

Effects of ultrasonication on the microstructures and mechanical properties of carbon nanotube films and their based composites

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Abstract: Carbon nanotube (CNT) film has been considered as a promising preform of CNTs for developing high performance composites that possess high content of CNTs. However, due to the intertube van der Waals interactions, CNTs in the films are always bundled together, making the evenly mixing of CNTs and resin materials challenging. In this work, an eco-friendly ultrasonic-assisted resin infiltration process has been developed, and its effects on CNT bundles **diameter**, CNT crystallinity, CNT film stretchability, and

the mechanical properties of CNT films and their based composites have been systematically investigated. It has been found that CNT bundles became thinner and the film stretchability became higher upon the ultrasonication, and thus the CNT film-based composites were strengthened accordingly. However, extensive sonication would severely destroy the crystal structures of CNTs and thus degrade the mechanical properties of CNT films and their based composites. The underlying mechanisms for the evolution of CNT networks during the ultrasonic treatment were also discussed.

Keywords: Carbon nanotubes, Composites, Resin infiltration, Mechanical Properties

1. Introduction

Due to their remarkable intrinsic mechanical, electrical and thermal properties [1-3], carbon nanotubes (CNTs) have been considered as the game-changing reinforcement for constructing high-performance and multifunctional composites [4-6]. At the early stages, CNT composites were prepared by dispersing CNTs powder into resin matrix [7, 8]. Enormous studies, however, have shown that the mechanical properties of these composites were far lower than expected [9], especially at high CNT loadings. This was mainly ascribed to the poor dispersion states of CNTs within resin materials as CNTs were prone to agglomerate due to their large surface areas and intertube van der Waals (vdWs) interaction [10, 11]. Moreover, the viscosity of the resin increased dramatically with increasing CNT content [12, 13], greatly reducing the processibility of resin materials.

According to Coleman's study [14], the strength and modulus of CNT composites are

positively correlated to CNT content, CNT alignment, and CNT/matrix interfacial load transfers. Extensive studies have found that mixing resin materials with macroscopic assemblies of CNTs, such as one-dimensional CNT fibers [15, 16] or two-dimensional CNT films [17-19], could fabricate composites with CNT content over 50 wt% [20, 21]. The alignment of CNTs within these composites could be enhanced through stretching prior to curing, and the strength of the composites containing high content aligned CNTs could exceed 2 GPa [22-24]. Meanwhile, some efforts have also been devoted to improve the interfacial load transfer efficiency by means of chemically modifying [24-26]. However, as CNT films are porous materials consisting of bundled CNTs, the resin infiltration processing is time-consuming [27] and always results in uneven resin distribution through the film thickness [28]. Mikhalech et al. [29] prepared block CNT composites by the process of resin penetration into CNT macroscopic assembly, and found resin enrichment regions and voids in the samples with low and high CNT content, respectively. This inhomogeneous distribution of the resin tended to retard the fully utilization of CNTs. On one hand, the load could not transfer efficiently between adjacent CNTs/CNT bundles due to the absence of the resin in the void areas. On the other hand, the resin rich regions were relatively weak, leading to earlier fracture of composites. Moreover, it is challenging for the resin materials to fully infuse into the bundles and wet all individual CNTs [7]. Thus, at a given CNT content, more CNTs could be utilized for strengthening the composites as the **diameter** of CNT bundles decreased.

In the present study, we proposed an eco-friendly ultrasonic-assisted resin infiltration processing to reduce the **diameter** of CNT bundles and enhance the homogeneity of resin

distribution within CNT composites. The effects of applied ultrasonication on CNT bundles **diameter**, CNT crystallinity, CNT film stretchability, and subsequently the mechanical properties of CNT films and their based composites have been systematically investigated. The underlying mechanisms for the evolution of CNT networks during the ultrasonic treatment were also discussed.

2. Experimental

2.1 Materials

CNT films with thickness of 7-9 μm , which were fabricated by using the Float Catalyst Chemical Vapor Deposition (FCCVD) method [30], were supplied by Suzhou Creative Nanotechnology Ltd., China. The film was used as received. Epoxy monomer (Trade name TDE85) and curing agent (Trade name DETDA) were supplied by Tianjin Jingdong Chemical Composites Co. Ltd., China. Analytical grade Acetone was purchased from Sinopharm Chemical Reagent Co. and used without any further purification.

2.2 Ultrasonic treatment of CNT films

CNT films were cut into pieces of $6\text{ cm} \times 6\text{ cm}$ size, and then immersed into the solvent (acetone). A home-made ultrasonication setup, as illustrated in Fig. S1, was used to generate sonication with a frequency of 40 kHz to the solution. The total sonication power was set as 72 W, and a series of sonication time (i.e. 0, 4, 8, and 16 min) were adopted to reveal its effect on the structures and properties of CNT films.

2.3 Fabrication of CNT film-based composites

Epoxy resin, where the mass ratio of epoxy monomer and curing agent was 5:2, was

diluted in the solvent (acetone), and a mechanical stirrer was used to mix and homogenize the solution. In the current study, a mass fraction of resin materials in the solution was set as 15%. CNT films of 6 cm × 6 cm size were then immersed in the epoxy resin solution at room temperature. The home-made ultrasonication setup was used to assist resin infiltration, as schematically illustrated in Fig. S2. A series of sonication time (i.e. 0, 4, 8, and 16 min) and sonication power (i.e. 36, 72, and 108 W) were adopted to reveal their effects on the structures and properties of CNT film-based composites. After infiltration process, the resin impregnated CNT films (CNT preregs) were placed in a vacuum oven at 50 °C for 0.5 h to remove the solvent, and then sandwiched between two layers of ventilated felt and peel ply under 20 MPa pressure and 75 °C for 1 h to remove the excess resin from the interior of CNT films. Finally, CNT preregs were cured through hot pressing under 20 MPa pressure, following the curing cycle of 90 °C for 1 h, 120 °C for 2 h, and 150 °C for 3 h.

2.4 Fabrication of aligned CNT film-based composites

CNT films of 6 cm × 6 cm size were immersed in the epoxy resin solution at room temperature for 1 h without ultrasonic treatment, or for 8 min under sonication with a power of 72 W. The obtained CNT preregs were stretched via a universal testing machine (E44, MTS, USA) at a speed of 0.3 mm/min at room temperature. To cure the aligned CNT preregs, solvent was firstly removed and the same curing procedures as mentioned above were implemented.

2.5 Characterization

The morphology of surface and cross-section of CNT composites was investigated via

a Scanning Electronic Microscopy (SEM, S-4800, Hitachi, Japan). SEM samples for cross-section evaluations were prepared by using a Dual Beam FIB system (FEI, Helios 5 UX, USA). The nanostructures of CNT bundles were also investigated by using a Transmission Electron Microscopy (TEM, Tecnai G2F20 S-Twin, FEI, USA). To prepare the TEM samples, a nearly transparent layer was carefully peeled from the CNT prepregs using tweezers and then spread onto a TEM microgrid. Atomic force microscopy (AFM, Multimode, Veeco, USA) was used to determine the roughness of CNT films/prepregs. The contact angle between epoxy and CNT films was investigated via Video-Based Optical Contact Angle Meter (OCA 15 EC, Dataphysics, Germany). The crystallinity and alignment of CNTs were investigated by Raman spectroscopy (LABRAM HR, Horiba-JY Corp, excitation wavelength 532 nm). Thermal performance of CNT films and their composites was evaluated through Thermal gravimetric analysis (TGA, NETZSCH 209 F1Libra), where the samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. Mechanical properties of CNT films and their composites were investigated via a tensile testing machine (Instron 3365, Instron Inc., USA) with a load cell of 10 N. All the samples were cut into the size of 2×30 mm, and at least five samples were measured for each kind of specimens.

3. Results and discussion

3.1 Structure and morphology of CNT films and their composites

3.1.1 Structure and morphology of CNT films

The size of the as-received CNT film is of about 90 cm×120 cm (Fig. S3). Fig. 1a₁-d₁

present the SEM images of CNT films before and after ultrasonic treatment in pure solvent. CNTs are mostly randomly aligned within all these films, and the films are of high porosity, making the resin infiltration possible. Figs. 1a₂-d₂ show the histograms of CNT bundle diameter, and the statistical analysis found that the diameter of CNT bundles increased with sonication times, where it was about 21.6 nm in the untreated CNT film, while it increased to 24.5, 28.3 and 33.4 nm after ultrasonic treatment for 4, 8 and 16 min, respectively.

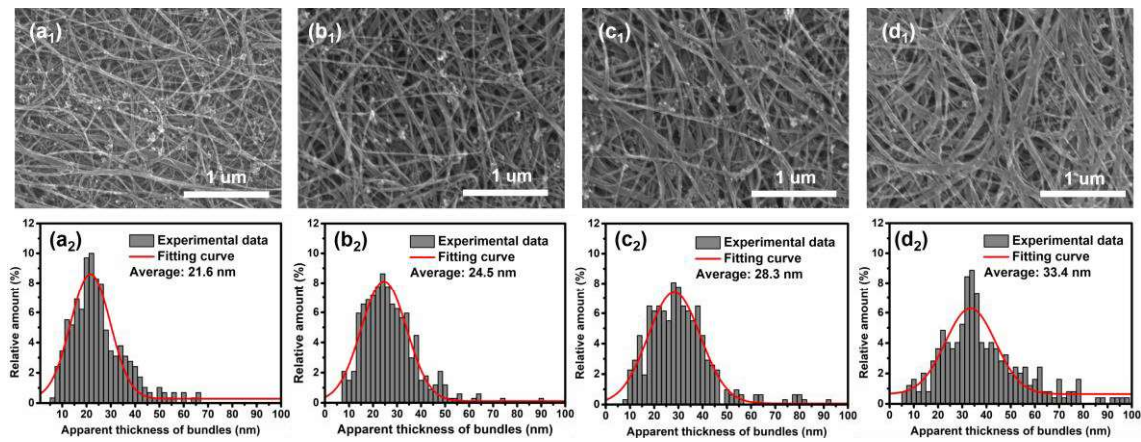


Fig. 1. (a₁-d₁) SEM images and (a₂-d₂) histograms of CNT bundles diameter of the CNT films after ultrasonic treatment in pure solvent for (a) 0, (b) 4, (c) 8 and (d) 16 min, respectively.

As mentioned earlier, CNTs are prone to adhere to each other to form bundles due to the intertube vdWs interaction, and these bundles form branched networks within the films [31]. Fig. 2a shows the TEM image of a typical branched CNT bundles within a CNT film, where a 42 nm thick bundle split into two thinner branches of 16 and 26 nm thick. When the ultrasound waves propagate in the solution, the induced bubbles experience the process of formation, growth, and collapse, resulting in cavitation effect, and the instantaneous temperature and pressure induced by bubble collapse can be as high

as 5000 K and 50 MPa, respectively [32]. The strong shock waves between the branches radiate to all directions and push the individual branches to further separate with each other when the impact force exceed the vdWs interaction between CNTs. This sonication induced de-bundling processing was schematically illustrated in Fig. 2b. As the cavitation bubbles continue to explode, large CNT bundles can be divided into smaller ones. However, when the sonication was stopped, these exfoliated small bundles would like to re-assemble into large bundles again under the intertube vdWs interaction, thus resulting in thickened bundles. Fig. 2c schematically illustrated this de-bundling and re-bundling process.

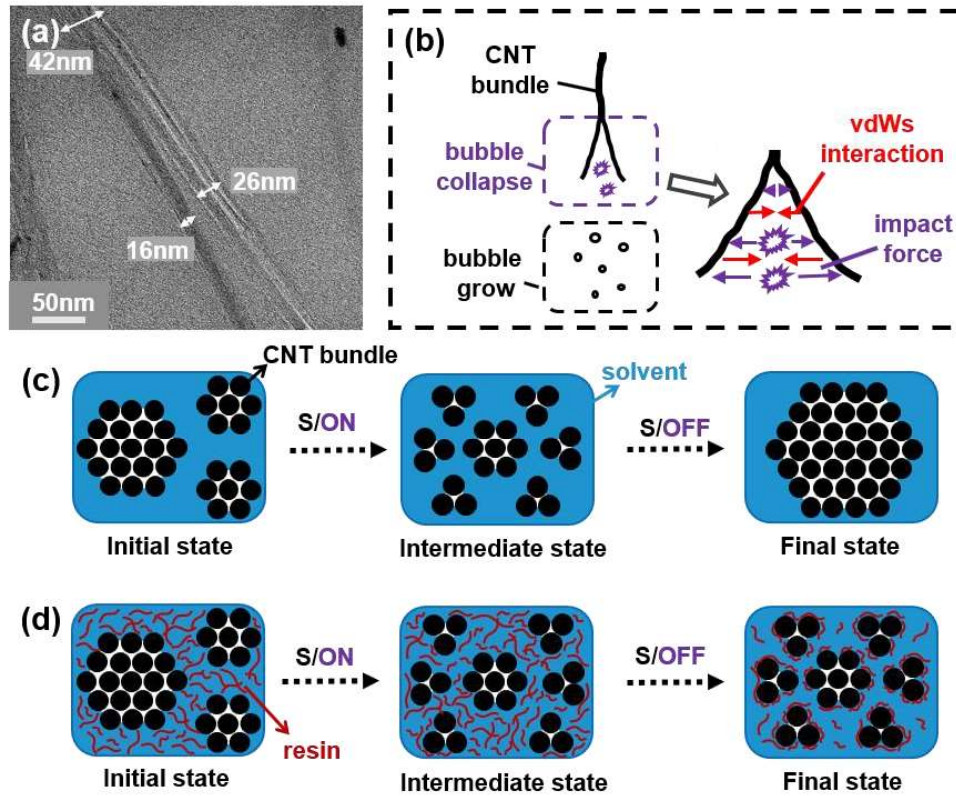


Fig. 2. (a) TEM image of branched CNT bundles, (b) schematic of the de-bundle processing and structural evolution of bundles in (c) pure solvent and (d) resin solutions.

3.1.2 Structure and morphology of CNT film-based composites

Fig. 3a₁-d₁ show the SEM images of CNT prepregs before and after ultrasonication.

For a better imaging of surface CNTs, CNT prepregs were washed by immersing them in acetone for 2h to remove excessive resin materials from the prepregs surface. TGA analyses (Fig. S4) showed that the weight content of CNTs in the films before and after this processing was about 59.0% and 90.3%, respectively. Contrary to pure CNT films, the diameter of CNT bundles within CNT prepregs decreased with increasing sonication time. Specifically, for the samples without ultrasonic treatment, the average diameter of CNT bundles was 61 nm, and some large bundles over 70 nm thick can be observed (Fig. 3a₁). After sonicated for 4, 8 and 16 min, the average diameter of CNT bundles decreased to about 59, 39 and 28 nm (Fig. 3b₁-d₁), respectively.

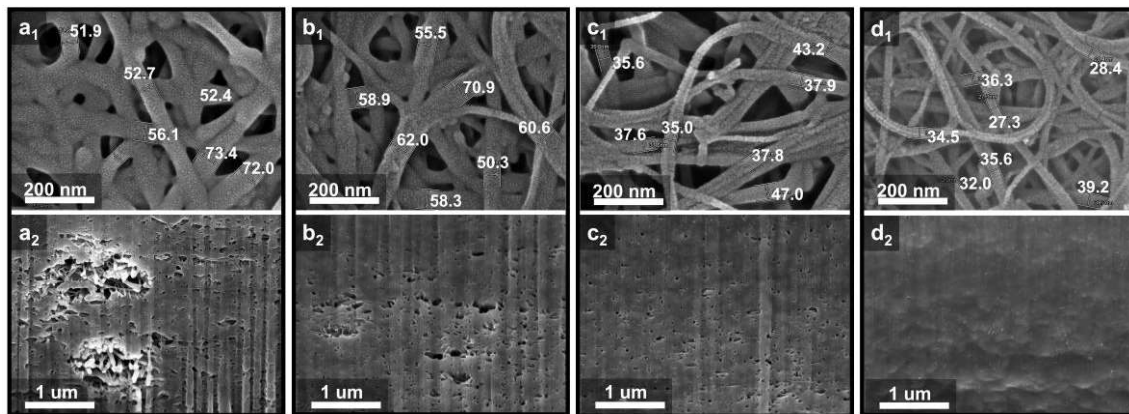


Fig. 3. (a₁-d₁) SEM images of the microscopic morphology of washed CNT prepregs, (a₂-d₂) Cross-section morphology of cured CNT composites, where a, b, c and d correspond to sonication time of 0, 4, 8 and 16 min, respectively.

Similar to the sonication of CNT films in pure solvent, it is also expected that during the sonication of CNT films in resin solutions, large bundles separated into smaller ones when the energy provided by ultrasonication exceeded the vdWs cohesive energy between CNTs. The resin materials then got into the enlarged interbundle areas and wrapped onto CNT surfaces (Fig. 2d), thus preventing the bundles from re-bundling after

the sonication was stopped. This de-bundling process increased the interface area between CNTs and matrix and thus promoted the stress transfer efficiency in composites [33]. It is worth noting that the de-bundling effect was less obvious for a short sonication time (such as 4 min in the present study), as the provided sonication energy was might not enough to overcome the vdWs cohesive energy between CNTs. When the sonication time increased to 8 or 16 min, the diameter of CNT bundles decreased dramatically, suggesting a stronger de-bundling effect.

In addition to the microstructure, the effect of ultrasonication on the macroscopic structure of CNT preregs was also investigated. As shown in Fig. S5a, the color of resin solution became darker with the increase of sonication time, indicating that CNTs escaped from the films and then dispersed into resin resolution. Besides, AFM characterizations, as shown in Fig. S5b-e, found that the roughness parameter Ra (arithmetic average roughness) of washed CNT preregs increased from 18.9 nm to 25.7 nm, suggesting that the surface of washed CNT preregs became rougher with the increase of sonication time. Under the ultrasonic condition, CNTs and their bundles separated from each other, resulting in looser network structure and rougher surface. Furthermore, infrared spectroscopy analyses of the above solutions, the details of which can be found in the supplemental materials (Fig. S6), have found that the sonication process not only had almost no effects on the structures of resin, but also did not induce chemical reactions between CNTs and resin.

To reveal the effect of ultrasonication on the resin distribution within CNT film-based composites, the cross-sections of these materials were characterized through SEM

analyses (Fig. 3a₂-d₂). For composites without sonication treatment, enormous large voids can be found (Fig. 3a₂), indicating poor resin infiltration. After sonicated for 4 min, large voids disappeared, while small voids still existed (fig. 3b₂). The number and size of voids further decreased after sonicated for 8 min (Fig. 3c₂), and no visible voids could be found after sonicated for 16 min (Fig. 3d₂), indicating that the resin were almost thoroughly infiltrated into the voids in the CNT network. The contact angle between epoxy and washed CNT prepreps was also tested and it has been found that the contact angle decreased with the increasing of sonication time (Fig. S7). This might be explained by the reason that with the increase of sonication time, CNT film got looser, and a looser CNT film absorbs the liquid resin more easily than a dense one. Furthermore, Qiao et al.'s study showed that ultrasonication could reduce the surface energy and viscous force of the liquid [34]. In this respect, resin with lower surface energy were able to further wet CNTs during the process of ultrasonic assisted resin infiltration.

The weight content of CNTs in the composites, which was investigated via TGA analyses, is in the range of 54.1% to 59.0% (Fig. S8). Although more resin might permeate into the interior of the CNT film due to sonication, excess resin between CNT bundles was squeezed onto the film surface under pressure and then absorbed by the ventilated felt (Fig. S9).

3.2 Properties of CNT films and their based composites.

3.2.1 Properties of CNT films

Previous studies have found that the crystallinity of CNTs in solutions always reduced upon ultrasonication, and this reduction could be quantitatively evaluated by calculating

the variation of I_G/I_D , where I_G and I_D represented the intensity of peak G and D, respectively, in their Raman Spectra [35, 36]. Fig. 4a shows the Raman spectra of CNT films before and after the ultrasonic treatment. The value I_G/I_D of pristine CNT films was 5.0 and decreased with the increase of sonication time, reaching to 3.3 after sonicated for 16 min, which implied that the ultrasonication played a detrimental role on the crystalline structures of CNTs within CNT films. This is mainly due to the reason that when the energy provided by the collapse of cavitation bubbles exceeded the bonding energy of C=C bonds within CNTs, these bonds would broke and thus resulted in new defects.

The TGA curves of pure CNT films after sonicated for different time were shown in Fig. 4b. Residual mass of untreated CNT films at 600°C was 97%, indicating a satisfactory thermal stability. The 3% mass loss was owing to the decomposition of amorphous carbon and alkane, which were the byproducts of the FCCVD process. After sonicated for 4, 8 and 16 min, the residual mass was 92.1%, 88.6% and 84.9%, respectively, indicating that thermal stability of CNT films decreased with the increase of sonication time. This also confirmed that upon ultrasonication, new CNT defects generated and thus the crystallinity of CNTs decreased.

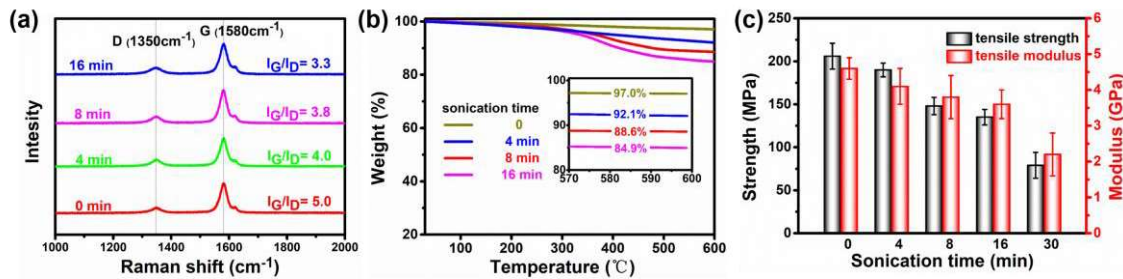


Fig. 4. (a) Raman spectra, (b) TGA curves and (c) mechanical properties of CNT films after sonicated in pure solvent for different time.

The tensile mechanical properties of different CNT films were compared in Fig. 4c.

The strength and modulus of untreated CNT films were 206 MPa and 4.6 GPa, respectively. With the increase of sonication time, the strength and modulus decreased, and they were as low as 80 MPa and 2.2GPa, respectively, after sonicated for 16 min. This can be explained by the following two aspects. On one hand, as mentioned earlier, ultrasonication created larger bundles, and these larger bundles would create large pores within CNT assemblies [37], which inhibited the stress transfer between CNTs inside CNT films. On the other hand, longer sonication time induced more defects on CNTs, which would also be detrimental to the mechanical properties of CNT films.

3.2.2 Properties of CNT film-based composites

Different sonication time and power were applied to investigate the effect of ultrasonication on the mechanical and electrical properties of CNT composites. The stress-strain curves and tensile mechanical properties are shown in Fig. 5a-c. The strength and modulus of the composites without ultrasonic treatment are 467 MPa and 10.9 GPa, respectively, which are over 2 times of pure CNT films. This indicated that the resin infiltration would effectively enhance the tensile mechanical properties of CNT films, which was in consist with previous studies [38]. By increasing the sonication time, the tensile mechanical properties of CNT composite films increased firstly and then decreased. After sonicated for 8 min, the tensile strength and modulus reached to the maximum of 583 MPa and 14.6 GPa, respectively, which were 24.8% and 33.9% higher than these of untreated ones. However, when further increasing the sonication time to 16 min, the strength and modulus of samples were reduced and even lower than those of untreated samples. The electrical conductivity of CNT composites treated with different

sonication time was also investigated. Similar to the trend of tensile strength, the conductivity of these composites increased firstly and then decreased with the increase of sonication time. However, the effect of ultrasonication on conductivity seemed to be less significant due to the presence of resin (Fig. S10).

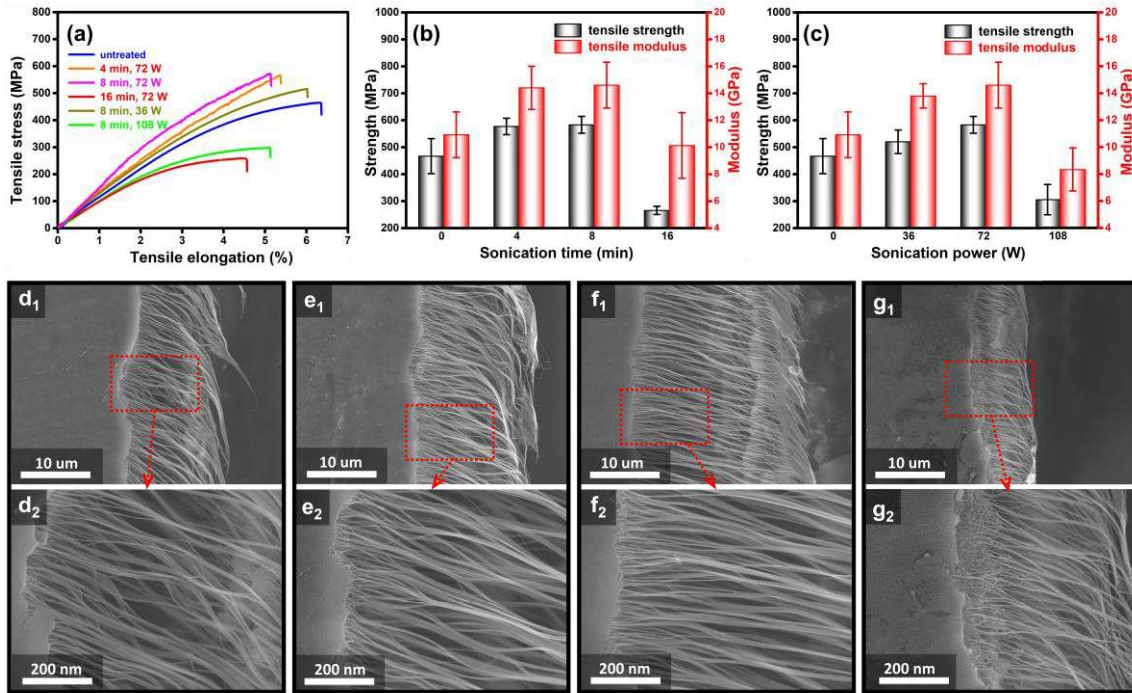


Fig. 5. Tensile mechanical properties and fractographies of CNT composites: (a) typical stress-strain curves, sonication (b) time and (c) power depend of the tensile mechanical properties, and low (d_1 – g_1) and high (d_2 – g_2) magnification SEM images of fractographies of CNT composites, where d, e f and g correspond to sonication time of 0, 4, 8 and 16 min, respectively.

To further reveal the structure dependence of the tensile properties of CNT composites, the fractographies of these composites were characterized through SEM analyses. As shown in Fig. 5d–g, CNT bundles were pulled out from the resin matrix in the fractured area. For the untreated composites, sparse, large diameter CNT bundles can be observed in the high magnification SEM image (Fig. 5d₂), resulted in limited reinforcing efficiency

and undesirable mechanical properties. For the composites which sonicated for 4 min (Fig. 5e) and 8 min (Fig. 5f), CNT bundles which pulled out from the resin were thinner, which was in consist with the thinning trends indicated in Fig. 3a₁-d₁. In this respect, more CNTs could thus interact with resin materials and share the loading within these composites, leading to higher load transfer efficiency and mechanical properties [33]. As the sonication time was extended to 16 min, although CNT bundles were also thinner, their length was significantly shorter (Fig. 5g) due to excessive sonication energy, as confirmed by the aforementioned Raman and TGA analyses, resulting in degraded mechanical properties.

The effect of sonication power on the mechanical properties of CNT composites were also investigated and shown in Fig. 5c. For all these samples, the sonication time was set as 8 min. Similar to the dependence of sonication time, the tensile strength and modulus increased firstly and then decreased. In summary, with the increase of sonication energy, CNT bundles diameter decreased while the defects ratio of CNTs increased, which played positive and negative roles on the mechanical properties of CNT composites, respectively. The balance of these two effects is the key to obtain high-performance CNT composites.

3.3 Properties of stretched CNT film-based composites

Stretching has been found to be an effective strategy of enhancing the alignment of CNTs and the properties of CNT composites [23, 35]. In this study, CNT preregs, without and with ultrasonic treatment, were stretched to evaluate the effect of ultrasonication on stretchability of preregs and mechanical properties of composites. The load-strain curves during the stretching process were shown in Fig. S11. It can be

seen that the preregs without ultrasonic treatment can be stretched by $20.5\pm3.5\%$, while preregs with ultrasonic treatment can be stretched further, reaching to $27.0\pm1.6\%$. The enhanced stretchability might be due to the reason that CNT bundles in the ultrasonic treated preregs were thinner, and CNTs and resins were more evenly mixed, making the preregs less susceptible to microcracks during the stretching process.

Fig. 6a and b show the microscopic images of the surfaces of oriented preregs after stretching without and with ultrasonic treatment, where it can be seen that CNTs in the latter possessed better alignment and were more densely packed. The alignment of CNTs can be quantitatively evaluated by $I_{G//}/I_{G\perp}$, where $I_{G//}$ and $I_{G\perp}$ represents the intensities of the G-band measured when the incident laser beam is in parallel and perpendicular directions to directions of stretching [39]. As shown in Fig. 6c, $I_{G//}/I_{G\perp}$ was 1.2 for the original films, and it increased to 2.2 and 3.2 for the stretched CNT composites without and with ultrasonic treatments, respectively. This means that ultrasonication plays a positive role on the stretching-enhanced alignment of CNTs in the composites, and thus leads to enhanced mechanical properties of the cured composites. The stress-strain curves and mechanical properties of composites before and after stretching process are shown in Fig. S12 and Fig. 6d, respectively. After stretching, the tensile strength and modulus of the aligned composites without ultrasonication were about 0.9 GPa and 48.9 GPa, respectively, and increased to 1.3 GPa and 104.3 GPa for ultrasonic treated composites, which were 44% and 113% higher than aligned composites without ultrasonication. This also confirms that stretching is an effective strategy of enhancing the mechanical properties of CNT composites.

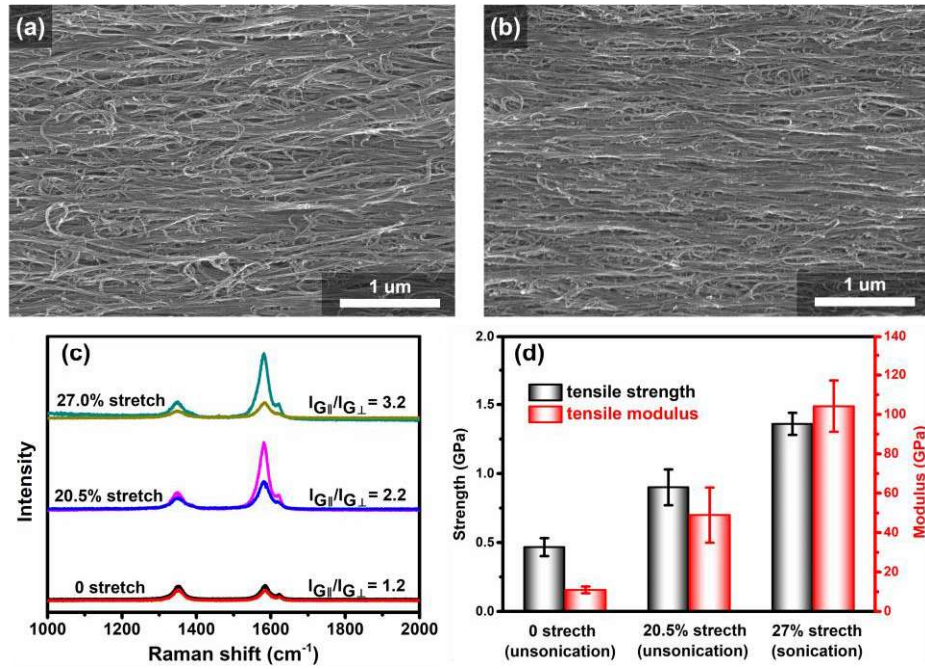


Fig. 6. Structures and mechanical properties of stretched CNT composites: SEM images of the surface of CNT prepregs stretched by (a) 20.5±3.5% and (b) 27±1.6%, (c) polarized Raman spectra and (d) mechanical properties of composites before and after stretching process.

4. Conclusions

In this study, the ultrasonic-assisted resin infiltration processing was developed to fabricate high performance CNT film-based composites. The structural evolution and properties of CNTs, CNT films and their composites before and after ultrasonic treatment were systematically investigated. It has been found that ultrasonication could on one hand destroy the crystallinity of CNTs, and on the other hand reduce the diameter of CNT bundles in solutions. However, due to the intertube vdWs interaction, these thinner bundles re-stacked into large ones in solutions without resin materials upon the ceasing of sonication. In these respects, the mechanical properties, thermal stability and structural

integrity of CNT films were degraded with the sonication energy.

In the resin solutions, the resin materials could wrap onto the exfoliated thinner bundles, thus restricted them from re-bundling. This de-bundling process enriched the interfaces between CNTs and resin materials, and thus improved the load transfer efficiency. The mechanical properties of CNT composites increased firstly and then decreased with the increase of sonication energy, where the reduction is mainly due to the reduced crystallinity of CNTs induced by ultrasonication. By optimizing the process parameters, the tensile strength and modulus of the composites were increased by 25% and 34%, respectively, compared with the samples without ultrasonic treatment. Moreover, the ultrasonic treated CNT preregs possess better stretchability, and after stretching, the strength and modulus of ultrasonic treated CNT composites were 44% and 113% higher than that of untreated composites.

It should be mentioned that the ultrasonic-assisted process developed here is a controllable, eco-friendly and scalable process, and can be adopted to fabricate composite materials containing other nanofillers.

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