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Research on the dispersion of carbon nanotubes and their application in solution-processed polymeric matrix composites: A review

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Abstract. This review highlights and categorizes the approaches for preparation of CNTs dispersion and polymer/CNTs composites via solution-based strategies. Carbon nanotubes (CNTs) demonstrate unique physical and chemical properties, which allow several exciting potential applications in various fields including nanocomposites. Presently, the commercialized application of CNTs is still quite limited due to the formation of CNTs bundles, which significantly degrade the properties. Therefore, well dispersion of CNTs in nanocomposites is quite important, especially for CNTs/polymer composites, as a small amount of CNTs can improve the composite properties dramatically. This article will review the research on the dispersion of CNTs (including covalent and non-covalent functionalization) and the fabrication of CNTs/polymer composites through solution-based strategies by using the CNT dispersions. Moreover, the factors influencing the properties of CNTs/polymer composites will be discussed as well as the future outlook.

Keywords: carbon nanotubes; covalent; non-covalent; functionalization; solution

1. Introduction

Carbon nanotubes (CNTs), classified into single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), are one-dimensional cylinders constructed by sp^2-carbon with a high aspect ratio. Due to the extraordinary mechanical, thermal, and electrical properties, CNTs have attracted tremendous attention and have been widely used in various fields, including nanomedicine, nanoelectronics, and nanocomposites (De Volder *et al*. 2013). In the field of nanocomposites, one of the most typical applications is being used as reinforcing filler for polymer matrix (McGinnis *et al*. 2018, Zhang *et al*. 2019, Chen *et al*. 2018). The CNTs were added into the polymer matrix for mechanical reinforcement due to their excellent mechanical properties and lower density (Gojny *et al*. 2004). The Young's moduli, strength, and toughness for individual CNTs were reported to be 0.27-0.95 TPa, 10-63 GPa, and 770-1240 J g^{-1}, respectively, much higher than other alternative reinforce agents (Yu *et al*. 2000a, b). Further enhanced mechanical properties of CNTs, such as Young's modulus up to 1.34 TPa and tensile strength over 80 GPa were achieved from superstrong CNTs and parallel aligned CNTs which were prepared by newly developed approaches (Zhang *et al*. 2011, Bai *et al*. 2018). On the other hand, the thermal and electrical conductivity of CNTs are reported to be as high as 6000 W/m·K and 10^6 S/cm, respectively (Berber *et al*. 2000). The combination of these remarkable properties makes CNTs ideal fillers for the fabrication of polymer composites with enhanced mechanical, electrical, and thermal performance.

For large enhancement in the properties of CNTs/ polymer composites, well distribution of CNTs in the polymer matrix is quite important. The well-distributed CNTs in matrix can form interconnected networks to provide a more uniform load transfer and reduce the stress concentration centers efficiently (Bagchi *et al*. 2018). However, due to the van der Waals and hydrophobic interactions between the strings, CNTs tend to aggregate and exist as random bundles, which degrade the composite properties significantly. Therefore, great effort has been dedicated for improving the distribution of CNTs in the polymer matrix. Up to now, two broad categories of strategies have been developed for improving the CNTs distribution: 1) debundling (or dispersing) CNTs before the mixing with polymer matrix, and 2) directly adding the CNTs into the matrix and then debunding and mixing simultaneously. The former is related to the dispersion of CNTs in an appropriate solvent and subsequent mixing with polymer through solution-based techniques. The latter is mostly based on the mechanical exfoliation of CNT bundles in polymer melts, such as melt mixing. Since centrifugation can be employed to exclude the CNT bundles in the initially prepared CNTs dispersion, solution-based methods are preferred for the fabrication of well-dispersed CNTs/ polymer composites, especially those with relatively low CNTs content.

In this review, we will explore the progress of solution-based strategies for the preparation of CNTs/polymer composites, which covers the dispersion of CNTs and subsequent fabrication of the composites. While the

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dispersion of CNTs in various solvents can be achieved through covalent or non-covalent functionalization (Georgakilas *et al*. 2008, Singh *et al*. 2009, Mallakpour and Soltanian 2016, Liang *et al*. 2017, Liu *et al*. 2018, Rubio *et al*. 2011), fabrication of the composites can be relied on solution mixing, in-situ polymerization, or latex mixing. Finally, the factors influencing the properties of CNTs/ polymer composites will be reviewed.

2. Dispersion of carbon nanotubes

Due to the high hydrophobicity and strong van der Waals interactions, CNTs have shown very poor solubility and exist as insoluble bundles. Since the promising properties of CNTs are closely related to the individual tubes, the formation of bundles significantly limits their applications in many fields including electronic device, nanodetector, drug carrier, and polymer matrix composites. Therefore, the preparation of debundled CNTs has emerged as a key issue for promoting their practical applications. On the other hand, for the facility of processing, aqueous dispersion of CNTs was preferred, as they can be easily processed through various solution-processing approaches, including spin-coating, drop-casting, printing, and solution mixing.

Two major approaches, covalent and noncovalent functionalization have been developed for the preparation of CNT dispersions. While covalent functionalization can drastically improve the dispersibility of CNTs through grafting soluble functional groups or hydrophilic chains, noncovalent functionalization is realized by the adsorption of dispersants on the sidewall of CNTs via noncovalent interaction, including van der Waals force, hydrogen bonding, hydrophobic interaction, and electrostatic attraction (Premkumar *et al*. 2012).

2.1 Dispersion of CNTs via covalent functionalization

Two approaches have been developed for the covalent functionalization of CNTs: indirect and direct chemical functionalization of the sidewall of CNTs. The indirect way usually involves the generation of active points on the surface of CNTs and subsequent grafting of soluble chains at the activated sites through chemical reaction, typically amidation and esterification reactions, as shown in Figs. 1 and 2. One of the most typical examples is to use strong acid to oxidize the CNTs, resulting in the generation of oxygen-containing functional groups, such as -COOH, -CHO, and -OH, on the surface of CNTs. With further chemical modification, stable CNT dispersion can be obtained (Tonga *et al*. 2020, Wojtera *et al*. 2020, Song *et al*. 2020, Noor *et al*. 2020). Note that the oxidization with a strong acid (such as nitric acid or mixture of concentrated sulfuric and nitric acids) solely doesn't endow CNTs with sufficient dispersibility, as reported by Tsang *et al*. (1994) and Liu *et al*. (1998). Therefore, grafting soluble chains is necessary for the preparation of stable CNTs dispersion.

Haddon's group firstly reported some strategies for the preparation of dispersible CNTs through amidation reactions between oxidized CNTs and octadecylamine or 4-tetradecylaniline, as shown in Fig. 1 (Chen *et al*. 1998, Hamon *et al*. 1999). The shortened (or oxidized) CNTs were either directly coupled with octadecylamine by the formation of zwitterions (**1** in Fig. 1) through an acid-base reaction, or reacted with oxalyl chloride to form an acyl chloride intermediate for the subsequent amidation reaction with 4-tetradecylaniline (**2** in Fig. 1). After the reactions, the long alkyl chain bonded to the surface of CNTs act as solubilizing agents, which endow promising dispersibility of the functionalized CNTs in most organic solvents. On the other hand, to increase the aqueous dispersibility of CNTs, the same group carried out the covalent functionalization with a water-soluble polymer, poly (m-aminobenzene sulfonic acid) (PABS). The resulted SWCNT-PABS (**3** in Fig. 1) exhibited much higher conductivity than that of the neat PABS (Zhao *et al*. 2004).

The strategies developed by Haddon and co-workers were then pushed forward by other groups for different purposes. Zhu *et al*. (2003) performed the acid treatment (H_2SO_4/HNO_3) and subsequent fluorination to obtain fluorinated nanotubes (F-SWCNTs) with the dispersibility of more than 1 mg/mL in dimethyl ether (DME), tetrahydrofuran (THF) and 2-propanol. The F-SWCNTs were solution mixed with epoxy resin to achieve a good distribution of CNTs in epoxy matrix. Pompeo and Resasco (2002) grafted glucosamine to the acyl chloride-activated CNTs, and obtained the final functionalized CNTs with good dispersibility (0.1-0.3 mg/mL, **4** in Fig. 1). By treating MWCNTs with strong acids (H_2SO_4/HNO_3) and subsequently grafting with an amino-triethyleneglycol chain to impart positive charges, Samori *et al*. (2010) obtained functionalized MWCNTs with good dispersibility (**5** in Fig. 1). Using the obtained sample, they developed a straightforward method for assessment of the number of functional groups on CNTs, based on potentiometric titration. Wojtera *et al*. (2020) performed the conversion of carboxyl groups on CNTs to amide derivatives, which subsequently reacted with fluorescent dye through amidation reaction. The resultant fluorescent dye grafted CNTs exhibited good dispersibility and showed great potential in fluorescent biosensors.

The esterification reaction is another efficient approach for covalent functionalization of CNTs (Fig. 2). By introducing cationic species, Li *et al*. (2013) synthesized dodecyl quaternary ammonium bromides functionalized SWCNTs through esterification reaction (**6** in Fig. 2). The functionalized SWCNTs showed good water-dispersibility in the pH range of 6.87 - 11.25, and were used as filler for PVA-based composites. Furthermore, polymeric segments such as poly(ethylene glycol) (**7** in Fig. 2) (Kalinina *et al*. 2011), poly(vinyl alcohol) (PVA, **8** in Fig. 2) (Lin *et al*. 2003), DNA (Hazani *et al*. 2003), and protein (Kam *et al*. 2004) have also been covalently bonded to the surface of CNTs through either esterification or amidation reaction, for pursuing aqueous dispersibility.

The condensation reaction between hydroxyl group and silicon methoxy group was also employed for the chemical functionalization of CNTs. Song *et al*. (2020) demonstrated

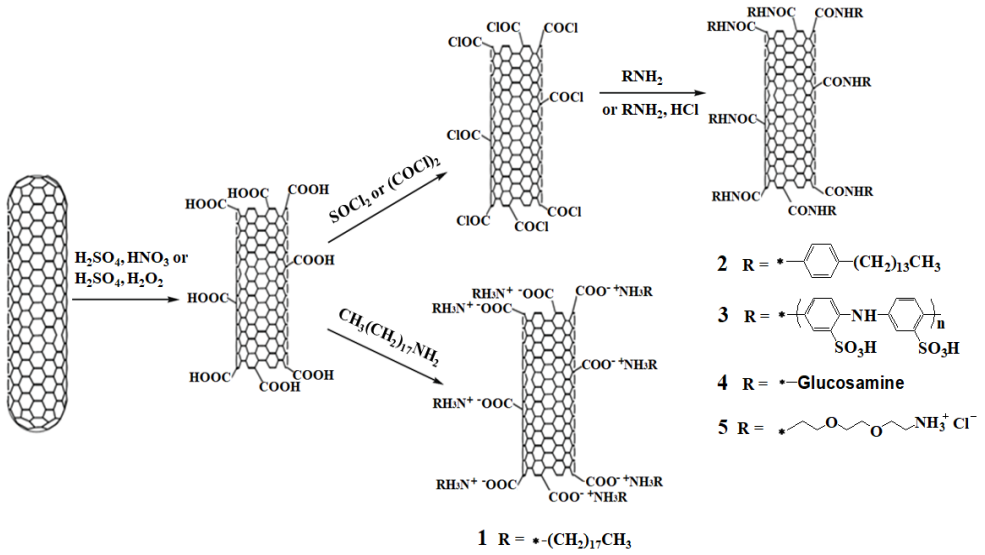

Fig. 1 Covalent functionalization of CNTs through amidation reactions

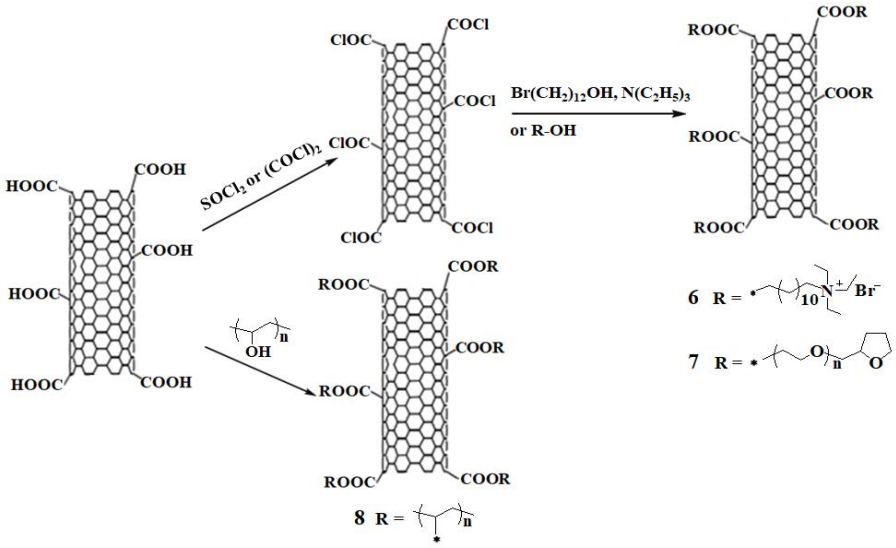

Fig. 2 Covalent functionalization of CNTs through esterification reactions

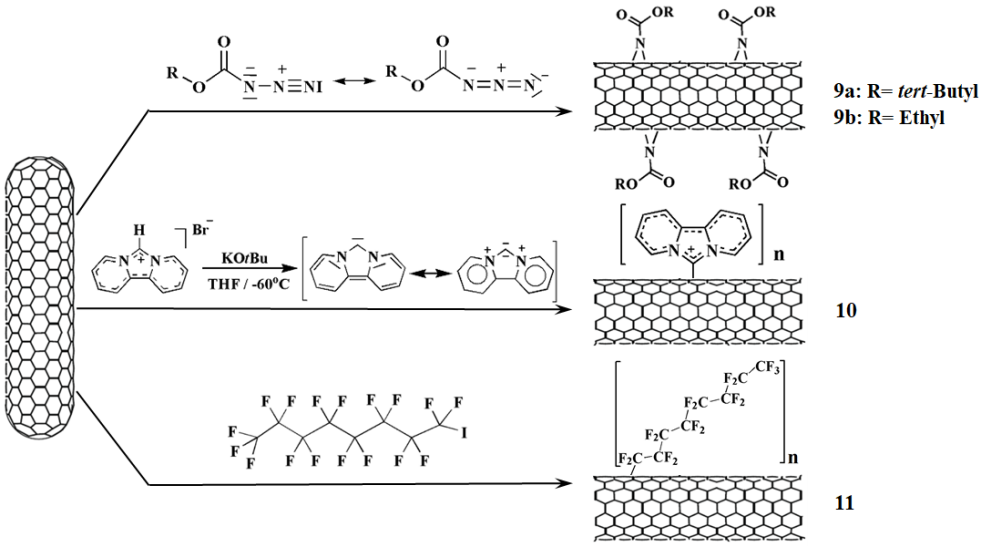

Fig. 3 Sidewall functionalization of CNTs by the addition of nitrene, nucleophilic carbene, and radical, respectively (Holzinger *et al*. 2001)

the reaction of hydroxylated CNTs with poly[3 -(trimethoxysilyl)propyl methacrylate] grafted conductive carbon black (CCB-PMPS), which offered a CNTs based hybrid filler with good dispersibility in THF.

Accompanying with the indirect method mentioned above, direct functionalization of the sidewall of CNTs has also been extensively investigated. The direct modification was mostly achieved by employing the addition (or cycloaddition) reaction of CNTs with nitrenes, carbenes, azomethine ylides, or radicals (Georgakilas *et al*. 2002a, b, 2008, Holzinger *et al*. 2001, Karousis *et al*. 2011). Since the strong-acid oxidation treatment in indirect functionalization significantly shortened the CNT length, direct modification through addition reaction was preferred for preparing the dispersions of long CNTs with low defect density. Furthermore, the direct chemical functionalization is considered to be more facile than the indirect modification due to the avoidance of using oxidative and hazardous acid.

Holzinger *et al*. (2001) reported the addition reactions of SWCNTs with nitrene, nucleophilic carbene, and the perfluorinated alkyl radical, respectively (Fig. 3). They found that the derivatized SWCNTs through the reactions with alkyl azidoformate (**9** in Fig. 3, where R = ethyl or *tert*-butyl) and dipyridyl imidazolidene (**10** in Fig. 3) showed good dispersibility in dimethyl sulfoxide (DMSO). The reaction with alkyl azidoformate was extended to nitrene bearing more complex substituents such as aromatic groups, dendrimers, long alkyl chains, and oligoethylene glycol units, which resulted in functionalized SWCNTs with promising dispersibility in various organic solvents including 1,1,2,2-tetrachloroethane (TCE), DMSO, and 1,2-dichlorobenzene (1,2-DCB) (Holzinger *et al*. 2003). They obtained the highest dispersibility of 1.2 mg mL^{-1} in DMSO and TCE for the SWCNT adducts obtained through the addition reaction with nitrenes bearing crown ethers.

The 1,3-dipolar cycloaddition of azomethine ylides, generated by thermal condensation of *a*-amine acids and an aldehyde was approved to be an effective approach for functionalization of CNTs. Georgakilas *et al*. (2002a, b, 2008) reported that the reaction of CNTs with aldehyde and modified glycine resulted in derivatives with good dispersibility in $CHCl_3$, CH_2Cl_2, acetone, methanol, ethanol, and water. Typically, the dispersibility in $CHCl_3$ was close to 50 mg mL^{-1} without sonication, among the highest level at that time. In the same year, they successfully prepared amine-functionalized and water-dispersible CNTs through the 1,3-dipolar cycloaddition with *N*-functionalized glycine, bearing a Boc (*tert*-butyloxycarbonyl)-protected amino end group (Fig. 4). The procedure was then adopted for the preparation of CNTs modified with amino acids and peptides for biomedical applications (Prato *et al*. 2008). Phenol groups were also grafted to the surface of SWCNTs *via* 1,3-dipolar cycloaddition, which resulted in stable dispersions in a range of polar solvents including water. The stable dispersions allowed the preparation of polymer/CNTs composites by mixing the components in solution at room temperature. In fact, homogenous, coherent, and transparent CNT composite films and/or gels were achieved due to the good compatibility of the functionalized CNTs and polymers or layered aluminosilicate clay minerals.

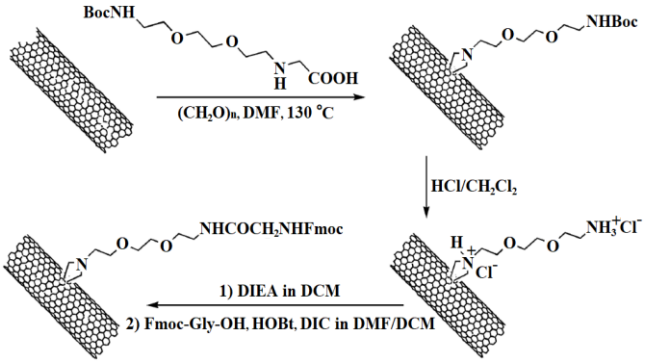

Fig. 4 Functionalization of CNTs based on the 1,3-dipolar cycloaddition reaction to the sidewall of CNTs. (Georgakilas *et al*. 2002b)

2.2 Dispersion of CNTs via noncovalent functionalization

Noncovalent functionalization of CNTs was normally realized by the adsorption of dispersants on the sidewall of CNTs *via* noncovalent interactions, including van der Waals force, hydrogen bonding, hydrophobic interaction, and electrostatic attraction (Premkumar *et al*. 2012). The molecules of surfactants either stack on the surface of CNTs or helically wrap around the CNTs sidewalls. Since covalent functionalization significantly disrupts the extended π-conjugation of the sp^2-carbon framework and thus alters the intrinsic electronic and mechanical properties of CNTs, noncovalent functionalization has attracted particular attention as it preserves the conjugated structure and the intrinsic properties of CNTs. In a typical noncovalent functionalization process, the choice of dispersants is the most critical step. A wide variety of dispersants, including surfactants (Liu *et al*. 2019a, Dai *et al*. 2020), biomolecules (Nakashima *et al*. 2003, Zheng *et al*. 2003), aromatic compounds (Liu *et al*. 2013b, 2017, 2018, Backes *et al*. 2009), ionic-gemini molecule,(Hou *et al*. 2018), and polymers (Liang *et al*. 2017, He *et al*. 2019, Schneider *et al*. 2020, Shamshoom *et al*. 2018), have been extensively investigated.

Surfactant-assisted dispersion is a very common technique for the preparation of CNT dispersions. Surfactants were initially used as dispersing agents for the purification protocols of raw carbon materials (Rao *et al*. 1997), and then for spectroscopic characterization (O'Connell *et al*. 2002). In 2003, Moore *et al*. (2003) and IsIam *et al*. (2003) compared a series of anionic, cationic, and nonionic surfactants and polymers in terms of their capability to disperse individual SWCNTs through ultrasonication in liquid phase. They claimed that sodium dodecylbenzene sulfonate (SDBS) gave the most well-resolved spectral features and/or most stable and concentrated SWCNTs dispersions. Typically, IsIam *et al*. (2003) presented the SDBS stabilized SWCNTs dispersion with the concentration of 20 mg mL^{-1}, which was stable for more than 2 months. Wenseleers *et al*. (2004) dispersed SWCNTs efficiently by forming stable micelle structures of surfactants. They found that bile salt detergents were

extremely efficient in solubilizing pristine individual SWCNTs by forming micelles, which provided an unusually unperturbed environment for spectroscopic investigations. Liu recently reported that surfactant, such as SDBS, sodium cholate (SC), sodium deoxycholate (SDC), and sodium dodecyl sulfate (SDS) can be used for debundling of SWCNTs in solid phase by ball-milling (Fig. 5) (Liu *et al*. 2019a). The debundled SWCNTs powder was readily dispersed in water by simply shaking with hand (Fig. 5). In this case, more than 60% of SWCNTs were dispersed by using SC, showing much better performance than other surfactants.

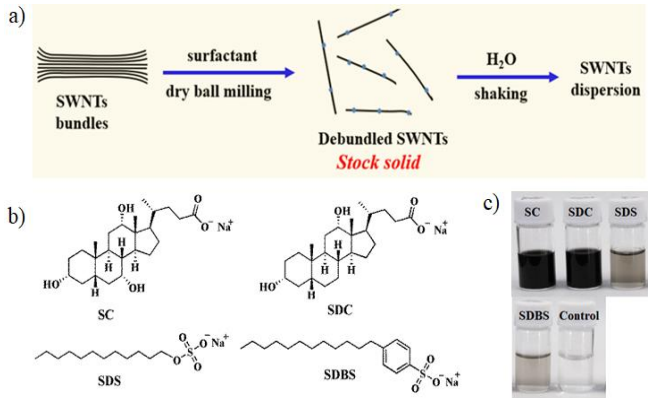

Fig. 5 (a) Schematic of the preparation of SWNTs dispersion through solid phase exfoliation; (b) Chemical structures of SC, SDC, SDS, and SDBS; (c) Photographs of aqueous CNTs dispersions by use of different surfactants (Liu *et al.* 2019a)

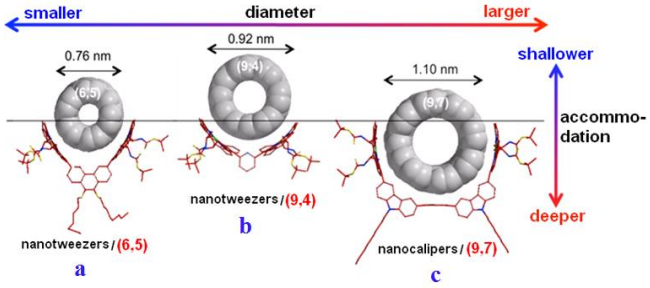

Fig. 6 Computer-generated molecular modeling of the complex structures of (6,5)-, (9,4)-, and (9,7)-SWCNTs with chiral diporphyrin nanotweezers (a) and (b) and nanocalipers (c), respectively. (Liu *et al.* 2013b)

In addition to the surfactants, biomolecules such as DNA, peptides, and proteins are also reported to be effective dispersing agents. As a typical bio-macromolecule, DNA was initially used by Zheng *et al*. (2003) and Nakashima *et al*. (2003) for the dispersion and/or separation of SWCNTs in aqueous solutions. Due to π–π stacking and helical wrapping of DNA on the surface of SWCNTs, the SWCNTs could be effectively dispersed in water with the assistance of ultrasonication for further separation and applications. Hirano *et al*. (2009) demonstrated the enhanced dispersion of SWCNTs (more than one order of magnitude) in water with proteins as the dispersant through the addition of fluoroalcohols as co-solvents. Other biomolecules such as peptides are also proved to be good dispersants for CNTs (Antonucci *et al*. 2017).

Recently, tailored small molecules and polymers have attracted increasing attention as new kinds of dispersants to target the specific CNT species. We and others designed a serial of tweezer- and caliper-shaped molecules, namely nanotweezers and nanocalipers, for the selective dispersion of SWCNTs and DWNTs (Fig. 6) (Liu *et al*. 2013a, b, 2014, 2017, Backes *et al*. 2011). Due to the strong π-π and C-H-π interactions, the nanotweezers-CNTs and nanocalipers-CNTs showed good stability in methanol, enabling further centrifugation for the diameter and/or metallicity selectivity. Note that by introducing chiral units to the molecules (Fig. 6), handedness discrimination of CNTs was achieved in addition to the diameter and metallicity discrimination (Liu *et al*. 2013b, 2014, 2017). Flat molecules such as the perylenes, pyrene and triphenylene derivatives, and metallo-porphyrins (Fig. 7), are also widely used as dispersants for CNTs (Backes *et al*. 2009, Liu *et al*. 2013b, 2018). The flat

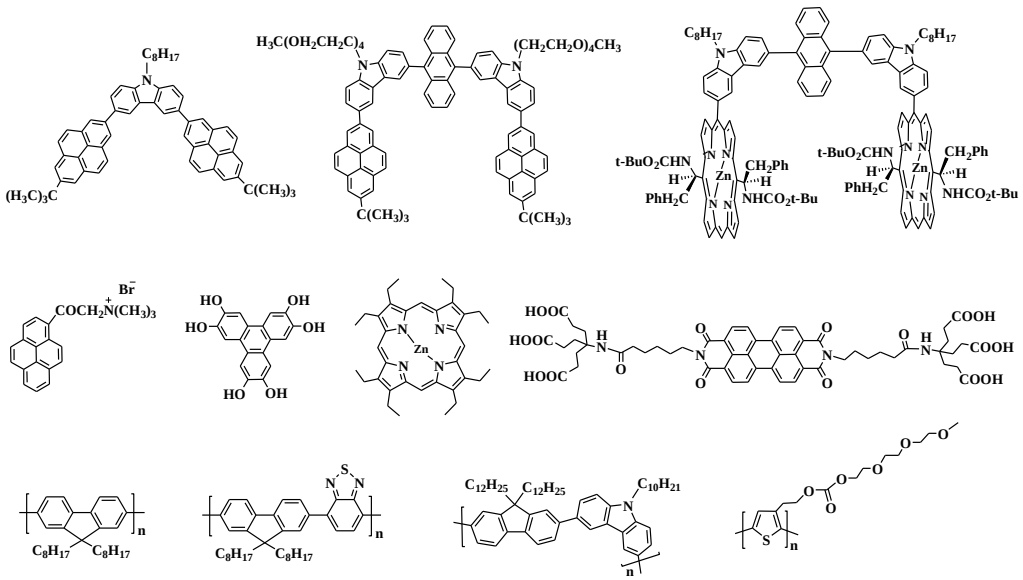

Fig. 7 Typical rationally designed small molecules and polymers for the noncovalent functionalization of CNTs

one-atom thickness and π-conjugated structural characteristics are considered to facilitate exfoliation of CNTs bundles as a wedge with the aid of bath sonication and stabilization of the result debundled CNTs through π-π interactions. On the other hand, polymeric dispersants based on polyfluorenes, polythiophene, polycarbazole, and benzene units (Fig. 7) were also designed and were systematically investigated for dispersing SWCNTs by different groups (Liang *et al*. 2017, He *et al*. 2019, Shamshoom *et al*. 2018, Schneider *et al*. 2020, Kim *et al*. 2020, Li *et al*. 2018). Typically, Shamshoom *et al*. (2018) designed a macrocycle-containing polyfluorene derivative for the efficient dispersion of SWNTs, which resulted in dark and concentrated nanotube dispersion (600 μg mL^{-1}). Among the various dispersants reported so far, the triphenylene-based dispersant namely 2,3,6,7,10,11-hexahydroxytriphenylene, was reported to be more efficient than the others in terms of the dispersing efficiency index (DEI) (Liu *et al*. 2018).

3. Preparation and properties of CNTs/polymer composites

Due to the unique mechanical, electrical, and thermal properties, CNTs were widely used as fillers in polymer matrix for pursuing enhanced properties that cannot normally be achieved by conventional composites or virgin polymers. However, the aggregates of CNTs were reported to significantly reduce the mechanical properties of the composites, as they can be dissociated under a relatively small tensile at the direction perpendicular to the axis of CNTs. Therefore, well distribution of CNTs in polymer matrix is very important for achieving promising mechanical properties. Several approaches such as solution mixing, melt mixing, in situ-polymerization and latex mixing have been developed for the preparation of CNTs/polymer composites. Among them, the solution-based techniques are considered to be more efficient than melt mixing for achieving well distribution of CNTs in polymer matrix, as the CNTs bundles can be exfoliated in appropriate solvents before mixing with the matrix solution. This critical review mainly focuses on the preparation and properties of solution-processed CNT/polymer composites.

3.1 Solution mixing

Solution mixing is perhaps the most common method for preparing polymer/CNTs composites due to the well dispersion of CNTs in the polymer matrix and facility for molding the composites to various shapes (such as different size and thickness). In a typical solution mixing process, the CNTs are firstly dispersed (or individualized) in an appropriate solvent through either covalent or noncovalent functionalization; subsequently, the dispersed CNTs are added into the polymer solution, followed by molding the mixture through solution-based technologies, such as casting, spin-coating, filtration, and co-precipitation (Fig. 8) (Nallabothula *et al*. 2019). In most cases, the same solvent is used for the dispersion of CNTs and dissolution of polymer, to avoid possible precipitation during the mixing process. The following sections will systematically discuss

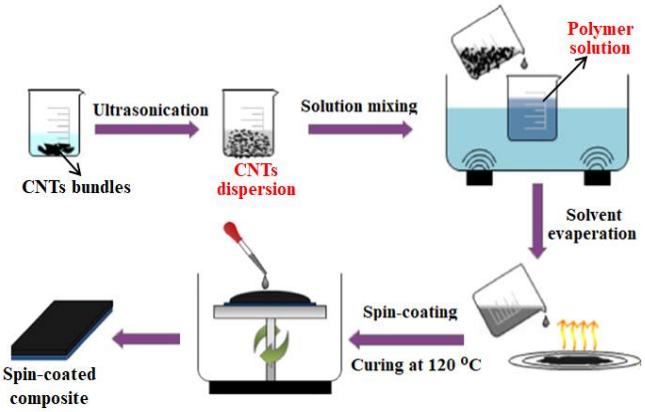

Fig. 8 Schematic depicting the fabrication of CNT/polymer composite thin film through solution mixing. (Nallabothula *et al*. 2019)

the distribution of CNTs in polymer matrix through solution mixing, based on covalent or noncovalent functionalization of CNTs.

3.1.1 Solution mixing based on non-covalent functionalization of CNTs

In an early report about solution-processed CNT/polymer composite, pristine MWCNTs were ground to fine powders and sonicated in chloroform ($CHCl_3$) to form a suspension for the solubilization of polymer matrix (Jin *et al*. 1998). The resulted suspension was transferred into a Teflon mold and dried in ambient conditions overnight. Through this solution process method, reasonably good distribution of MWCNTs in polymer matrix was achieved. In the subsequent studies, other solvents such as *N,N'*-dimethylacetamide (DMAc), *m*-cresol, and chlorobenzene, were also used for the dispersion of CNTs and subsequent preparation of their composites (Yuan *et al*. 2011, Wang *et al*. 2015, 2018). Yuan *et al*. (2011) dispersed MWCNTs in DMAc through sonication with a high-power tip sonicator, and to the resultant dispersion, different quantities of poly (amic acid) solution were then added. After further sonication, the mixture was directly cast into films and followed by thermal imidization at 100℃. The final polyimide (PI)-based composite (MWCNTs/PI composite) exhibited ultrahigh electrical conductivity as well as high mechanical properties. Typically, the electrical conductivity of the MWCNT/PI composite reached 38.8 S cm^{-1} at CNT loading of 30 wt%, which was the highest reported value for conventional solution-processed nanotube composites. Zhou *et al*. (2019) designed a star-like co-polybenzimidazole (co-PBI) for the dispersion of carbon nanomaterials (including SWCNTs, MWCNTs, and graphene) in DMAc and fabrication of their composites. The dispersing effect of aromatic polymers on CNTs was significantly promoted by tailoring their molecular architecture from linear to star-like configuration (Fig. 9(a)). In this work, polymer co-PBI worked as both dispersant and matrix for CNTs. Due to the strong π–π interactions between MWCNTs and the aromatic rings in co-PBI, MWCNTs were uniformly distributed in the solution-processed MWCNTs/co-PBI composite at MWCNTs concentration up to 2 wt%, which resulted in

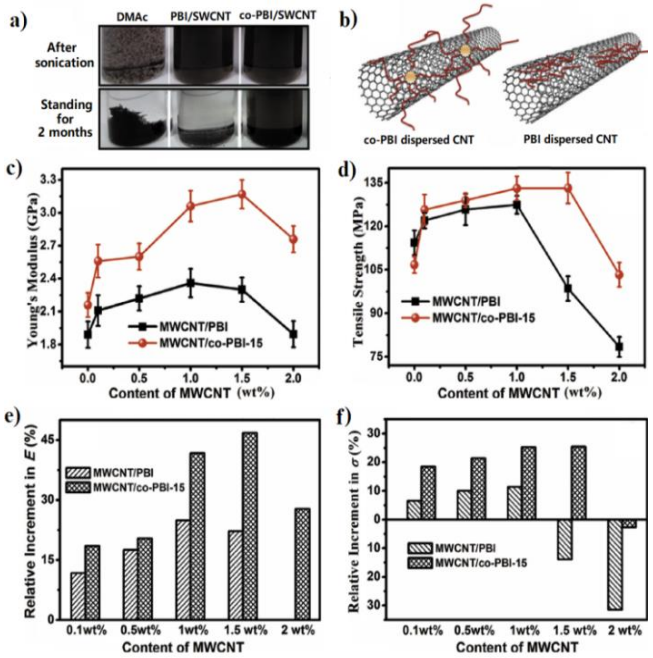

Fig. 9 Photographs of dispersion of SWCNTs (a) and proposed dispersion mechanism (b) by using PBI and co-PBI as the dispersants. Comparison of Young's modulus (c) and tensile strength (d) of MWCNTs/PBI and MWCNTs/co-PBI composites. Comparison of the relative increment in Young's modulus (e) and tensile strength (f) of MWCNTs/PBI and MWCNTs/co-PBI composites (Zhou *et al.* 2019)

much higher mechanical performance than that of linear PBI-based composite (MWCNTs/PBI). For example, when the loading of MWCNTs was 1 wt%, the Young's modulus and tensile strength of MWCNTs/co-PBI was 3.06 GPa and 133.1 MPa, corresponding to the increments of 41.7% and 25.3%, respectively, as compared with that of neat co-PBI (Fig. 9). These values were higher than that of MWCNTs/PBI, which were 2.36 GPa and 127.4 MPa, corresponding to the increments of only 24.9% and 11.4%, respectively (Fig. 9). The enhanced mechanical properties by adding CNTs might be attributed to the following reasons; 1) greater uniform stress spreading offered by the uniformly dispersed CNTs in the matrix; 2) CNTs make the matrix more crystalline, and the crystalline composite is stronger than the amorphous ones; 3) as the fillers, CNTs have much stronger mechanical properties than polymeric matrix (Shahlol *et al.* 2020).

In a recent work by Mirka *et al.* (2019), an alternating copolymer based on fluorene and 2,5-dimethoxybenzene was designed for the selective dispersion of semiconductive SWCNTs (*sc*-SWCNTs). The polymer/ SWCNTs dispersion was directly formed in toluene under sonication. Since the centrifuged sample showed an *sc*-SWCNTs purity > 99%, it was used for the fabrication of *sc*-SWCNT TFTs through soak and drop-cast techniques. The authors claimed that the device exhibited maximum hole and electron mobilities of 19 and 7 $cm^2/V{\cdot}s$, respectively, with on/off ratios as high as 10^7. Other newly designed polymer such as pentiptycene polymer was used as CNTs dispersant for the fabrication of polymer/SWNTs composite for benzene, toluene, and o-xylene detection (Luo *et al.* 2020).

Using the π-π interaction between CNTs and aromatic units of solvent molecules, Wang *et al.* (2015, 2018) demonstrated that pristine CNTs can be dispersed in *m*-cresol and chlorobenzene, respectively. Through solution mixing the CNTs dispersion with conjugated polymer solutions, nanocomposites with enhanced electronic and thermoelectric properties were obtained. Wang *et al.* (2018) dispersed SWCNTs in anhydrous chlorobenzene through vigorous stirring. To the dispersion, a donor-acceptor-type conjugated polymer based on benzo-[1,2-b:4,5-b′]-dithiophene (BDT) was added. After continuously stirring to completely dissolve the polymer, the mixture was drop-cast on glass substrate under ambient conditions to form the conjugated polymer/SWCNT composite. With the increasing amount of SWCNTs in the composite, the Seebeck coefficient decreased, and the electrical conductivity increased gradually. The maximum Seebeck coefficient and electrical conductivity of the composite with a 1:10 mass ratio of polymer to SWCNTs were 68.1 $\mu V\ K^{-1}$ and 529.3 S cm^{-1}, respectively. Furthermore, the highest power factor of 116.7 $\mu W\ m^{-1}\ K^{-2}$ was obtained at approximately 95℃.

Although several specific organic solvents (such as *m*-cresol and chlorobenzene mentioned above) can disperse CNTs directly, environmental-friendly (especially less toxic) solvents, such as water, alcohol, or simple water/ organic mixture, are preferred in green chemical industry. Therefore, CNTs dispersions stabilized with appropriate dispersant in environmental-friendly solvents were also widely studied for the composite preparation. He *et al.* (2019) synthesized four thermally cleavable polythiophene derivatives and used them for the dispersion of SWCNTs in ethanol. Through drop-casting process, the film with network structures of the polymer/SWCNTs composite was obtained. After thermal cleavage of the solubilizing group through decarboxylation, the resultant composite film showed an electrical conductivity of 35 S cm^{-1}, about 250 times higher than that before thermal cleavage. In the study by Qu *et al.* (2018), the solution of hydrophilic pyridinium salt polymer in DMF/H_2O (1/4) was mixed with SWCNTs in water through stirring. Due to the strong π-π interaction between the polymer and SWCNTs surface, uniform dispersion was obtained, which was drop-casted on a clean glass substrate to form a composite film. The well dispersion of SWCNTs in the polymer matrix endowed maximum electrical conductivity and power factor of 159 S cm^{-1} and 46.4 $\mu W\ m^{-1}\ K^{-2}$, respectively. Surfactant, most typically SDBS was also employed in dispersing SWCNTs in aqueous solution for the preparation of magnetically sensitive SWCNTs and their composites through the solution mixing (Liu *et al.* 2019b).

3.1.2 Solution mixing based on covalent functionalization of CNTs

Generally, the covalently functionalized CNTs are much easier to form uniform suspension than pristine CNTs. Therefore, numerous reports employed the suspension of covalently functionalized CNTs for the nanocomposite

preparation through solution-based processing techniques. Perhaps, the conversion of pristine CNTs to oxidized or carboxylized CNTs (CNTs-COOH) by acid treatment is the easiest way to obtain aqueous dispersible CNTs. Considering the facility of this approach, several papers have demonstrated the preparation of polymer/CNTs-COOH composites by solution mixing, with the property enhancement through adding the CNTs-COOH (Shaffer and Windle 1999, Du *et al*. 2015, Das *et al*. 2018, Sui *et al*. 2019, Tonga *et al*. 2020)

In an early example described by Shaffer *et al*., the CNTs were oxidized by the mixture of concentrated nitric and sulphuric acid (1:3) to produce an electrostatically stable dispersion of CNTs in water (Shaffer and Windle 1999). After careful mixing the CNTs dispersion with PVA aqueous solution followed by subsequent casting and water evaporation, composite films with a wide range of CNTs loadings were obtained. Using the same method of acid oxidation, Du *et al*. (2015) prepared carboxylized MWCNTs (MWCNTs-COOH) and subsequently fabricated their nanocomposites with PVA through solution mixing and casting. They investigated the microstructures, conductivity, and electroactive shape memory properties of MWCNTs-COOH/PVA films, and found that the highest thermal conductivity (0.45 W/m·K) was obtained at the MWCNTs content of 20 wt%. Furthermore, the shape of the composite could be fully recovered to the original form within 35 s at a constant voltage of 60 V (Fig. 10). The systematic analysis revealed that the enhanced performance was attributed to the reinforcement of MWCNTs, leading to the improved electrical and thermal conductivities of the PVA matrix. Das *et al*. (2018) reported that the existence of polar functional groups, such as carboxyl (-COOH) on the surface of SWCNTs endowed a strong matrix-filler interaction between the functional groups and the PVA chain. Furthermore, the strong electronegativity of oxygen led to a high value of dipole moments, which resulted in a proper orientation of SWCNTs in the PVA matrix through the dipole-dipole interaction. Therefore, the solution-processed PVA/SWCNTs-COOH composite exhibited hysteresis behavior. The CNTs-COOH has also been dispersed in organic solvents for the preparation of nanocomposites with polymer matrix. Sui *et al*. (2019) systematically compared the dispersion quality of CNTs in thermoplastic polyurethane (TPU) matrix with different preparation methods: solution mixing and melt mixing. They used DMF for the suspension and solubilization of MWCNT-COOH and TPU, respectively. After adding the suspension of MWCNT-COOH into the TPU solution dropwisely and subsequent mixing, the TPU/MWCNT-COOH composites were coprecipitated by pouring the mixture into a non-solvent for TPU, deionized water. It was found that a better dispersion can be obtained by using solution mixing at MWCNTs-COOH content ≤ 5.0 wt%.

Other than carboxyl, amine and hydroxyl groups, long alkyl chains have also been chemically bonded with CNTs for improving the dispersibility of CNTs in various solvents (Song *et al*. 2021, Li *et al*. 2013, Konnola and Joseph 2016). Li *et al*. (2013) synthesized a new type of water-soluble SWCNTs (N^+-SWCNTs) by grafting with dodecyl

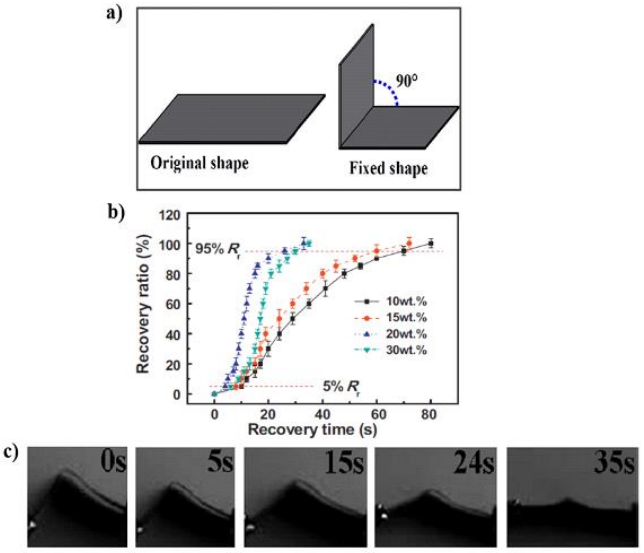

Fig. 10 (a) The original shape and the fixed shape for PVA/MWCNTs samples. (b) The relationship of recovery time and recovery ratio for PVA composites with different contents of MWCNTs. (c) Electroactive shape recovery behavior of PVA composites with 20 wt.% MWCNTs loading (Du *et al*. 2015)

quaternary ammonium bromides. The introduced cationic species ensured not only high solubility of N^+-SWCNTs but also improved stability of the aqueous dispersions. The aqueous N^+-SWCNTs dispersion was well mixed with aqueous PVA solution and poured into a glass mould for the preparation of PVA/N^+-SWCNTs nanocomposite. Since the key issues including uniform dispersion of CNTs and enhancement of interfacial interaction between PVA and nanotubes have been well treated, the tensile strength and Young's modulus of composite films with 0.3 wt% N^+-SWCNT increased by 33% and 32%, respectively, as compared to that of neat PVA film. Konnola and Joseph (2016) demonstrated a novel functionalization by grafting carboxyl-terminated poly (acrylonitrile-*co*-butadiene) (CTBN) on the sidewall of MWCNTs to obtain MWCNT-*g*-CTBN, which was mixed with epoxy resin in acetone by sonication. After the evaporation of the acetone and mixing with molten hardener at 180℃, post-curing was done at 200℃ to obtain the final composite. It was found that the incorporation of MWCNT-*g*-CTBN in the epoxy matrix imparted tremendous improvement in mechanical strength as well as fracture toughness when compared with pristine MWCNT/epoxy composites. The mechanism for this improvement can be attributed to the well dispersion of MWCNT-*g*-CTBN in the matrix through solution mixing, and the improved interfacial interaction between nanotubes and matrix through chemical bonding.

For improving the compatibility between CNTs and polymer matrix, researchers have also investigated the dispersing properties of CNTs functionalized with chemical chains that are structurally close to the matrix polymer. Due to the similarity or identity of the chemical units in CNTs and matrix, interfacial interaction was significantly enhanced, which could be beneficial for the CNTs

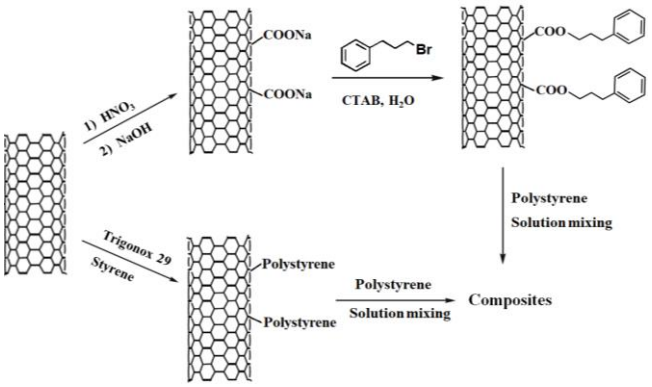

Fig. 11 Chemical functionalization of CNTs with phenyl-containing chains for the preparation of composites with polystyrene. (Faraguna *et al.* 2017)

dispersion. Faraguna *et al*. (2017) prepared phenyl propane ester functionalized and polystyrene grafted MWCNTs, respectively (Fig. 11). Both of them showed good dispersibility in the toluene solution of polystyrene. Since both the grafted chains (phenyl propane ester or polystyrene) and matrix (polystyrene) contained phenyl units, the functionalized MWCNTs and polystyrene showed good compatibility, resulting in uniform composite through solution mixing (Fig. 11). The authors systematically investigated the dispersion, electrical and thermal properties of the composite, and found that solution-mixed nanocomposites exhibited lower percolation thresholds than that of melt-mixed samples.

As mentioned so far, solution mixing is a very effective technique for preparing nanocomposites of CNTs with soluble polymers, either in aqueous or organic solutions. Considering the environmental pollution, the aqueous solution is preferred, as most of the organic solvents, such as THF, acetone, toluene, and DMF are toxic and harmful to human health. However, the poor aqueous solubility of most polymers significantly limited the wide applications of solution mixing. Therefore, other alternative solution-based processing techniques have also been developed and extensively investigated.

3.2 In-situ polymerization

To a certain degree, in-situ polymerization is another solution-processing technique for the preparation of CNT/polymer composite, as the polymerization was mostly performed in solution phase. In a typical in-situ polymerization, the CNTs were firstly uniformly dispersed in an appropriate solution either with or without the polymerization monomer. After adding monomer and/or initiator, the mixture was stirred under specific conditions to obtain the CNT/polymer nanocomposite. The main advantage of this method is that it enables the preparation of CNT composites with insoluble and thermally unstable polymers, which cannot be processed by solution and melt mixing. Besides, it is a very convenient processing technique allowing the preparation of composites with high CNT loading and good CNT dispersion. During the polymerization, the initially synthesized polymers, either bonded to or wrapped on the surface of CNTs, significantly improve the compatibility between CNT and polymer matrix, resulting in a uniform distribution of CNTs in polymer matrix even at high CNTs loading. Due to the numerous advantages, in-situ polymerization has been widely used in the preparation of nanocomposite, as in the case of solution mixing mentioned above.

Initially, in-situ radical polymerization was employed for the synthesis of poly (methyl methacrylate) (PMMA)/MWCNT composites by Jia *et al*. (1999). In this work, MWCNTs and radical initiator 2,2'-azobisisobutyronitrile (AIBN) were directly added into MMA to initiate the reaction. The authors believed that π-bonds in MWCNTs were initiated by AIBN and therefore MWCNTs could participate in the PMMA polymerization. SEM images revealed that only relatively thin PMMA layers were wrapped on the surface of CNTs, which demonstrated the PMMA molecules in the composite being rather small. Therefore, an improved in-situ process was proposed (Jia *et al*. 1999). The AIBN was put into MMA and stirred for 75 min to allow the initial polymerization of MMA before adding MWCNTs. Since the PMMA molecules grew larger than those in the one-pot experiment mentioned above, the resulted CNTs were wrapped with thicker PMMA layers and were better dispersed in the PMMA matrix. Yao *et al*. (2010) prepared SWCNTs/ polyaniline (PANI) hybrid nanocomposites through an in-situ polymerization using SWCNT as the template and aniline as the reactant. In this work, the SWCNTs were dispersed in 1 M HCl by sonication at room temperature for 2 h and followed by adding the aniline monomer. To the mixture, ammonium peroxidisulfate (APS) as the oxidant was added dropwisely (in 1 M HCl) to initiate the reaction. Detailed analyses revealed that the polyaniline grew along the surface of SWCNTs forming an ordered chain structure during the SWCNT-directed polymerization process. This ordered chain structure of the PANI was considered to contribute to an enhanced carrier mobility of the SWCNT/PANI nanocomposites. Conductivity and power factor of composites with 41.4 wt% SWCNTs reached 1.25×10^{4} S/m and 2×10^{-5} W m^{-1} K^{-2}, respectively, which was more than one order of magnitude higher than that of pure PANI. However, the thermal conductivity of the SWCNTs/PANI composite did not change much even with high SWCNT content. This can be attributed to the phonon scattering effect of nanointerfaces produced by the SWCNT/PANI nanocable structure. Liang *et al*. (2016) demonstrated that surfactant SDS dispersed SWCNTs can be used for the preparation of PPy/SWCNT composites through in-situ polymerization. The pristine SWCNTs were firstly dispersed in water or aqueous ethanol (H_2O+EtOH) with the aid of SDS by sonication. To the homogeneous dispersion, pyrrole monomer was added and stirred for 20 min. Due to the interfacial attractions of π–π interactions and van der Waals forces between SWCNTs and pyrrole, most of the pyrrole monomers were adsorbed on the SWCNT surfaces. After adding iron sulfate aqueous solution dropwisely, in-situ polymerization occurred on the SWCNT surfaces, resulting in a wrapping layer of PPy on

SWCNTs. The composites were washed and filtrated under vacuum to achieve stretchable, super flexible, and mechanically stable thermoelectric films. The super flexibility of the films was confirmed by both direct observations under various deformations (including bending, rolling, and twisting) and quantitative measurements of the minimum bending radii (< 0.6 mm). With SWCNT:Py ratio of 60 wt%, the nanocomposite prepared in aqueous ethanol showed the electrical conductivity and power factor of 399 ± 14 S cm^{-1} and 19.7 ± 0.8 μW m^{-1} K^{-2}, respectively. These values are the best for PPy-based composites reported so far.

The in-situ polymerization was also carried out in organic solvent such as DMF and 1,2-Dichlorobenzene (1,2-DCB), as they were reported to be good solvents for CNT dispersion (Nayak *et al*. 2012, Allen *et al*. 2014). Nayak *et al*. (2012) dispersed MWCNTs in DMF, to which a premixed aqueous solution containing an appropriate molar ratio of monomer (*N*-hydroxymethyl acryl amide), cross linker (*N*,*N*-methylene-bis-acrylamide), and initiator (APS) was added. After adding a catalyst (*N*,*N*,*N*,*N*-tetramethylethylene diamine), the slurry was gently stirred, and subsequently cast into a Teflon mold at room temperature to form a gelled composite. Conductivity of the composite film was found to increase significantly with the MWCNTs concentration due to the formation of continuous conductive pathway at high MWCNTs concentration. Allen *et al*. (2014) dispersed SWCNTs in oDCB in the presence of poly (3-hexyl thiophene) (P3HT), which led to gel-like properties and alignment of SWCNTs. After adding the corresponding monomer, pyrrole (Py) or 3,4-ethylenedioxythiophene (EDOT), the mixture was coated on a glass slide into a film or extruded from a syringe to form fibers (Fig. 12). The SWCNT film or fibers was brought to contact with $FeCl_3$ solution containing phytic acid for initiating the polymerization of the conducting polymer. In this system, phytic acid was used to cross-link the PPy and PEDOT. The oxidant, $FeCl_3$, doped both the polymer and the SWCNTs, leading to highly conductive composites. The conductivities of SWCNT/P3HT/PPy and SWCNT/P3HT/PEDOT composite films reached 2800 and 3300 S/cm, respectively. These films open up the possibility of using SWCNT/conjugated polymer films as solution-processable transparent electrodes. On the other hand, conductivity of the as-prepared composite fibers reached 170 S/cm. Since all the additives here are inexpensive or at low concentrations, this approach enables large-scale processing.

For achieving better dispersion of CNTs in polymer matrix, chemical functionalization of CNTs was performed before in-situ polymerization (Mun *et al*. 2008). Functionalizing the CNTs with polymers that are structurally close to the matrix polymer is considered to be the best approach, as such modification ensures better compatibility of the functionalized CNTs with the matrix and limits the microscopic phase separation in the nanocomposites. As a typical example, Mun *et al*. (2008) demonstrated the fabrication of poly (ethylene terephthalate) (PET) hybrids with triphenyl phosphonium (Ph3P) functionalized MWCNTs via in-situ polycondensation. The pristine

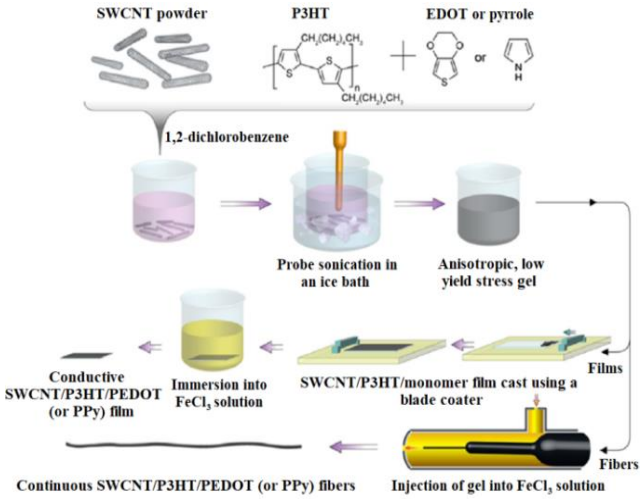

Fig. 12 Scheme illustrating the method to use in-situ polymerization to form conductive films and fibers (Allen *et al.* 2014)

MWCNTs were treated with HNO_3, thionyl chloride ($SOCl_2$) and (2-hydroxyethyl) triphenyl phosphonium bromide in sequence to obtain the functionalized MWCNTs (Ph3P-MWCNTs). The Ph3P-MWCNTs were then mixed with ethylene glycol under stirring. To this suspension, a mixture of dimethyl terephthalate (DMT) and a few drops of isopropyl titanate was added. The resultant mixture was allowed to react under heating with a steady stream of N_2 gas to obtain the final Ph3P-MWCNT/PET hybrid. Characterization showed that the adding of a small amount of functionalized MWCNTs can significantly improve the thermal and electrical properties of the composite fiber prepared by melt-spun.

In general, in-situ polymerization can be applied to prepare composites of CNTs with almost any polymer. However, limitations also exist. In the case of insoluble polymer, the solubility of the oligomers decreases gradually with the polymerization undergoing. Finally, only relatively low molecular weight polymers could be obtained as the matrix of the nanocomposite. Therefore, the choice of an appropriate solvent that can well disperse CNTs and dissolve polymer monomers simultaneously is very important for achieving high molecular weight polymer matrix.

3.3 Latex mixing

To a certain degree, latex mixing is an innovative solvent-based approach for incorporation of nanofillers into polymer matrix. This approach is particularly useful for polymers exhibiting relatively poor solubility and low decomposition temperature that cannot be processed by solution mixing and melt mixing. Since most polymers have latex forms in which discrete polymer particles with sizes of ~50 nm are stably suspended in aqueous medium, latex technology offers a wide platform for the preparation of polymer nanocomposites. Preparation of nanocomposites through latex mixing involves the dispersion of fillers, preparation of polymer latex, mixing the fillers with

polymer latex, and co-coagulation.

In the case of CNTs as the filler, the dispersion of CNTs was directly added to the polymer latex and mixed carefully (Grossiord *et al*. 2005, 2010, Nish *et al*. 2007, Moradi *et al*. 2015, Wu and Chen 2008). After removing the solvent, a uniformly dispersed CNT/polymer composite can be formed. Grossiord *et al*. (2005, 2010) demonstrated the preparation of polystyrene-SWCNTs composites by latex mixing. The pristine SWCNTs were firstly debundled with the assistance of surfactant (such as SDS or polysaccharide) to form a stable aqueous dispersion. The SWCNTs dispersion was then mixed with polystyrene latex particles obtained by emulsion polymerization. After freeze-drying and subsequent processing, a composite consisting of homogeneously dispersed SWCNTs in polymer matrix was obtained. The authors claimed that this technique has advantages including facile, versatile, reproducible, absence of toxic solvents, and good incorporation of SWCNTs into the polymer matrix. Latex mixing was further used to fabricate composites based on other CNTs species such as MWCNTs or other polymer matrices such as polypropylene. Grossiord *et al*. (2008) prepared MWCNTs/ polystyrene composites through a similar approach based on latex mixing. Electrical conductivity of the composite film was systematically investigated. A drastic increase in the conductivity was observed for the composites when the MWCNTs content reached about 1.5 wt%, indicating the percolation threshold for the formation of a conductive MWCNTs network in polystyrene matrix. The maximum conductivity was reported to be 1 S m^{-1} for this MWCNTs/ polystyrene film. The excellent electrical properties render this type of nanocomposites extremely attractive from a technological point of view.

In addition to the composites based on single-size latex mentioned above, composites derived from a binary latex system were also investigated. Moradi *et al*. (2015) synthesized two differently sized (30 and 70 nm) poly (methyl methacrylate-*co*-*tert*-butyl acrylate) latexes by emulsion polymerization for composite preparation. Through mixing the latexes with SWCNTs dispersion and subsequent spin-coating process, conductive composite film was prepared on a glass plate. They found that the conductivity of the film was closely related to the content of smaller particles, overall solid content, and the spin-coating conditions. A maximum conductivity of 371 S/m was obtained when the smaller latex particles (30 nm) content was at 3-5%. These conductive composites have potential application prospects in the field of electronics.

4. Factors influencing the properties of CNTs/ polymer composites

For achieving large enhancement in the properties of CNTs/polymer composites, it is quite important to understand the factors influencing the properties of composites, as well as how they work. This part will systematically discuss the effect of functionalization, size (including length, diameter, and aspect ratio of CNTs) and dispersion state of CNTs on the properties of CNTs/polymer composites.

4.1 Functionalization

Functionalization of CNTs is very important for improving their dispersibility and thus affects the physical properties of CNT/polymer composites (Menezes *et al*. 2018, Xing *et al*. 2016, Ma *et al*. 2007, 2010, Gulotty *et al*. 2013). The chemical functionalization of the CNT surface is expected to maximize the shear strength of the composite interface and promote the dispersion of CNTs. Covalently grafted long chains are entangled with polymer matrix, which ensures good stress transfer from matrix to CNTs. Besides, the functional groups make the CNTs more compatible with the polymer and solvent, which helps to significantly improve the dispersion of nanotubes and further the properties of composite materials.

Menezes *et al*. (2018) studied the effect of functional groups of MWCNTs on the mechanical properties of composites using HDPE as the matrix. As shown in Table 1, the pristine MWCNT based composite (HDPE/P-MWCNT) exhibited higher Young's modulus and tensile strength than the pure matrix HDPE. After the incorporation of functional groups, such as carbonyl or octadecylamine (ODA), on the surface of CNTs, the resulted composites (HDPE/MWCNT-COOH and HDPE/MWCNT-ODA) showed further enhanced mechanical properties. Meanwhile, the toughness decreased significantly from 26 N mm/mm^3 to 3-4 N mm/mm^3, and the elongation at break remained unchanged. Systematic study revealed that the surface functional groups of MWCNTs affected the interaction of the components from two main points: the structural and polarity similarity between the functional chains and polymer matrix. Similar structural and polarity are benefit for the nanoscale mixing and thus improve the mechanical properties significantly.

In addition to HDPE, PS and epoxy were employed as matrix respectively for the investigation of functionalization effect of CNTs. Xing *et al*. (2016) used functionalized CNTs containing phosphorus and nitrogen to enhance the thermal, mechanical and flame retardant properties of CNTs/PS composites. The results showed that the addition of aminated MWCNTs (A-MWCNT) or diphenylphosphinic chloride functionalized MWCNT (DPPA-MWCNT) to PS matrix can effectively enhance both physical and mechanical properties. Compared with PS/A-MWCNT, PS/DPPA-MWCNT showed higher glass transition temperature, better thermal stability and tensile strength due to the high dispersion and interfacial interaction between DPPA-MWCNT and PS matrix. Ma *et al*. (2010) compared the effects of silane- and amino-functionalization on the mechanical and thermo-mechanical properties of epoxy-based composites. In both cases, the incorporation of functional groups (silane or amino) on the surface of CNT significantly enhanced the mechanical properties of resultant composites, due to the higher surface energy and much better wettability with epoxy than the pristine CNTs. When comparing the silane- and amino-CNTs, composites containing silane-CNTs showed higher flexural modulus than that of amino-CNTs, and the difference diminished at high CNT content, such as 0.5 wt% CNTs (Fig. 13(a)). On the contrary, much higher flexural strength was obtained from the composites containing amino-CNTs at the CNT content of 0.5 wt% (Fig. 13(b)). These observations suggest that amino-CNTs are more effective in enhancing the

Table 1 Mechanical properties of HDPE/MWCNT composites with different functionalization (Menezes *et al.* 2018)

Sample	Young's moduli (MPa)	Tensile strength (MPa)	Elongationat break (%)	Toughness (N mm/mm^3)
HDPE Pure	(38 ± 4) x 10	26 ± 1	(15 ± 3) x 10	26 ± 5
HDPE/P-MWCNT	(47 ± 6) x 10	28 ± 1	16 ±2	4 ± 1
HDPE/MW CNT-COOH	(50 ± 5) x 10	29 ± 1	16 ±6	4 ± 1
HDPE/MW CNT-ODA	(53 ± 3) x 10	30 ± 1	15 ±2	3 ± 1

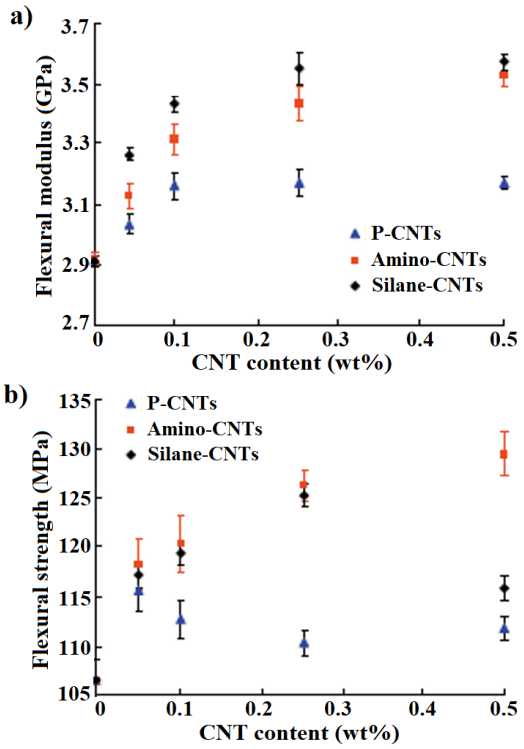

Fig. 13 Flexural properties of different functionalized CNTs composites with different contents of CNTs (Ma *et al.* 2010)

mechanical properties of the composites, especially at high CNT contents.

The effects of functionalized MWCNTs and SWCNTs on thermal conductivity of CNTs/polymer composites were compared by Gulotty *et al.* (2013) and Chen and Han (2020). In both cases, the addition of as-grown CNTs resulted in the enhancement of thermal conductivity of the composites, as compared with pure epoxy resin. However, the introduction of carboxylic groups on the surface of CNTs led to quite different performance between SWCNTs and MWCNTs. While carboxylic functionalization degraded the performance of SWCNTs fillers (the thermal conductivity dropped about 25%, almost to the neat epoxy value), no noticeable effect was observed for MWCNTs fillers. These results indicated that the contribution of the outer wall to the heat conduction in MWCNTs was marginal, and the heat transportation was mainly achieved by the inside walls, which were not affected through the functionalization. In the case of SWCNTs, the carboxylic functionalization generated surface defects to reduce the transmission of acoustic phonons, resulting in a decrease of thermal conductivity.

4.2 Dispersion of CNTs

Due to the nanometer radial size and high surface energy, CNTs are easy to agglomerate and exist as aggregates in polymer matrix. Since poor dispersion of CNTs makes the interfacial force between CNTs and matrix relatively weak, the loaded force cannot be effectively transferred from the matrix to CNTs, resulting in poor mechanical properties. Therefore, the homogenous dispersion or distribution of CNTs in polymer matrix is extremely important.

Since most of the polymers are non-conductive, the dispersion state of CNTs is particularly important for improving the electrical conductivity of CNT/polymer composites. Xie *et al*. investigated the effects of MWCNTs and polymer coupling treatment on the dispersion and electrical property of the resultant composites (Xie *et al.* 2010). They found that the factors degrading the dispersion of CNTs (such as an excessive amount of CNTs, weak sonication conditions) significantly decrease the electrical property of MWCNT/polymer composites. Nallabothula *et al.* (2019) used ultrasonic and mechanical stirring to disperse MWCNTs, and then prepared MWCNTs/polymer composites by compression molding and spin-coating, respectively. Through ultrasonic treatment and subsequent compression molding, the MWCNTs were well dispersed in the polymer matrix at the WMCNTs content of 3%, resulting in an enhanced conductivity of 72 S/cm. On the contrary, the composite films prepared by mechanical stirring and subsequent spin-coating exhibited a large number of CNTs aggregates, resulting in a much smaller conductivity of 0.41 S/cm.

Mechanical properties such as tensile strength and failure strain of CNTs/polymer composites are also closely related to the dispersion quality of the CNTs. Gupta *et al.* (2013) prepared MWCNTs/epoxy composites with different degree of MWCNTs dispersion through several processing methods. They found that homogeneous dispersion of MWCNTs in matrix resulted in enhanced mechanic properties, and worse dispersion or aggregates led to a decrease in the properties. Typically, the tensile strength of the composite prepared by the combination of microfluidic processing and planetary shear mixing was 15% higher than that of pure epoxy resin. On the other hand, the tensile strength of composite prepared by the combination of ultrasonic and planetary shear mixing or planetary shear mixing solely was 15% less than that of pure epoxy resin. These results can be attributed to the dispersion quality of MWCNTs in the polymer matrix. While the combination of microfluidic processing and planetary shear mixing resulted in a relatively homogeneous dispersion of MWCNTs, ultrasonic treatment plus planetary shear mixing or planetary shear mixing solely resulted in poor dispersion of MWCNTs. Kong *et al.* (2012) prepared poly(dimethyl siloxane) (PDMS) based nanocomposites through solution mixing and mini-extruder respectively. The dispersion state of MWCNTs in the PDMS was estimated by optical microscope in transmission mode. It was found that the composites

prepared by mini-extruder showed better CNTs dispersion, thus higher tensile strength and thermal conductivity than the solution mixing processed composites, which showed better electrical conductivity due to a higher aspect ratio of CNTs. Composites prepared by other dispersion methods such as probe sonication, batch mixing and mechanical stirring, were also investigated and a similar conclusion was drawn (Yazdani *et al*. 2016).

In summary, poor dispersion of CNTs in polymer matrix is prone to form larger aggregates and cracks, which reduce the mechanical strength of the nanocomposites. On the other hand, well-dispersed CNTs are more effective than the agglomerated ones in transferring external loads. Additionally, the CNTs networks in the well-dispersed CNTs/polymer composites are also benefit for the electron transfer process, thus resulting in good electrical properties.

4.3 CNTs size

In addition to the functionalization and dispersion of CNTs, the dimensions of CNTs also affect the properties of CNTs/polymer nanocomposites, including electrical and thermal conductivity, fatigue crack growth rates, Young's modulus, and tensile strength. Generally speaking, a high aspect ratio of CNTs can enhance the properties of composites more effectively.

Zhang *et al*. (2008) investigated the effect of CNTs length and diameter on the fatigue behavior of CNTs/epoxy composites. They found that the fatigue crack growth rates were largely depended on the length, diameter, and dispersion quality of CNTs in the matrix. The small diameter, large length, and well dispersion of CNTs were beneficial for reducing the fatigue crack growth rates. Singh *et al*. (2010) and Gulotty *et al*. (2013) studied the length effect of CNTs on the electrical and thermal conductivity of conducting polymer/CNTs composites, respectively. In the case of the same CNTs content, higher electrical and thermal conductivity were obtained by using longer CNTs (Figs. 14 and 15).

The relationship between the mechanical properties and CNTs dimensions were also investigated (Martone *et al*. 2011, Wan *et al*. 2005, Greenfeld and Wagner 2015). Martone *et al*. (2011) and Wan *et al*. (2005) reported that the CNTs length or aspect ratio is critical to both the load transfer efficiency and effective modulus of the composites. In the case of the same CNTs loading, the composites containing CNTs with larger length or aspect ratio, exhibited much better mechanical properties, including tensile strength and Young's modulus.

In addition to the factors mentioned above, the molecular weight of polymers and processing method of the composites are also reported to affect the properties of CNTs/polymer composite, although the influence sometimes may not so pronounced (Faraguna *et al*. 2017, Gupta *et al*. 2013, Kong *et al*. 2012).

5. Conclusions and future outlook

In conclusion, CNTs have emerged as highly promising fillers for polymer-based composites. A range of new composites have been fabricated and demonstrated astonishing mechanical and electrical properties. The

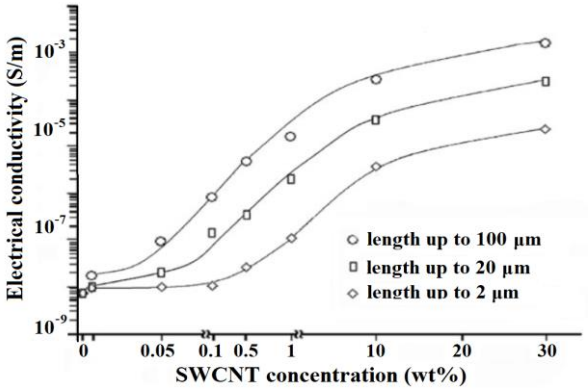

Fig. 14 Variation in electrical condyctivity of P3OT/SWCNT composite films for different concentrations of SWCNTs as a function of length of nanotubes. (Singh *et al.* 2010)

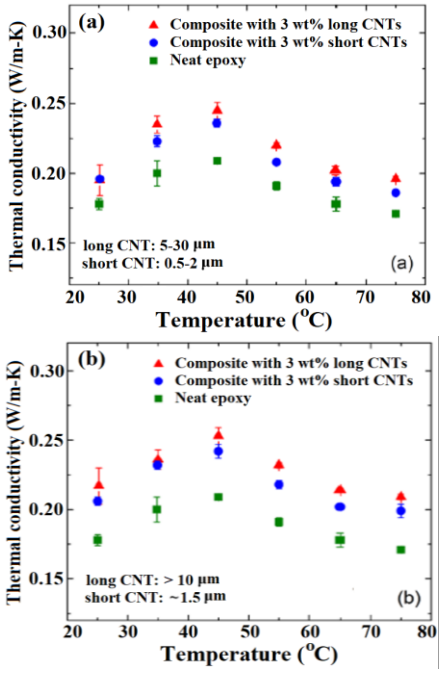

Fig. 15 Thermal conductivity of epoxy-based nanocomposites with SWCNTs (a) and MWCNTs (b) of different length. Note that longer CNTs perform better in terms of the thermal conductivity enhancement in both cases (Gulotty *et al.* 2013)

pioneer works revealed that the distribution quality of CNTs in polymer matrix was the most important factor influencing the composite properties. Therefore, extensive research has been conducted for pursuing well distribution (or dispersion) of CNTs in the matrix. This article reviews the latest methods that have been proposed to disperse CNTs in various solvents, as well as the techniques developed for CNTs/polymer composites fabrication by using the CNTs dispersions.

Various approaches based on covalent or non-covalent functionalization have been developed for the preparation of CNTs suspension. The well-dispersed CNTs suspension enabled many solution-related approaches for CNTs/polymer composites fabrication, such as solution mixing,

in-situ polymerization, and latex mixing. Compared with melt blending, the solution-based approaches are likely to provide more uniform distribution of CNTs in the polymer matrix, as the CNT bundles can be exfoliated in the solution phase before mixing with the polymer matrix. The review summarized the merits and disadvantages of each fabrication method, and discussed appropriate approaches for polymers with different dissolution characteristics (soluble in either aqueous or organic solvents). Finally, the influence of functionalization, dispersion quality, and lateral size of CNTs on the properties of CNTs/polymer composites was reviewed. From the above review, the factors resulting in better compatibility and distribution of CNTs in the matrix are beneficial to the composite properties. Additionally, longer CNTs are easy to form interconnected networks to generate higher mechanical property and electrical conductivity.

There is a large interest in the CNTs/polymer composite materials due to a broad range of important applications. Although extensive investigation has been performed, fabrication of high-performance CNTs/polymer composites that can satisfy practical applications is still challenging. Therefore, further breakthroughs should be made in the following aspects in the near future

(1) Solution-based approaches are quite efficient for fabricating well-distributed CNTs/polymer composite, especially with low CNTs concentration. The composites in solution phase can be easily processed into film for various important device applications. However, solution-based techniques are mostly limited to relatively small-scale production. More effort should be dedicated to develop scalable solution-based approaches for promoting the practical applications.

(2) Due to the high hydrophobicity and strong van der Waals interactions, CNTs have existed as insoluble bundles. Therefore, debundling and dispersing of CNTs are quite important for their applications in polymeric composites. While the debundling process involves appropriate exfoliants or covalent functionalization, the dispersing of CNTs is related to the interfacial interaction of CNTs with the polymer matrix and solvent employed. More attention should be paid to improve the distribution of CNTs in polymer matrix.

(3) For solution-based techniques, the choice of solvent is quite important. Only the good solvents for both CNTs and polymer matrix can provide well distribution of CNTs in the matrix. Since the functionalization of CNTs significantly alters the solubility of CNTs, the choice of solvent would be relying on the functional groups grafted on CNTs and the structure of polymer matric.

(4) The composites of CNTs and conductive polymer will be of particular importance in the near future due to the great potential in flexible electrodes for displays, supercapacitors, as well as thermal conductive devices. The surface engineering should be addressed for improving the charge transfer between CNTs and conductive polymer, thus the conductivity of the composites.

(5) Although quite low content of CNTs is needed for fabrication of high-performance CNTs/polymer composites, the practical applications require huge quantities of CNTs. Therefore, the development of new cost-effective approach for CNTs preparation is also important.

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