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Research Article

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Manipulating conductive network formation via 3D T-ZnO: A facile approach for a CNT-reinforced nanocomposite

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Abstract: To achieve an efficient conductive network while preserving the properties of carbon nanofillers is a challenging and essential issue for the fabrication of highly conductive polymeric nanocomposites. The present paper reports a facile approach to manipulate the network formation in the polymer matrix via introducing the tetrapod ZnO whisker (T-ZnO) in the carbon nanotube (CNT)-reinforced epoxy composite. The influence of T-ZnO on the CNT dispersion was evaluated by UV-Vis spectroscopy, rheological measurement, scanning electron microscopy (SEM), and electrical and mechanical properties of the bulk composite. The results showed that the CNTs tend to disperse more uniformly with an increase in T-ZnO loading. An optimized ratio of 1:2 between CNTs and T-ZnO was found to significantly enhance the electrical conductivity by 8 orders of magnitude. A low percolation threshold of 0.25 wt% CNTs was achieved in this hybrid CNTs/T-ZnO composite, which is only 40% of the threshold value in the pure CNTs/epoxy. The flexural strength and modulus of the hybrid composite were also improved noticeably in comparison to the CNTs/epoxy. The mechanism for increasing the performance of the nanocomposite was analyzed. These results indicated that the T-ZnO can assist to efficiently improve the dispersion and the formation of the conductive network, which is beneficial to the enhancement of the mechanical and electrical performance of the nanocomposite.

Keywords: carbon nanotubes, tetrapod ZnO whiskers, mechanical property, electrical property

1 Introduction

Carbon nanotubes (CNTs) are considered to be one of the most promising carbon nanofillers for the fabrication of high-performance multifunctional polymeric nanocomposites due to its ultrahigh aspect ratio and superb mechanical, electrical, and thermal properties [1–4]. However, the strong tendency to aggregate from the van der Waals interactions not only prevents CNTs to release its full potential but also brings negative consequences, such as micro-defects and poor interfaces, to the composites. To improve the dispersibility of CNTs, various approaches have been developed to treat CNTs, which can be divided into two categories: covalent modification (chemical functionalization) and noncovalent modification (physical or surfactant treatment) [5]. Covalent modification is to graft functional groups on the sidewalls of CNTs via chemical or physical treatments such as acids [6–8], plasma [9–12], UV/ozone [13], and ultrasonication [14]. This method can effectively improve the mechanical property of the nanocomposite by disintegrating CNT bundles and strengthening its interfacial bonding with the surrounding polymer matrix. However, this process inevitably leads to the disruption of the extended π conjugation in nanotubes and hinders its pristine material properties. In comparison, noncovalent modification can largely maintain the intrinsic properties of CNTs via coating various

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surfactants such as sodium dodecyl sulfate (SDS) [15,16], polyaniline (PANI) [17,18], Triton X-100 [19], poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) [20,21], and gelatin [22] on the nanofillers. However, in practical situations, the property of the noncovalently treated nanofillers is likely to be influenced by the surfactants, for example, some insulated surfactants may hinder the conductive pathways of nanofillers and decrease the electrical conductivity of the bulk composite [22]. Moreover, some surfactants do not have strong interaction with nanofillers that can be easily removed during washing and filtering procedures. Therefore, it is still a challenging and important issue to achieve high-quality dispersion while maintaining the integrity of the nanofillers.

The hybridization of CNTs with other cost-effective multifunctional filler offers an alternative to solve the above problem. The synergistic effect of hybrid fillers on the electrical conductivity of some polymers has been investigated, such as the combinations of CNTs/GNP/epoxy [23], CNTs/CB particle [24,25], and GO/T-ZnO/epoxy [26]. A favorable synergistic effect would decrease the percolation threshold and facilitate the formation of the electrical conductive network in polymer matrices. Some research efforts have been devoted to incorporate T-ZnO into the polymer to improve the thermal conductivity due to its unique structure that is easy to form the conductive network [27,28]. Tetrapod-shaped ZnO whisker (T-ZnO) exhibits a 3D shape in the form of four arms interconnected together via a core at angles 109° with respect to each other [29]. It can be expected that the needle-like legs of T-ZnO can insert into large agglomerates to cause disentanglement during its mixing process with nanofillers in the polymer matrix. If so, the dispersion of CNTs in the polymer matrix can be manipulated via simply control the amount of T-ZnO adding in the solution and eventually facilitate the formation of interconnected conductive networks in the composite. Moreover, the good mechanical property of T-ZnO filler can also be beneficial to the enhancement of mechanical properties of the bulk polymer composites. To the best of author's knowledge, the effect of T-ZnO on the dispersibility of CNTs for the improvement of the nanocomposites' multifunctional properties has not been reported so far.

In the present paper, the influence of T-ZnO on the dispersion quality and rheological, electrical, and mechanical properties of CNTs/epoxy nanocomposite was comprehensively investigated. It was shown that the addition of T-ZnO not only improves the dispersion of CNTs but also contributes to the formation of conductive networks, resulting in notably improved electrical and mechanical performances. A proposed mechanism for property enhancement with the addition of T-ZnO has been discussed.

2 Experimental

2.1 Materials

CNTs (trademarked as TNM1) with an average diameter of 25 nm and a length of 10–30 μm were purchased from Chengdu Organic Chemicals Co., Ltd, Sichuan, China. Commercial epoxy resin (GCC-135) and curing agent (GCC-137) were purchased from Kunshan green follow chemical industry Co., Ltd, (China). The ratio between the two components was 3:1 by mass. T-ZnO whiskers were provided by Chengdu Crystrealm (China). The used chemicals were purchased from a commercial source at an analytical reagent standard without further purification.

2.2 Preparation of nanocomposites

The calculated amount of mixed raw CNTs and T-ZnO was sufficiently dispersed by mechanically stirring for 30 min. Then, the mixture was added into epoxy and stirred for another 30 min. After that, the curing agent was added to the CNTs/T-ZnO/epoxy mixture at a ratio of 10:3. The mixture was then mechanically stirred for 30 min at room temperature, followed by degassing under vacuum for 2 h before being casting into the aluminum mold. The mold was kept in an oven, and the mixture was cured at 60°C for 6 h followed by post-curing at 120°C for 4 h. Finally, a different mixing ratio of CNTs/T-ZnO was prepared and tested to investigate possible synergistic effects that can improve the dispersion of CNT in the matrix.

2.3 Characterization

A scanning electron microscope (SEM) was used to investigate the morphologies of the fracture surfaces of the composite after the three-point flexural test. The dispersing state of CNTs/epoxy with and without the addition of T-ZnO was measured by UV-visible spectra analysis using a Shimadzu UV-3600Plus device in the wavelength range of 200–1,100 nm. The rheological measurements were performed with a rotational rheometer (TA DHR-1, USA) on 60 mm diameter parallel plates with 1 mm gap at 80°C. A frequency sweep was conducted on the liquid nanocomposite system (CNTs/epoxy, CNTs:T-ZnO (1:2)/epoxy, both without hardener) at controlled stress (1 Pa) between 0.1 and 100 rad/s within the linear viscoelastic range (LVR). The electrical conductivities of tested samples were measured by a two-point measurement with a Keithley 6517B device at room temperature. The dimension of the specimen is 59 mm in length, 12 mm in width, and 3 mm in thickness. The conductive silver-epoxy paste was adhered to on both sides of each sample as electrodes to reduce possible contact resistance. A three-point bending test was conducted with a span length of 50 mm and a crosshead rate of 2 mm/min, according to ASTM D790. Each test data was the average value of six repeated samples.

3 Results and discussion

3.1 Fabrication and characterizations of CNTs/T-ZnO/epoxy composite

The fabrication process of CNTs/T-ZnO/epoxy nanocomposite is shown in Figure 1. It is observed that T-ZnO whiskers are a 3D crystal structure with four needle-like legs joined together via a core at an angle ca. 109° with respect to each other. As such, to utilize the excellent structural feature of T-ZnO as an effective dispersion filler, the first step is to mix CNT with T-ZnO through proper mixing procedures to form a pre-dispersed CNTs/T-ZnO hybrid filler. After that, most of the severely entangled agglomerates can be broken into smaller ones, which facilitated the formation of a continuous conductive network. Then, CNTs/T-ZnO/epoxy nanocomposites with concentrations of 1.0, 2.0, 3.0, and 4.0 wt% CNTs/T-ZnO hybrid and with a fixed concentration of 4.0 wt % CNTs/T-ZnO at different mix ratios were fabricated. To examine the predispersed results of the CNT, several techniques have been applied to analyze the dispersion of CNTs/T-ZnO in both the solvent and epoxy matrix.

To understand the dispersion and distribution of the nanofillers in the epoxy, we analyzed the SEM images of the fracture faces of the nanocomposite, as shown in Figure 2(a)–(d). It can be seen from Figure 2(a) and (b) that lots of large agglomerates (marked with the red circulars) are observed, which implies that the CNTs are severely entangled and nonuniformly distributed over the whole matrix. With the addition of T-ZnO, there is less probability of CNT aggregation on the fracture surface of the CNTs/T-ZnO/epoxy when compared with the pristine CNTs one, while the T-ZnO was uniformly distributed (marked with red arrows) as shown in Figure 2(c) and (d). Moreover, from the comparison of Figure 2(a) and (b) to Figure 2(c) and (d), it shows that there were noticeable differences in the morphologies of the pristine CNT and CNTs/T-ZnO nanocomposites: the former has a relatively smooth fracture surface while the latter

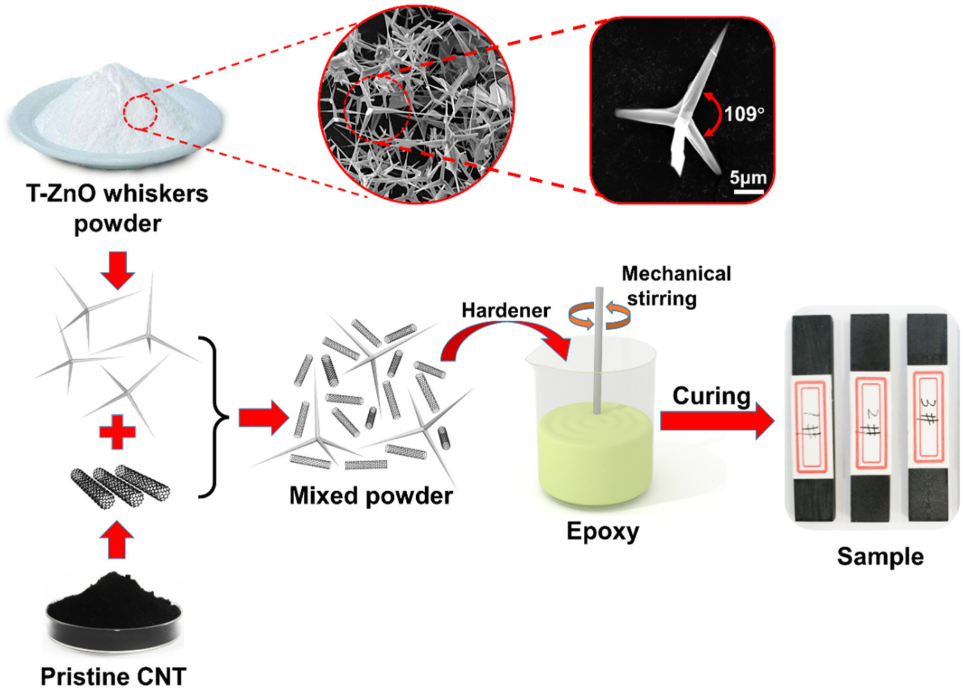

Figure 1: Structure of T-ZnO and schematic of the fabrication procedure of CNTs/T-ZnO/epoxy nanocomposite.

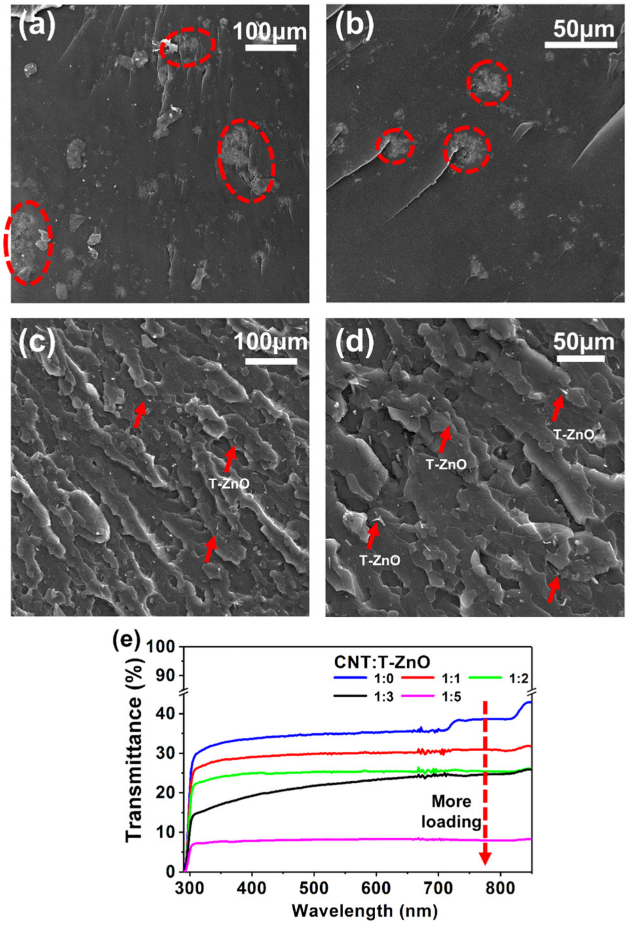

Figure 2: (a) and (b) SEM images of fracture surface pristine CNT; (c) and (d) CNT:T-ZnO (1:2) epoxy-based nanocomposite. (e) Comparison of UV-vis spectra and dispersion states of 4.0 wt% uncured CNTs/T-ZnO/epoxy diluted in the ethanol (1:50 wt%).

presents a relatively rough one. This phenomenon suggests that the addition of T-ZnO can not only improve the dispersibility of CNTs in the epoxy but also increase the fracture toughness of the polymer matrix via homogenization of the stress distribution [30].

UV-vis transmission spectra can be used to describe the dispersion state of the nanofiller in the solution [31]. Figure 2(e) shows the UV-vis transmission spectra of pristine CNT and different ratios CNTs/T-ZnO mixture in the ethanol solution. For each UV-vis measurement, the absolute amount of filler was made identical by applying the appropriate dilution factor. It can be observed that the pristine CNT solution has the highest transmittance. This is due to a large number of agglomerates that enable the light source to penetrate the solution. Interestingly, for the CNTs/T-ZnO hybrid, the transmittance decreases as the T-ZnO percentage increases, and the more T-ZnO was added, the lower transmittance was presented. The reason for the improvement of CNTs/T-ZnO/epoxy is probably that the spatial four-needle structured T-ZnO can act as a physical needle to detach the aggregation of CNTs in the solution.

The rheological behavior of polymer nanocomposite is strongly dependent on the dispersion state of the filler, filler type, and the interactions between the fillers and the polymer matrix. Figure 3(a), (b), (d), and (e) shows the storage modulus (G', elastic property) and loss modulus (G'', viscous property) as a function of angular frequency for CNTs/epoxy and CNTs:T-ZnO (1:2)/epoxy systems. It can be seen that both G' and G'' curves increase notably with an increase in the angular frequency, while the slopes of G' and G'' gradually decrease as the filler loading increase. This phenomenon is due to a strong interaction between nanofiller and epoxy chains. A plateau at low-frequency range ($\omega < 1$) of G' is observed in CNTs:T-ZnO (1:2)/epoxy systems when the filler loading is 3 wt%, indicating a transition from “liquid-like” to “solid-like” viscoelastic behavior occur (see Figure 3(a)) [32]. Moreover, a “pseudo-solid-like” behavior, a symbol of the formation of a continuous network, is achieved as the amount of filler increase to 4 wt% [33]. However, there is no obvious plateau for all frequencies range for the CNTs/epoxy system, which can be explained that the poor dispersion state of pristine CNT develops discrete aggregates, instead of a continuous network, allowing the free-flowing of the epoxy chains [34]. The difference between CNTs/epoxy and CNTs:T-ZnO (1:2)/epoxy systems with respect to G' and G'' is due to the hybridization of CNT with T-ZnO improved dispersion state of nanofillers in the polymer matrix [26].

It is widely accepted that a Newton fluid demonstrates nearly invariant complex viscosity (η^*) [35]. Figure 3(c) and (f) show the complex viscosity versus the angular frequency. At low filler loading, the suspensions exhibit the typical Newtonian viscosity plateau for both systems. In CNTs/T-ZnO/epoxy composite, as the filler loading increases, the low-frequency complex viscosity significantly increases. This is attributed to the chain mobility of epoxy being restricted by the nanofillers. A strong shear thinning behavior was found with a filler loading of 4.0 wt%, which further proved that a continuous network was formed [36]. For filler loading above 2.0 wt%, the orders of magnitude of CNTs/T-ZnO/epoxy suspension are more viscous than that of the pristine CNT/epoxy, implying that the interaction between fillers and epoxy was more pronounced. This observation was consistent with the G' results.

3.2 Electrical and mechanical properties

Figure 4(a) compares the electrical conductivities of epoxy composites filled with different concentrations of

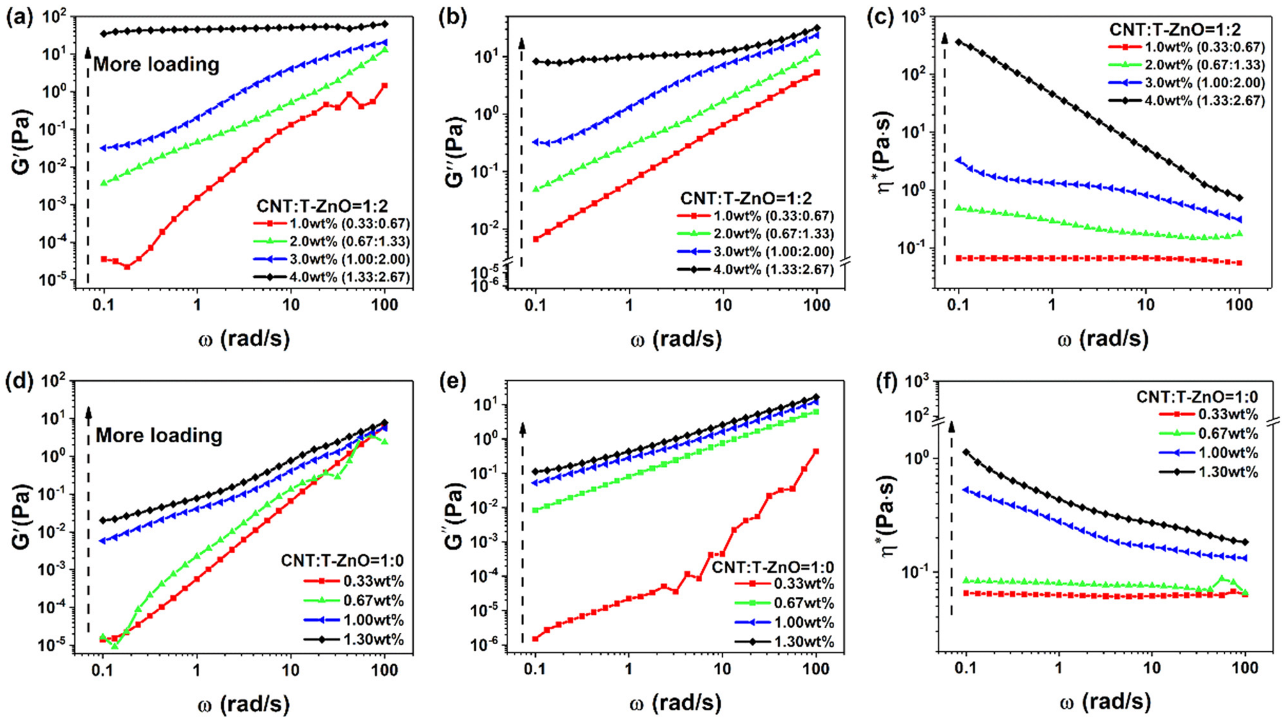

Figure 3: Storage modulus G', loss modulus G'', complex viscosity η^* of the epoxy-based nanocomposites as a function of angular frequency at 80°C (a)–(c) for CNTs:T-ZnO (1:2) and (d)–(f) for pristine CNT.

CNTs/T-ZnO under the mass ratio of 1:1, 1:2, 1:3, and 1:5. It can be found that the CNTs/T-ZnO hybrid system shows a significant improvement in conductivity when the mix ratio of CNTs:T-ZnO is 1:2, whereas the conductivity of CNTs/T-ZnO/epoxy at other mass ratio is lower than that of pristine CNT/epoxy. The enhancement may be attributed to the effective formation of a conductive network from the synergetic effect between CNTs and T-ZnO. To further investigate this hypothesis, the samples of CNTs/T-ZnO at a ratio of 1:2 were specifically tested. Figure 4(b) shows the electrical conductivity of the CNTs:T-ZnO (1:2) hybrid system as a function of the CNT concentration. Here, to study the influence of T-ZnO on the percolation threshold of the composite, the following power-law equation was used:

$$\sigma(p) \propto (p - p_c)^t \tag{1}$$

where σ represents the DC conductivity, p is the concentration of conductive filler, p_c is the fraction at

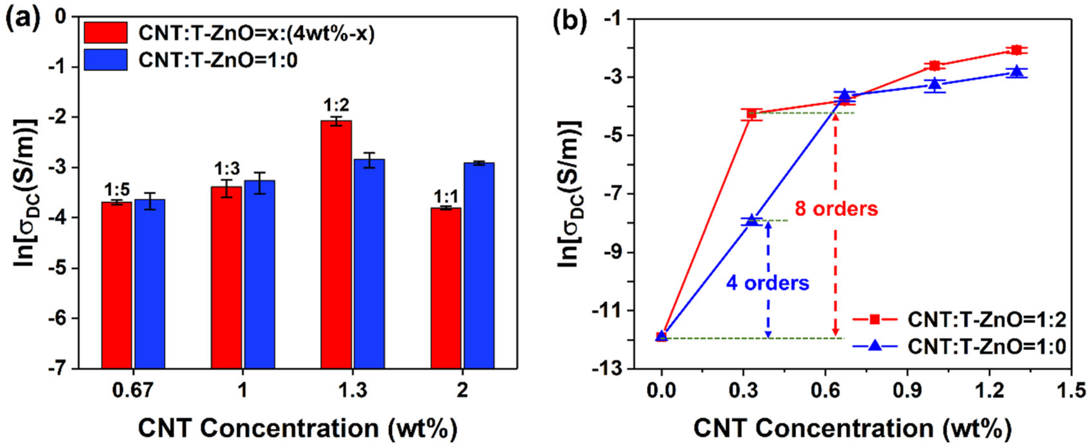

Figure 4: (a) Influence of mixing ratio on electrical conductivities of epoxy nanocomposite with and without T-ZnO; (b) electrical properties of pristine CNTs/epoxy, CNTs:T-ZnO (1:2)/epoxy under different nanofiller loadings.

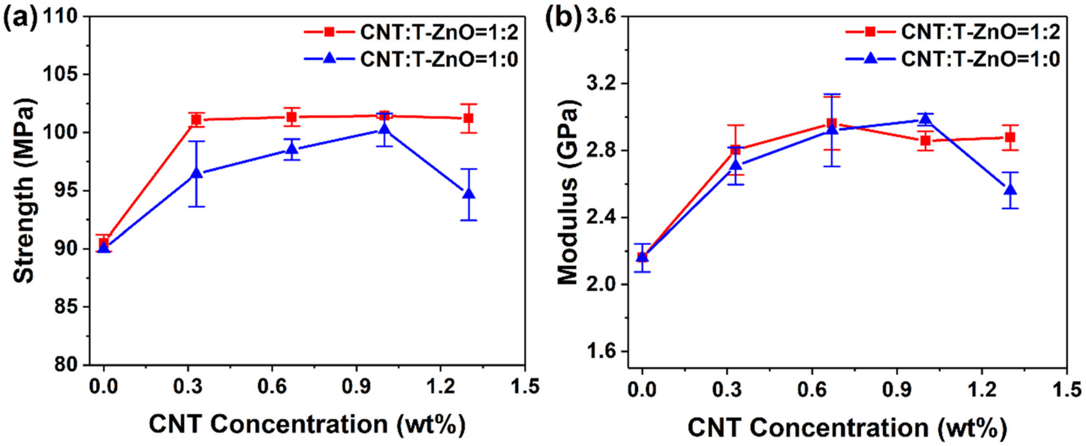

Figure 5: (a) Flexural strength and (b) flexural modulus of CNTs/epoxy nanocomposites with and without T-ZnO.

the percolation threshold, and t is a critical percolation exponent reflects the dimensionality of the conductive networks.

The percolation threshold derived from equation (1) is 0.75 wt% (0.25 wt% CNTs:0.5 wt% T-ZnO) for the CNTs/T-ZnO hybrid sample while for the pristine CNTs/epoxy, the threshold value is 0.67 wt% which means the addition of T-ZnO can significantly improve the dispersion and network formation in the composite. Moreover, the value of exponent t for the CNTs/T-ZnO one is 3.44, which is much bigger than the pristine CNT case ($t \approx 1.5$) and also bigger than 2 (which is believed to indicate the three-dimensional network formation). The high exponent value can be related to the formation of tunneling percolation network [37]. Therefore, it can be deduced that in the CNTs/T-ZnO/epoxy system, an effective conductive network was established at a lower filler loading than for the single CNT filled system, which means that combining 1D CNTs with 3D T-ZnO facilitates the formation of conductive pathways in the resin.

Figure 5 shows the flexural properties of CNTs/epoxy nanocomposites with and without the addition of T-ZnO. Nanocomposites containing CNTs/T-ZnO hybrid fillers exhibited better performances than the pristine CNTs/epoxy composite. With an increase in the filler content, both the flexural strength and modulus of the nanocomposites reinforced with T-ZnO increased consistently, whereas they became saturated after a peak at filler content at 1.0 wt% for strength and 3.0 wt% for modulus. This result can be interpreted by 3D T-ZnO that possesses a spatial four-needled structure which allows the stress of the sample to be uniformly distributed. For the pristine CNT system, the flexural strength and modulus became declined at a filler content above 1.0 wt%. It is suspected that the decrease was caused by poor dispersibility of pristine CNTs and nonuniformly distribution in the epoxy matrix. In addition, a shorter error bar of flexural strength and modulus for CNTs/T-ZnO system indicated a stable and homogenous CNT distribution in the matrix, which can be achieved with the help of T-ZnO (see Figure 5). The electrical performance of the present CNTs/T-ZnO hybrid (1:2) composite is also compared with other epoxy-based nanocomposites from various treatment methods as shown in Table 1. It can be observed that the present method can achieve a relatively high electrical conductivity with the lowest percolation value. This result demonstrates the impressive efficiency of T-ZnO on the manipulation of conductive networks in the composite when compared with other physical or chemical treatment methods. In addition, the strengthening effect of T-ZnO also attributes to the overall mechanical performance of the composite, which showed excel improvements when compared with other results.

3.3 Mechanism analysis

From the above results, we propose a possible mechanism for interpreting the influence of T-ZnO in the improvement of dispersibility and the formation of a conductive pathway in the composite, as shown in Figure 6. Pristine CNTs tend to be highly entangled due to the strong intertube interaction, especially for CVD-grown CNT (Figure 6(a)) [42]. When large amounts of needle-shaped T-ZnOs are introduced in the polymer matrix, the sharp tips will effectively penetrate into aggregates and break them into many small agglomerates, as shown in Figure 6(a). However, the extent of aggregates breakage is believed to

Table 1: Comparison of the electrical and mechanical properties of the CNTs/T-ZnO/epoxy with other epoxy-based nanocomposites in the literature

Filler type		**CNTs**	**CNTs (polyaniline)**	**CNTs (acid)**	**GNP/CNTs**	**GNP/CNTs**	**CNTs/T-ZnO**
Method		**Mechanical mixing + ultrasonication**	**Mechanical mixing + casting**	**Ultrasonication**	**Mechanical stirring + sonication**	**Three-roll milling + hot pressing**	**Mechanical stirring**
Electrical property	Percolation threshold (wt%)	0.5	0.6	0.4	0.62	—	0.25 (CNTs)
	Mixed ratio	—	—	—	2:8	1:4	1:2
	Maximum electrical conductivity (S/m)	10^{-2}	10^{-3}	3×10^{-3}	10^{-2}	2×10^{-3}	8×10^{-3}
Reference		[38]	[39]	[40]	[23]	[41]	Our work

be controlled by the loading of T-ZnO in the polymer, as already demonstrated by the UV-vis spectrum and electrical conductivity results in Figures 2 and 4. Assuming that the total amount of hybrid nanofillers (T-ZnO/CNTs) is fixed and the mass ratio between T-ZnO and CNT is 1:1, most of the CNTs are still in an entangled state because the proportion of T-ZnO is relatively low. In this case, an effective conductive pathway is difficult to be established owing to the agglomerated CNTs nonuniformly distributed in the resin, as shown in Figure 6(b). With an increase in T-ZnO, more agglomerates are broken into smaller ones and constructed into conductive networks as plotted in Figure 6(c). However, the proportion of T-ZnO should not be too high, such as at a ratio of 1:5 since the formation of conductive paths is hindered by the excessive addition of T-ZnO, as shown in Figure 6(d). It shows that the ratio of 1:2 is the optimum choice to achieve the best electrical performance with a suitable dispersion state. Further detailed investigations will be conducted to verify the present hypothesis.

4 Conclusions

In this article, a T-ZnO whisker was used as a complement filler to hybridize CNTs, which not only improves the dispersion of CNTs but also constructs high-efficient conductive networks within an epoxy resin. This can be confirmed from multiple results that the epoxy-based nanocomposites with CNTs/T-ZnO hybrid fillers exhibited a synergistic effect for both electrical and flexural properties when CNTs/T-ZnO ratio of 1:2 was used. UV-visible spectra analysis, scanning electron microscope analysis, rheological measurements, electrical measurement, and three-point bending tests have been conducted and verified that T-ZnO can effectively improve the dispersion state, electrical and mechanical properties of the CNTs/T-ZnO/epoxy when compared with the CNTs/epoxy composite. In summary, this study showed that the hybridization of CNTs with T-ZnO is a facile approach that offers an alternative to effectively improving the dispersibility of CNTs, resulting in good electrical and mechanical properties of epoxy-based nanocomposites.

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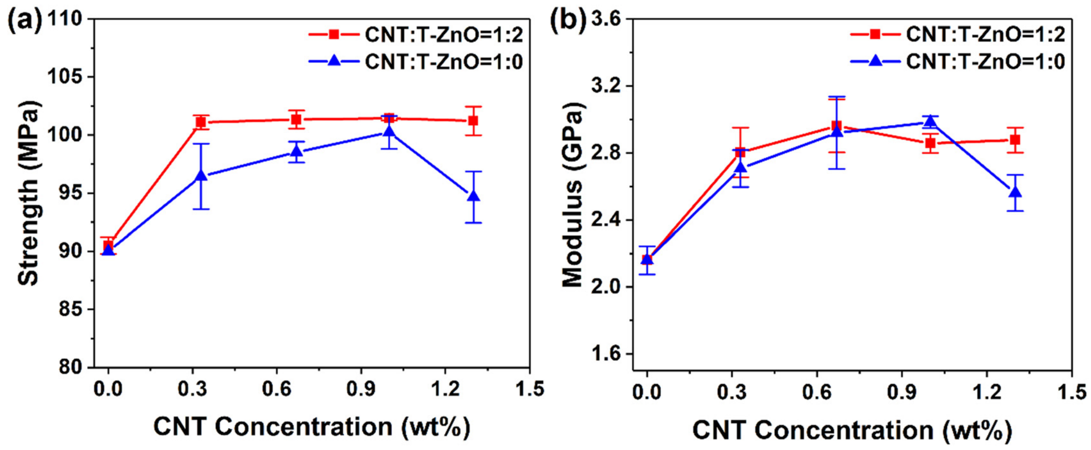

Figure 6: Possible mechanism of the manipulation effect of T-ZnO in the network formation in the epoxy resin under different CNTs:T-ZnO ratios. (a) CNTs agglomerates reduced from T-ZnO. (b) CNTs:T-ZnO = 1:1. (c) CNTs:T-ZnO = 1:2. (d) CNTs:T-ZnO = 1:5.

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