60 and 1.56 μm were obtained respectively, which showed a slightly reduced particle size compared with the raw SCNCs. Meanwhile, the regular morphology of CSCNCs and legible primary NPs were still maintained, which means that the structure of SCNCs had little change during the heat treatment process.

To explore the structural stability of thermally treated products, the suspensions of SCNCs and CSCNCs were subjected to ultrasound sonication at 22 kHz for different durations (Fig. S1). After 2 min ultrasound, these two materials were still intact with very little broken pieces, which indicated a stable structure to some extent. However, some of the SCNCs were seen to be broken into fragments after 3 min, and more of the

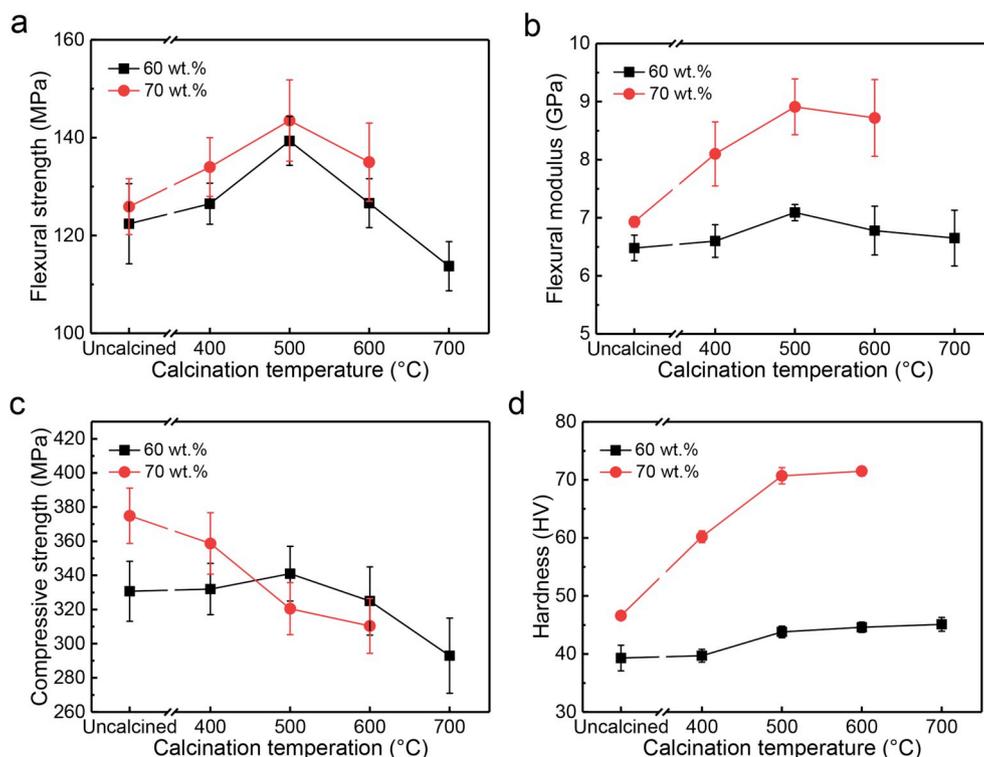


Fig. 4. The effect of heat treatment temperature of CSCNCs on (a) flexural strength, (b) flexural modulus, (c) compressive strength, and (d) hardness of the DRCs.

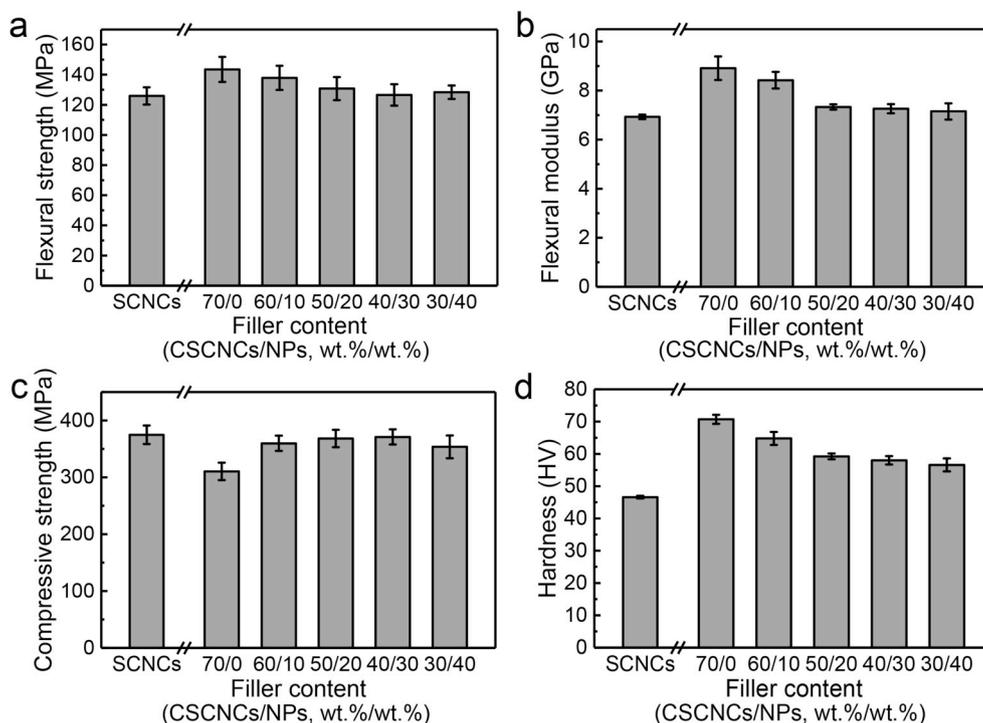


Fig. 5. The effect of mass ratio of the CSCNCs and NPs on (a) flexural strength, (b) flexural modulus, (c) compressive strength, and (d) hardness of the DRCs.

SCNCs were destroyed for longer sonication times. Meanwhile, the destruction of CSCNCs was inconspicuous after another 2 min of sonication, which confirmed that the stability of SCNCs was dramatically enhanced after the heat treatment process.

To understand the structure of CSCNCs better, their pore size distributions were determined by BJH cylindrical pore model (Fig. S2). Clearly, after keeping at 400 and 500 °C for 3 h, the average pore diameters declined from 13.08 to 11.49 and 10 nm, respectively, which may provide a more compact structure and densified silica framework. Thus, this structure may have a potential to reduce fractures of the CSCNCs during loading [26]. In addition, since the pore diameter of CSCNCs-500 (10 nm) was approximated with the theoretical value (9.54 nm) of cylindrical pore model, the further increase of temperature to 600 and 700 °C may not cause a continual drop of the pore diameters of CSCNCs (9.99 and 9.97 nm respectively).

Fig. 3 shows the FT-IR spectra of SCNCs and CSCNCs before and after calcination and the corresponding grafting ratios. Compared to the unmodified samples, the modified SCNCs and CSCNCs appeared a new absorption band at 1722 cm^{-1} , which was mainly attributed to the stretching vibration of C=O [31], and the other peaks were exactly the same. This proved that the surfaces of fillers were successfully modified with γ -MPS. Additionally, the intensity of characteristic peak decreased as the heat treatment temperature increased, proving the gradual decrease of grafting ratio. To further quantitatively evaluate the grafting ratio, TG test was performed (Fig. S3), and the values were calculated [33]. Fig. 3b shows the variety in grafting ratios of the SCNCs with different calcination temperatures. The SCNCs showed the highest grafting ratio of 3.72 wt%. The γ -MPS was more difficult to be grafted after 400 °C heat treatment since this process destroys the hydroxyl groups attached on the silica particle surface. As a result, the grafting ratio reduced to 2.70 wt%. Further increase of the calcination temperature to 500, 600 and 700 °C led to falling grafting ratios to 2.49, 2.17 and 1.81 wt%, respectively.

3.2. Characterizations of the DRCs

The mechanical tests of CSCNCs-based DRCs were conducted to

analyze the effect of calcination process on the effectiveness of CSCNCs. Fig. 4 shows the flexural properties, compressive strength and hardness of DRCs obtained by filling CSCNCs with different contents and calcination temperatures. The CSCNCs-700 was very difficult to be filled to 70 wt% probably due to its low grafting ratio. When the calcination temperature was increased from 400 to 700 °C, the flexural performances of DRCs were enhanced and then reduced, achieving the maximum amount (135.80 MPa, 6.99 GPa for a 60 wt% filler content, and 143.50 MPa, 8.91 GPa for a 70 wt% filler content) when the DRCs were filled with the CSCNCs-500. This result may be attributed to a fact that the CSCNCs-500 has more strong internal structure than the CSCNCs-400, which is evidenced by the decreasing pore diameter (Fig. S2f). Therefore, the DRCs filled with the CSCNCs-400 are more susceptible to be damaged than that filled with the CSCNCs-500. Although the grafting ratio of CSCNCs-500 is lower than that of the CSCNCs-400, the positive impact of the stronger fillers outdoes the negative effect owing to the lower grafting ratio. In addition, as the temperature further rose to 600 or even 700 °C, the grafting ratio dropped significantly, giving rise to a worse adhesion between the resin matrix and CSCNCs. Meanwhile, the pore sizes remained constant, which denoted that the inner structure of CSCNCs may not be further reinforced. Therefore, the composites filled with CSCNCs-600 and CSCNCs-700 had overall decreasing performances.

Compared to the SCNCs, the CSCNCs endowed the DRCs obviously enhanced mechanical properties except for the compressive property. Under a 70 wt% loading, the DRCs filled with CSCNCs treated at all experimental temperatures had much better flexural properties and higher hardness than the SCNCs-filled DRCs, which is due to the stronger structure of CSCNCs caused by more compacted NPs inside. In particular, the DRCs filled with 70 wt% CSCNCs-500 (DRCs-CSCNCs) showed significant improvements in flexural strength (14%), flexural modulus (29%) and hardness (52%) compared to the DRCs loading 70 wt% SCNCs (DRCs-SCNCs), while the compressive strength decreased by 17%.

Although the DRCs-CSCNCs had enhanced flexural properties and hardness, the compressive strength should also be improved. Here, the NPs as building blocks for the original CSCNCs-500 were used as co-

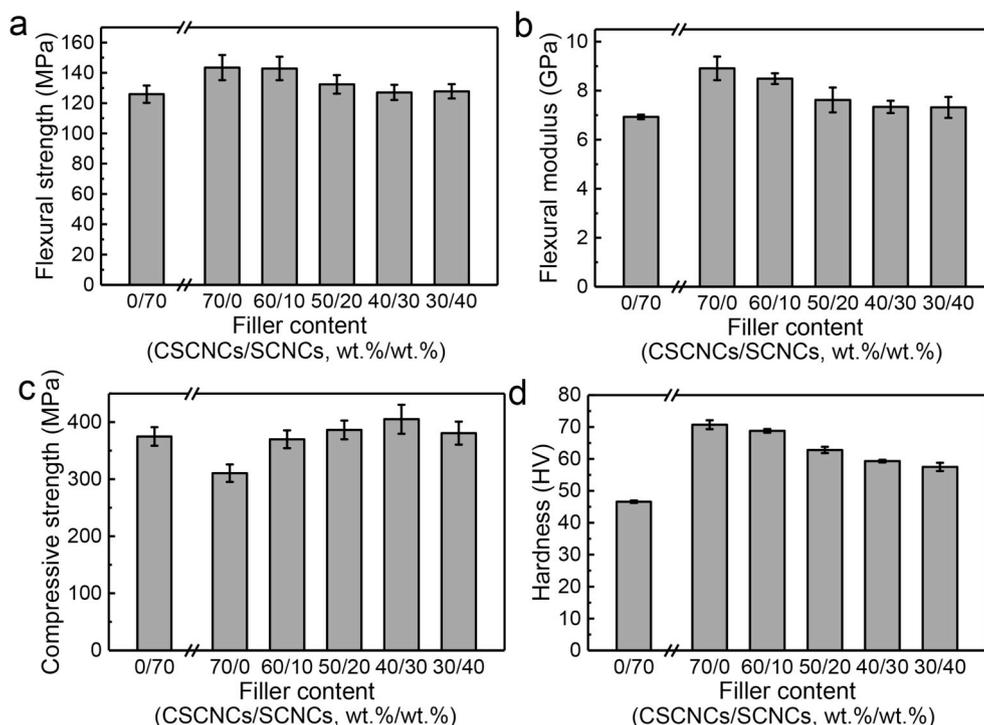


Fig. 6. The effect of mass ratio of the CSCNCs and SCNCs on (a) flexural strength, (b) flexural modulus, (c) compressive strength, and (d) hardness of the DRCs.

fillers for this purpose. Fig. 5 exhibits the mechanical performances of the DRCs prepared by filling CSCNCs and NPs with different mass ratios. With a 70 wt% filler content, the flexural properties and hardness of DRCs can reach the maximum values for DRCs-CSCNCs, and then were decreased with the increasing supplement of NPs. However, the compressive strength of DRCs-CN 60-10 (CSCNCs: NPs = 60: 10, wt./wt.) (359.9 ± 13.5 MPa) was significantly enhanced compared to that of the DRCs-CSCNCs (310.5 ± 15.2 MPa), and was close to that of the DRCs-SCNCs (374.9 ± 16.2 MPa). Moreover, the flexural properties and hardness of DRCs-CN 60-10 were significantly higher than that of DRCs-SCNCs. The possible reason is that the NPs, instead of the resin matrix, might embed into the interstices existing in composites, which reduces the space among particles and increases the packing of fillers, thereby generating an improved comprehensive property [18]. Noticeably, all the DRCs reinforced with a certain amount of CSCNCs presented dramatic improvements in hardness, mainly attributed to the enhancement of filler strength after the heat treatment process [26,37].

Based on the encouraging results obtained by a filler mixture of CSCNCs and NPs, to further improve the overall performance, the SCNCs were adopted as co-fillers of the CSCNCs for the DRCs because the SCNCs had been proved for a better strengthening effect than the NPs [33]. Fig. 6 shows the mechanical strengths of DRCs prepared by filling CSCNCs and SCNCs having various mass ratios. The corresponding stress-strain curves of three-point bending test were plotted on Fig. S4. Obviously, the filler composition had significant effects on the flexural properties. The addition of CSCNCs can harden the DRCs, while a SCNCs-filled sample can deform more (Fig. S4). As raising the proportion of CSCNCs, the slope of linear region also increased in the strain-stress curves [38]. In addition, the great performances in flexural properties and hardness of DRCs-CSCNCs were comparative with that of the DRCs filled 60 wt% CSCNCs and 10 wt% SCNCs (DRCs-CS 60-10), while the compressive strength of DRCs-CS 60-10 was well above that of the DRCs-CSCNCs, having no significant difference compared to that of the DRCs-SCNCs (Table S2). These results denoted that the advantages of CSCNCs and SCNCs can be combined when they were both incorporated in the DRCs. The possible reason, why the enhancement effect of SCNCs is greater than NPs, is that the broken SCNCs imbedding

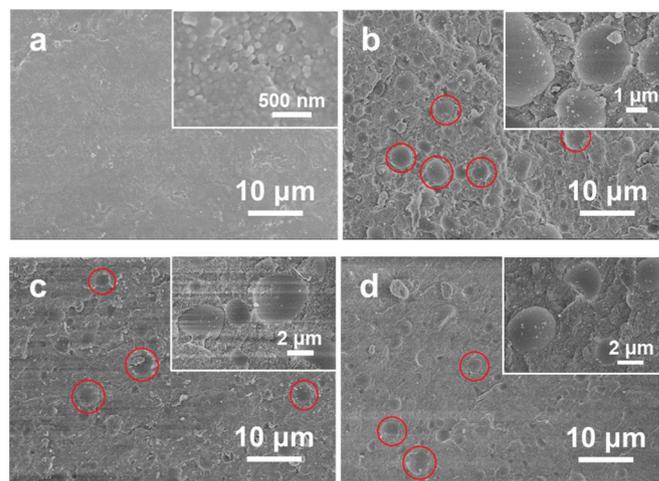


Fig. 7. SEM images of the fracture surfaces of DRCs with different CSCNCs/SCNCs ratios: (a) DRCs-CSCNCs, (b) DRCs-CS 60-10, (c) DRCs-CS 50-20 (CSCNCs: SCNCs = 50/20, wt./wt.), (d) DRCs-CS 40-30 (CSCNCs: SCNCs = 40/30, wt./wt.). Red circles shown in image (b), (c) and (d) represent complete CSCNCs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

into the interstices may not only increase the filler packing, but also provide a tighter interfacial bond with the resin matrix due to its porous structure (Fig. S5).

The fracture surfaces of DRCs with different CSCNCs/SCNCs ratios are shown in Fig. 7. The DRCs-SCNCs showed a flat surface, indicating the weak resistance of DRCs to the applied force. The unobservable SCNCs structure provided evidence that the unstable aggregation of NPs in SCNCs may result in the destruction in DRCs after mixing and extruding in the three-roll extruder. After 500 °C heat treatment, CSCNCs manifested a stronger construction, most of which can be completely found in the fracture surfaces (Fig. 7b). The DRCs-CSCNCs displayed coarse cross-section surfaces with a number of curved steps,

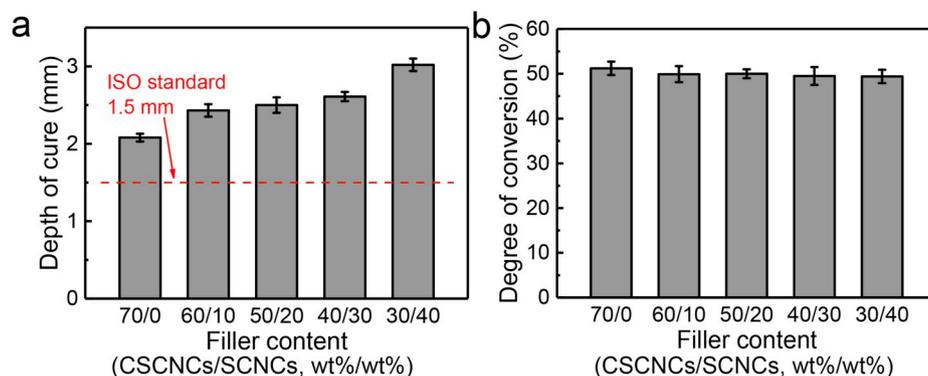


Fig. 8. The effect of mass ratio of the CSCNCs and SCNCs on the (a) depth of cure and (b) degree of conversion of DRCs.

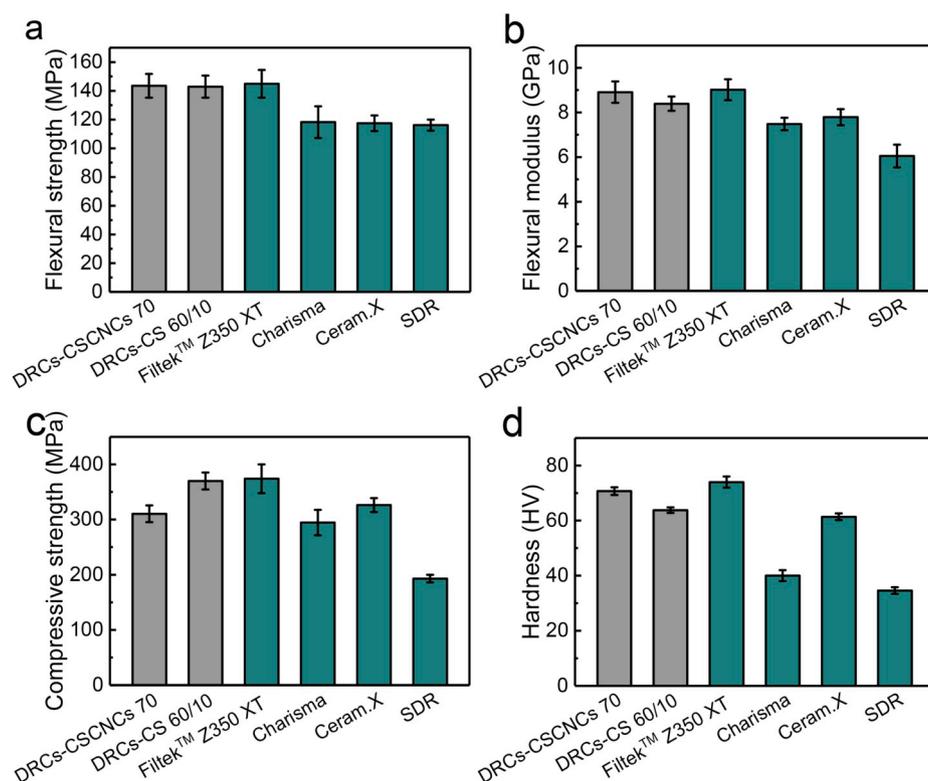


Fig. 9. (a) Flexural strength, (b) flexural modulus, (c) compressive strength, and (d) hardness of our products and four kinds of commercially available DRCs.

suggesting the capability of crack deflection of the CSCNCs and the higher fracture energy of DRCs [39]. With the decrease of content of the CSCNCs, the fillers with the entire structure reduced dramatically (Fig. 7c and d).

Fig. 8 shows the cure depth (Fig. 8a) and conversion degree (Fig. 8b) of DRCs prepared by filling CSCNCs and SCNCs with different mass ratios. As shown in Fig. 8a, the cure depth of all the experimental samples exceeded the standard (1.5 mm) in ISO 4049: 2009, and had an uptrend with the increase of the proportion of SCNCs in the DRCs. The possible reason of this increasing trend is that the pore size of CSCNCs has a significant decrease compared with the SCNCs, which makes it harder for light to pass through. Meanwhile, some of the SCNCs were crushed to original nanoscale particles during the mixing process. The loose particles enabled higher light scattering and reflection so that much higher depth of cure can be exhibited for the DRCs filled with more SCNCs [40]. Furthermore, the conversion degree of samples having different filler compositions exhibited no significant difference. These results are probably because the degree of conversion may only be impeded in the

composites where the filler size approaches the 470 nm wavelength of curing unit [41,42]. Although some of the SCNCs were crushed, the particle diameter and primary particles of SCNCs and CSCNCs were the same and dramatically discrepant with the wavelength. Therefore, there was a similar degree of conversion for the DRCs with different CSCNCs/SCNCs ratios.

For better comparisons, we bought four kinds of representative and commercial DRCs with SiO₂/ZrO₂ nanoclusters, silica/silicate glass as fillers, and evaluated the above four samples in the same instrument. Remarkably, most of the commercial DRCs were loaded with more than 70 wt% or 55 vol% fillers, and more than one component (as shown in Table S1). The corresponding mechanical properties are shown in Fig. 9. It was obvious that all the DRCs filled with nanocluster fillers (our products and Z350) had higher properties than the DRCs filled hybrid fillers (Charisma and Ceram.X) and the bulk fill material (SDR). The flexural properties and compressive strength of our products were comparable with Filtek™ Z350. Additionally, some commercial Ba-glass fillers were also adopted to prepare the DRCs. Compared to the Ba-glass

powders (Fig. S6), the CSCNCs/SCNCs fillers had much higher strengthening effect in mechanical properties of DRCs due to their unique nano-micro structures. These results suggested that the DRCs prepared by the combination of CSCNCs and SCNCs may achieve great properties even in the condition of single filler component and lower filler content.

4. Conclusions

In this study, the structure-reinforced SCNCs were obtained by combining spray-drying with calcination treatment. The calcined SCNCs (CSCNCs) at a relatively low temperature of 500 °C achieved obvious improvements in the flexural properties and hardness of DRCs except the decrease of compressive strength in comparison to the SCNCs. To obtain the overall performance including compressive strength, the CSCNCs were used together with the SiO₂ NPs or SCNCs which were built from SiO₂ NPs. The results indicated that the SCNCs had a better strengthening effect than the NPs. And the combined filling of 60 wt% CSCNCs and 10 wt% SCNCs can make the compressive strength of DRCs increase to the same level with that of the DRCs filled with 70 wt% SCNCs. Moreover, the corresponding flexural strength, flexural modulus and hardness kept a great improvement of 14%, 23% and 48%, respectively. More importantly, the as-prepared DRCs had better mechanical properties than many commercial products even in the condition of single filler component and lower content of fillers. Therefore, it could be envisioned that the introduction of CSCNCs as fillers may have a new sight for the fabrication of DRCs having greatly enhanced mechanical properties.

Declaration of competing interest

I confirm that all the co-authors have read and approved this manuscript. No related work is in the press with any other journal. There are no known potential conflicts of interest with this work.

CRediT authorship contribution statement

Dan-Lei Yang: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **Qian Sun:** Supervision, Writing - review & editing. **Hao Niu:** Validation, Formal analysis. **Rui-Li Wang:** Investigation, Resources. **Dan Wang:** Resources. **Jie-Xin Wang:** Conceptualization, Methodology, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compositesb.2020.107791>.

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