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# Dramatic increase in electrical conductivity in epoxy composites with uni-directionally oriented laminae of carbon nanotubes

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## HIGHLIGHTS

- Composites with uni-directionally oriented laminae of carbon nanotubes were prepared.
- Conductivity of epoxy composite with lamellar structure were dramatically increased.
- Epoxy composite with lamellar structure shows good compressive performance.

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## ABSTRACT

Carbon nanotubes (CNTs) felts of aligned lamellar structure were prepared by ice templating and then infiltrated by liquid epoxy resin by vacuum pressure impregnation (INCNT/EP). Conventional physical blending method was also used to prepare carbon nanotube/epoxy composite as a comparison (PHCNT/EP). Microstructal observations of INCNT/EP fracture surfaces revealed the formation of a three-dimensional (3D) framework composed of unidirectionally oriented CNTs lamellae, which lead to a dramatic increase in electrical conductivity of the composite, by 15 orders of magnitude compared to pure epoxy and by 3 orders of magnitude compared to PHCNT/EP composite. Electrical conductivity of the INCNT/EP composite reached to 0.158 S/cm at CNT loading of 1.31 wt%. Meanwhile, improvements in Young's modulus (up to 25.5%) and yield strength (up to 12.2%) of the INCNT/EP composite under compressive loadings compared to pure epoxy were obtained. It is also observed that INCNT/EP composites show stable compressive behaviour and can effectively resist the sudden decrease of stress due to its skeleton structure of CNTs lamellae after the strain of *ca*. 50%.



## 1. Introduction

In recent years, intense research efforts are focused in nanocomposite research for the development and characterisation of materials reinforced with carbonaceous and ceramic nanofillers such as graphene, carbon nanotubes (CNT), silica, titania, alumina, etc. CNTs, discovered in 1991 by Iijima [1], are currently considered as high-potential nanoreinforcements for their outstanding thermal, electrical and mechanical properties. A vast number of studies in the literature report that use of CNTs as reinforcements in polymer matrices can lead to composites with exceptional mechanical and electric properties; these encouraging findings will eventually expand the usage of polymers in the electronics and other industries [2–4]. On the other hand, there are still important open concerns towards preparation of high performance CNT/polymer composites, the main challenge being achievement of high loading and homogeneous dispersions of the tubes in the continuous matrix phase [5]. The problem arises from the fact that CNT tend to spontaneously agglomerate, bundle together and entangle in the presence of most common solvents used for composite preparation, hence promoting introduction of critical defects in the composite volume [6]; not unexpectedly the problem gets bigger as CNT loading increases. To improve dispersion of CNTs in polymer matrices, several preparation processes have been suggested in the literature. The physical blending method is considered as the most convenient and practical way to prepare CNT/polymer composites from an industrial point of view while ultrasound [7] and high speed shearing [8] are more often used to efficiently disperse CNTs in the polymer matrix. Ultrasonicated CNTs may tend to re-agglomerate upon removal of the high acoustic energy [9]. Dispersion efficiency can be significantly improved through the usage of compatibilizers [10], surfactants [7] or even chemically functionalized tubes wherein carboxylic acid and

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hydroxyl groups are introduced on the outer walls of the tubes upon soaking in concentrated sulfuric or nitric acids or other strong oxidizing reagents [11]. However, it is still very hard to fabricate CNT/polymer composites with satisfactory electrical performance by physical blending method, for CNTs being non-oriented within the matrices. Dassios et al. [12,13] grew large dense vertically aligned CNTs array, then filled the CNT arrays with liquid epoxy resin and poly-vinyl alcohol (PVA) with the assistance of acetone as thinning medium. Chechenin et al. [14] measured electrical transport performance in similar composites and found great electrical conductivity values up to 0.85 S/cm, while, the shape and size of the composites were severely limited by the CNT array dimensions, so it is not suitable for practical application. An attractive alternative to fabricate highly conductive polymer composites would be the use of electrically conductive CNT felts or foams [15] as preformed CNT network, and polymer matrices can be infiltrated into the network. In this approach, the process of homogeneous dispersion of the tubes in the polymer matrix can be avoided, meanwhile, as the conductive network is already established by the CNT network, the conductivity of the composite will be well enhanced. Freeze casting was used to fabricate graphene monoliths with a cork-like structure [16]. The resulting biomimetic graphene-based monoliths exhibit a combination of ultralow density, superelasticity, good electrical conductivity and high efficiency of energy absorption. By infiltrating polymers into such 3D grapheme networks [17–20], electrically conductive polymer composites with improved mechanical properties were obtained.

In the present study, electrically conductive CNT/epoxy resin composites with uni-directionally oriented laminae of carbon nanotubes were prepared, and the methodology presented here is highly customizable shape and size. The main principle relies on ice templating for the preparation of porous CNT felts [21], wherein ice crystals play the role of templates for CNT grown. The felts were realized via freeze drying, and then filled with liquid epoxy resin by vacuum pressure impregnation at high temperature (INCNT/EP). Physical blending method was also used in the preparation of independent CNT/epoxy resin composites (PHCNT/EP) for benchmarking purposes. The compressive behaviour and electrical conductivity of the two types of composites were investigated and compared.

## 2. Experimental

Pristine multi-walled carbon nanotubes of diameters in the range of 8–15 nm and lengths of *ca.* 50 μm were provided from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. The epoxy resin used was liquid diglycidyl ether of bisphenol-A (DGEBA, E44) with an epoxide number of 0.41–0.47 (Nantong Xingchen Synthetic Material Co., Ltd., China). 4,4′-dichlorodiphenyl sulfone (Wuhan Yuancheng Gongchuang Science and Technology Ltd., China) was used as curing agent. Sodium carboxymethyl cellulose (CMC, Aladdin Reagent Ltd., Shanghai, China) was used as binder to prepare CNTs felt.

The preparation process of INCNT/EP composites can be categorized into main stages:

The first stage, depicted schematically in Fig. 1, aimed to prepare lamellar CNTs felts through freeze drying. In this stage, aqueous CMC solutions at mass fractions of 0.8 wt% were prepared by addition of CMC powder into distilled water with subsequent mechanical stirring for 2 h. CNTs were then added into the solution at predetermined weight loadings (1.00 wt%, 1.25 wt%, 1.50 wt%, 1.75 wt%, 2.00 wt%). Dispersion of CNTs in the solution was achieved by mechanical stirring for 30 min and then ultrasonication for 1 h at 1500 W in a Bilon-1500 ultrasonic emulsifying dispersion bath (Bilon Biological Technology Co., Ltd., Shanghai, China), able to maintain the suspension at room temperature during homogenization. The dispersed solution was then poured into a 100 × 50 × 5 $mm^3$ polytetrafluoroethylene mould and the mould was freezed into the cold trap of freezing dryer. During the freezing process, upper cover of the cold trap was opened, which created a temperature gradient in the cold trap, the temperature on the bottom is about −80 °C. The freezing process lasted for 10 h and finally dried under vacuum for 36 h. The obtained felts adopt the size of the mould, and the thickness of the felt is constant in this work. The apparent density (ρ) of the prepared CNT felt was calculated using the formula: $\rho = m/V$, where $m$ and $V$ are measured weight and volume of the sample in natural state, respectively, and the calculations are shown in Table 1.

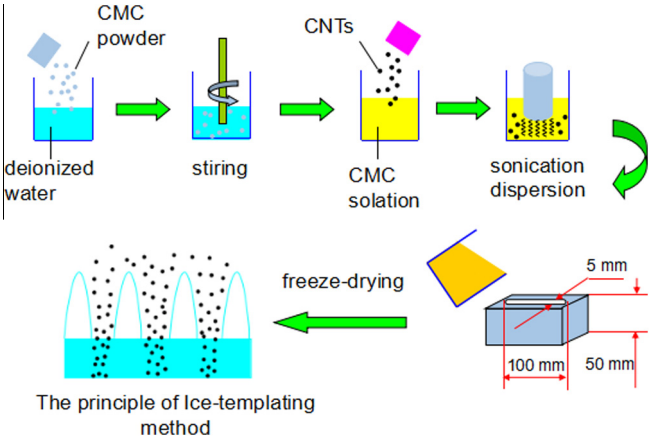


**Fig. 1.** Schematic illustration of freeze drying method for the CNTs felts.

In the second stage, vacuum pressure impregnation was adopted to infiltrate E44 epoxy resin into the CNTs felts. To decrease its high room temperature viscosity, the resin was heated to 100 °C and then diluted with the curing agent at a weight ratio of 4:1 (epoxy:curing agent) with simultaneous mechanical stirring for 20 min. The stirred mixture was stored in the oven at 130 °C until the mixture become transparent and any evidence of curing agent grains had disappeared. The CNT felts were subsequently submerged into the liquid epoxy and inserted in a VO400 vacuum oven (Memmert, Germany) for two 15-min cycles of vacuum pressure impregnation at 140 °C. Curing of the epoxy was performed by continuous residence at 140 °C for 12 h. The cured composites were machined into specimens of dimensions of 4 × 5 × 6 $mm^3$ for compressive tests and of 23 × 11 × 4 $mm^3$ for electrical conductivity tests. CNTs mass fraction in the composites was calculated using the formulas: $W = n \times \rho \times V_c/m_c$, $n = w_1/w_2$, where $W$ is CNTs mass fraction in the composites, $\rho$ is apparent density of the prepared CNT felt, $V_c$ and $m_c$ are volume and weight of the composite, $w_1$ and $w_2$ are mass fraction of CNT and CMC in the solution, and $n$ is the mass ratio of CNT and CMC in the CNT felt.

For PHCNT/EP composite preparation, E44 epoxy was initially heated to 100 °C for lowering of viscosity and CNTs were added with subsequent ultrasonication for 1 h in a water bath heated at 90 °C for maintenance of the low viscosity. Curing agent was then added into the CNT-epoxy suspension at a weight ratio of 4:1 (epoxy:curing agent) and mechanical stirring followed for 20 min. The thermal cycle for curing the epoxy was identical to the previous case. CNT loading in the PHCNT/EP composite was 1.00 wt%, 1.25 wt%, and 1.50 wt%, respectively.

Specimens of pure epoxy, INCNT/EP composite, and PHCNT/EP composite were tested in compression in a SANS CMT-4304 SANS Universal Testing Machine (Sans Materials Testing Co. Ltd., Shenzhen, China) with crosshead displacement speed of 0.5 mm/min.

**Table 1**
Statistical results in Young's modulus, yield strength, conductivity of INCNT/EP composite, and density, conductivity of CNT felt.

| CNT loading in solution (wt%) | Density of CNT felt ($mg/cm^3$) | CNT loading in composite (wt%) | Young's modulus (GPa) | Yield strength (MPa) | Conductivity (S/cm) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | INCNT/EP | INCNT/EP | INCNT/EP | | CNT felt | |
| | | | | | PA-D | PE-D | PA-D | PE-D |
| 0 | 0 | 0 | 1.57 ± 0.046 | 135.07 ± 0.43 | ~1E−16 | ~1E−16 | / | / |
| 1.00 | 19.8 | 0.87 | 1.89 ± 0.051 | 150.79 ± 0.54 | 0.139 ± 0.012 | 0.043 ± 0.004 | 0.158 ± 0.015 | 0.062 ± 0.004 |
| 1.25 | 22.4 | 1.08 | 1.84 ± 0.049 | 150.74 ± 0.49 | 0.147 ± 0.011 | 0.073 ± 0.007 | 0.165 ± 0.014 | 0.090 ± 0.005 |
| 1.50 | 25.3 | 1.31 | 1.97 ± 0.054 | 150.65 ± 0.53 | 0.158 ± 0.012 | 0.088 ± 0.008 | 0.174 ± 0.016 | 0.110 ± 0.006 |
| 1.75 | 28.0 | 1.51 | 1.91 ± 0.048 | 149.75 ± 0.48 | / | / | / | / |
| 2.00 | 30.7 | 1.74 | 1.91 ± 0.045 | 151.51 ± 0.56 | / | / | / | / |

Scanning electron microscopy (SEM, Hitachi S-2700, Tokyo, Japan) was employed for the micro-structural characterization of the failed specimens. Volume electrical conductivity of the specimens were measured by two-wire method using a Keithley 6220 DC current source (Heithley, Cleveland, USA). Specimens were fixed onto a circuit board and their two ends were connected to the circuit board by copper wires fastened with silver paste. The circuit board was then plugged into the slot of the current source for electrical conductivity measurement, and the impressed currents were 10 mA, 10 mA, and 0.1 mA in the measurements of CNT felt, INCNT/EP and PHCNT/EP composites, respectively. Because the electrical resistivity of PHCNT/EP composites are large, the impressed currents were low to avoid excessive voltage.

## 3. Results and discussion

The macroscopical appearances of pure epoxy, the CNT felt prepared by ice templating and the as-machined INCNT/EP composite are shown in Fig. 2. As shown in Fig. 2b, the CNT felt was foam-like, with grooves parallel to ice growth direction (the direction of temperature gradient as indicated by the red arrow) on the surface of the felts observable by naked eye. Upon manipulation of manual flattening, the felt had apparently good structural stability and resilience, it would quickly return to its original shape. Experiments at different CNT loadings revealed felt stability enhancements with tube loading, while stability was poor at low loadings. As successful vacuum infiltration requires a minimum structural stability of the infiltrated material, a tube concentration of 1.00 wt% in solution was established herein as the lowest necessary. The typical texture of as-machined INCNT/EP composite specimens is shown in Fig. 2c, the direction of original grooves on the felt is retained in the specimens. By optical examination, INCNT/EP composites exhibited homogeneity and very smooth surfaces without obvious open porosity, the findings indicate a very good degree of infiltration. The CNTs felt microstructure was further investigated under SEM as shown in Fig. 3, and Fig. 3a, b show in the direction parallel to and perpendicular to ice growth direction, respectively. The results indicate that the CNT felts formed three-dimensional (3D) frameworks composed of unidirectionally oriented lamellae comprised of CNTs and CMC. CMC in this work acts as binder of CNTs to form a stable structure satisfied with infiltration requirement, if there is no CMC, CNTs are connected by van der Waals force which is too weak for infiltration. Fig. 4 shows the existence of CNTs in the INCNT/EP composite, it indicates that the tubes appear capable of retaining the structure of the felt with unidirectionally- oriented lamellae clearly observable.

### 3.1. Compressive behaviour

Compressive behaviours of INCNT/EP and PHCNT/EP composites were tested, and the loading direction was parallel to orientation of the felt. The statistical Young's modulus, yield strength of the two composites with different CNT loadings are presented in Tables 1 and 2, respectively, and their variation is depicted schematically in Fig. 5. It is observed that the Young's modulus and yield strength performance of the two kinds of composites have improved compared to that of pure epoxy even at 0.87 wt% tube loadings, a pure result of nanotube presence, and the INCNT/EP composite is superior to the PHCNT/EP composite. The Young's modulus of INCNT/EP was 1.97 GPa at 1.31 wt% tube loadings, approximately 25.5% higher than that of pure epoxy, and the yield strength of INCNT/EP was 151.51 MPa at 1.74 wt% tube loadings, approximately 12.2% higher than that of pure epoxy. Improvement of mechanical properties of INCNT/EP composite can be owning to the reinforce-

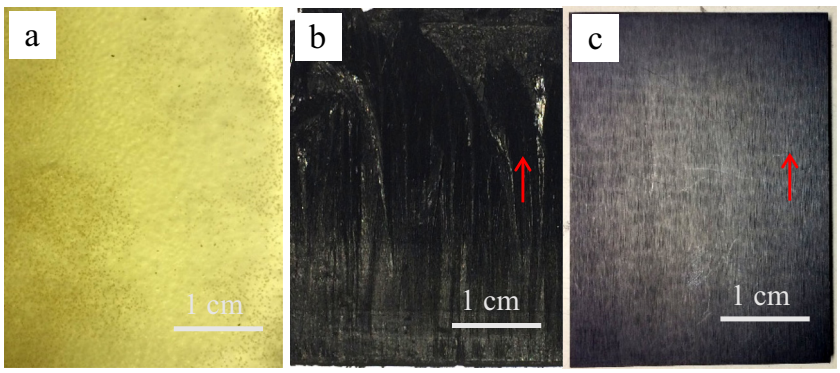


**Fig. 2.** Digital photographs of (a) the pure epoxy, (b) the CNTs felt, and (c) INCNT/EP composite.

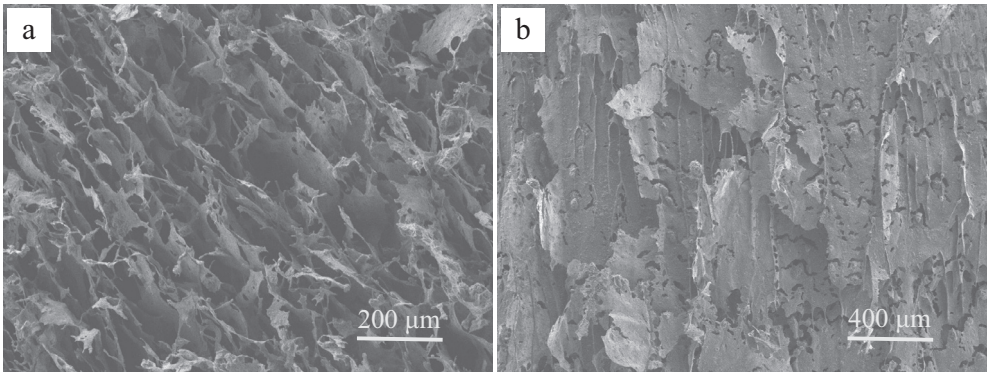


**Fig. 3.** SEM micrographs of the CNTs felt (a) parallel to and (b) perpendicular to ice growth direction.

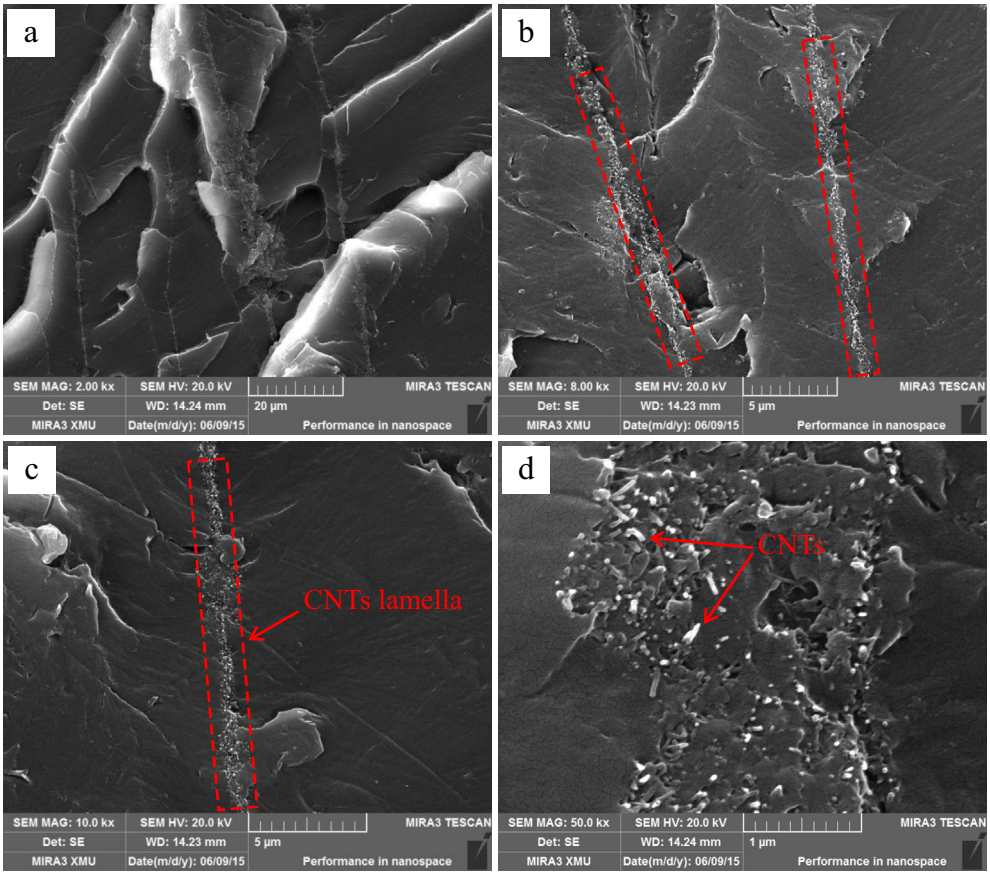


**Fig. 4.** Fractured surface SEM micrographs of INCNT/EP composite. (a) Three-dimensional (3D) framework composed of unidirectionally oriented CNTs lamellae, (b) magnifying image of CNTs lamellae, (c) single CNTs lamellae, and (d) internal structure of CNTs lamellae.

**Table 2**
Statistical results in Young's modulus, yield strength, conductivity of PHCNT/EP composite.

| CNT loading in composite (wt%) | Young's modulus (GPa) | Yield strength (MPa) | Conductivity (S/cm) |
|---|---|---|---|
| 0 | 1.57 ± 0.046 | 135.07 ± 0.43 | ~1E−16 |
| 1.00 | 1.82 ± 0.043 | 148.74 ± 0.51 | 2E−4 ± 1E−5 |
| 1.25 | 1.79 ± 0.045 | 148.16 ± 0.49 | 4E−4 ± 1.5E−5 |
| 1.50 | 1.75 ± 0.039 | 148.26 ± 0.45 | 6E−4 ± 1.4E−5 |

ment of CNT lamellae, and eliminating the defects of cracks on the CNT lamellae as shown in Fig. 3b may get a further improvement of mechanical properties, which will be showed in our later works. Interfacial strength is also one of the most critical influence on mechanical properties of the composite, so we will also try to further enhance the interface.

The typical stress-strain behaviours of pure epoxy and the two kinds of composites are presented in Figs. 6 and 7. The mechanical responses of the three materials began with an elastic regime, when the stress reached to a limitation, the molecular chain of the resin began to move, and the instable regime occurred. Instability in pure epoxy occurred at *ca.* 5% strain, while, at *ca.* 7.5% strain in two kinds of composites. Pure epoxy and PHCNT/EP composite had similar compressive behaviours, there was an abrupt decline of stress in the instable regime when the strain reached

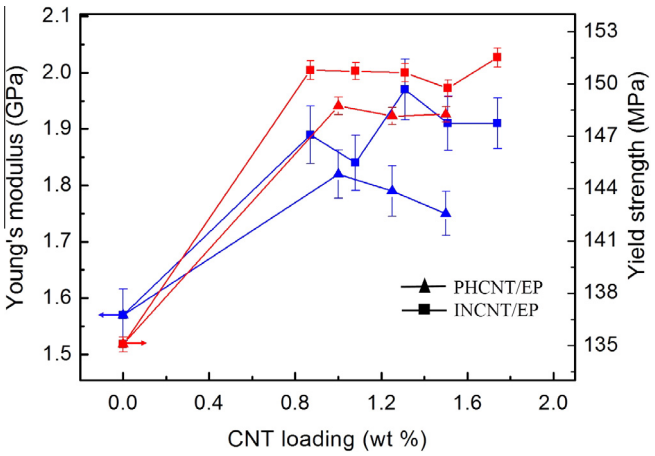


**Fig. 5.** Effect of CNT loading on Young's modulus and yield strength of INCNT/EP composite and PHCNT/EP composite.

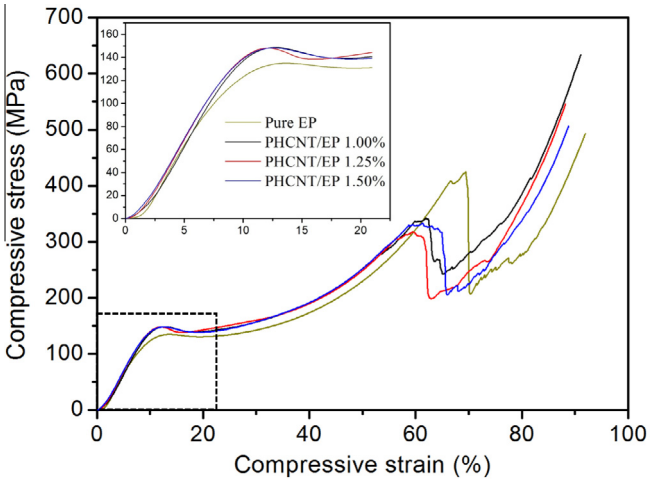


**Fig. 6.** Compressive stress-strain curves of pure epoxy and PHCNT/EP composites.

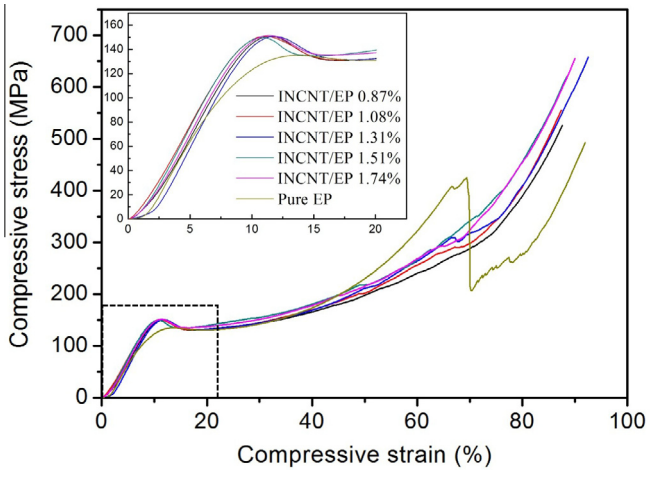


**Fig. 7.** Compressive stress-strain curves of pure epoxy and INCNT/EP composites.

to a critical point as shown in Fig. 6, which was resulted from the rapid propagation of cracks in the materials. However, such phenomenon cannot be seen in the stress-strain behaviours of INCNT/EP composites. Before *ca.* 50% strain, mechanical responses of the pure epoxy and INCNT/EP were alike as shown in Fig. 7, but after this point, the variations occurred. There was no abrupt decline of the stress, but just slightly decline in the stress-strain behaviours of INCNT/EP composites. It indicated that INCNT/EP composites can effectively prevent the abrupt structural failure, which can be owned to its lamellar structure. When the cracks propagated through the CNTs laminae, most of the energy will be absorbed, so the CNTs laminae just act as many buffer layers, and prevent the rapidly propagating of cracks. SEM images of the failed composite specimens are shown in Fig. 8, and CNTs lamellae are clearly observable in Fig. 8b, while, CNTs in Fig. 8d are in a mess.

### 3.2. Electrical conductivity

Volume electrical conductivity of PHCNT/EP, INCNT/EP composites and CNT felts of both reinforcement directions parallel to the CNT lamellae (PA-D) and perpendicular to the CNT lamellae (PE-D) were measured and the statistical results are summarized in Tables 1 and 2 while the variations are schematically represented in Fig. 9. It is observed that INCNT/EP composite conductivity exhibits the same directionality dependence with the orientation of CNT felt and it is greater compared to that of PHCNT/EP composites. More specifically, electrical conductivity of INCNT/EP composites in the direction parallel to the CNT lamellae increases dramatically, by 15 orders of magnitude, compared to pure epoxy resin and by 3 orders of magnitude compared to PHCNT/EP composites. Pure epoxy conductivity reaches *ca.* $10^{-16}$ S/cm, while that of INCNT/EP composites with a tube loading of 1.08 wt% is 0.147 S/cm and of PHCNT/EP composites *ca.* $10^{-4}$ S/cm. The latter value compares favorably with literature findings [22]. No work has been reported to obtain such increase in electrical conductivity in epoxy composites with such low CNTs loading as INCNT/EP. CNT felt has oriented lamellar structure wherein CNT lamellae form a fine conductive network, so it has good conductivity of 0.174 S/cm at the density of 25.3 g/cm$^3$. After infiltrating with epoxy, conductivity of the composite is 0.158 S/cm, the value is just a little smaller than that of CNT felt. Therefore, the infiltration process causes slight deterioration of the network structure of the felt. The dramatic increase in INCNT/EP conductivity compared to pure epoxy can be attributed to such a conductive network within the epoxy matrix. CMC acts as binder to prepare the felt, it wrap up CNT to form CNT lamellae, as CMC is insulator, it has bad effect on the electrical conductivity of the foam. Decreasing the content of CMC will enhance the electrical conductivity of the felt, while, a suitable amount of CMC should be used to ensure the foam's structural stability for infiltration. It is observed that conductivity of PE-D of the INCNT/EP composite is not much lower than that of PA-D. The reason is that the two-dimensional CNT lamellae shows orientation along the ice growth direction only, and there is no orientation in other directions, so it can also form a conductive network in other directions. Thus, the conductivity of PE-D of the composite will not too much lower than that of PA-D. One can notice that conductivity of INCNT/EP composites increases only slightly with increasing CNT loading. This behaviour can be attributed to presence of defects on the CNTs lamellae, as demonstrated in Fig. 4b, which reduce the integrity of the conductive network formed by the tube laminaes, thus impeding the increase in the conductive paths hence also in electrical conductivity. The particular findings indicates that eventual improvement of the CNTs felt preparation method for decreasing the amount of defects in the lamellae may associate with great improvements in electrical conductivity. This topic is currently under investigation by our lab and will be dealt with in a forthcoming publication.

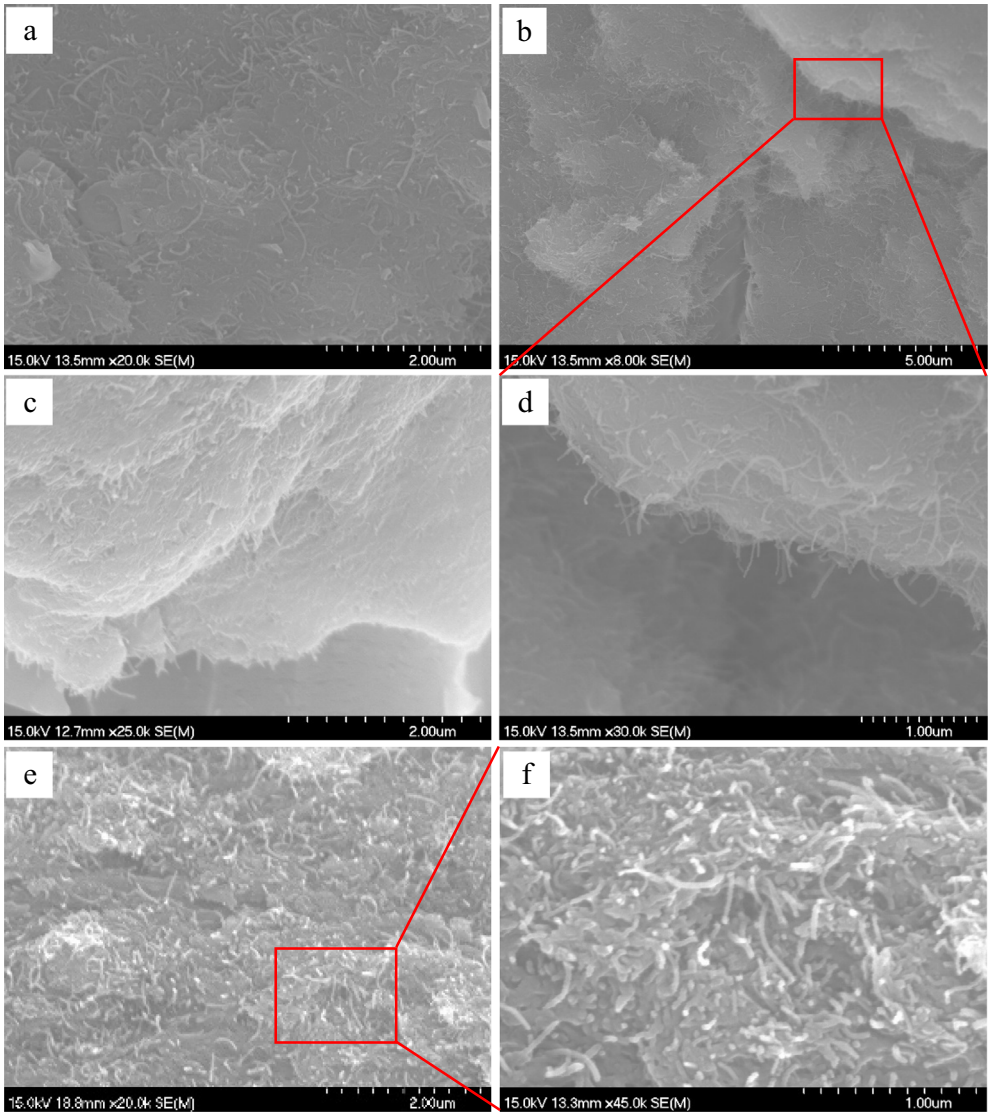


**Fig. 8.** SEM images of composite failed under compression. (a–d) INCNT/EP composite and (e, f) PHCNT/EP composite.

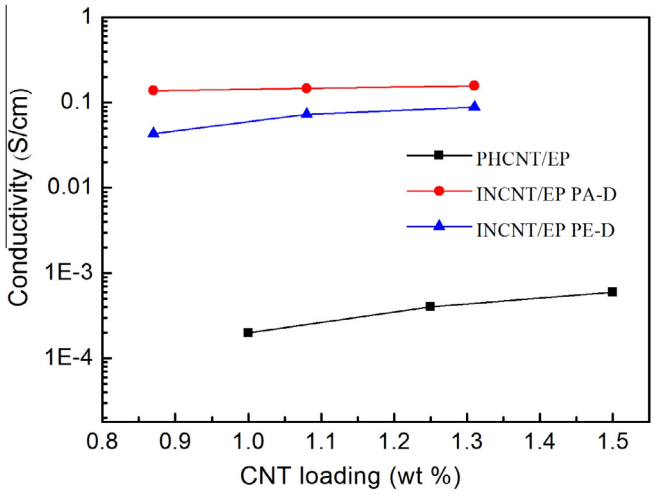


**Fig. 9.** Effect of CNT loading on conductivity of INCNT/EP composite and PHCNT/EP composite.

## 4. Conclusions

In the present paper, three-dimensional CNT felts comprised of unidirectionally -aligned tube lamellae prepared by ice templating were infiltrated by epoxy resin through vacuum pressure impregnation. The resulting INCNT/EP composites retained the structural integrity and resilience of the felt. Compressive test indicated that INCNT/EP composites have an improved Young's modulus (up to 25.5%) and yield strength (up to 12.2%) compared to pure epoxy, and it can effectively prevent the abrupt structural failure due to its lamellar structure which act as stress buffer layers. On the other hand, formation of a fine conductive network of the CNT lamellae in the epoxy matrix enables it's the dramatic increase in INCNT/EP electrical conductivity increases, by 15 orders of magnitude compared to pure epoxy and by 3 orders of magnitude compared to the PHCNT/EP composites.

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