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Mechanical Properties of Carbon Nanotubes-Polymer Composites

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<http://dx.doi.org/10.5772/62635>

Abstract

Carbon nanotubes (CNTs), as a one-dimensional material, have outstanding mechanical properties such as extreme tensile strength and Young's modulus. At present, to prepare pure CNTs materials is quite difficult and the mechanical properties of the materials are limited in a low level. Because of their extraordinary mechanical properties and high aspect ratio, CNTs are considered to be ideal candidates for polymer reinforcement. In addition, CNTs/polymer composite materials are much easier to prepare than pure CNTs materials, so they have been paid much attention by researchers recently. However, challenges must be faced to prepare the CNTs/polymer composite with ultimate mechanical properties. So in this chapter, the main concerns are how to disperse CNTs in polymer matrix to prepare homogenous composite dispersions, how to prepare homogenous CNTs/polymer composite using possible fabricating processes based on the homogenous dispersions, how to increase the fiber mechanical properties especially through the enhancing interaction between polymer and CNTs, controlling the amount of CNTs and enhancing their orientation in the matrix.

Keywords: mechanical property, carbon nanotube, polymer, composite, dispersibility

1. Introduction

In recent years, because stronger, lighter, or less expensive compared to traditional materials, high-performance composite materials have increasingly become an essential in a wide range

of structural applications [1, 2]. As early as in ancient times, people have realized that the combination of two or more materials could form new materials which had better properties than either of the materials compositions. For example, ancient people in China began to use straw to reinforce mud to form bricks as building materials, and to use hemp or silk to reinforce paint and so on [3, 4]. Nowadays, composite materials are used extensively in various areas, not only in the aerospace industry but also in a large and increasing number of commercial mechanical engineering applications.

Composites are made up of reinforcements and matrix materials, in which the latter surrounds and supports the former by maintaining their relative positions, and conversely, the reinforcements impart their special mechanical and physical properties to enhance the matrix properties [1]. With their rapid development and because of their advantages in good processibility and high mechanical properties, polymers have gradually replaced many of the conventional materials as matrix of composites in various applications. In order to obtain high-strength, high-modulus, and light-weight composites used in harsh loading conditions such as aerospace components, anti-bullet, high temperature resistance, etc., strong and light reinforcing fibers such as Kevlar, carbon fiber, ultrahigh-molecular-weight polyethylene fiber and glass fiber are always selected to suit the requirements [5]. Provided the fibers are mechanically well attached to the matrix, they can greatly improve the overall properties of composites. Recently, fiber-reinforced composite materials have increasingly gained popularity in high-performance materials.

Carbon nanotubes (CNTs) as one of the strongest and stiffest materials in terms of tensile strength and elastic modulus in nature have received much attention since their discovery by Iijima in 1991 [6]. Their excellent mechanical properties result from the covalent sp^2 bonds formed between the individual carbon atoms. It has been shown that CNTs are very strong in the axial direction, Young's modulus on the order of 270–950 GPa and tensile strength 11–63 GPa [7]. Furthermore, CNTs as one-dimensional materials possess some basic characteristic and advantages of fiber, which have inspired interest in using CNTs as a filler in polymer-based composites to obtain ultra-high performance structural materials with enhanced mechanical properties [8, 9]. A lot of efforts have been made to explore CNTs/polymer composite materials in both academy and industry. The structure, morphology, mechanical properties, and possible applications of these composite materials have been extensively investigated with some very promising results. They have been proven to be very effective fillers in polymers.

However, CNTs have large specific surface area, bending fiber-like shape, and strong van der Waals interactions which are easy to make the CNTs agglomerate and entangled, and difficult to be dissolved in water or organic solvents, or disperse in polymer [10]. The agglomeration of CNTs will lead to difficulties of stress transfer from matrix to the reinforced materials CNTs efficiently, and adversely lower the mechanical properties of the CNTs/polymer composite. So, how to enhance the dispersibility of CNTs in polymer matrix has been one of the most concerns in the field of CNTs reinforced polymer-based composite materials. Therefore, functionalization of CNTs is extremely important for their dispersion, stress-transfer, and potential applications in polymer composites [11]. In this chapter, we will focus on the

dispersibility of CNTs in polymer matrix through enhancing the interaction between CNTs and polymer, the processing of the composites, and the mechanical properties of the composites.

2. Dispersion of CNTs in polymers

Dispersity of CNTs in polymer and the stress transfer from the matrix to CNTs have significant effects on reaching optimum mechanical properties for CNTs/polymer composites. Only if CNTs disperse homogeneously in polymer matrix, effective stress transfer in the whole composite materials will be guaranteed; conversely, poor dispersity of CNTs in polymer matrix will lead to poor stress transfer, which not only cannot play their role in increasing mechanical properties but also can possibly weaken the original properties of the matrix. Therefore, the reinforcement of CNTs to polymer matrix is to great extent dependant on the dispersity of CNTs in the matrix.

To improve the dispersity of CNTs has two approaches: macroscopical mechanical mixing and functionalizing CNTs to build interaction between the interfaces of CNTs and polymer matrix. The interaction through bonding has another significant effect, that is, strengthening stress transfer effect. Obtaining a good dispersion of CNTs in the polymer matrix is very challenging. Ultrasonication, physical or chemical functionalization are common to achieve a good dispersity of CNTs in polymer matrix with enhanced mechanical properties.

2.1. Ultrasonic dispersion

Ultrasonication generates alternating low-pressure and high-pressure waves in liquids, causing high-speed impinging liquid jets and strong hydrodynamic shear-forces. So, ultrasonic device can be used as a high-speed mixer and agitator [12]. Ultrasonication is a common tool used to break up CNTs agglomerates in solution, but pure ultrasonication treatment of CNTs is not common, for the dispersion effect is not so satisfactory: some of CNTs re-aggregate or some of them deposit in a short period of time once sonication stops. **Figure 1** shows the photos of MWCNTs aqueous solutions in different standing time after sonication. The solutions sonicated 20 min, 1 hr and 2 hr all deposited after standing 30 min.

Generally, ultrasonication of CNTs always combines with application of surfactants to obtain better dispersion effect: ultrasonication is used to disperse CNTs, and surfactants are used as stabilizers. Sodium dodecyl sulfate (SDS) [13, 14], dodecyl benzene sulfonic acid (DBSA) [15, 16], and sodium dodecyl benzene sulfonate (SDBS) [17] are commonly used as surfactants. The process is simply that CNTs mix with surfactants and the mixture are then sonicated. During sonication, CNTs are gradually exfoliated and disentangled from aggregates and bundles and

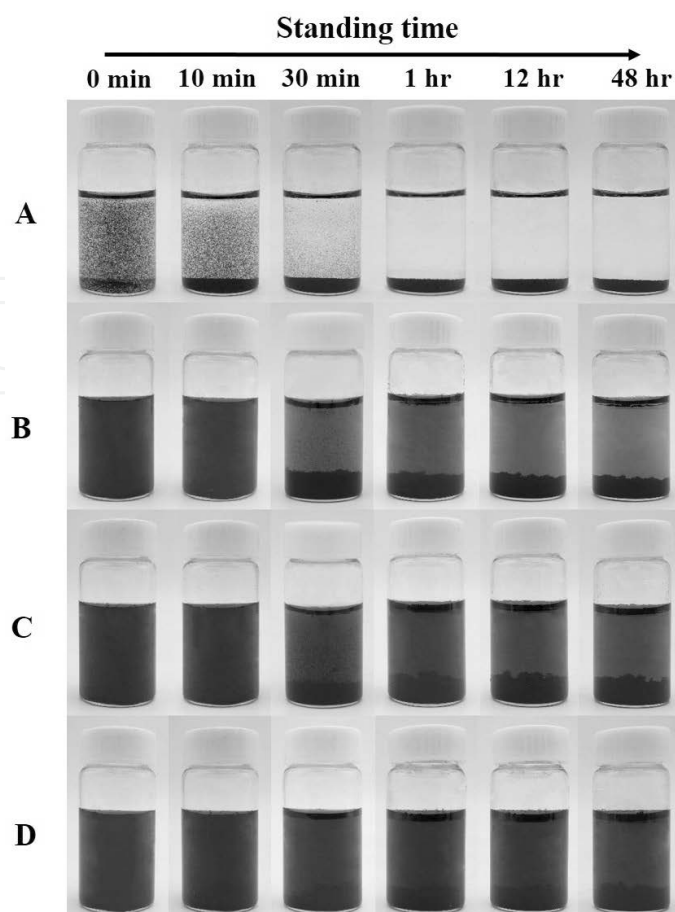


Figure 1. Digital images of MWNTs aqueous suspensions after ultrasonication and standing for different time. Ultrasonication time: A. 0 min; B. 20 min; C. 1 hr; D. 2 hr.

stabilized by surfactants. **Figure 2** shows the photos of MWCNTs aqueous solutions added SDBS in different standing time after sonication. Clearly, the addition of SDBS distinctly improves the dispersity and stability of MWCNTs in water.

CNTs dispersions often foam heavily during ultrasonication, and these foams consequently reduce the dispersion efficiency. This bubble problem can often be solved by adding antifoam agents such as oligomers of polyether and polysiloxane to eliminate air layers or to reduce foams [18].

The destruction of CNTs in suspensions by use of ultrasonication was described as early as 1996. Ultrasonic treatment of CNTs causes a considerable amount of defects including buckling, bending, and dislocations in the carbon structures [19]. So suitable ultrasonication time and energy output have to be considered before CNTs are treated.

2.2. Covalent functionalization

Covalent functionalization of CNTs can greatly improve the stress transfer from the matrix to CNTs besides dispersity, but it usually introduces structural defects to the surface of CNTs. The functionalization of CNTs can be achieved by either direct introduction of oxygen

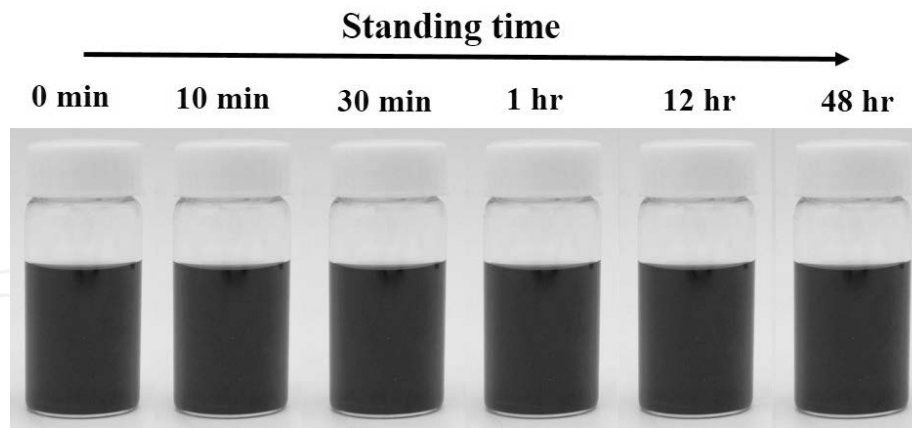


Figure 2. Digital images of MWNTs aqueous suspensions changed with the standing time after ultrasonication for 10 min in the presence of SDBS.

containing groups to the sidewalls of CNTs by acid treatment, or on this basis further introduction of polymer chains through its chain ends directly reacting with the oxygen containing groups on CNTs (*ex situ*), or commonly through the monomers reacting with the groups on CNTs to introduce polymer chains, that is, *in situ* polymerization.

2.2.1. Acid treatment

The most common procedure used for covalent attachment of oxygen containing reactive groups to CNTs is the treatment with inorganic acids. Usually, the nanotubes are treated through being refluxed with a mixture of concentrated nitric and sulfuric acid with the ratio of volume 1 to 3 although their concentrations may be slightly different [20–23]. However, accidentally, the ratio of the acids changes, for example, CNTs were oxidized with the mixture of 83 mL of sulfuric acid and 133 mL of nitric acid (65%) [24]. Concentrated nitric acid [25] and the mixture of hydrogen peroxide and sulfuric acid (vol = 1:4) [26] are also selections for oxidizing CNTs. These oxidative treatments usually result in shortening of the CNTs' length and formation of surface reactive groups, such as hydroxyl, carbonyl, and mainly Carboxyl. Furthermore, the inorganic impurities of the Al-Fe catalyst used in the preparation of CNTs are solubilized by the acids and the concentration of the impurities is gradually decreased with treatment time [20, 23, 26, 27]. It has been shown that acid functionalized CNTs has good dispersibility in water and organic solvents, and the carboxylic functional groups give a stronger nanotube-polymer interaction, leading to enhanced values in mechanical properties of the CNTs/polymer composite [27, 28]. Acid-treated MWCNTs show homogeneous dispersion and scarcely any precipitates are observed. Because the sidewalls of the MWCNTs carry more dissociated carboxyl groups after oxidization, the nanotubes can stabilize via an electrostatic stabilization mechanism [29]. Saito et al. consider that this shortened MWCNTs after acid treatment could be dispersed in the polar solvents such as ethanol, DMSO, and DMF more easily than the crude MWCNTs. Moreover, these dispersion liquids of the MWCNTs are stable without aggregation for more than one month. This phenomenon can be ascribed to the

reduction of their length and the effect of the solvation brought by the introduced hydrophilic group, i.e., the carboxyl group [20].

At moderate temperature, only little sidewall damage happens with the increase of the acid treatment time, whereas at high temperature, much shorter nanotubes are resulted [26].

Being different from reaction of CNTs with concentrated acids, carboxylic functional groups can be introduced on the CNTs through a photosensitized dry oxidation induced by ultraviolet radiation [30, 31]. Organic acid could also be used as an oxidative, for example, trifluoroacetic anhydride/H₂O₂ (3:1, 60% H₂O₂) were used to functionalize single-walled carbon nanotubes (SWCNTs), in addition to oxygen-based functional groups, trifluoroacetic groups were covalently attached to the SWCNTs. Moreover, these modified SWCNTs were shortened into ca. 300 nm in length during functionalization, resulting in exfoliation of nanotube ropes to yield small bundles and individual nanotubes. The resultant SWCNTs were easily dispersed in polar solvents such as dimethylformamide, water, and ethanol [32].

2.2.2. Grafting macromolecular chains

Polymer-functionalized CNTs, compared to the unmodified ones, usually show relatively good dispersibility in organic solvents and high compatibility with polymer matrix in CNTs/polymer composites. The functionalized CNTs containing active groups (predominantly carboxyl) can further cooperate with polymers through esterification or amidation reactions between the groups on the CNTs and those on the polymer chains, [21, 33, 34] and conversely, treated or functionalized macromolecular chains can also directly attach on pristine CNTs [29, 35, 36].

Most of the approaches require the pre-modification of CNTs to introduce functional groups to CNTs surfaces, which can react to the groups on polymer chains, leading to the chains grafted onto CNTs. For example, after CNTs are acidic functionalized, polyvinyl alcohol (PVA) grafts to the tubes through esterification as shown in **Figure 3**. PVA-functionalized CNTs are soluble in the same solvent of neat PVA, thus allowing the intimate mixing of the nanotubes with the matrix polymer, so the functionalization of CNTs by polymer is an effective way for the homogeneous nanotube dispersion to obtain high-quality polymeric carbon nanocomposite materials [37]. Grafting different kind of polymer onto CNTs from the matrix polymer which is however compatible with the former polymer is another example. Massoumi et al first prepared carboxylated MWCNTs by acid treatment, then poly(ethylene glycol)-grafted MWCNTs (PEG-MWCNTs), whereas finally obtained PVA/MWCNTs-PEG nanocomposite and PVA/starch/MWCNTs-PEG nanocomposite [21].

Sometimes, polymer chains are not necessary to graft onto CNTs, but only some groups which are well compatible with polymer are needed to connect with CNTs. For instance, amino groups grafted MWCNTs possess good compatibility with the matrix PEEK, so simply by mixing the MWCNTs with PEEK, the composite with significantly increased storage modulus, glass transition temperature, and friction coefficient was prepared [27].

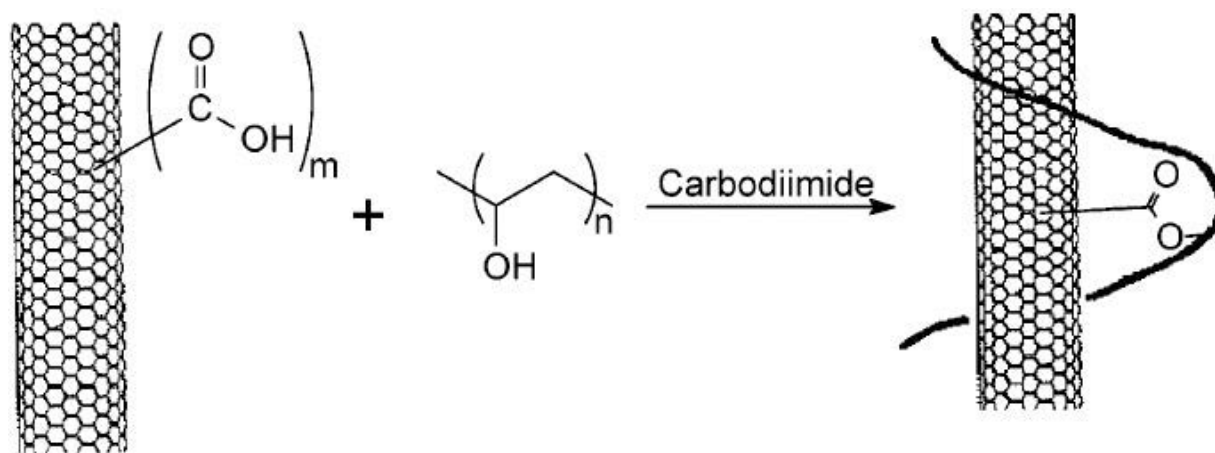


Figure 3. Schematic of functionalized CNTs with PVA in carbodiimide-activated esterification reactions [37].

On the other hand, the use of pristine or unmodified CNTs in the preparation of polymer functionalized CNTs has shown several advantages such as preventing the CNTs from damage. It is reported that polymer grafted CNTs have better reinforcement than pristine CNTs. This kind of polymer functionalized CNTs can be realized through free-radical polymerization, ozonization of polymer, Friedel-Crafts reaction and etc. [29, 35, 36, 38]. Through a radical coupling reaction involving polymer-centered radicals, polystyrene and poly[(*tert*-butyl acrylate)-*b*-styrene] are used to functionalize shortened SWCNTs [36]. Ozonization of polymers produces alkylperoxide and hydroperoxide groups in polymer chains, which can decompose into radicals by heating. As the radicals are reactive toward the sp^2 hybrid carbons of CNTs, the ozonized polymer chains can be grafted onto the CNTs through the reaction between CNTs sidewalls and the radicals of polymer chains as shown in **Figure 4** [35].

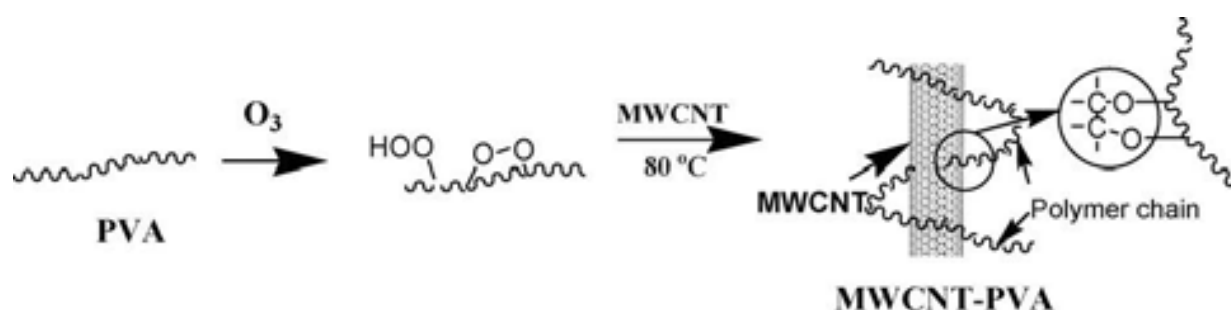


Figure 4. Reaction mechanism of ozonized PVA grafting onto MWCNT [35].

After Friedel-Crafts reaction has been successfully applied for the chemical functionalization of CNTs through grafting small molecules onto CNTs [39, 40], researchers are increasingly interested in application of Friedel-Crafts for functionalization of CNTs using polymer. The approach is more feasible than the traditional carboxylation because the surface treatment of

CNTs before the grafting of polymer chains to the CNTs is not needed. Wu et al. [41] successfully functionalized MWCNTs with high percentage of grafting via Friedel-Crafts alkylation. The PVC-grafted MWCNTs could be dispersed well in organic solvent and the dispersion was quite stable. Moreover, it has been shown that Friedel-Crafts alkylation is a less destructive or nondestructive reaction for efficient dispersion and functionalization of CNTs.

In our previous work [29], PVA was grafted onto MWCNTs by Friedel-Crafts alkylation reaction with anhydrous aluminum chloride (AlCl_3) as a catalyst. MWCNTs, PVA, and DMSO were first mixed and dissolved, then the catalyst AlCl_3 was added, and the mixture reacted and terminated. The reaction product was centrifuged and washed with distilled water until no AlCl_3 could be detected, and finally, the functionalized MWCNTs (f-MWCNTs) were obtained. In the experimental procedures, AlCl_3 reacted with the hydroxyl on PVA and formed carbocations, which then attacked the benzene rings on MWCNTs surface due to their inherent electrophilicity. Subsequently, the PVA chains were grafted onto MWCNTs as depicted in **Figure 5**.

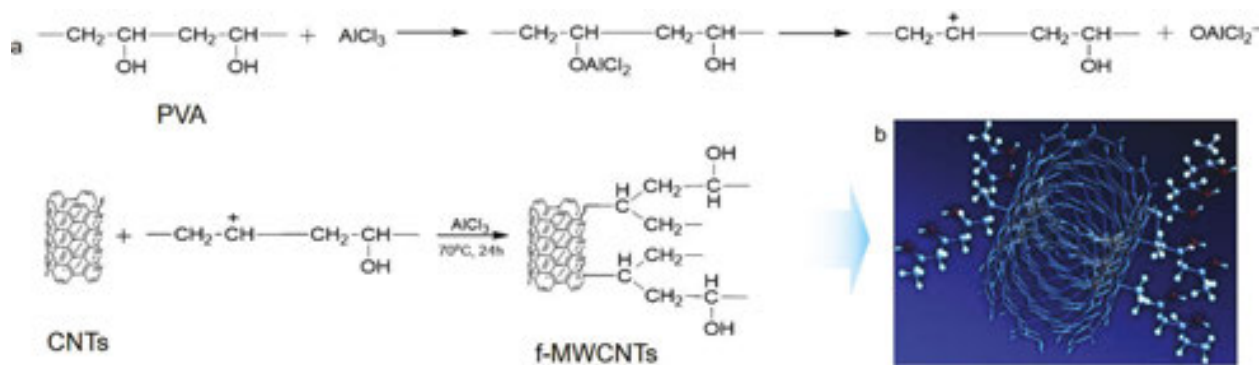


Figure 5. (a) Functionalization of MWCNTs with PVA by Friedel-Crafts alkylation reaction and (b) cartoon depicting of f-MWCNTs structure [29].

Figure 6 shows TEM images of pristine MWCNTs (p-MWCNTs), f-MWCNTs and carboxyl group functionalized MWCNTs (c-MWCNTs) treated by a mixture of nitric and sulfuric acid in DMSO/ H_2O . p-MWCNTs are aggregate obviously as shown in **Figure 5a**, whereas f-MWCNTs are homogenously dispersed without distinct destructive structural damages (**Figure 5b**). In comparison, c-MWCNTs present serious fragmentation (**Figure 5c**). It is clear that functionalization of MWCNTs by Friedel-Crafts alkylation reaction is relatively much gentler than acid treatment. Images of single p-MWCNT and f-MWCNT tubes clearly show that the surface of the p-MWCNT is clean and smooth, while the surface of f-MWCNT is surely wrapped with PVA chains (**Figure 5d** and **5e**).

UV detector can be used to measure the transmittance of MWCNTs in the supernatant, which is used to characterize the dispersibility of the MWCNTs, that is, the higher the transmittance, the worse the dispersibility. The UV-vis spectra of the samples after storage for different periods of time are recorded as shown in **Figure 7**. For p-MWCNTs, the transmittance is almost

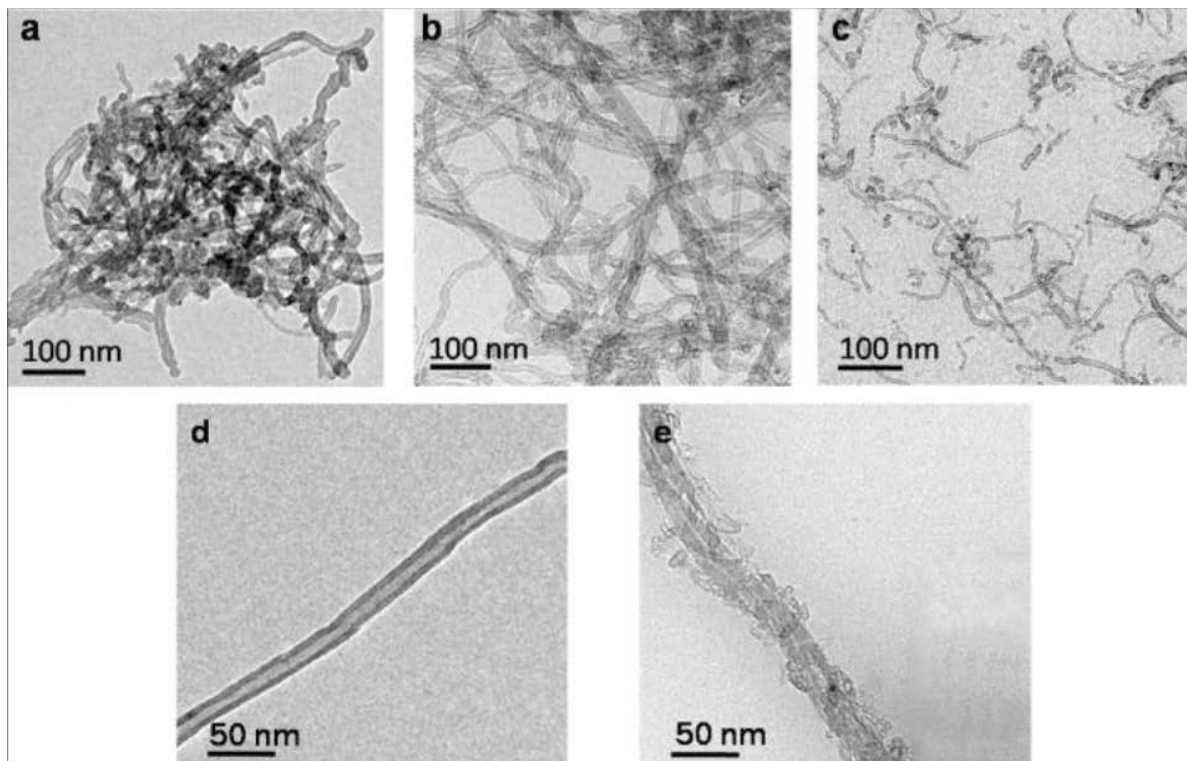


Figure 6. TEM images of (a) p-MWCNTs, (b) f-MWCNTs, (c) c-MWCNTs, (d) single p-MWCNTs, and (e) single f-MWCNTs in DMSO/H₂O [29].

100% after the first three days, indicating that the MWCNTs are relatively rapidly precipitated. However, the transmittance of modified MWCNTs, whatever f-MWCNTs or c-MWCNTs, increases only about 20% in the first three days and keeps stable in the following days, proving their good dispersibility which is apparently related with the interaction between PVA and MWCNTs.

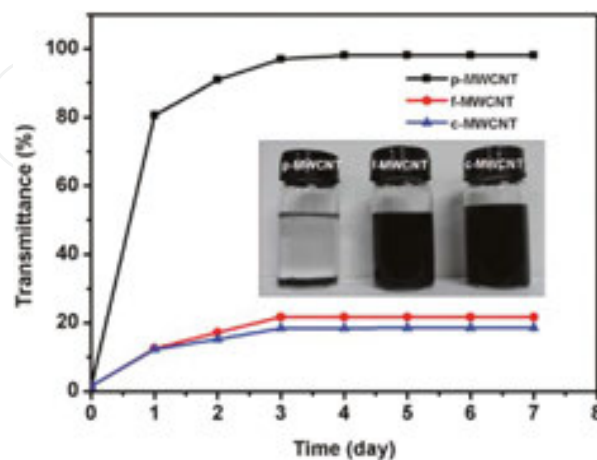


Figure 7. UV-vis transmittances of p-MWCNTs, f-MWCNTs and c-MWCNTs. The content of MWCNT is 0.05 wt%. Inset: image of the dispersed samples after 7 days [29].

2.2.3. In situ polymerization

The main feature of in situ polymerization is that it enables polymer macromolecules from the starting material of monomers to graft onto the convex walls of CNTs, which can provide a better nanotube dispersion and formation of a strong interfacial interaction between the nanotube and the polymer matrix. In addition, in situ polymerization is a very convenient technique that allows the preparation of composites with high nanotube loading and provides very good miscibility with almost any polymer type [8, 38]. It is believed that this simple in situ polymerization method is in general scalable for large-scale production of CNTs/polymers composites [42]. Step polymerization is often applied to prepare CNTs reinforced polymer nanocomposites by in situ polymerization of monomers [43, 44]. In the in situ grafting reaction, CNTs first have to graft reactive groups on the side wall, which then react with reactive groups of monomers to form covalent bond. For example, synthesis of MWCNTs-reinforced polyimide (PI) nanocomposites by in situ polymerization of monomers is as follows: MWCNTs associated with acyl groups were formed and then participated in the reaction with the monomers through the formation of amide bonds. The mechanical properties of the resultant MWCNTs-PI nanocomposites were significantly enhanced at a very low loading (0.5 wt. %) as shown in **Figure 8** [45].

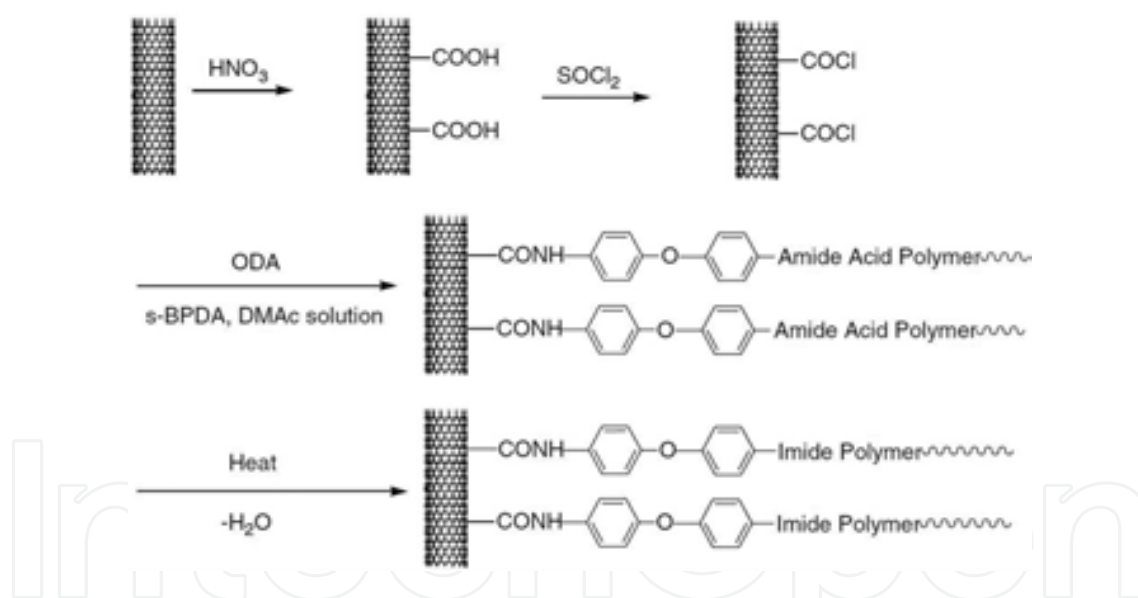


Figure 8. Outline of the preparation of MWNT-polyimide nanocomposite films [45].

MWCNTs modified by functional amine groups via ozone oxidation followed by silanization were incorporated into a vegetable oil-based polyurethane (PU) network via in situ polymerization to prepare CNTs/PU nanocomposites. Storage modulus, glass transition temperature, Young's modulus, and tensile strength of the nanocomposites increased with increasing the MWCNTs loading up to 0.8%. However, increasing the MWCNTs content to 1.2 wt % resulted in a decrease in thermomechanical properties of the nanocomposites [38]. A SWCNTs/nylon 6 graft copolymer was prepared by in situ polymerization of caprolactam with SWCNTs possessing carboxylic acid and amide functionalities. The results show that SWCNTs with a

higher concentration of carboxylic acid groups can form a stronger SWCNTs-polymer interfacial interaction, which consequently improves the mechanical properties [43]. Diamine and dianhydride were reacted with carboxylated MWCNTs in situ to give a homogeneous MWCNTs/poly(amic acid) mixture and then to give a series of MWCNTs/PI composites after imidization. Tensile tests show the elastic modulus and the yield strength of the composites increase, and the failure strain decreases [44].

Besides, in situ polymerization can also be realized through radical polymerization [46]. The composites of f-MWCNTs/polyacrylonitrile (PAN) copolymer were prepared by in situ solution polymerization. Acrylonitrile (AN) and acrylamide (AM) dissolved in DMSO/H₂O solvent and f-MWCNTs mixture suspension was initiated by AIBN, reacted and finally PAN grafted MWCNTs were obtained. Compared with p-MWCNTs as shown in **Figure 9a**, the f-MWCNTs (**Figure 9b**) are not destructed after the functionalization and have a more compact morphology. As shown in **Figure 9c** and **9d**, p-MWCNTs settle obviously, whereas f-MWCNTs are disentangled and dispersed uniformly.

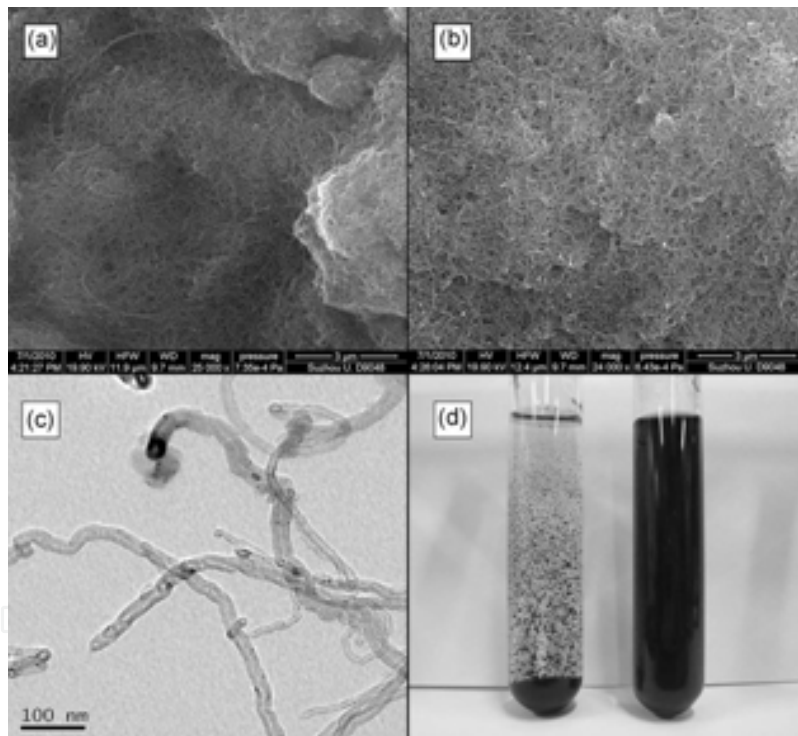


Figure 9. SEM images of (a) p-MWCNTs (b) f-MWCNTs, TEM images of (c) f-MWCNTs, and (d) photograph of p-MWCNTs (left) and f-MWCNTs (right) [46].

2.3. Noncovalent functionalization

Functionalization of CNTs by chemical processes not only causes damage to different extent which will restrict the reinforcement of the CNTs but also is difficult to be commercially available due to the complicated operations. Noncovalent modification is now adding its appeal for many researchers since it is more feasible than covalent modification [47, 48]. The

dispersion of CNTs noncovalent modified in polymer is generally achieved by interaction of secondary van der Waals bonding or hydrogen bonding among polymer, dispersant, and CNTs surface [49]. Non-covalent treatment has the possibility of adsorbing various groups on CNTs surface without disturbing the π system of the graphene sheets of CNTs. So the non-covalent surface treatment by surfactants or polymers has been widely used in the preparation of both aqueous and organic solutions containing high weight fraction of well dispersed CNTs. Generally, ionic surfactants are suitable for CNTs/water-soluble while nonionic surfactants are used in the case of organic solvents [50].

2.3.1. Synthetic surfactant

2.3.1.1. Ionic surfactants

Several synthetic ionic surfactants are reported to efficiently disperse bundled nanotubes into suspensions of individual nanotubes, particularly for SWCNTs [13, 51, 52]. For example, SWCNTs could be suspended in aqueous media as individuals surrounded by SDS adsorbed phase [53]. Diouri et al. prepared CNTs/SDS aqueous solution with the help of ultrasonication, then the solution mixed with PVA aqueous solution to achieve the CNTs/PVA composites with required CNTs loadings [14]. An extensive all-atom molecular dynamics study on the morphology of SDS surfactant aggregates adsorbed on SWCNTs has been carried out. The calculations reveal that the nanotube diameter is the primary factor that determines the morphology of the aggregates [54]. SDS makes CNTs have satisfied dispersibility, but compared with oxidized CNTs, CNTs stabilized by surfactant SDS exhibit weaker interactions with the matrix PVA [55].

SDBS could be used to solubilize high weight fraction SWCNTs in water by the nonspecific physical adsorption. A series of anionic, cationic, and nonionic surfactants and polymers have been tested for their ability to suspend individual SWCNTs by Moore et al [49]. For the ionic surfactants, SDBS gives the most well resolved spectral features, while for the nonionic systems, surfactants with higher molecular weight suspend more SWCNTs and have more pronounced spectral features. The dispersing power of a range of surfactants has been explored by Islam et al. [13]. The results show that NaDDBS (i.e. SDBS)-CNTs dispersions are by far the most stable. The adsorption and the self-assembly of SDBS on SWCNTs are investigated via all-atom molecular dynamics simulations [56]. The results show that the self-assembly of SDBS depends on the surface coverage but to a small extent on the SWCNTs diameter, and controlling the morphology of the surfactant aggregates will lead to the selective stabilization of aqueous CNTs dispersions. The aggregation kinetics of SWCNTs and MWCNTs, initially dispersed by SDBS, are evaluated. The results show that the CNTs could be effectively suspended in aqueous solution using the surfactant (SDBS), and that increased electrolyte concentrations will induce aggregation [57].

Regarding cationic surfactant, Regarding cationic surfactant, dodecyl trimethylammonium bromide (DTAB) could form exceptionally stable SWCNTs dispersions [58]. Cetyltrimethylammonium bromide (CTAB) modified CNTs in H_2SO_4 aqueous solution assisted by sonication

led to uniform dispersion of the embedded CNTs in polydiphenylamine (PDPA) and a reinforced PDPA nanocomposite. [59].

The ratio of surfactant to CNTs is sure to have effect on the dispersibility of CNTs, but the concentration of the surfactant is found to be a more important factor on the resulting dispersibility than the ratio [51].

2.3.1.2. Non-ionic surfactant

Another fraction of surfactants is nonionic surfactants such as polyoxyethylene 8 lauryl ($\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{-CH}_2)_7\text{OCH}_2\text{CH}_3$), nonylphenol ethoxylate (Tergitol NP-7), polyoxyethylene octyl phenyl ether (Triton X-100), Tween-60, polysorbate-80 and so on [50, 52, 60–62].

It is clearly seen that after the surface treatment by Triton X-100, large agglomerates and closely packed CNTs are significantly loosened without breakage or shortening of CNTs. The surfactant-treated CNTs/epoxy nanocomposites exhibit much better performances including storage modulus, flexural strength, and flexural modulus than those without treatment for CNTs. The above observations are attributed to the 'bridging' effects between the CNTs and epoxy introduced by the hydrophobic and hydrophilic segments of the nonionic surfactant [60]. With the surfactant polyoxyethylene 8 lauryl as an additive, the nanotubes are dispersed better. Through the introduction of only 1 wt. % CNTs in epoxy, the glass transition temperature increases from 63 to 88°C and the elastic modulus increases by more than 30% [63]. Some polymers such as PEO-PPO-PEO triblock can also enhance the suspendability of CNTs. This is easily explained with steric stabilization by the adsorbed surfactant or polymer layer [49].

A molecule with a π -conjugated backbone built from aromatic thiophene and dialkoxyphe-nylene units and substituted imidazolium groups (TPO) is recently designed to obtain ultra-stable SWCNTs dispersion in aqueous medium. TPO provides synergistic π - π stacking, charge transfer and cation- π interactions. The dispersions even prepared using very low concentration of TPO (0.5 mg/mL) or SWCNTs (0.02 mg/mL) show long-time stability for twelve months [64]. Blanch et al. [51] systematically studied into the ability of some well-known surfactants and polymers to disperse SWCNTs. The smaller ionic surfactants are generally more effective dispersants than larger polymer and surfactant molecules. However, an effective dispersant for the CNTs by a certain technique may not necessarily perform well by a different method. Optimal concentrations for dispersion of the CNTs are determined for the anionic surfactants SDBS and DOC as well as some nonionic such as Triton X-405, for example, the optimal surfactant concentrations for CNTs dispersion are approximately 1.6% (DOC), 0.5% (SDBS), and 3% (Triton X-405). Exceeding the optimum concentrations is detrimental as it leads to agglomeration of the CNTs. As stated above, SDBS is excellent in dispersing CNTs, whereas SDS has turned out to be the most promising surfactant out of the following four sets of surfactants: SDS, CTAB, SDS + CTAB and Tween, for the effective dispersion of hydrophobic MWCNTs in rubber latex [62].

2.3.2. Non-synthetic surfactants

Recently, natural molecules as surfactants have been used in functionalization of CNTs by physical interaction. Liu et al. [65] described a non-destroyable surface decoration of CNTs with biopolymer chitosan via a controlled surface-deposition and cross-linking process. Nakamura et al. [66] discovered that a green tea solution could dissolve SWCNTs without aggregation in an aqueous medium. In our previous study [67, 68], the strength and modulus of PVA fibers are extremely increased by introduction of MWCNTs functionalized with natural surfactants. π - π stacking between the benzene rings of surfactants and CNTs is the major interaction between CNTs and the surfactants.

2.3.2.1. Tea polyphenols

As non-covalent modification, using green tea to disperse SWCNTs in water was first reported by Nakamura et al. [66] and now has drawn a great deal of attentions. Tea polyphenols (TP) is the extract powder from tea, which is biocompatible and biodegradable. TP-functionalized MWCNTs and the composites with PVA were prepared in our previous work [67]. TP dissolved in DMSO/H₂O (vol = 3:1) was mixed with MWCNTs (MWCNTs:TP wt. = 1:3). After the mixture was sonicated and homogenized, the prepared PVA solution was poured into the dispersion of MWCNTs/TP and stirred to form MWCNTs/TP/PVA dispersion. **Figure 10** illustrates the interaction between PVA and MWCNTs: π - π interaction between MWCNT and TP, and hydrogen bond between TP and PVA.

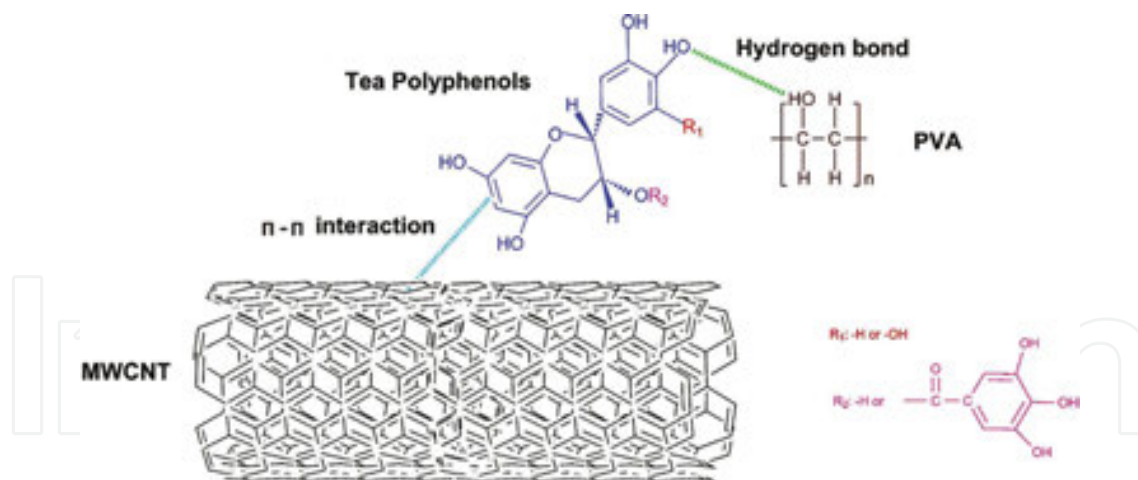


Figure 10. Structure of PVA/MWCNTs composites with TP as a surfactant [67].

As shown in **Figure 11a**, TEM images of pristine MWCNTs in DMSO/H₂O display apparent aggregation and entanglement, while MWCNTs modified by TP in DMSO/H₂O are separated and homogeneously distributed (**Figure 11b**). After adding PVA, the MWCNTs are still well distributed as shown in **Figure 11c**. Because the non-covalent interactions exist between MWCNTs and PVA through the 'bridge' effect of TP, TP-functionalized MWCNTs can be well dispersed in PVA, leading to a stable dispersion with the help of sonication and mechanical

homogenization. As further evidences, the dispersions in the bottles in **Figure 11** show the similar results to the TEM images.

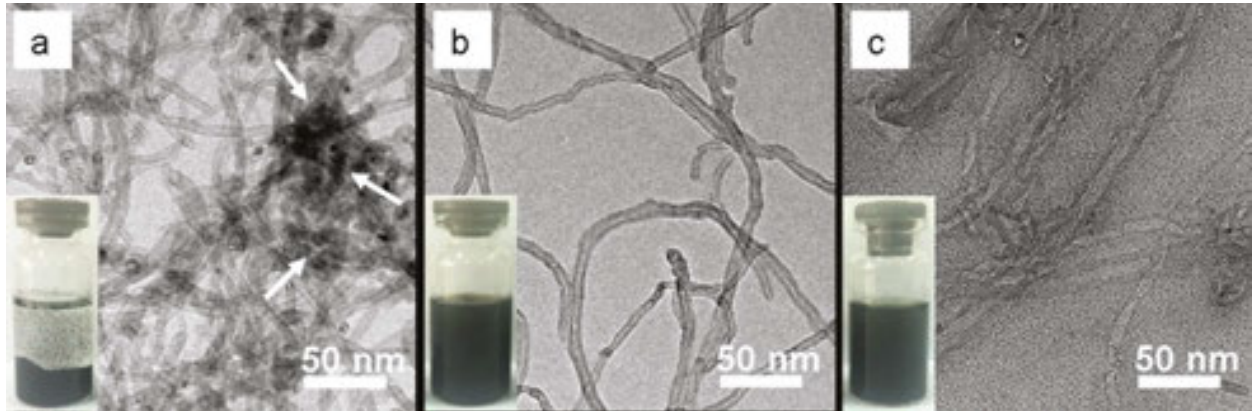


Figure 11. TEM images of (a) MWCNTs/DMSO/H₂O, (b) MWCNTs/TP/DMSO/H₂O, (c) MWCNTs/PVA/TP/DMSO/H₂O. MWCNTs:TP (wt) is 1:3, and the concentrations of MWCNTs are 0.2 wt.% (insets are MWCNTs dispersions in the corresponding media after staying 2 hr) [67].

2.3.2.2. Rosemary acid

Rosemary acid (RosA) is an extract from rosemary, an evergreen shrub with aromatic linear leaves, which is green, non-toxic and environment-friendly. Like TP, it possesses the conditions: π - π stacking between RosA and CNTs and hydrogen bonds between RosA and polymer matrix. Besides, in comparison with TP, its more hydroxyl groups and added carboxyl group provide CNTs more chances to interact with polymer. **Figure 12** shows the illustration of the interaction between PVA and RosA-modified MWCNTs (m-MWCNTs). π - π stacking exists between MWCNTs and RosA on m-MWCNTs, and hydrogen bonds are supposed to be formed between hydroxyl groups of RosA and PVA, so that PVA and MWCNTs can be connected.

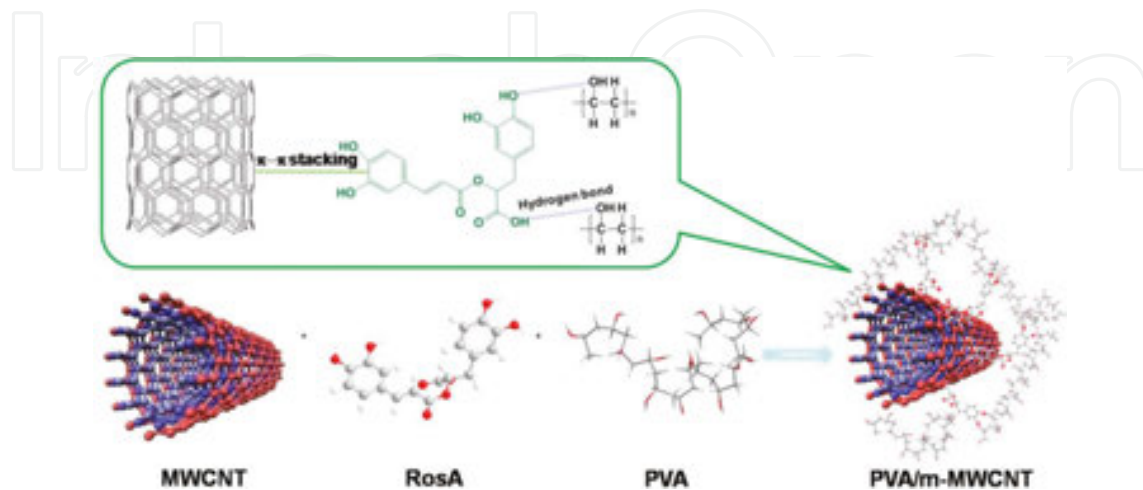


Figure 12. Schematic illustration of the structure of PVA/m-MWCNTs composites [68].

As shown in **Figure 13a**, pristine MWCNTs (p-MWCNTs) exhibit almost 100% UV transmittances after staying one day, indicating poor dispersibility in the solution, while as the introduction of RosA, the transmittance quickly decreases, proving obviously improved dispersibility of m-MWCNTs. Apparent aggregation of p-MWCNTs can be seen in **Figure 13b**, whereas m-MWCNTs are clearly separated and homogeneously distributed as shown in **Figure 13c**. The inset picture provides much intuitive evidences for the dispersibility of p-MWCNTs and m-MWCNTs.

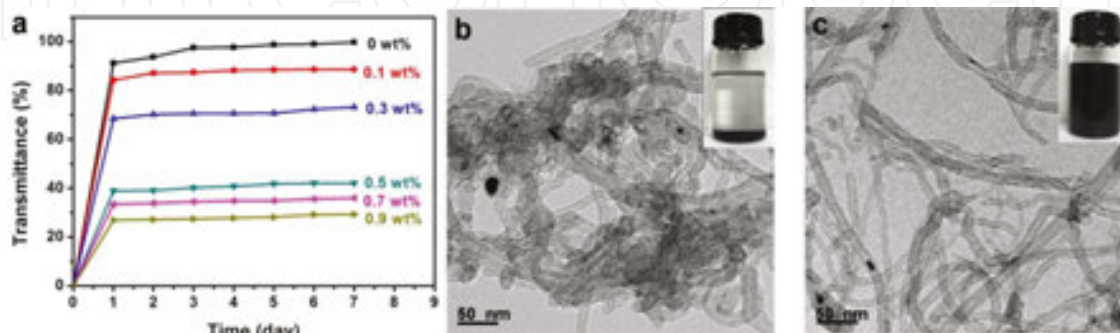


Figure 13. UV-vis transmittances of the MWCNTs dispersions in DMSO/H₂O (vol ratio = 3/1) with different concentration of RosA marked on the ends of the curves (a) and TEM images of p-MWCNTs, (b) m-MWCNTs (c) in DMSO/H₂O. The inserts are the corresponding MWCNTs dispersions after staying for 7 days [68].

3. Processing of CNTs/polymer composites

Polymeric materials mainly include plastics, fiber, and rubber (elastomer), so they can be the representatives as matrices to composite with CNTs. This section will briefly describe the fabrication of the CNTs/polymer composites based on three kinds of typical synthetic materials: fiber, film, and elastomer.

3.1. Composite fiber

Fiber processing has its own advantages, one of which is that it can be drawn in large draw ratio. That means it has higher possibilities to enhance mechanical properties of the composites through the orientation of related structural units. Ideal CNTs fibers, comprising axially aligned and highly packed CNTs, could have much higher specific modulus and specific strength than those of commercial carbon and polymeric fibers, but so far the modulus and strength values are still low [69]. To date, no breakthrough has been reported in the specific strength and specific stiffness of CNTs fibers. The outstanding mechanical and physical properties of individual CNTs have provided the impetus for researchers in developing high-performance fiber polymeric materials based on CNTs because they can be handled much more conveniently than the individual CNTs [70].

3.1.1. Solution spinning

Manufacturing CNTs-based fibers commonly uses solution spinning, which can be divided into two processes: dry spinning during which the solvent in fiber forced from the spinning hole is removed by evaporation by heating, and wet spinning during which the solvent in fiber is removed by coagulation in another fluid. In general, mechanical properties of neat CNTs fibers prepared by dry spinning are far higher than those of the fibers prepared by wet spinning [71]. However, dry spinning has disadvantages such as difficulties in process scalability and mass production, which thus affects the structural characteristics and physical properties of CNTs-based fibers, while the wet spinning is a relatively simple technique with advantages of commercially ready availability [72, 73]. So a number of researches have been conducted to make CNTs/polymer composite fibers by wet spinning. Vigolo et al. firstly reported the wet spinning of SWCNTs/PVA composite fibers via a coagulation method [74] and the composite fibers prepared by wet spinning were measured to have 230 MPa of tensile strength and 40 GPa of Young's modulus. Dalton et al. [75] manufactured mechanically strong SWCNTs/PVA gel fibers by using a modified coagulation-based wet spinning method. The composite fibers had 1.8 GPa of tensile strength and 80 GPa of Young's modulus. Fibers with high loading, as high as 23 wt% of SWCNTs, were successfully produced through wet spinning [76].

Besides, a dry-jet wet spinning is generally used to prepare high strength and high modulus fibers, and it is expected to use this spinning process to produce high-performance polymer/CNTs composite fibers. In our previous work [29, 67], f-MWCNTs/PVA composite dispersion was forced through a spinning hole into an air gap of 5 mm and then into cold methanol coagulating bath (**Figure 14a**). Postdrawing was carried out in a tube oven between two 6.5-cm-diameter rollers at a temperature about 200°C and draw ratio 8–12. Postdrawing could lead to increased orientation and crystallization of the fibers and thus to improvement in both strength and modulus. The spinning dope was extremely uniform due to good dispersibility of MWCNTs in PVA, the fiber formation was quite easy to be controlled, and the drawn fibers

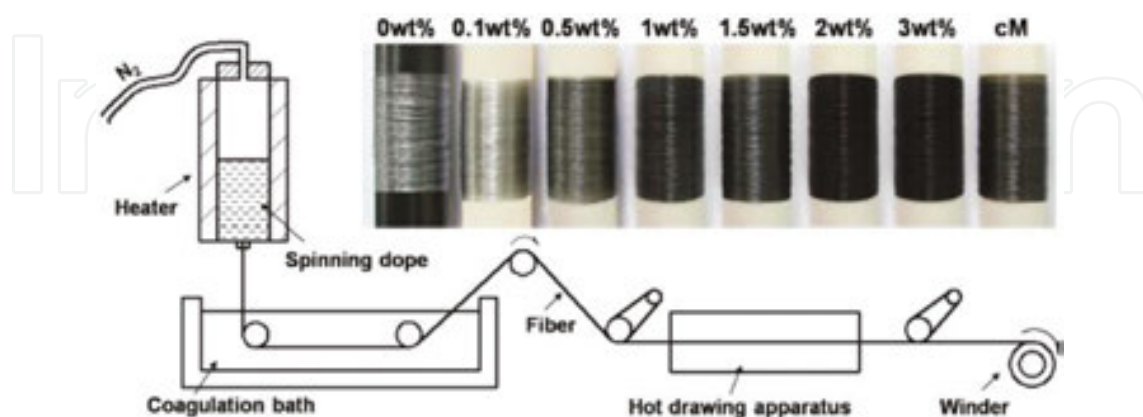


Figure 14. (a) Spinning apparatus for preparing PVA/f-MWCNTs composite fibers. (b) Photograph of the composite fibers with different f-MWCNTs loadings (marked on the tops) and cM represents the composite fiber with 0.5 wt% MWCNTs containing carboxyl groups [29].

were quite smooth and uniform at certain MWCNTs loadings (**Figure 14b**), and thus the fibers obtained expected mechanical properties.

A method for manufacturing sheath-core structured composite fibers was developed using wet spinning techniques as shown in **Figure 15**. The core portion of a fiber was prepared using CNTs solution while the sheath used a fiber-forming polymer such as PVA. The CNTs solution was injected into the inner nozzle and the PVA polymer solution to the outer nozzle. The inner and outer diameters of the spinneret were 0.3 and 0.5 mm. The interfacial contact between the core and sheath was found to be good and did not hinder the flexibility of the resulting fibers so they could be easily woven into fabric. The spinning technology used here is scalable and compatible with mass production methods in industry [77].

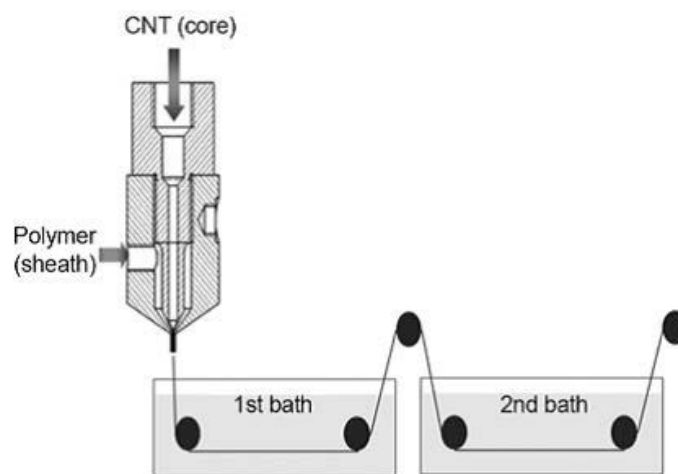


Figure 15. The wet spinning process used to produce the sheathcore structured CNT/PVA fiber [77].

Composite fibers can also be differently prepared through wet spinning. MWNTs solution was forced through a spinneret into a rotating bath of acidic PVA solution, the pH of which was 2 adjusted by adding concentrated hydrochloric acid. The MWNTs/PVA composite fibers were then collected in a water bath and drawn upward for drying. The toughness of the composite fibers is approx. $563 \text{ J} \cdot \text{g}^{-1}$ which exceeds by far the toughness of materials such as aramid or spider silk [24].

3.1.2. Melt spinning

Melt spinning is the simplest method for fiber manufacturing. If a polymer can be melted under reasonable conditions, its conversion to a fiber by melt spinning is preferred over the solution-spinning process, mainly as the former does not involve the use of solvents and the problems associated with their use, namely, their removal, recovery, the associated environmental concerns and the low spinning speeds [78]. Melt spinning is also a common approach used for preparation of CNTs/polymer composite fiber, but it is not well suited to make composite fibers containing a large fraction of CNTs. Indeed, the presence of CNTs results in a strong increase in the viscosity of the polymer, which makes the polymer containing CNTs extrusion and the fiber spinning particularly difficult. In contrast, wet spinning of CNTs/polymer solutions

allows inclusion of greater fractions of CNTs, provided that the nanotubes are homogeneously dispersed in the polymer solutions [79]. Moreover, the macromolecular chains and CNTs in the melt are seriously entangled, so to achieve high orientation of the chains and CNTs is extremely difficult, which hinders enhancement of the mechanical properties of the composite fiber.

The melt spinning of CNTs/polymer can generally be completed in following three steps. The melt-compounding of polymer and CNTs is conducted in a twin-screw extruder at a high CNTs concentration to firstly produce a masterbatch, then the masterbatch is diluted to the desired CNTs concentration by mixing with the desired amount of neat polymer, and finally, the mixture is melted and spun in suitable apparatus and the obtained as-spun fiber is drawn continuously or separately. The processing of CNTs/polymer composite is commonly needed to transfer to a screw extruder, and then the molten CNTs/polymer composite is forced through a spinneret with a constant-speed drive, which could be adjusted to modify the mass flow rate of the polymer. The spinning hole on the spinneret is a cylindrical capillary, which is generally less than 1 mm in diameter. The extruded thread is wound-up on a rotating package at a speed of several hundred or thousands meters per minute [80]. Sometimes, if melt spinning is in small scale and in low melt viscosity, a melting apparatus, piston-barrel system, such as capillary rheometer, can also be used (**Figure 16**) [81].

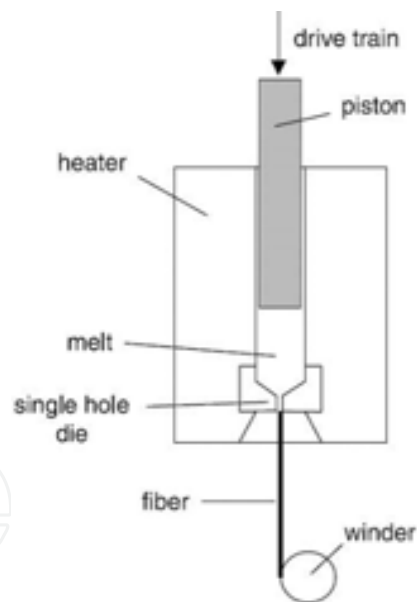


Figure 16. Schema of the piston type spinning device [81].

3.1.3. Electrospinning

Electrospinning is an electrostatically induced self-assembly process wherein ultra-fine fibers are produced. Recently, the electrospinning technique has also been used for the alignment of CNTs in a polymer matrix, leading to high-strength, high-modulus, and even high electrical conductivity. It has been established that electrospinning a polymer solution containing well-

dispersed CNTs leads to nanocomposite fibers with the embedded CNTs oriented parallel to the nanofiber axis due to the large shear forces in a fast fiber-drawing process [82].

Fiber collection methods for electrospinning can be divided into two classes: continuous filament wound on roller and felt piled by short fibers collected on nets or sheets. Commonly, the nanofibers are collected in felt due to ease of processing. For example, when MWCNTs/PAN dispersion in DMF was electrospun, a flat metal net covered in aluminum foil was served as a grounded counter electrode to collect the short fibers to form a felt after several hours' spinning. Because the MWCNTs have good dispersibility in PAN solution, even if the loadings of MWCNTs increase, the fibers are formed in uniform diameter and smooth surface as shown in **Figure 17a–Figure 17e**. On the other hand, with the increase of the loadings of MWCNTs, that is, the conductivity of the spinning solution rises, the improved Coulomb force and static electricity facilitate the formation of small-diameter fibers (**Figure 17f**).

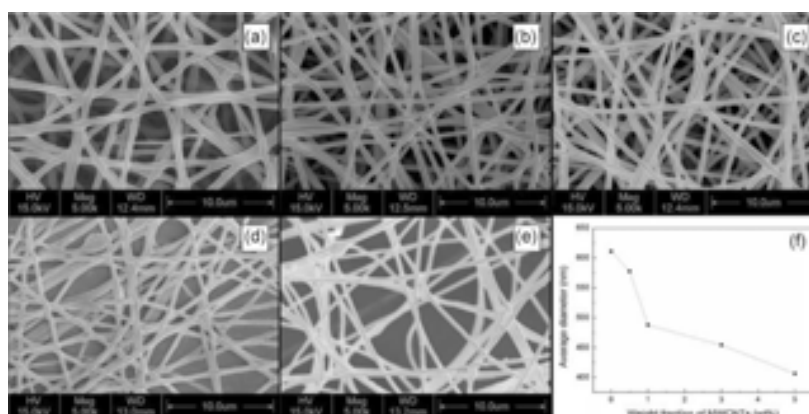


Figure 17. SEM images of PAN/f-MWCNTs composite nanofibers with different f-MWCNTs concentrations (a) 0 wt%, (b) 0.5 wt%, (c) 1 wt%, (d) 3 wt%, (e) 5 wt%, and (f) diameter distribution of nanofibers [46].

Particularly, electrospinning set-up with water as collector (**Figure 18**) was used to obtain aligned fiber samples and then the fiber was drawn out using a mechanical roller to obtain continuous fiber bundles [83]. As evident from **Figure 18**, individual fibers within the fiber bundles are tightly packed and aligned together. The stiffness and strength are seen to increase by 32% and 28%, respectively, when 3 wt.% CNTs is added to neat PVDF fibers, which can be attributed to the nano-reinforcement effect of the CNTs.

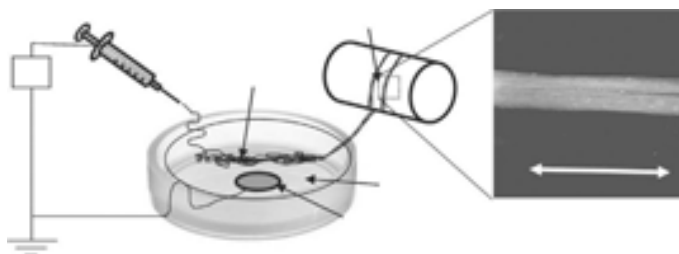


Figure 18. Schematic of the electrospinning setup used to obtain continuous self-assembled yarn structure [83].

3.2. Composite film

Film or membrane is one of the major products of plastics family. The composite film consisting of CNTs and polymer has extensive application because of its excellent mechanical and electrical properties. Casting is a common process to prepare the composite film, and a micrometer order uniform thickness film can be obtained after being dried naturally or at heating condition. For example, uniform MWCNTs/PVA, MWCNTs/cellulose, and MWCNTs/PS composite films can be prepared by casting [35, 84, 85]. The storage modulus for a 6 wt. % MWCNTs/PS composite cast film at 80°C is up to 122% of neat PS and the glass transition temperature increased significantly with an increase in MWCNTs concentration [85]. In order to manufacture highly stretchable, twistable, transparent, and conductive polymer and CNTs bilayer films, an efficient spin-coating and curing method is applied. In general, the spin-coating technique is known as one of the most promising processes to provide desired film uniformity, easy control of thickness, short operation time, and high reproducibility without environment limit [86]. For instance, defect-free MWCNTs were dispersed in deionized water to obtain a stable aqueous solution with the aid of SDBS. After spin-coating the aqueous MWCNTs solution on glass plates, polydimethyl siloxane (PDMS) was applied on the surface of the MWCNTs layer and then was cured. Finally, the MWCNTs/PDMS bilayer films were peeled off easily from the glass plates (**Figure 19**) [87].

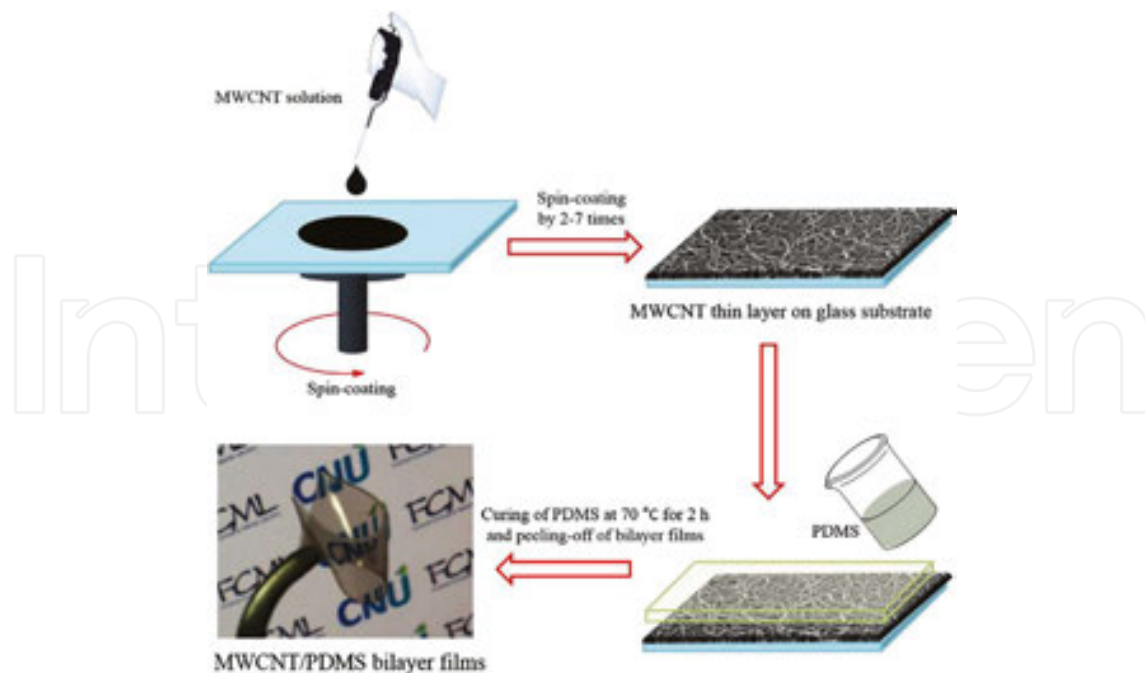


Figure 19. Schematic procedure to manufacture MWCNTs/PDMS bilayer films by spin-coating of MWCNTs solution and following curing of PDMS [87].

A novel in situ bulk polymerization method to prepare vertically aligned carbon nanotubes (VACNTs)/polymer composite films was developed to prevent CNTs condensation that could disturb CNTs orientation during liquid phase processing. A VACNTs array was infiltrated with styrene monomer with a certain amount of polystyrene-polybutadiene (PS-PB) copolymer that acted as a plasticizer, which confirms that the addition of PS-PB into the matrix can improve the elongation at break of the CNTs/PS composite film. These CNTs/polymer composite membranes show high gas and water permeability comparable to the other VACNTs composite membranes, potentially enabling applications that may require membranes with high flux, flexibility, and durability [88].

3.3. Elastomers

The unique properties of elastomers especially their high and reversible deformability are of great industrial importance. However, on account of their low elastic modulus, they are generally compounded with a reinforcing filler. The reinforcement of elastomers is probably one of the most important processes in rubber industry, especially in modern tire manufacture industry. Generally, reinforced elastomers show an increase in modulus, hardness, tensile strength, abrasion, and tear resistance as well as resistance to fatigue and cracking [89]. The conventional reinforcing fillers such as carbon blacks (CBs) and silicas have been widely used, while due to the advantages of CNTs as stated above, they as reinforcing fillers of elastomers have attracted much researchers' attention. Potential applications of CNT-filled rubber composites range from industrial applications such as rubber hoses, tire components, and sensing devices, to electrical shielding and electrical heating devices [90].

3.3.1. Reinforced natural rubber

Toluene is often used as a dispersant for CNTs in natural rubber (NR). For example, NR containing all the formulation ingredients could be dissolved in the suspension of CNTs and toluene. After NR/CNTs dispersion was mixed, the toluene was carefully removed, and the mixture was cured and formed sheets under certain pressure and temperature. The CNTs bring significant improvements in the mechanical properties with regard to the pure polymer. It is demonstrated that the intrinsic potential of CNTs is excellent reinforcing filler in elastomeric materials and small filler loadings substantially improve the mechanical behavior of the soft matrix [89]. Similarly, Fakhru'l-Razi reported that the preparation of MWCNTs/NR nanocomposites was carried out by a solvent-casting method using toluene as a solvent. Using this technique, CNTs can be dispersed homogeneously in the NR matrix in an attempt to increase the mechanical properties of these nanocomposites. There is an increase in the initial modulus for up to 12 times over pure NR. Application of the CNTs can result in rubber products having improved mechanical, physical, and chemical properties, compared with existing rubber products reinforced with CB or silicone [91].

Silane functionalization of MWCNTs could offer NR better performance in terms of property improvement when loaded in elastomeric composites. The MWCNTs are initially subjected to aminopropyltriethoxysilane (APS) treatment to bind amine functional groups ($-NH_2$) on the nanotube surface. Successful grafting of APS on the MWCNTs surface through Si-O-C linkages

is confirmed. Loading of silane-functionalized MWCNTs in the ENR (epoxidized NR) matrix results in a significant improvement in the mechanical, electrical, and thermal degradation properties of the composite materials, when compared to gum or pristine MWCNTs-loaded materials. As expected, the modulus of the composites at various strains increases significantly with an increase in nanotube loading. For instance, the 100% modulus increases to 106% when pristine CNTs are loaded, whereas it increases to about 120% when aminosilane-functionalized CNTs are loaded [92].

3.3.2. Reinforced synthetic elastomer

The process of reinforcing silicone rubber by MWCNTs needs following several steps. Silicone rubber resin was dissolved in petroleum ether to obtain homogeneous solution; fumed silica, KH550, and water were added to the above solution and agitated; Fe_2O_3 was added to the above mixture and agitated; MWCNTs or their suspension was added into the above mixtures and dispersed by ultrasonic treatment and agitation; the above mixture was desolventized in vacuum oven; curing agent and catalyst were added into the mixtures and stirred followed by moving into a mould for curing to obtain the composites. When 5 phr of MWCNTs was added, the room temperature vulcanized (RTV) silicone rubber composite reinforced by MWCNTs achieved good comprehensive performance. Its tensile strength, tear strength, elongation, and onset decomposition temperature reach 2.0 MPa, 11.7 kN/m, 238%, and 510°C, respectively, while the above said values for the composite with untreated MWCNTs are only 1.1 MPa, 7.0 kN/m, 83%, and 484°C, respectively [93].

Reinforcement of thermoplastic polyurethanes (TPUs) by MWCNTs was also carried out by solution method. MWCNTs were ultrasonicated by a dipping tip sonicator at room temperature in tetrahydrofuran-THF (0.1% volumetric solution of nanotube). TPU pellets were then added to the ultrasonicated solution and mixed with a magnetic stirrer. The solution was then poured in a Petri dish in order to allow THF evaporation at room temperature and to obtain reinforced TPU films. Such films were further dried in a vacuum oven. Typical mechanical properties (Young's modulus and yield strength) are improved and the strain energy dissipation is also increased [94].

Although solution blending is common to incorporate MWCNTs into an elastomer, this approach is not suitable for industrial practice due to its higher environmental and economic costs. Melt blending is the most convenient and efficient technique for the preparation of CNTs reinforced elastomers although it also has some disadvantages, so melt blending is a good selection to prepare CNT-reinforced elastomers. For example, appropriate amounts of CNTs were compounded into the elastomers styrene-butadiene rubber (SBR) and nitrile-butadiene rubber (NBR) by melt-mixing using a two-roll open mill. The elastomer compounds were vulcanized with the aid of sulphur at 150°C and at 3000 psi using a compression molding to obtain thin sheets (0.8 mm thick). The composites of CNTs/rubber show the improved properties such as resistance to solvent swelling, enhanced glass transition temperature, and improved storage and loss moduli [95].

4. Mechanical properties of the composites

4.1. The amount of CNTs

As it can be understood, mechanical properties of CNTs/polymer composites are improved due to effective CNTs reinforcement in the composites. In comparison with pure polymer, addition of functionalized CNTs causes an increasing in elastic modulus and yield strength, which is due to good dispersibility of CNTs and stress-transfer effect from the matrix to the CNTs caused by good interfacial interaction between the CNTs and the matrix. However, the optimum added amount of CNTs to polymer has to be carefully considered to obtain ultimate mechanical properties of the composite. For instance, Young's modulus, tensile strength, and storage modulus of the CNTs/PP nanocomposites can be increased with increasing CNTs content, but CNTs tend to aggregate into bundles in the matrix and hence the mechanical properties of the composite are reduced when CNTs over a certain amount, usually 2–3 wt. % [96].

Liu et al. [61] reported that mechanical properties of CNTs/polymer nanocomposite materials are greatly dependent on the content of CNTs. Within a limited weight fraction, mechanical properties of the nanocomposites increase significantly with addition of CNTs, and they reach the optimum when the content of CNTs is around 2 wt. %. The breaking strength of MWCNTs/poly(p-phenylene terephthalamide) (PPTA) nanocomposites containing 2 wt.% MWCNTs increases from 212 MPa up to 327 MPa, with a 54.2% increase compared to the pure aramid membranes. Being different from strength, with low volume fraction of CNTs, the modulus of the nanocomposite material exhibits a linear relationship with the content of the CNTs, and when the content of CNTs is further increased, the enhancement effects are weakened. The enhancement mechanism of MWCNTs/PPTA nanocomposites can be simply described as follows. The thread morphology of CNTs which can overlap with each other and strong π - π bond effects and van der Waals forces among adjacent nanotubes can result in the interweaving between nanotubes, leading to network-like structure. The structure has excellent stress transfer effect due to the strong interfacial forces between CNTs and the aramid matrix, and the CNT network can inter-pass throughout the layered structures of MWCNTs/PPTA nanocomposite membranes, which can greatly enhance the interaction between adjacent layers, hindering the slippage under tensile stress, that is to say, these layered structures are mechanically locked, improving the stiffness and tensile strength of nanocomposites. However, when the loading of CNTs exceeds a certain value, cluster structures inducing stress concentration will be formed which will become the sources of break, weakening the reinforcement of CNTs.

Similarly, the ultimate tensile strength of MWCNTs/ABS composites is enhanced with the increase in MWCNTs loading up to 70 MPa at a load of 3 wt.% MWCNTs and the values slightly decrease with further increase as shown in **Figure 20a**. When the MWCNTs loading is 10 wt. %, the strength significantly declines to 57 MPa, but this value is still higher than that of neat ABS. The variation of Young's modulus with the different loadings of MWCNTs loading is different from the strength (**Figure 20b**) and the modulus of the composites shows a linear

increase till the largest loadings in the experiment. **Figure 20c** shows that percentage elongation decreases with an increase in MWCNT loading [2].

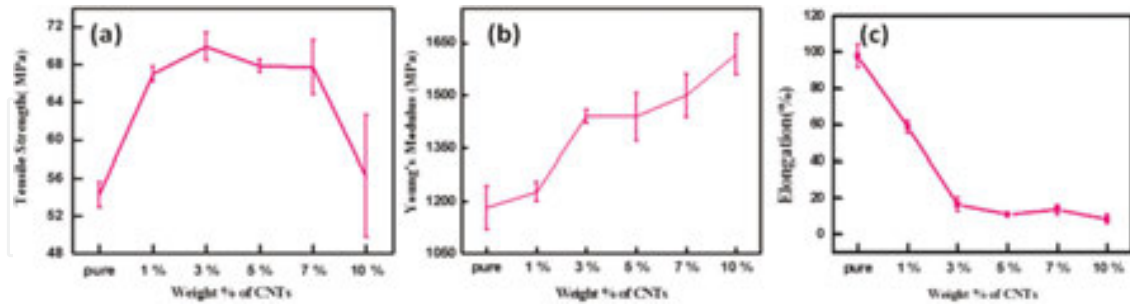


Figure 20. (a) Tensile strength, (b) Young's modulus, and (c) % elongation of MWCNTs/ABS composites with respect to the weight percentage of MWCNTs [2].

Similar trends are shown in our previous study as shown in **Figure 21** [29]. The addition of small amount of f-MWCNTs except acid-treated MWCNTs (c-MWCNTs) leads to a significant increase in the tensile strength of f-MWCNTs/PVA composite fibers, but the strength decreases when f-MWCNTs further increase from ultimate value 926MPa at 2 wt.% f-MWCNTs to about 805 MPa at 3 wt.% f-MWCNTs. However, Young's modulus keeps increasing with the increase of the MWCNTs loadings, and the break strain shows gradually decrease. The increase of Young's modulus and the decrease of the break strain reflect that at the same time of reinforcement the ductility decreases with the increasing MWCNTs loadings.

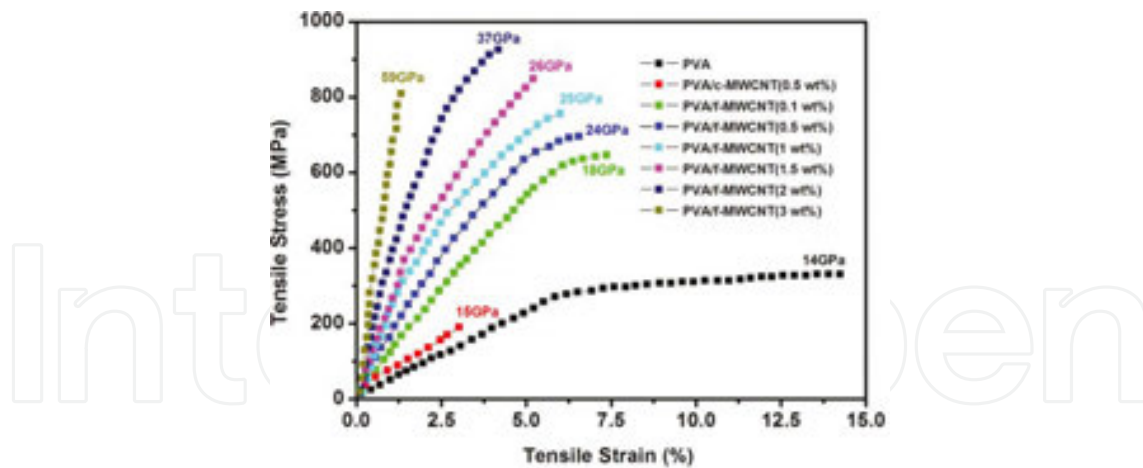


Figure 21. Stress-strain curves of PVA/f-MWCNTs composite fibers, the values on the tips of curves are Young's modulus of the corresponding fibers [29].

In order to explain this, a cross-sections of pure PVA- and TP-treated MWCNTs and PVA composite fibers (**Figure 22a** and **22b**) were prepared by breaking the fibers in liquid nitrogen to give an intact surface fracture (**Figure 22a'** and **22b'**). The pure PVA fiber shows evidently ductile fracture (**Figure 22a'**), whereas the fiber containing MWCNTs exhibits a typical feature of stiff and rigid fracture behavior with clear-cut fracture cross section [97]. On the contrary,

for brittle polymer, such as cellulose, with a CNT loading of 5 wt %, the tensile toughness reaches 5.8 MJ/m^3 , about 346% higher than that of neat cellulose film. The explanation is that the interfacial hydrogen bonding facilitates the stress transfer and simultaneously reduces the density of hydrogen bonding network of cellulose so as to obviously enhance the plastic deformation of the nanocomposite [98].

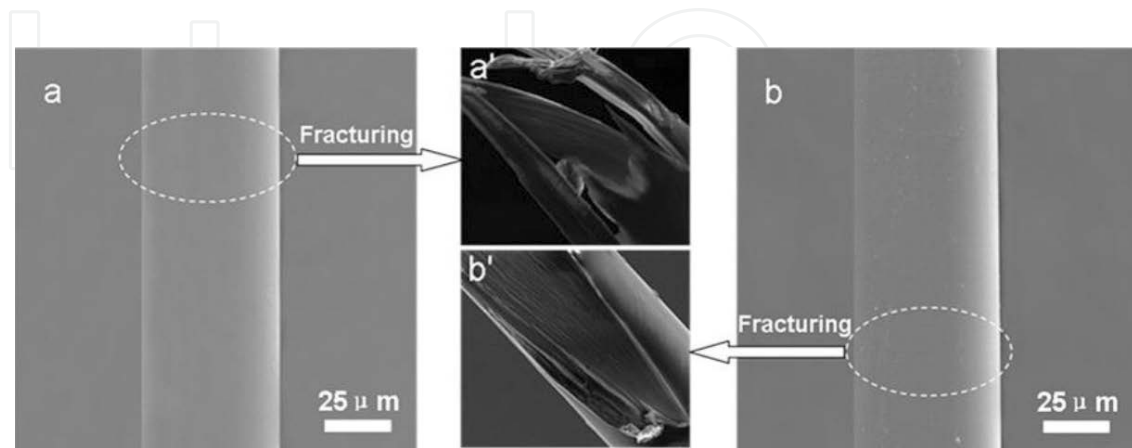


Figure 22. SEM images of (a) pure PVA and (b) MWCNTs/PVA composite drawn fibers prepared with 0.2 wt% MWCNTs loading; (a') the fractured cross-section of PVA fiber (a) and (b') is the fractured cross-section of MWCNTs/PVA composite fiber [67].

Different from the statement above, the incorporation of large amount CNTs in polymer matrix can still significantly enhance the nanocomposite tensile strength. The CNTs (1 wt. %)/PP nanocomposite shows 18% improvement in the tensile strength, while the 20% CNTs (20 wt. %)/PP nanocomposite exhibits an extremely high tensile strength, 1.8 times that of the unfilled polymer. This finding proves that high concentrations of CNTs can be incorporated in PP without degrading the tensile strength [97].

Sample		Specific tensile strength ($\text{kgf}\cdot\text{cm}^{-2}$)	Specific modulus ($\text{kgf}\cdot\text{cm}^{-2}$)	Elongation at break (%)
In situ composite nanofibers	PAN	188.2	88.5	45.2
	0.5% f-MWCNTs/PAN	213.4	309.2	42.8
	1% f-MWCNTs/PAN	310.3	553.9	40.1
	3% f-MWCNTs/PAN	246.8	371.9	39.6
	5% f-MWCNTs/PAN	208.6	287.5	35.7
Ex situ composite nanofibers	0.5% f-MWCNTs/PAN	194.7	280.3	40.7
	1% f-MWCNTs/PAN	297.4	455.1	38.9
	3% f-MWCNTs/PAN	219.6	292.8	36.0
	5% f-MWCNTs/PAN	201.7	217.4	33.4

Table 1. Mechanical properties of PAN, ex situ composite and in situ composite nanofibers.

At the same CNTs loadings, the mechanical properties of covalent treated CNTs-based composite are obviously higher than those of non-covalent treated CNTs based composite. For instance, the strength of TP-treated MWCNTs and PVA composite fiber are 643 MPa when the MWCNTs loadings are 0.6 wt.%, whereas the strength of PVA grafted MWCNTs and PVA composite fiber is 695 MPa at a load of 0.5 wt.% MWCNTs, indicating that the latter has stronger stress transfer effect due to covalent interaction between PVA and MWCNTs than the former [16, 46]. On the other hand, at the same CNTs loadings, the mechanical properties of the polymer composite containing CNTs functionalized by in situ polymerization are higher than those by ex situ polymerization as shown in **Table 1**. [46].

4.2. Orientation of CNTs

As we know, the mechanical properties such as tensile strength and Young's modulus of polymeric materials depend strongly on the orientation of the polymer chains. Similarly, as far as conventional fiber reinforcement is concerned, unidirectional composites show the highest improvements in strength and modulus. Therefore, it is expected that alignment of CNTs is important for improving mechanical properties [81]. So, the approach to improving the mechanical properties of CNTs/polymer nanocomposites is through alignment of CNTs by taking advantage of their exceptional anisotropic properties of CNTs arising from the one-dimensional structure of CNTs with extremely high aspect ratios. CNTs alignment can be achieved using various routes, including mechanical force, magnetic field, electric field, shear flows, and electrospinning [83, 99].

In the route of mechanical force, the composite materials are stretched usually by drawing, making CNTs orient along the drawing direction. Hot stretching of the MWCNTs/epoxy prepregs can markedly improve the mechanical properties of the composites. The improved mechanical properties of stretched composites derive from the increased MWCNTs volume fraction and the reduced MWCNT waviness caused by stretching. With a 3% stretch ratio, the MWCNTs/epoxy composites achieve the best tensile strength and elastic modulus [100]. Fiber drawing allows both the nanotubes and the polymer chains to be aligned, leading to enhance-

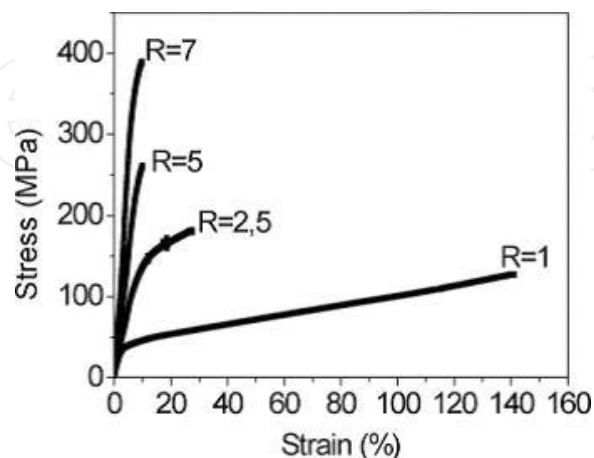


Figure 23. Stress-strain curves of MWCNTs/PA12 (7 wt. %) fibers with different draw ratio (R) values [101].

ment of the mechanical properties of the composites. As shown in **Figure 23**, the stress of MWCNTs (7 wt. %)/PA12 composite fibers increases with the draw ratio obviously [101].

The alignment of MWCNTs in bulk epoxy matrices can be realized by application of external electric field. The alignment gives rise to much improved electrical conductivity, elastic modulus, and quasi-static fracture toughness compared to those with CNTs of random orientation. The storage modulus of MWCNTs/epoxy composite can increase by 50% [102]. The Young's moduli of the 0.3 wt.% CNTs/epoxy nanocomposites with and without CNTs orientation are about 40% and 15% higher than that of the neat epoxy, respectively. The additional 25% enhancement in modulus clearly demonstrates the effectiveness of the alignment [99].

In addition, the shear forces during electrospinning present in the liquid jet result in automatic alignment of well-dispersed nanotubes [103]. **Figure 24** clearly demonstrates the significant increases in Young's modulus and tensile strength of the functionalized MWCNTs reinforced PMMA nanofibers obtained by electrospinning. The significant improvements in modulus and strength are likely related to the good dispersion and orientation of the CNTs within the polymer and to the strong interfacial adhesion due to the nanotube surface modification [104].

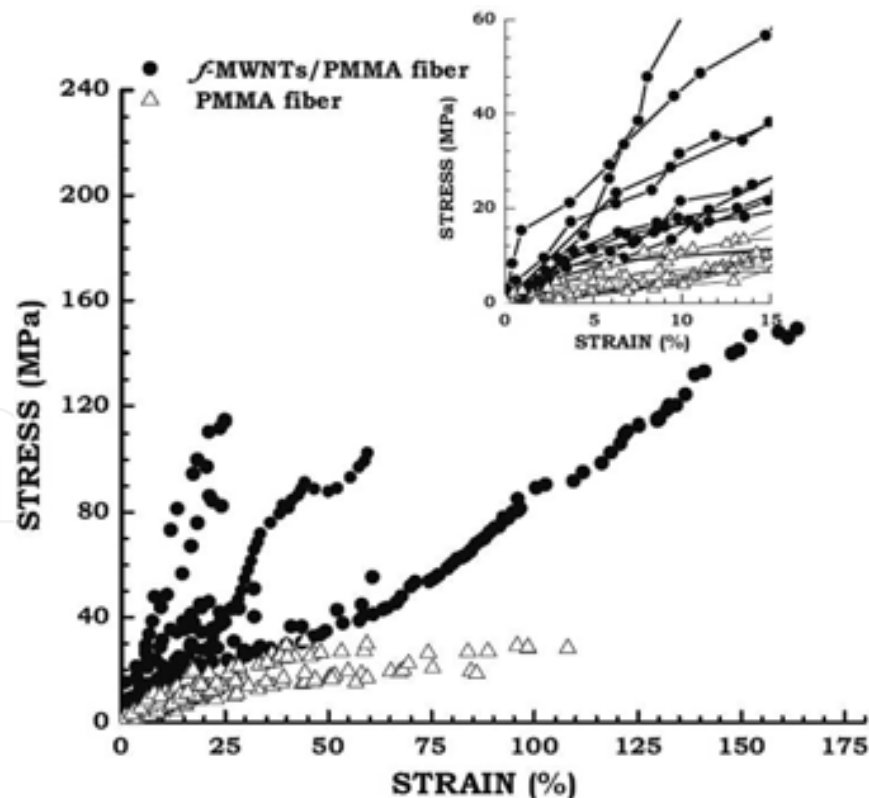


Figure 24. Stress-strain curves of electrospun PMMA nanofibers and CNT/PMMA nanofibers. The inset is a magnified view of the initial range (up to 15 %) of strain from which Young's modulus was calculated by linear regression [104].

There is an obvious difference in the intensity of the G band on polarized Raman spectra for different polarization directions after hot-stretching, which can be correlated to the alignment of CNTs in the composites. Normally, the degree of CNT alignment can be evaluated by the depolarization factor R , the ratio of the peak intensities of the G band in the two polarization directions, i.e., parallel (VV configuration) and perpendicular (VH configuration) to the fiber axis. The marked increase in R can be ascribed to the better alignment of CNTs after hot-stretching. For instance, the R values of MWCNTs/PAN composite are 1.03 and 2.95 for samples before and after hot-stretching, respectively, indicating the big difference between both R values, that is, much better alignment of CNTs after hot-stretching [105]. Besides, the orientation of CNTs can directly be characterized by TEM image as shown in **Figure 25**, in which the oriented CNTs can clearly be seen.

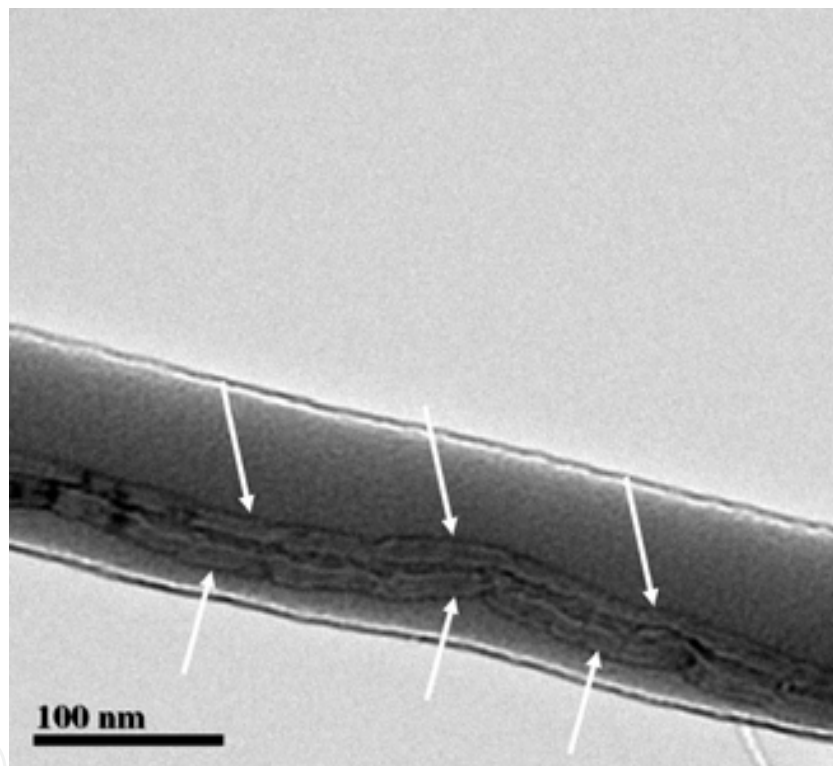


Figure 25. Representative TEM image of PVDF fibers filled with 2 wt.% CNTs [83].

In our previous paper [67], we presented a structure model of MWCNTs/PVA composite fiber as shown in **Figure 26**. TP-functionalized MWCNTs connects with PVA by non-covalent interactions and disperses uniformly in PVA matrix. It is considered that there are 'constrained regions' in the composite, which are composed of MWCNTs, constrained PVA molecular chains, and the surfactant TP molecules combined by H-bonding and π - π stacking among them. After the fiber is drawn, all the elements in the 'constrained regions' as a whole align along the fiber axis, which greatly increases orientation effect of all the elements in the composite, further strengthens the interactions between MWCNTs and PVA chains, and consequently forms a structure possessing high mechanical properties.

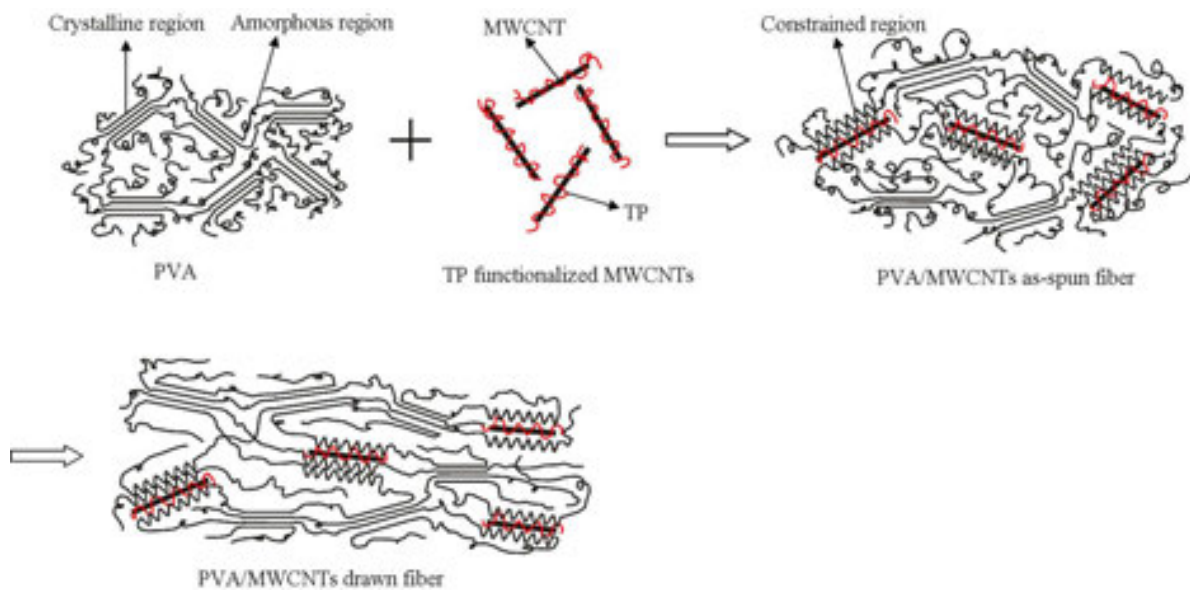


Figure 26. Proposed structural model of PVA/MWCNTs composite fiber [67].

5. Concluding remarks

Recently, CNTs have been widely used to incorporate into polymers to develop high-performance composite materials. Dispersibility of CNTs in polymer and the stress transfer from the matrix to CNTs have significant effects on reaching ultimate mechanical properties for CNTs/polymer composites. Mechanical processes to disperse CNTs such as ultrasonication have limited dispersing effect, and they generally are applied together with other dispersing processes so as to enhance the disperse effect of CNTs. Both covalent and non-covalent functionalization of CNTs can well disperse CNTs in polymer matrix, but at the same time have their disadvantages, such as, CNTs structure damage for covalent functionalization or weak interaction between matrix and CNTs for non-covalent functionalization. Due to better stress transfer, the mechanical properties of covalent functionalized CNTs/polymer composite are higher than non-covalent functionalized composite. As a one-dimensional material, CNTs are quite suited to reinforce polymeric fiber, which moreover can be easily drawn in a high draw ratio, leading to high orientation of CNTs and polymer chains. In addition to dispersibility of CNTs in the matrix, the amount and orientation are two important factors which cannot be ignored. Optimum amount and high orientation of CNTs should be considered in order to achieve excellent mechanical properties of CNTs/polymer composite. CNTs reinforcement makes the mechanical properties of polymer increase several times higher than the neat polymer in some of literatures, which conforms that CNTs are very effective fillers for polymers. However, the challenges the researcher should still face are how to optimize various factors in preparing CNTs/polymer composite in order to reach its ultimate mechanical properties, and how to scale up from laboratory and thus realize mass production.

Acknowledgements

This chapter was performed with the support of a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials. The authors also thank Mr. Yajun Li, Mr. Yao Cheng and Miss Juan Li for their kind assistances.

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