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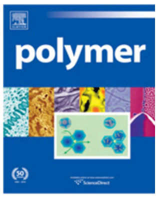

Feature Article

# Assessing the strengths and weaknesses of various types of pre-treatments of carbon nanotubes on the properties of polymer/carbon nanotubes composites: A critical review

Suryasarathi Bose [a], Rupesh A. Khare [b], Paula Moldenaers [a,*]

[a] Department of Chemical Engineering and Leuven Materials Research Center, Katholieke Universiteit Leuven, Willem de Croylaan 46, B-3001 Leuven, Belgium
[b] Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

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ABSTRACT

The current state of research in polymer/carbon nanotubes (single wall and multiwall) composites has been reviewed in context to various types of pre-treatments presently employed. The fundamental aspects of carbon nanotubes are briefly discussed and various strategies designed to alter the dispersion stability and quality of nanotubes in the composites is highlighted. A complete survey of the published data is provided and both the opportunities and the limitations in the frame of covalent and non-covalent type of pre-treatments of carbon nanotubes are juxtaposed. In this context, diverse proposed mechanisms behind different molecular level interactions between nanotubes and the functional moieties are addressed. The effects of these pre-treatments on electrical and rheological percolation thresholds are assessed as they provide an alternative means to evaluate the state of dispersion of carbon nanotubes in the composites. In this regard, the influence of various pre-treatments on the nature of charge transfer mechanisms, system dimensions etc. deduced from different parameters of classical percolation theories are also discussed. These transport parameters offer a vital clue on the nature of the pre-treatment and the effects it has on the structure–property correlations.

## 1. Introduction

Since their discovery, carbon nanotubes (CNT) [1] have attracted the interest of both the scientific and the industrial community with a hope to revolutionize various frontiers in the field of nanotechnology. The intriguing properties associated with CNT were believed to open new avenues in the material world, especially in the field of polymer-based composites. Since then various techniques to incorporate CNT in polymer matrices were designed with a desire to fabricate new advanced materials with multi-functional properties. Some of these properties were directed towards transferring the unique electrical properties associated with CNT to rather insulating polymer matrices with the aim of obtaining conducting composites. The possibility to achieve reasonably high conductivity at low CNT content owing to its high aspect ratio (*L*/*D*, where *L* is length and *D* is diameter of CNT) makes them an ideal candidate to be harnessed for several potential applications. Such high aspect ratio facilitates CNT to form a 'network-like' structure in the composites at a particular; often low concentration termed as 'percolation'. However, in order to exploit the exceptional properties of CNT one has to design strategies to generate in a reproducible way a stable and uniform dispersion of CNT in the composites. The strong inter-tube van der Waals' forces impede the uniform dispersion of CNT and the nanotubes are often dispersed as aggregates in the matrix. In addition, certain properties of the host polymer matrix like wetting, polarity, crystallinity, melt-viscosity etc. add to the challenge of obtaining a percolative 'network-like' structure of CNT in the composites at a desired concentration. Hence the level of percolation varies vastly with the matrix polymer. With growing demand of efficient translation of CNT properties to the composites, the research community worldwide has been hunting for novel strategies that counterbalance the strong inter-tube van der Waals' forces and further retain the 'network-like' structure of CNT right from preparation/processing of the composites to the end use. For this purpose, various strategies have been adopted and the opportunities and challenges involved have been addressed in numerous journal publications. Several review articles have been published in past few years on various aspects of polymer/CNT composites [2–10]. The present article is a critical review emphasizing mainly the strengths and the weaknesses of different types of

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[*] Corresponding author. Tel.: +32 16 32 23 59; fax: +32 16 32 29 91.
*E-mail address:* paula.moldenaers@cit.kuleuven.be (P. Moldenaers).

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pre-treatments currently employed to tailor the dispersion of CNT in the matrix polymers. It has been well understood that certain typical parameters of CNT viz. chirality, lengths and diameters, impurities, structural defects etc. vary significantly from batch to batch and hence comparing results obtained by different research groups becomes very intricate. Hence, in this review we present a comprehensive collection of published data which compares the effects of different pre-treatments viz. covalent and non-covalent functionalization of CNT on electrical, thermal and structural properties of the composites with respect to pristine CNT. In the literature data reviewed here the strategy employed for the pre-treatments are either indigenously developed in the laboratory or the pre-treated CNT are procured from the same source as that of pristine CNT. By comparing in this way we hope to provide insights into the strengths and weaknesses of various pre-treatments and thereby minimize the effects of other influential factors that stem from the source of production. The influence of different pre-treatments on the electrical and rheological percolation thresholds are also discussed as they provide an alternative means to evaluate the state of dispersion of CNT in the composites. The influence of the pre-treatments on the transport properties, nature of charge transfer mechanisms, system dimensions (2D/3D networks) etc. are also highlighted which are deduced from various analytical models of classical percolation theories. These crucial transport parameters demand close inspection as they provide a vital clue on the nature of pre-treatment and the influence it has on the structure–property correlations.

## 2. CNT: fundamental aspects

In order to comprehend various aspects of polymer/CNT composites, thorough understanding of the chemistry, structure and properties of CNT is vital. Given the brevity of the article we only briefly describe this here. In concept, CNT are cylindrical shells made by rolling graphene sheets. A graphene sheet consists of a monolayer of $sp^2$-bonded carbon atoms where each atom is connected to three carbon atoms in the $x$–$y$ plane and a weak delocalized '$\pi$-electron' cloud in the $z$ axis which gives CNT its unique electrical properties [11]. There are two basic types of CNT viz. SWNT (single wall carbon nanotubes) and MWNT (multiwall carbon nanotubes). SWNT consist of a single graphene sheet, which is a planar array of benzene molecules, involving hexagonal rings with double and single carbon–carbon bonding. MWNT comprise an array of such nanotubes that are concentrically nested. The high polarizability of the '$\pi$-electron' cloud leads to strong van der Waals' forces of attraction between CNT and the weak inter-planar interactions of the graphene sheet, which provide its solid lubricant quality, impede matrix adhesion. Thus, these inherent characteristics of CNT seriously hamper the uniform dispersion in the polymer matrix.

The unique properties associated with CNT are dictated by various aspects viz. synthesis methods employed, degree of graphitization, defects, chirality, diameter and degree of crystallinity and entanglements [12]. A brief synopsis highlighting some of these aspects influencing the intrinsic characteristics of CNT has been presented in Ref. [8]. Concerning the structure effect, it has been reported that the end-caps of nanotubes are highly reactive as compared to the sidewalls [13] which themselves contain defect sites viz. Stone–Wales defects, $sp^3$-hybridized defects and vacancies in the nanotubes lattice. This intrinsic defect chemistry paves way to tether many different types of chemical moieties onto the defect sites which can further be utilized to tailor the polymer/CNT interface. In addition, the delocalized '$\pi$-electron cloud' can be utilized to facilitate adsorption of different moieties onto the surface of CNT via various types of specific interactions viz. 'CH–$\pi$', '$\pi$–$\pi$' stacking, 'cation–$\pi$' etc. These two routes for tailoring the CNT surface will be elaborated on below.

## 3. Strategies designed to alter the dispersion quality and stability of CNT

The high specific surface area, large $L/D$ and high waviness induces entanglements and close packing in CNT. In case of SWNT it has been found that they are tightly bound by van der Waals' forces of attraction of 0.5 eV/nm leading to either bundles or ropes [14]. It is well understood over the years that the key to exploit the unique properties associated with CNT lies in its uniform and stable dispersion in the host polymer matrix. To realize this, some of these strategies are directed towards improving the dispersion of CNT by mechanical means viz. ultrasonication prior to composite preparation or more recently during the fabrication of the composites by ultrasound assisted extrusion [15], high shear mixing, latex technology, *in situ* polymerization, solid-state mechanochemical pulverization, coagulation spinning or by using external magnetic/electric fields etc. A recent review gives a brief synopsis of these methods [8]. Next to these methods are the ones that manipulate the surface energy of CNT either chemically (covalent functionalization) or physically (non-covalent functionalization). In this article we mainly emphasis on these pre-treatments and summarize both the opportunities and the limitations in context to electrical, thermal and structural properties of polymer/CNT composites.

### 3.1. Covalent treatments

The inherent characteristics of CNT viz. pyramidization and misalignment of '$\pi$-orbital' of the $sp^2$-hybridized carbon atoms make them more reactive than the graphene sheets and in turn pave way for covalent attachment of chemical moieties at end and defect sites or at the sidewall [13]. It is believed that covalent attachments of chemical species modify the stacking properties of CNT possibly by altering the hydrogen bonding and tends to debundle the tubes wherein the chemical species may intercalate between the bundles [14]. This route greatly enhances the solubility of CNT in the common solvents and aids in dispersing them in many polymer matrices. In addition to assisting in debundling, these treatments also improve significantly the phase adhesion with the host matrix and thus help in engineering the polymer/CNT interface. Due to the presence of fullerene-like end-caps which are sensitive to oxidation, the oxidation of CNT may be readily performed to create oxidized CNT [16–18]. They further serve to tie up with many different functional groups including zwitterionic linkages [19], amide bonds [20], esters [21], amines [22], fluorescein molecules [23], peptide nucleic acid [24] etc. and even can be tagged with metal coordination compounds [25,26]. Recently, inorganic nanoparticles have also been reported to be chemically attached to the SWNT surfaces via their end and defect sites [27]. Alternatively, a high degree of functionalization is also possible through the sidewall involving fluorination [28], ozonolysis [29], osmylation [30], organic functionalization involving diazonium compounds [31], derivatives with azomethine ylides [32], organometallic approach [33], electron reduction of benzophenone [34], anchoring with nickel(II) salen complex [35], addition of nitrenes, carbenes or radicals [36,37] etc. Recent reviews give an exhaustive overview of the current state of art of various open-end and sidewall covalent functionalization of CNT [38].

The various functional moieties attached through covalent functionalization of CNT enable to reactively couple with the available functional groups in the matrix polymer. This manifests itself in a stronger interface and an efficient stress transfer. The stress transfer at the interface between the nanotubes and the matrix critically controls the mechanical properties of the composites. Though the covalent route enables to tune various properties of polymer/CNT composites via chemical coupling, the consequences of these routes also demand careful inspection. For instance, the covalent treatments result in loss of intrinsic electrical properties affecting the gap at the Fermi level which greatly influences the metallic properties of metallic CNT [39]. In addition, this route adversely influences the *L*/*D* of the nanotubes which greatly affects the percolation threshold of CNT in the composites. Covalent treatments are also believed to decrease the phonon-scattering length affecting the thermal conductivity [40]. It also induces loss in symmetry and decreases the maximum buckling force of CNT [41]. Thus the covalent functionalization can strongly influence the intrinsic characteristics of CNT which further reflects in the overall performance of the polymer/CNT composites.

Table 1 summarizes a comprehensive collection of published data which compares the influence of covalent pre-treatment on various properties of the composites with respect to pristine CNT. The polymer matrices in column 1 are arranged alphabetically. The strategy employed for pre-treatment, the opportunities and the challenges addressed are arranged in columns 2–4. After a close inspection it is quite evident from the literature data reported in Table 1 that covalent functionalization has a profound positive effect on the structural properties of the composites viz. tensile strength and modulus, flexural strength and modulus, impact strength, storage modulus etc. of the composites. The improvements in structural properties in various polymer/functionalized CNT composites are addressed in connection with improved dispersion and efficient load transfer via reactive coupling between the functional moieties present on the surface of CNT and the available functional groups in the matrix polymers. The most interesting results of Table 1 are highlighted below. For example, Zou et al. [42] reported significant improvements in tensile strength and modulus (45% and 90% respectively as compared to neat epoxy) on utilizing very low concentrations of polyacryloyl chloride functionalized MWNT (0.1 wt%) in epoxy matrix. These improvements were addressed in connection with employing mild acid treatments and further magnifying the functional groups by polyacryloyl chloride which tethers more covalent bonds with the matrix epoxy. Yang et al. [43] reported simultaneous improvements in stiffness, strength, ductility and toughness using functionalized MWNT in polyethylene oxide (PEO) matrix. The storage modulus, Young's modulus, yield stress, tensile strength, ultimate strain, and toughness of PEO has been found to increase by 113%, 228%, 166%, 442%, 1240%, and 4080%, respectively at an optimal concentration of functionalized MWNT (1.5 wt%). These improvements were attributed to enhanced dispersion and better compatibility of phenoxy grafted MWNT with PEO. Ramanathan et al. [44] reported enhanced phase adhesion between amide functionalized MWNT and poly(methyl methacrylate) (PMMA) manifesting in significant improvements (above theoretical predictions) in elastic modulus of the composites (see Fig. 1). The results of various other polymer/CNT composites were also compared here (as indicated in Fig. 1). The effects of different functional moieties on the interaction potential and phase adhesion of polyamide 6 (PA6)/MWNT composites have been investigated by Meng et al. [45]. They realized that interactions such as the hydrogen bonds among the acid-modified MWNT (A-MWNT) led to a compact stacking morphology, resulting in a poor dispersion as compared to diamine-modified MWNT (D-MWNT). Fig. 2 illustrates the electron microscopy images of tensile fractured surfaces of the nanocomposites. Fig. 2(a and b) shows the aggregation and pull-apart of unmodified MWNT (U-MWNT) resulting from the incompatibility of the U-MWNT and PA6 matrix. Meng et al. [45] also realized that the pullout of U-MWNT was the dominant failure mechanism manifesting weak interfacial adhesion between U-MWNT and PA6 matrix. In contrast, Fig. 2c–f illustrate that both A-MWNT and D-MWNT were effectively dispersed (as compared to U-MWNT) in the PA6 matrix with minimal pullout and the plastic deformation of PA6 matrix controlled the overall failure mechanism in the nanocomposites. The storage modulus, glass transition temperature, tensile strength (Fig. 2g), Young's modulus and crystallization temperature of PA6 were found to be improved significantly on incorporation of D-MWNT. Several other publications reporting significant improvements in structural properties of the composites upon utilizing covalent functionalized CNT have been summarized in Table 1.

Table 1 also reflects the limitations associated with covalent functionalization. It is quite evident from the literature data reviewed here that this route disrupts the extended π-conjugation of CNT and adversely influences the electrical characteristics of the nanotubes. The observed lower electrical conductivity in several composites utilizing functionalized CNT were addressed in context to the harsh acid treatment conditions during functionalization process, defects, lower *L*/*D*, encapsulation/coating/wrapping due to reactive coupling/grafting etc. For instance Kim et al. [46] investigated different oxidizing conditions of MWNT on the percolation thresholds in epoxy/MWNT composites. These authors found that electrical percolation threshold greatly depends on the oxidizing time. Bose et al. [47] observed that though the percolation threshold of MWNT (of both amine functionalized and pristine) in melt-mixed PA6/acrylonitrile–butadiene–styrene (ABS) blends remained almost unaltered however, the absolute values of DC conductivity were higher for blends with pristine MWNT. Moreover, above percolation threshold the blends with pristine MWNT showed orders of magnitude higher electrical conductivity as compared to amine functionalized MWNT. They correlated these observations to lower *L*/*D* of amine functionalized MWNT. In addition, they reported that the dielectric constants for the blends were also higher for pristine MWNT at all concentrations. Ma et al. [48] reported possible wrapping on functionalizing MWNT with silane that led to decreased electrical conductivity in epoxy/MWNT composites (see Fig. 3). Similar observations were also reported in poly(L-lactic acid) (PLLA)/MWNT composites [49]. However, we note that few research groups also reported enhanced conductivity on employing chemical functionalized nanotubes. For instance Yuen et al. [50] observed improved electrical conductivity and reduced percolation threshold in polyimide (PI) matrix employing silane grafted MWNT. In addition, there are few experimental studies which report no appreciable change in the electrical conductivity on using functionalized CNT and in contrast there are few other studies which report synergistic improvements in structural, thermal and electrical properties on employing functionalized CNT (see Table 1).

It is evident that the disadvantages of covalent functionalization with regards to electrical conductivity are negligible as compared to the improved dispersion and compatibility with the matrix, which further leads to enhanced structural properties in the nanocomposites. Hence, optimizing the conditions during chemical treatments can play a crucial role in rendering optimal macroscopic properties. In Section 4, we discuss how chemical pre-treatments influence the geometrical and physical networks of CNT in the composites as manifested from electrical and rheological percolation thresholds respectively.

### 3.2. Non-covalent treatments

An efficient alternative to tailor the polymer/CNT interface and yet preserving the integrity of the tubes is realized by non-covalent

**Table 1**
Summary of the experimental results of the reviewed publications involving covalent type of pre-treatment of CNT (arranged alphabetically with respect to the polymer matrices).

| Matrix | Strategy | Opportunities | Challenges/Remarks | Ref. |
|---|---|---|---|---|
| Cynate ester<br>Bisphenol A dicynate | Utilizing acid functionalized MWNT with epoxy bridges | Uniform dispersion; Improvements in flexural and impact strength; increase in $T_g$, moderate improvements in storage modulus | | [140] |
| Epoxy | Utilizing acid functionalized MWNT under different oxidation conditions | Improved dispersion, Low percolation threshold (where oxidizing conditions are mild) | Increase in percolation threshold with increase in oxidation time (due to partial damage of the crystalline structure) | [46] |
| Epoxy | Functionalization of MWNT through strong acid oxidation (here MWNT is used in conjunction with glass fiber) | Improved dispersion, mechanical properties | Reduced electrical conductivity (functionalization disrupted the electrical structure of MWNT); Reduced $T_g$ (crosslinking density of functionalized MWNT/epoxy/glassfibre nanocomposite is decreased because of the interference of functionalized groups on the MWNT) | [141] |
| Epoxy | Utilizing acid and amino functionalized MWNT | Improved dispersion, $T_g$, impact strength | Amino functionalized MWNT showed better properties than acid functionalized (amino functionalized MWNT adhere to epoxy matrix through chemical bonds -$NH_2$ and -NH groups) | [142] |
| Epoxy | Functionalizing SWNT by polyamidoamine dendrimer | Improved dispersion, tensile strength, storage modulus | Reduced elongation at break, reduced $T_g$(as compared to neat epoxy due to presence of excess amine groups) | [143] |
| Epoxy | Functionalizing acid functionalized MWNT with polyacryloyl chloride | Significant improvements in thermal, tensile strength and modulus | | [144] |
| Epoxy | Functionalization of MWNT with different amino groups | Improvements in mechanical properties (dependent on the molecular structure of modifier) | Reduced $T_g$ (methylene radicals and hexylene groups induce flexibility and make the epoxy segments move more easily) | [145] |
| Epoxy | Functionalization of MWNT with silane | Improved dispersion, thermal stability, flexural modulus and strength | Decrease in electrical conductivity after modification due to wrapping | [48] |
| Epoxy | Utilizing amine functionalized MWNT | Improved curing kinetics, $T_g$, flexural strength, storage modulus | Damping property decreased (as compared to neat epoxy) | [146] |
| Epoxy | Utilizing triethylenetetramine functionalized MWNT | Improved dispersion, impact, bending strength, enhanced thermal conductivity | Functionalization led to decrease in crystallinity of MWNT | [147] |
| Epoxy | Grafting of butylamine on $CF_4$ plasma treated SWNT | Improved dispersion, mechanical and electrical properties | | [148] |
| Epoxy | Plasma assisted functionalization of MWNT with maleic anhydride | Improved dispersion, tensile strength and modulus; elongation at break, improved electrical conductivity | | [149] |
| Epoxy | 1. Utilizing acid functionalized MWNT.<br>2. Esterification of MWNT with phenyl glycidyl ether (PGE) and diglycidyl ether of bisphenol A (DGEBA) | Significant improvement in dispersion, flexural strength and modest increase in elastic modulus (in both cases) | Decrease in flexural strength and elastic modulus in acid functionalized MWNT | [150] |
| Epoxy | Grafting of hardener through diazotization reaction | Improved dispersion, elastic and storage modulus | Decrease in glass transition temperature (reduced cross-linkage) | [151] |
| Epoxy | Utilizing amine functionalized of MWNT | Increase in thermomechanical properties and $T_g$ | | [152] |

**Table 1** (*continued*)

| Matrix | Strategy | Opportunities | Challenges/Remarks | Ref. |
|---|---|---|---|---|
| Epoxy | Functionalization of acid functionalized SWNT by dicarboxylic acid acyl peroxide treatment followed by reaction with diamines | Significant increase in storage modulus, ultimate tensile strength and tensile modulus |  | [153] |
| Epoxy | Utilizing triethylenetetramine and carboxylic acid functionalized MWNT | Improved dispersion and mechanical properties with TETA functionalized MWNT | Reduced tensile strength and modulus with acid functionalized MWNT | [154] |
| Epoxy | Acid functionalization in different media | Better electrical conductivity of composites with MWNT functionalized in milder conditions | Better flexural properties of composites with MWNT functionalized in stronger conditions | [155] |
| Epoxy | Covalent grafting and non-covalent adsorption of polyethylenimine (PEI) on MWNT | Improved storage modulus of composites after covalent functionalization | Reduced electrical conductivity in both covalent and non-covalent modified MWNT composites | [156] |
| PA6 | Utilizing acid and diamine functionalized MWNT | Improved mechanical properties | Interactions such as the hydrogen bonds among the acid-modified MWNTs led to poor dispersion as compared to diamine functionalized MWNT. | [45] |
| PA 6,10 | Friedel craft acylation of MWNT with 4-chlorobenzoic acid | Improved dispersion and tensile strength |  | [157] |
| PAN | Fluorination of SWNT | Increased tensile strength and hardness | Composites with the fluorinated SWNT were not conducting because the fluorinated tubes are insulating | [158] |
| PANI | Utilizing acid, thermal and octadecylamine (ODA) functionalized SWNT | Composites with air oxidized CNT gave better electrical conductivity |  | [159] |
| PBO | Oligo hydroxyamide functionalized MWNT | Improved dispersion, tensile strength and modulus |  | [160] |
| PC | Oxidation with $H_2O_2$ followed by thermal and freeze drying of MWNT | Improved electrical conductivity | Better performance with freeze dried MWNT | [161] |
| PCL | Utilizing acid functionalized MWNT | Improved dispersion, storage modulus | Lower conductivity values for composites with acid functionalized MWNT due to destruction of $\pi$-network | [162] |
| PE | Grafting of PE on MWNT | Improved dispersion, tensile strength and modulus; toughness, yield strength and storage modulus |  | [163] |
| PE | Sidewall fluorination of SWNT | Improved dispersion and storage modulus |  | [164] |
| PEO | Utilizing acid and amine functionalized MWNT | Better electrical conductivity and improved dispersion for acid functionalized MWNT | Amine functionalization led to aggregation and poor electrical conductivity compared to pristine MWNT | [165] |
| PEO | Grafting of phenoxy on acid functionalized MWNT | Significant improvement in storage modulus, yield stress, tensile strength and toughness |  | [166] |
| PET | Functionalization of MWNT with benzyl and phenyl isocyanate | Improved tensile strength and modulus |  | [167] |
| PET | Utilizing acid and amine functionalized MWNT | Improved mechanical properties (higher with amine functionalized MWNT) |  | [168] |
| PET | Utilizing acid and acetic functionalized MWNT | Improved mechanical properties (higher improvement with acetic functionalized MWNT) |  | [169] |
| Phenoxy resin | Modification of MWNT with 1-(aminopropyl) imidazole | Improved dispersion and storage modulus | Decrease in glass transition temperature (due to plasticization) | [170] |
| PI | Silane grafting on acid functionalized MWNT | Improved electrical conductivity |  | [50] |

(*continued on next page*)

**Table 1** (*continued*)

| Matrix | Strategy | Opportunities | Challenges/Remarks | Ref. |
|---|---|---|---|---|
| PI | Utilizing acid and amine functionalized MWNT | Improvement in mechanical properties (better dispersion with amine functionalized MWNT) | Decrease in surface and volume conductivity after functionalization (less to some extent with amine functionalization) | [171] |
| PI | 1. PI-*g*-MWNT<br>2. Utilizing acid functionalized MWNT | Improved dispersion, electrical conductivity, tensile strength and modulus in PI-*g*-MWNT composites (as compared to acid functionalized MWNT) | | [172] |
| PI | Utilizing acid and amine functionalized MWNT | No change in electrical percolation threshold | No significant improvements in mechanical properties, Reduced electrical conductivity (high degree of modification disturbs the $\pi$-electron conjugation of the nanotubes) | [173] |
| PLA | Utilizing acid and hydroxyl functionalized MWNT | Improved dispersion (in case of acid functionalization), retards thermal depolymerization of PLA | Decreased thermal stability of composites with hydroxyl functionalized MWNT | [174] |
| PLLA | Grafting of PLLA on MWNT | Improved tensile strength, modulus and elongation at break | Decrease in conductivity due to coating of grafted PLLA on MWNT | [49] |
| PLLA | Utilizing MWNT-*g*-POSS | Improved mechanical properties | | [175] |
| PMMA | Utilizing amide functionalized CNT | Significant improvements (above theoretical predicted value) in storage modulus, electrical properties and thermal stability | | [44] |
| PMMA | Functionalization of MWNT with siloxanes | Significant improvements in thermal stability | Long siloxane chains resulted in plasticization of PMMA | [176] |
| PMMA | Covalent modification with vinyl monomer acryloyl chloride | | Reduced electrical conductivity due to possible encapsulation | [177] |
| PMMA | Oxidation of MWNT and *in-situ* polymerization of MMA | Increased storage modulus and glass transition temperature | | [178] |
| PP | 1. MWNT were heat treated in air at 500 °C for an hour<br>2. Utilizing acid and amine functionalization along with PP-*g*-MA and SEBS-*g*-MA | Improved electrical conductivity (SEBS-*g*-MA found to be better dispersant as compared to PP-*g*-MA) | | [179] |
| PP | Functionalization with undecyl generated by radical decomposition of Lauroyl peroxide | Improved yield strength and elongation at break, | Electrical percolation threshold greater than ∼3.6 wt% | [180] |
| PP | Covalent modification of CNT with intumscent flame retarding agent | Improved flame retardency and mechanical properties | | [181] |
| PP | grafting of PP on MWNT by melt reaction of PP-*g*-MA with amine functionalized MWNT | Improved mechanical properties | | [182] |
| PP | Silane functionalization of MWNT | Slight improvement in tensile strength | | [183] |
| PP | *In situ* grafting of PP on SWNT with benzoyl peroxide | Increased tensile strength and modulus | | [184] |
| PS | Functionalization of MWNT with 4-vinylaniline using diazo-coupling reaction | Improvement in mechanical and electrical properties | | [185] |
| PS | Covalent functionalization of acid functionalized MWNT with 4-vinylbenzyl chloride | Improvement in thermal and mechanical properties (as compared to acid functionalized MWNT) | | [186] |
| PS | Grafting of PS on SWNT by Fridel Craft's acylation | Improvement in electrical conductivity | | [187] |

**Table 1** (*continued*)

| Matrix | Strategy | Opportunities | Challenges/Remarks | Ref. |
|---|---|---|---|---|
| PS | *n*-butyl functionalization of MWNT with organometallic *n*-butyl lithium | Improved dispersion and improved tensile strength and modulus | Decrease in thermal stability with increasing functionality | [188] |
| PS | MWNT functionalized with chlorinated PP | Significant improvement in tensile strength, modulus and toughness | Improvements are limited to low volume fraction of MWNT | [189] |
| PS | Functionalization of SWNT with *p*-amino phenyl alkylene (APA) followed by grafting of PS on these sites with high bonding density | Significant improvements in tensile strength and modulus | | [190] |
| PSF | Modification of MWNT with long chain esters | Improved dispersion and electrical conductivity | No much change in electrical conductivity with increase in carbon atoms beyond 8 | [191] |
| PU | Grafting of PU on hydroxyl functionalized SWNT | Improved dispersion, Young's modulus | No significant improvement in elongation at break | [192] |
| PU | Utilizing hydroxyl functionalized SWNT | Improved dispersion | Reduced electrical conductivity after functionalization | [193] |
| PVA | Hydroxyl functionalization of SWNT | Improved dispersion, tensile strength and modulus | | [194] |
| PVA | Covalent functionalization of MWNT by Ferritin protein | Improved storage modulus and glass transition temperature | | [195] |
| PVA | Functionalization of SWNT by PVA through esterification | Improved dispersion and tensile strength | | [196] |
| PVA | Oxidation of MWNT | | Lower electrical conductivity | [197] |
| PVC | ATRP grafting of poly butyl methacrylate on MWNT | Significant improvement in dispersion, tensile strength, modulus and yield stress | | [198] |
| PVDF | Utilizing acid and ester functionalized MWNT | No change in electrical percolation threshold, increase in dielectric constant | | [199] |
| SAN | Using MWNT-*g*-PMMA | Improved dispersion, storage modulus, tensile strength, Young's modulus and toughness | | [200] |
| Silicone elastomer | Functionalization of MWNT with trichlorosilanes | | Reduced electrical conductivity after functionalization | [201] |
| Sylgard 184 silicone | Functionalization of MWNT with 7-octenyltrichlorosilane (7OTCS) and n-octyltrichlorosilane (*n*OTCS) | Improved dispersion and Young's modulus after functionalization | Terminal polar group present in 7OTCS had a major role in dispersion and improvement in mechanical properties | [202] |
| Vinyl ester | Functionalization of acid functionalized MWNT with POP backboned with amine groups | Improved electrical conductivity (POP with higher molecular weight gave better dispersion) | | [203] |
| Vinyl ester | Using maleic anhydride (MA) grafted on poly(oxyalkylene)amines (POA) functionalized MWNT | Improved flexural modulus and electrical conductivity (better dispersion achieved with higher molecular weight POA) | | [204] |

PA6 – polyamide 6; PA 6,10 – polyamide 6,10; PAN – polyacrylonitrile; PANI- polyaniline; PBO- poly(p-phenylene)benzobisoxazole; PC – polycarbonate; PCL – polycaprolactone; PE – polyethylene; PEO – polyethylene oxide; PET – polyethylene terepthalate; PI – polyimide; PLA – polylactic acid; PLLA – poly(L-lactic acid); PMMA – polymethylmethacrylate; PP – polypropylene; PS – polystyrene; PSF – polysulfone; PU – polyurethane; PVA – polyvinyl alcohol; PVC – polyvinyl chloride; PVDF – polyvinylidine fluoride; SAN – styrene acrylonitrile.

functionalization of CNT. This route is particularly attractive because of the possibility of adsorbing various groups of ordered architectures on the CNT surface without disturbing the extended $\pi$-conjugation of the nanotubes. In the last few years, the non-covalent surface treatment received lots of attention and various strategies have been proposed which caters the debundling of CNT in presence of the modifier. These approaches have been addressed in connection with surface coating/wrapping of low molecular weight surfactants (anionic/cationic) [51–63], polymers [64–67] and liquid crystalline $\pi$-conjugated oligomers [68]; absorption of hydrophilic non-charged polymer molecules and amphiphilic cationic polymer molecules [69–71], block copolymers [72–74],

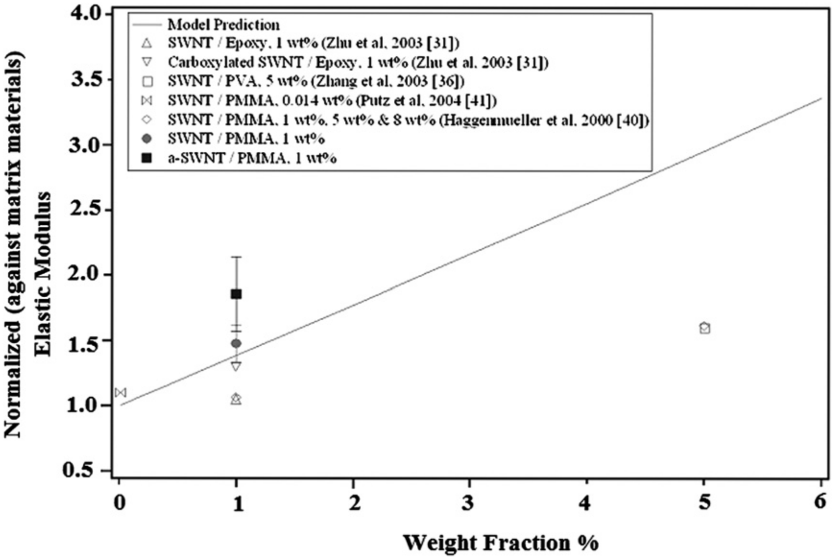

**Fig. 1.** Theoretical prediction (by Mori–Tanaka model) versus experimental results for the modulus values of PMMA/SWNT composites. The solid line shows the theoretical upper bound of normalized modulus values. Some data for the composites presented here exceed this upper bound, indicating significant interphase region with polymer of altered mobility and increased effective stiffness (Ramanathan et al. [44] – Reproduced by permission of Wiley, Copyright© 2005 Wiley Ltd. All rights reserved).

deoxyribonucleic acid (DNA) [75]; solvent free modification by tertiary phosphines [76]; functionalization by sodium lignosulfonate [77], six-armed star poly(L-lactic acid) [78], peptides [79], *meso*-tetraphenyl porphine and its metal (II) complexes [80]; ligand–lectin interactions with glycolipids [81]; sorption of endocyclic and exocyclic substitutions [82]; hybridization with porphyrins [83]; using ferrocene–amino acid conjugates [84]; establishing 'cation–π' type of specific interactions with metal salts [85,86]; 'π–π' stacking with aromatic molecules [87–89], azo dyes [90], pyrene carboxylic acids (PCA) [91]; room temperature ionic liquids (RTIL) [92–94] etc.

Among the various treatments, the RTIL has recently received immense interest on account of its efficient dispersion capacity of CNT and the formation of thermally stable bucky-gel [92]. It has been reported that homogeneous functionalization of SWNT in presence of RTIL viz. imidazolium ion containing liquids with different polymerizable functional groups can lead to mechanically reinforced, electroconductive and thermoconductive soft materials [95].

In this context the proposed mechanisms behind various molecular level interactions associated with the non-covalent treatments are summarized below. For instance, it has been suggested that SWNT dispersion by RTIL molecules is mediated by a local chemical environment and the strong 'π–π' interactions between CNT are shielded by the ionic liquids that prevent them from rebundling [96]. In case of amphiphilic polycations it is believed that hydrophobic alkyl pendant group of the polymer binds with the hydrophobic stem of the CNT surface while the positive charges provide compatibility with the polar solvent media and prevent re-aggregation [97].

In the case of charged surfactants such as sodium dodecylsulfate (SDS) or *tetra*-alkylammonium bromide the dispersion of nanotubes is stabilized by electrostatic repulsion between the micelles [98] and in the case of charge-neutral surfactants, such as polyvinylpyrrolidone (PVP) mainly due to the large solvation shell created by hydrophilic moieties assembled around the nanotube [99]. In this context, it has been suggested that simple alkyl chains of surfactants such as SDS, sodium dodecyl sulfonate (SDSA) and dodecyl tri-methyl ammonium bromide (DTAB) form non-specific hydrophobic interactions with CNT leading to loosely packing of surfactants around the nanotubes. Reports [100] show that the outermost nanotubes in a bundle are treated more than the innermost tubes and the nanotubes remain predominantly bundled even after surfactant treatments. Hence, mechanical methods viz. ultrasonication prior to surface treatment should be supplemented. Different hierarchical organization of surfactants on the nanotubes surface have been presented where the surfactant molecules can either be adsorbed perpendicular to the surface of the nanotubes, forming a monolayer or could be organized into half-cylinders oriented parallel to the tube axis or could assemble as half-cylinders oriented perpendicular to the tube axis (see Fig. 4) [101]. Further, it has been shown that the surface coverage of SDS molecules on the nanotubes surface is typically ~2–3 SDS molecules/nm$^2$ [102]. The interaction potential of CNT with the surfactants significantly depends on the concentration and the molecular architecture. For instance, it is believed that the presence of phenyl rings in sodium dodecyl benzene sulfonate (SDBS) makes it more efficient in solubilizing CNT as compared to SDS due to improved interaction between aromatic stacking of CNT and the phenyl ring.

In the context of polymer assisted dispersion, it has been suggested that to minimize strain in their conformations some polymers wrap around CNT in a helical fashion. For instance, PVP with a hydrophobic alkyl backbone and hydrophilic pendant group coils around CNT such that its backbone is in contact with the surface of CNT and pyrrolidone groups are exposed to water [99], in contrast to DNA which assembles in the opposite way [75]. In case of wrapping with conjugated poly(*m*-phenylenevinylene) (PmPV) system it has been found that the permanent dipole moments on PmPV play a vital role for induction of transient dipole in CNT, thereby providing effective van der Waals' interactions with the sidewalls [103,104]. Few other examples of different hierarchical assemblies of molecules on the CNT surface have been illustrated in Fig. 4.

It has been well appreciated that metal salts viz. sodium salt of 6-amino hexanoic acid (Na-AHA) [85,86] and certain phosponium-based salts [105] assist in significant debundling of the MWNT aggregates by establishing specific interactions viz. 'cation–π' and/

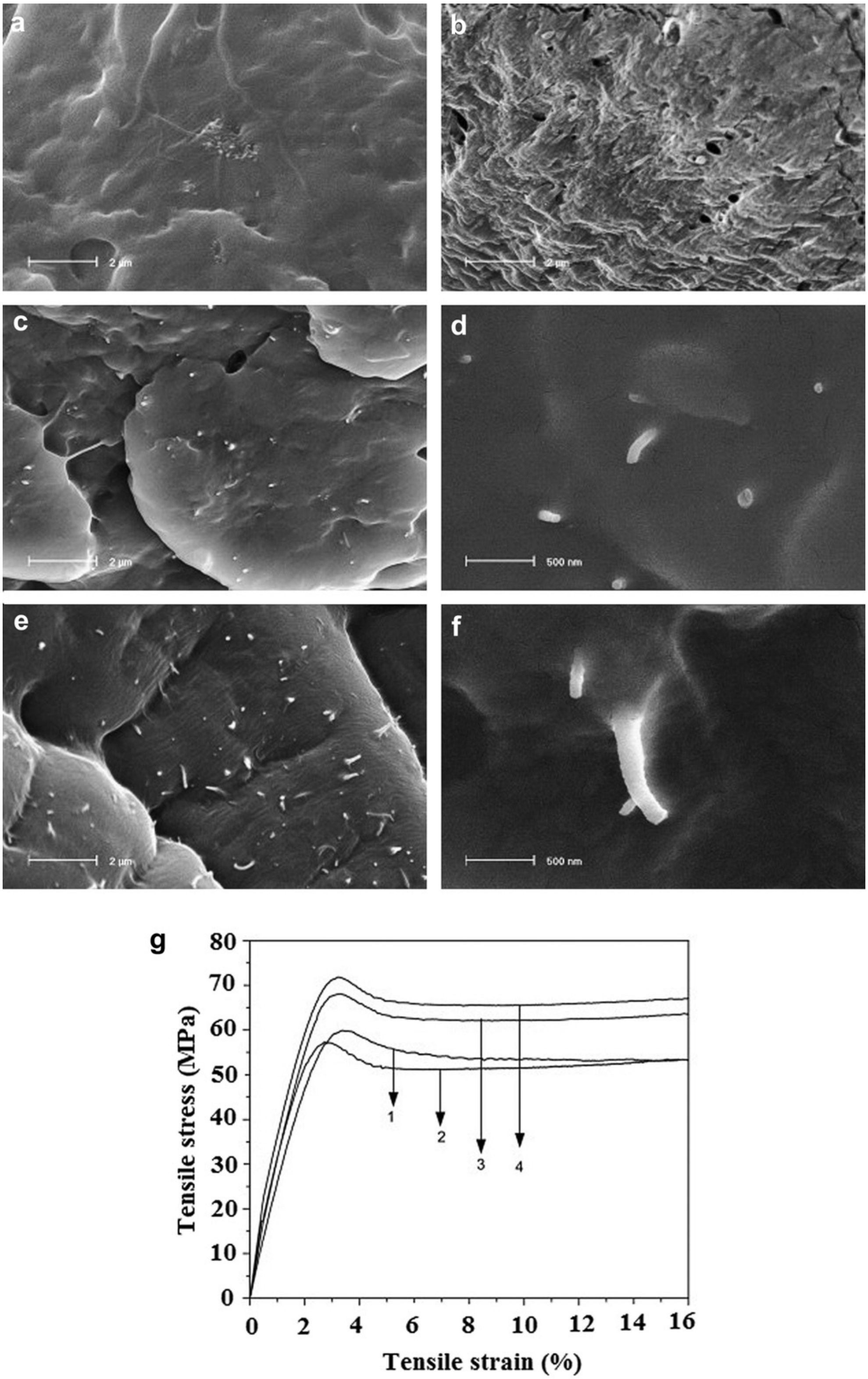

**Fig. 2.** SEM images of tensile fractured surfaces of (a and b, scale 2 μm) PA6/U-MWNT, (c and d, scale 2 μm and 500 nm respectively) PA6/A-MWNT and (e and f, scale 2 μm and 500 nm respectively) PA6/D-MWNT; g, Typical tensile stress–strain curves of (1) PA6, (2) PA6/U-MWNT, (3) PA6/A-MWNT and (4) PA6/D-MWNT (Meng et al. [45] – Reproduced by permission of Elsevier, Copyright© 2007 Elsevier Ltd. All rights reserved).

or '$\pi$–$\pi$' type of interactions with the extended '$\pi$-electron' clouds of the nanotubes. It is worth noting that 'cation–$\pi$' type of interactions exhibits a strength of 35–183 kJ mol$^{-1}$, which is significantly higher than either hydrogen bonding (1–40 kJ mol$^{-1}$) or '$\pi$–$\pi$' type of interaction (8–16 kJ mol$^{-1}$) [106,107]. The functional groups present in these salts take part in reactive coupling with the available functional moieties in the matrix during composite preparation and retain the percolative 'network-like' structure of

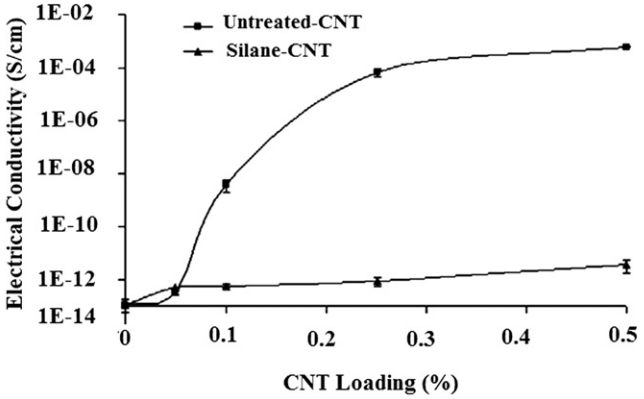

**Fig. 3.** Electrical conductivity of untreated and silane functionalized MWNT/epoxy composites (Ma et al. [48] – Reproduced by permission of Elsevier, Copyright© 2007 Elsevier Ltd. All rights reserved).

CNT. The dispersion stability of MWNT in presence of phosponium-based salts with respect to critical organic tail length and concentration has also been investigated. It has been found that in case of excess phosponium salts the nanotubes re-aggregate [105]. Similar phenomena have been observed in case of surfactants stabilized CNT suspensions and have been addressed in connection with attractive depletion-type of interactions [102]. Hence, the concentration and molecular architecture of the modifiers play a crucial role in the degree of exfoliation of CNT and one need to consider these factors in order to exploit CNT to bridge the gap between those of bulk and molecules.

Table 2 represents a comprehensive collection of published data that compares the effects of non-covalent type of pre-treatment on various properties of the nanocomposites with respect to pristine CNT. The columns are arranged accordingly as that of Table 1. Some of the more striking observations are summarized below. Exceptionally low electrical percolation thresholds (0.006 wt%) have been reported in PMMA/MWNT composites on account of '$\pi$–$\pi$' type of interactions with TFA (trifluoroacetic acid) and P3HT (poly(3-hexylthiophene)) [108]. Significant improvements in electrical conductivity have been reported in clay assisted dispersion of SWNT in epoxy matrix at very low concentrations (0.05 wt%) [109]. It has been proposed that the structure of SWNT in the composites changes from a discontinuous aggregated state to a continuous 3D network in presence of clay. Kodgire et al. [85] reported significant improvements in electrical conductivity in PA6/MWNT composites (see Fig. 5a) employing a unique reactive modifier (Na-AHA). These authors have found that specific interactions viz. 'cation–$\pi$' between $Na^+$ moieties and extended delocalized '$\pi$-electron' clouds of MWNT significantly facilitate in debundling the tubes (as can be seen from the TEM micrographs in Fig. 5b–e). Further, they observed that the concentration of Na-AHA played a critical role in the degree of exfoliation of MWNT. Similar observations were also reported in melt-mixed PA6/ABS blends where significantly low electrical percolation thresholds (~0.25 wt%) have been reported on utilization of Na-AHA modified MWNT [86]. Concerning the structural properties of the composites in view of non-covalent modifications few literatures report significant to moderate improvements. These effects have been addressed in context to enhanced dispersion of CNT owing to various types of interactions with the matrix and the results are summarized in Table 2. It is evident from the literature data reviewed here that the non-covalent treatment has a positive influence on the electrical properties of the composites. This is facilitated by better exfoliation/debundling and stable dispersion of CNT in the composites mediated by various types of specific interactions viz. 'CH–$\pi$', '$\pi$–$\pi$', 'cation–$\pi$' etc. In addition, unlike covalent treatment the intrinsic electrical properties of CNT are preserved in this type of treatment which further reflects in lower electrical percolation thresholds in the composites.

## 4. Evaluating the dispersion stability and quality of CNT

In this section the methods used to evaluate the dispersion stability and quality of CNT in composites are described. Although there are various methods to evaluate the morphology and the state of dispersion of CNTs viz. microscopic techniques involving optical, atomic force microscopy, scanning and transmittance electron microscopy [110–113]; dynamic light scattering [114], transient fluorescence emission [111], small angle neutron scattering [115,116], Raman spectroscopy [117,118], size exclusion chromatography [119], UV–vis spectroscopy [120], solution suspension stability [105] etc. we focus here on indirect methods. The latter includes AC electrical conductivity measurements and melt-rheological investigations; these have specific advantages as compared to the direct methods. The AC electrical conductivity measurements give insight into the percolative 'network-like' structure of CNT, nature of charge transfer mechanism viz. tunneling/hopping, system dimensions (2D/3D networks) etc. in the composites. The melt-rheological measurements elucidate the onset of physical gelling above a typical concentration of CNT. These indirect (*in situ*) methods provide in-depth insight in underlying concepts of percolation behavior and provide an important tool to evaluate the state of dispersion of CNT in the composites. In contrast, the morphology in the direct ('post-mortem') techniques like electron microscopy can only be viewed after the composite has solidified. Furthermore, electron microscopy can only represent the state of dispersion of CNTs in 2D in contrast to 3D in *in situ* techniques. However, in order to correlate the structure developed in the melt state with the solid-state morphology various direct methods are supplemented to get an overall perspective of the state of dispersion of CNTs in the composites. Given the brevity of the article, we focus here mainly on these *in situ* techniques to assess the state of dispersion of CNTs in the composites and also evaluate the strengths and weaknesses of various pre-treatments influencing the dispersion of CNTs in the composites.

There are ample literatures and an exhaustive review [10] discussing the electrical percolation threshold in various polymer/CNT composites, but this review focuses mainly on the literatures that investigate the influence of pre-treatments on electrical and rheological percolation threshold of CNT in the nanocomposites. In the subsequent sections we describe how these characterization tools reflect the nature of pre-treatments and also provide insights into the geometrical (electrical) and physical (rheological) networks of nanotubes in the composites.

### 4.1. Electrical percolation threshold

This section summarizes various concepts starting from the classical percolation theories used to estimate the electrical percolation threshold and get insights into the nature of charge transfer mechanisms; system dimensions (2D/3D networks) etc. in CNT-based polymer composites.

According to several analytical models, the electrical percolation threshold decreases in a hyperbolic fashion as a function of $L/D$ of the filler [121]. Simple models using continuum percolation consider the filler network as a group of non-interacting sticks or

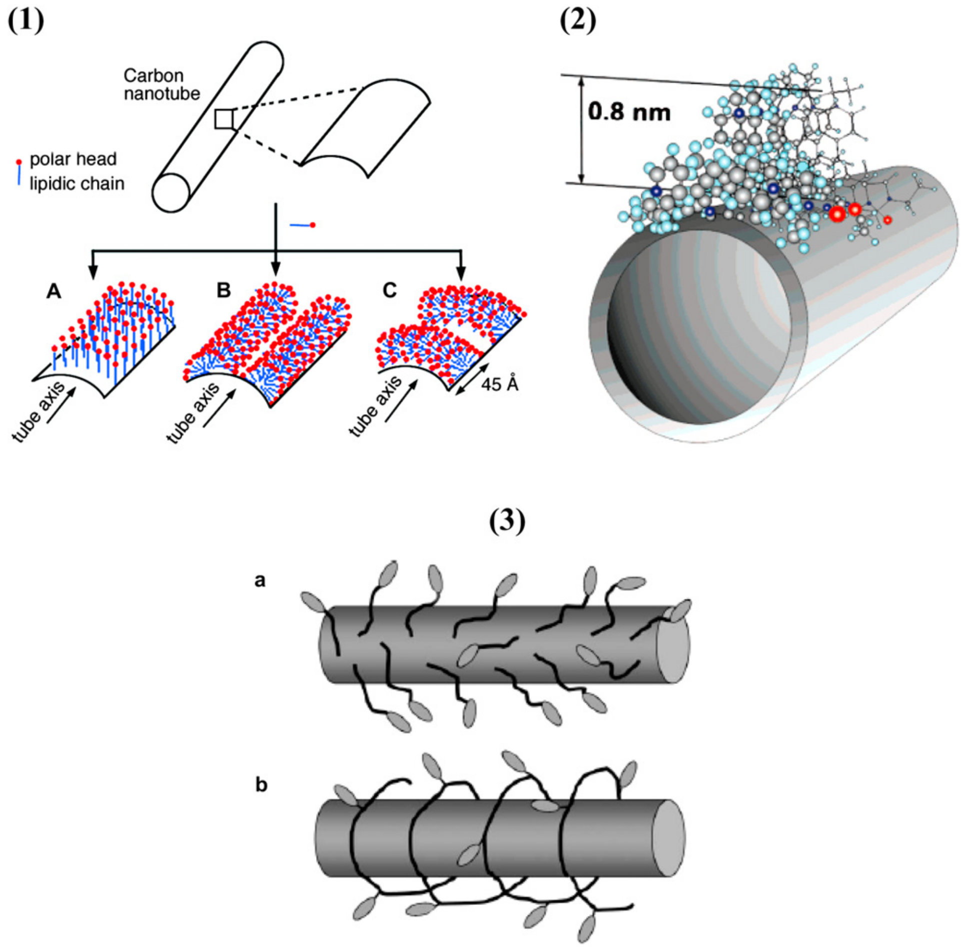

**Fig. 4.** (1) Different possible organizations of sodium dodecyl sulphate molecules on the surface of CNT, (A) adsorbed perpendicular to the surface, forming a monolayer; (B) organized into half-cylinders oriented parallel to the tube axis; (C) half-cylinders oriented perpendicular to the tube axis (Richard et al. [101] – Reproduced by permission of The American Association for the Advancement of Science, Copyright© 2003, The American Association for the Advancement of Science). (2) Structural schematics of the adsorption layer of polymer on SWNT. (Hydrophobic alkyl radicals in the side chains are omitted for clarity; their position is denoted by red spheres. Color coding of atoms: C-gray; H-light blue; N-purple. Hydrophilic part of the layer is facing the aqueous surrounding, while hydrophobic backbone is lying on the graphite wall) (Sinani et al. [97] – Reproduced by permission of American Chemical Society, Copyright© 2005, American Chemical Society). (3) Different modes of adsorption of ambiphilic molecules on SWNT surface: (a) molecular surfactant forming a micelle and (b) polymer wrapping around nanotubes (hydrophilic groups are represented by ellipsoids and hydrophobic groups by black lines) (Britz and Khlobystov [104] – Reproduced by permission of The Royal Society of Chemistry) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

rods, and suggest that the percolation threshold (in volume fraction) scales as 1/AR. Recently, the use of excluded volume concept shed more light in predicting the percolation threshold in polymer/CNT composites. This theory considers that the rod number density is roughly equal to the reciprocal of the excluded volume of the rods. A general relationship between the percolation threshold of systems with various geometries and their associated excluded volume has been discussed extensively by Balberg et al. [121]. In the isotropic case of randomly long sticks (length $L$ and radius $r$) and assuming CNT as long rigid sticks the proposed relation is:

$$(L/r)\Phi_c = 3 \tag{1}$$

where, $\Phi_c$ is the critical volume fraction of the stick.

The typical $L/D$ of CNT reported for most of the composites is in the range of 300–1000 which predicts $\Phi_c$ to be in the range of 0.005–0.0015 (from Eq. (1)). However, electrical percolations well below that predicted by the excluded volume concept have been reported for few polymers. These observations have been related to kinetic percolation which allows for particle movement and re-aggregation [10]. However, in most cases it has been observed that the percolation threshold of CNT in the composites is well above the predicted ones. As mentioned before, next to the inherent characteristics of CNT some of the physical properties of the polymers viz. wetting, polarity and crystallinity also add to the challenge in the formation of percolative 'network-like' structures manifesting in observed higher percolation threshold in various polymer/CNT composites.

In a typical AC electrical conductivity measurement one can find, above the percolation threshold ($p_c$), a finite conductivity manifesting in a plateau (DC conductivity) at low frequency corresponding to the electrical response of the percolating network. According to the classical percolation theory, a power law can be used to model conductivity of the form:

$$\sigma_{DC} = \sigma_o (p - p_c)^t \text{ for } p > p_c \tag{2}$$

where, $\sigma_{DC}$ and $\sigma_o$ corresponds to the DC conductivity of the composite and the conducting component respectively, $p$ is the concentration of the conducting component and $t$ represents

**Table 2**
Summary of the experimental results of the reviewed publications involving non-covalent type of pre-treatment of CNT (arranged alphabetically with respect to the polymer matrices).

| Matrix | Modification route | Improvement | Adverse/Remarks | Refs. |
|---|---|---|---|---|
| Epoxy | Non-covalent functionalization of MWNT with sodium salt of 2-aminoethanol | Improvements in electrical conductivity and storage modulus | | [205] |
| Epoxy | Non-covalent modification with non-ionic surfactant Triton X100 | Significant improvement in mechanical properties | No improvement in electrical conductivity | [206] |
| Epoxy | Modification of CNT with Palmitic acid in different ratios | Improvement in electrical conductivity and reduced percolation threshold after modification | 1:1 modification was found to be optimum based on electrical conductivity | [207] |
| Epoxy | Decoration of amino functionalized MWNT with Ag nanoparticles | Improved electrical conductivity (increased further after addition of AG nanoparticles) | Amino functionalized MWNT showed less electrical conductivity as compared to amino functionalized + Ag nanoparticles | [208] |
| Epoxy | Clay assisted dispersion of SWNT | Improved electrical conductivity | No effect on storage modulus | [109] |
| Epoxy | Titania doped hybrid structures of MWNT | Improved elastic modulus | Reduced electrical conductivity | [209] |
| PA6 | Cation-$\pi$ interaction of MWNT with Na-AHA | Improved electrical conductivity | | [85] |
| PA6 | Addition of $CaCO_3$ to MWNT in different ratios | Improved dispersion and electrical conductivity | | [210] |
| PA6 | Encapsulation of MWNT with SMA in mat | Improved mechanical properties | Reduced electrical conductivity due to encapsulation | [211] |
| PA6 | Encapsulation of SWNT with SMA | Improved tensile strength and elongation at break | Lower tensile modulus | [212] |
| PA6 | Encapsulation of SWNT with SMA | Improved tensile properties | | [213] |
| PC | Modification of MWNT with P3HT-*g*-PCL of different molecular weight based on $\pi$–$\pi$ interaction | Improved mechanical and electrical properties | Low DP P3HT-*g*-PCL had better $\pi$–$\pi$ interaction with MWNT giving higher improvements compared to high DP P3HT-*g*-PCL | [214] |
| PA6/ABS blends | Modification of MWNT with Na-AHA | Improved electrical conductivity | Plasticizing effect | [86] |
| PA6/ABS blends | Modification of MWNT with phosponium modifiers of different molecular architecture | Improved electrical conductivity | Plasticizing effect | [105] |
| PMMA | Use of co-solvent TFA and conjugated polymer P3HT establishing '$\pi$–$\pi$' type of interactions | Exceptionally low percolation threshold 0.006 wt% | | [215] |
| PMMA | Non-covalent $\pi$–$\pi$ interaction with P3HT-*g*-PMMA | Improved tensile strength, Young's modulus and elongation at break | | [216] |
| PPF | Surfactant assisted dispersion | Improved compressive modulus and yield strength. (Comparable compressive strength as compared to unmodified SWNT) | Decreased flexural strength and modulus | [138] |
| PS | Non-covalent modification of SWNT with PPE | Reduced percolation threshold | | [217] |
| PS | Dispersion of MWNT with cationic surfactant, SDS | | Processing temperature affects electrical conductivity near percolation threshold | [218] |
| PS | Non-covalent modification of SWNT and MWNT with P3HT-block-PS copolymer | Reduced percolation threshold | | [219] |
| PS | Non-covalent modification of SWNT with trialkyl immidazolium | Improved dispersion | | [220] |
| PS | Non-covalent modification of MWNT with pyrene functionalized styrene maleic anhydride block polystyrene copolymer | Improved electrical conductivity | | [221] |

PPF – poly(propylene) fumarate.

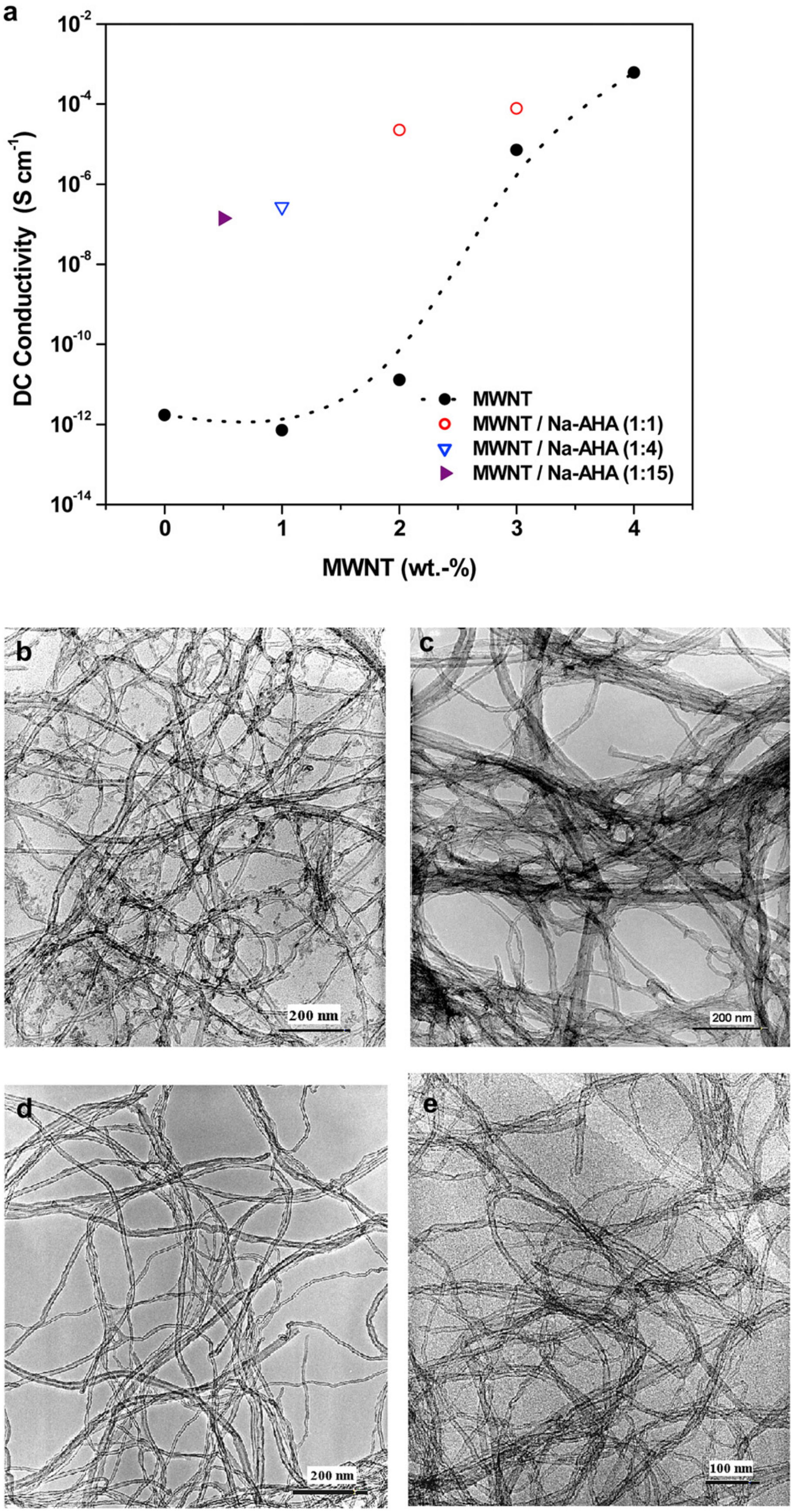

**Fig. 5.** (a) Variations in DC electrical conductivity of PA6/MWNT composites with purified MWNT and dependence with various ratio of MWNT/Na-AHA mixture. TEM image of (b) 'aggregated' MWNT in tetrahydrofuran (THF), (c) 1:1 mixture of MWNT and Na-AHA in THF, (d) 1:4 mixture of MWNT and Na-AHA in THF, (e) 1:4 mixture of MWNT and Na-AHA in distilled water (Kodgire et al. [85] – Reproduced by permission of Elsevier, Copyright© 2006 Elsevier B.V. All rights reserved).

conductivity exponent. The values of $t$ can be determined from the slope of the least-square on a log–log scale. It has been suggested that the theoretical value of exponent $t$ related to the composite system dimensions (2D/3D) ranges from 1.6 to 2.0 [121]. However, various values of $t$ have been reported. It is believed that $t$ can be affected by various parameters viz. temperature, filler matrix interface etc. The larger exponents than the predicted ones are often explained by Swiss–Cheese model [122] which suggests that the real critical exponent $t'$ can be evaluated from:

$$t' = t + (a/l)(1 - l/a) \tag{3}$$

where, $l$ is the tunneling distance coefficient and $a$ is the average distance between two nanotubes.

Further, it has been suggested that the polymer layer in the inter-nanotubes connections provides the highest resistance section in the electrical pathway through the network. This polymer layer is a barrier to efficient carrier transport between nanotubes and models for conductivity based on fluctuation-induced tunneling have been proposed [123]. Considering CNT agglomerates in the composites as near spheres, the resistance is dominated by inter-agglomerate distance and the DC conductivity follows the relation:

$$\ln \sigma_{\mathrm{DC}} \sim p^{-1/3} \tag{4}$$

However, in case of dynamic percolation process the filler moves closer to each other and the tunneling resistance is reduced. This disrupts the random distribution of the filler and the above relation fails (deviates from the exponential behavior).

From various analytical models it is quite evident that the percolation threshold has an intimate relationship with $L/D$ of CNT. Hence, it can be stated that any type of pre-treatments that affects $L/D$ of CNT would eventually influence the percolation thresholds in the composites. Rather, the 'effective $L/D$' (of disentangled CNT) seems to be more important in governing the percolation thresholds in the composites and the latter can be manipulated by various pre-treatments. The chemical functionalization of CNT adversely affects the 'effective $L/D$' due to the involvement of harsh chemical conditions. In contrast, non-covalent routes enable significant exfoliation of CNT mediated by the local environment of various modifiers and increase the 'effective $L/D$'. Different pre-treatments involve different levels of interactions between molecules and the matrix and greatly influence the charge transport mechanisms in the composites. Moreover, improved phase adhesion due to reactive coupling in chemical functionalization of CNT may lead to an insulating polymer layer on the CNT surface which further impedes efficient carrier transport. In case of non-covalent modifications it has been suggested that the hierarchical structures adsorbed on the surface via different specific interactions influence the charge carrier mechanisms in the composites. CNT are considered to be natural electron acceptors and hence they can form a pair with electron donors through van der Waals' and Coulombic interactions. In addition, it is believed that charge transfer may take place when CNT interact with electron deficient neutral or positively charged molecules through various specific interactions. For instance, SWNT/pyrene forms donor–acceptor nano-hybrids and can be electrostatically associated with strong electron donors like porphyrins and pthalocyanines [124]. Partial electron transfer from SWNT onto anthracene has been proposed on account of '$\pi$–$\pi$' interactions [124]. The type of functional groups on the surface of CNT also influences the nature of conduction mechanism. For instance, N–H groups on the surface have been suggested to form charge-transfer complexes and decrease the energy needed for charge carriers to hop from conducting cluster neighbors [125]. Further, it has been proposed that acid treatment induced COOH groups can form vacancy–COOH pairs [126] and improve the electrical conductivity in contrast to many papers which report reduced conductivity due to perturbed $\pi$-conjugation system on chemical functionalization. These examples illustrate the importance of CNT/molecule interactions that dominate the overall charge transport in the nanocomposites.

The influence of various pre-treatments also reflects in different parameters deduced from the analytical models discussed above but few literatures are encountered that investigate the influence of type of pre-treatment on the parameters deduced from classical percolation theories and compare in connection with the pristine CNT. For instance, Kim et al. [46] investigated in detail the influence of different type of oxidation treatment of MWNT on the percolation threshold of epoxy/MWNT composites. These authors claimed that purification of MWNT should be carried out in mild or basic conditions to avoid partial damage to the crystalline structure of MWNT. The type of oxidative treatment also reflects in the exponent $t$ (of Eq. (2)) and the slope (of Eq. (4)) which they addressed to changes in degree of dispersion, flaw density, difficulty in tunneling conduction and interfacial characteristics influenced by type of oxidation (see Fig. 6). Li et al. [127] explained tunneling type of conduction mechanism of carboxylic and ester functionalized MWNT in a polyvinyledine difluoride (PVDF) matrix as manifested from the linear relationships (of Eq. (4)). They claim that the carboxylic functional groups on the surface of MWNT decrease the tunneling current which manifests in a relatively slight increase in electrical conductivity with increasing concentration of MWNT. Further, they found that longer alkyl chains of ester functionalized MWNT are more compatible with the host matrix and showed lower percolation threshold as compared to carboxylic acid functionalized MWNT. The type of pre-treatments also reflects in the values of the dielectric constant of the composites and has been addressed in context to numerous 'mini-capacitors' formed as the concentration of MWNT increases. Valentini et al. [125] explained the conduction mechanism in epoxy/SWNT system by electron donation by the amine groups on SWNT surface and reduction in the hole-carriers in $p$-type SWNT which further decreased the conductance of the composites. This observation was further reflected in the current–voltage characteristic curves. They

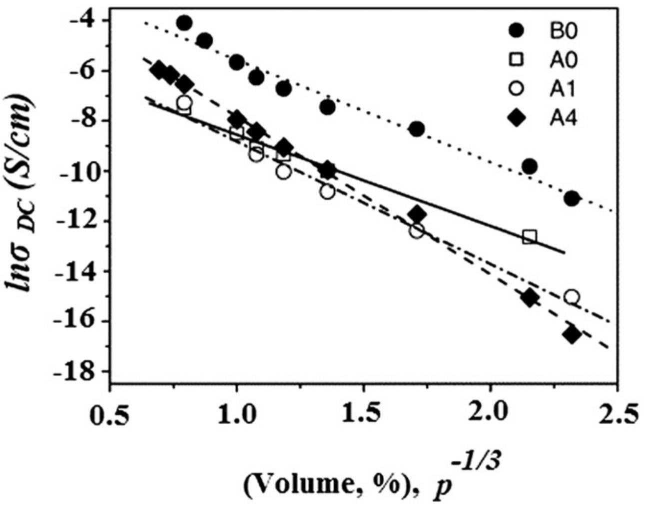

**Fig. 6.** Linear variation of ln $\sigma_{\mathrm{DC}}$ vs. $p^{-1/3}$ in oxidized MWNT/epoxy composites (The codes represent the treatment conditions of MWNT, B0: $H_2O_2/NH_4OH$ mixture (28.5%)/room temperature/for 4 h/pH:10.5; A0: $HNO_3$ (28.5%)/room temperature/for 4 h/pH:3.5; A1: $HNO_3$ (40%)/100 °C/for 1 h/pH:2.5; A4: $HNO_3$ (40%)/100 °C/for 4 h/pH:2.5) (Kim et al. [46] – Reproduced by permission of Elsevier, Copyright© 2004 Elsevier Ltd. All rights reserved).

explained that amine functionalized SWNT provide a vehicle for the proton transfer along hydrogen bonds and further contribute to the increase in intrinsic conductivity.

In context to non-covalent type of treatments, Cui et al. [128] compared the electrical conductivity of epoxy/MWNT composites with or without surfactant treatment. They report tunneling type of conduction mechanism in surfactant treated MWNT composites and addressed the observations in connection with the wrapping effect which was further confirmed by non-linear current–voltage characteristics. Zhao et al. [129] reported low percolation threshold and well-controlled dielectric properties in surfactant treated perfluoro alkoxy (PFA)/MWNT composite films. They addressed these findings in context to restricted relative movements and re-aggregation of SDBS coated MWNT. They also investigated the effect of $L/D$ on the electrical and dielectric properties however, they did not comment on the influence of surfactant treatment on the exponent $t$.

It is evident that the type of pre-treatment reflects in the charge transport properties estimated via various percolation models. The critical parameters deduced from these models provide a vital clue on the nature of charge transfer mechanism in the composites viz. hopping, tunneling and in addition provide insights into system dimensions (2D/3D) networks. Further, the charge transport properties reveal the degree of dispersion of CNT facilitated by various pre-treatments and the influence it has on the intrinsic characteristics of CNT.

### 4.2. Physical gelation

Rheological techniques have been widely used to detect the presence of internal structures in filled polymer composites. In context of polymer/CNT composites, melt rheological investigations shed light on the macroscopic connectivity of 3D network of CNT formed from various physical interactions. At a critical concentration of CNT, the viscoelastic response of the system undergoes a transition from 'liquid-like' to 'solid-like' behavior and this observation is manifested in a plateau in the storage modulus and a sharp rise in the melt-viscosity. The increase in modulus and melt-viscosity is due to physical gelling arising from the entangled network of nanotubes. It is believed that this behavior of CNT may even prevent individual tube motion and often referred as 'jammed solids' [130] in the literature. In most polymer composites (with few exceptions) the rheological percolation threshold has been reported to be well below the geometrical (electrical) percolation thresholds. According to Du et al. [131] different tube–tube distance is required for rheological and electrical percolation thresholds. For instance, the nanotubes should be approximately 5–10 nm distances apart for hopping type of charge transfer to occur whereas they contribute to the physical network as long as they are in the range of radius of gyration of the host matrix. Further, it has been reported that above the rheological percolation threshold it is the combined polymer–nanotubes network which is dominant rather than polymer–polymer network. This phenomenon is a plausible reason behind the fact that above the rheological percolation threshold the effect of increasing the concentration of CNT on the mechanical properties is minimal. Recently, it has been shown that a more homogeneous dispersion of CNT in the matrix leads to stronger solid like and non-terminal behaviors and the composites exhibits weaker temperature dependency [132].

The effect of chemical functionalization of CNT on the rheological percolation threshold is quite profound in contrast to the limitations in its role in electrical percolation threshold. It has been postulated that defect ridden tubes though adversely affect the electrical percolation threshold of the composites but significantly contribute to the physical network (rheological percolations) on account of various types of interactions with the matrix. Cynthia et al. [133] reported that the functionalized SWNT in PS matrix demonstrated a percolated 'network-like' structure at concentrations well below that of pristine SWNT (see Fig. 7). This behavior has been addressed in connection with better dispersion and improved compatibility with the polymer matrix. Further, these authors compared the relative influences of functionalized and un-functionalized SWNT on the chain dynamics of PS. They reported that SWNT do not significantly affect the dynamics of the polystyrene (PS) chains on length scales comparable to the entanglement length which manifested roughly the same composition dependency of functionalized and un-functionalized SWNT in PS matrix (see Fig. 7). Similar observations were reported by Zhou et al. [134] where the rheological percolation thresholds in case of PMMA modified MWNT were significantly lower as compared to its unmodified counterpart. This behavior has been explained with context to the PMMA chains grafted on the surface of MWNT that can entangle with the polymer chains to form a continuous nanotubes–polymer chains network, even when the gap between nanotubes is larger than the radius of gyration of PMMA chain. In a detailed investigation, Lee et al. [135] compared the viscoelastic response of heat treated, acid treated and amine treated MWNT in a polypropylene (PP) matrix. Storage modulus values in the composites were reported to be improved for both heat-treated and acid treated MWNT on account of homogeneous dispersion and stronger interactions between MWNT and PP matrix. However, the viscoelastic properties for the amine treated MWNT were reported to be decreased which has been attributed to excessive hydrogen bonding between amine functional groups leading to aggregation of nanotubes in PP matrix. In contrast, the rheological percolation thresholds were almost unaffected in acid treated and purified MWNT in PA6 matrix whereas significant differences were noted in electrical properties [136]. Besides melt interfacial reactions with the matrix the AR of CNT also plays a significant role in rheological percolation threshold. This was realized by Bose et al. [47] in melt-mixed PA6/ABS blends with amine functionalized MWNT which showed delayed percolation threshold as compared to pristine

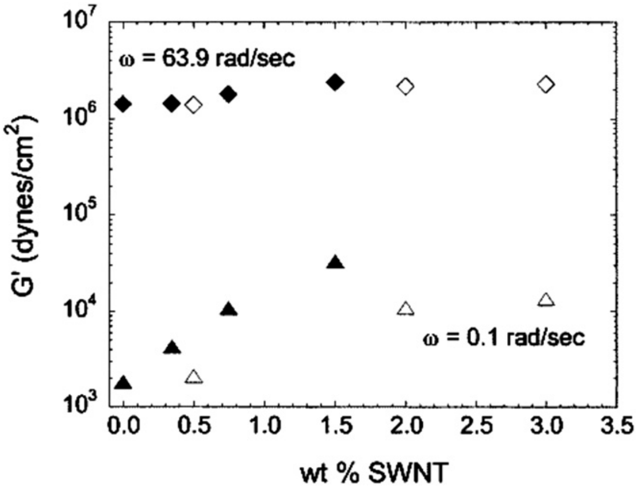

**Fig. 7.** Comparison of storage modulus ($G'$) values at two frequencies for the functionalized SWNT composites (filled symbols) and the un-functionalized SWNT composites (open symbols). The diamonds correspond to a frequency of 63.9 rad/s at 170 °C and the triangles represent data at 0.1 rad/s (Mitchell et al. [133] – Reproduced by permission of American Chemical Society, Copyright© 2002, American Chemical Society).

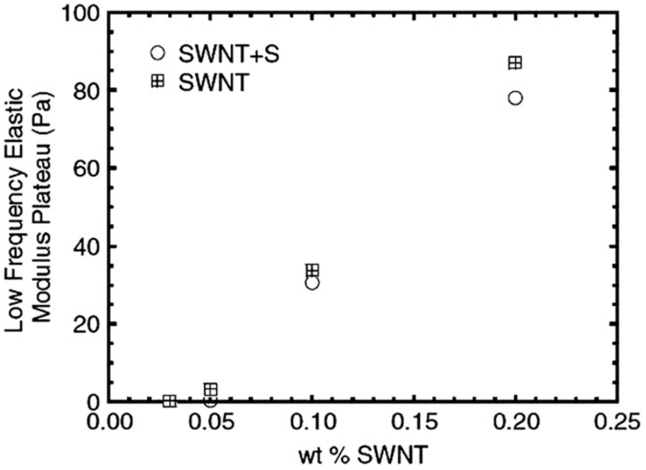

**Fig. 8.** Concentration dependence of low frequency elastic modulus for PFA/SWNT composites (Shi et al. [138] – Reproduced by permission of IOP Publishing Limited).

MWNT. Further, they concluded that it is the 'effective AR' which is a dominant factor in controlling both electrical and rheological percolation thresholds.

Very few articles were encountered comparing the influence of non-covalent treatments of CNT with their unmodified counterparts on the rheological percolation thresholds. Few literatures on wrapping and surfactant-mediated dispersion of CNT on the rheological properties are discussed here. In case of SMA encapsulated SWNT in a PA12 matrix a 'better' percolated structure has been reported as compared to PA12/SWNT composites [137]. It has been suggested that the process of encapsulation by SMA copolymer led to finer dispersion of SWNT and enhanced interfacial adhesion between PA12 and SMA modified SWNT. The rheological percolation thresholds have been reported to be slightly delayed in surfactant treated SWNT in poly(propylene fumarate) matrix (as inferred from the low frequency elastic modulus plots, Fig. 8) for the reasons which needed further investigations as claimed by the authors [138]. The rheological percolation threshold (~0.25 wt%) has been found to coincide with the geometrical percolation threshold in PA6/ABS blends with Na-AHA modified MWNT [86]. This was attributed to higher degree of exfoliation of MWNT rendered by Na-AHA. Thus both covalent and non-covalent treatments influence significantly the physical network of CNT in the composites on account of different levels of molecular interactions with the macroscopic chains. In summary, the rheological percolation threshold offers a vital clue on the nature and extent of interaction potential of CNT with the matrix and helps in understanding the underlying concepts of polymer-nanotubes networks and the effect of CNT on the chain dynamics.

## 5. Conclusion and outlook

The recent advances in polymer/CNT composites in the framework of different types of pre-treatments currently employed to manipulate the dispersion stability and quality of CNT in the composites have been reviewed. Different strategies followed in numerous journal publications have been discussed and the strengths and weaknesses of various pre-treatments have been summarized. In this context, diverse proposed mechanisms concerning the interaction potential of different molecules with CNT have been highlighted. Further, the influences of the pre-treatments on the geometrical and physical networks of CNT have been addressed. Several transport parameters deduced from different analytical models have been discussed in connection with different types of pre-treatments. These transport parameters offer a vital clue on the nature of the pre-treatment and on the degree of dispersion of CNT in the composites.

It is evident from the statistics of Fig. 9a that covalent modifications of CNT has been much emphasized as it enables efficient tailoring of the polymer/CNT interface through reactive coupling between the functional moieties on the CNT surface with the available functional groups of the polymer. This strategy significantly improves the structural properties of the nanocomposites (see Fig. 9b). However, this route perturbs the extended $\pi$-conjugation system of CNT and adversely influences the intrinsic

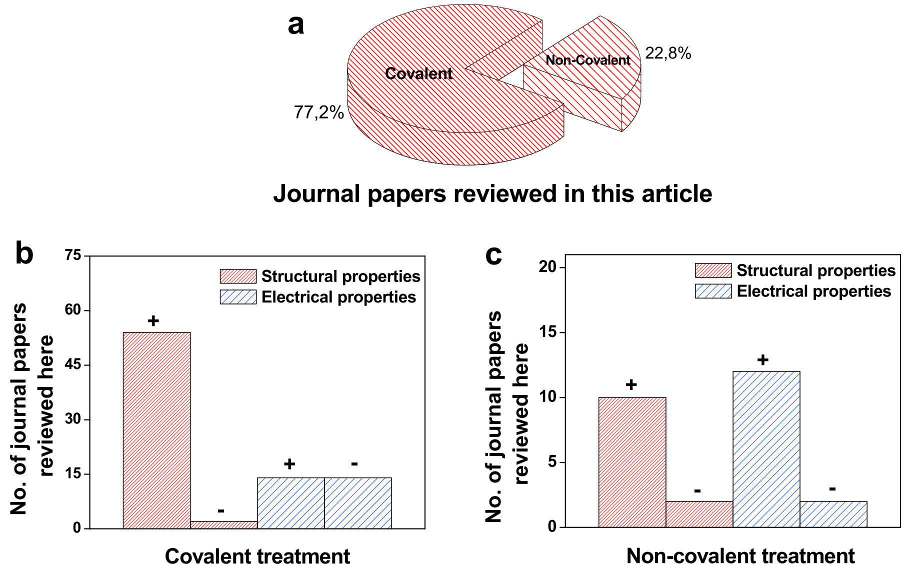

**Fig. 9.** (a) Overall statistics of the journal papers reviewed in this article which addresses the influence of various pre-treatment in polymer/CNT composites and compares with respect to pristine CNT; (b) Statistics showing the strengths (+) and weaknesses (−) of covalent and non-covalent types of pre-treatment on the composite properties (statistics also includes paper which report simultaneous improvement in both structural and electrical properties).

electronic characteristic of the nanotubes though few studies report a positive influence as well (see Fig. 9b). Hence, the typical conditions during chemical functionalization become extremely vital and carefully selecting the optimum conditions can lead to optimal macroscopic properties.

An alternative route to oxidative treatments is the non-covalent treatments which allow the adsorption of different hierarchical structures on the CNT surface through various specific interactions. This route also preserves the integrity of the tubes which further results in positive influence on the electrical conductivity of the composites (see Fig. 9c). In addition, on account of various types of interactions with the host this route also shows moderate to significant improvements in the structural properties of the composites (see Fig. 9c). However, the concentration and the molecular architecture of the molecules are the vital parameters and needs thorough understanding to realize the extent of interaction potential. Recently, a study by Simmons et al. [91] demonstrated that stable dispersions of SWNT can be achieved by employing a simple and effective non-covalent functionalization with PCA without substantial altering the *L*/*D* and introduction of defects. This route besides leading to improved dispersion of SWNT in polycarbonate (PC) matrix also led to improved bond strength as manifested from Raman strain shift analysis. Such strategies can possibly be extended to other aromatic compounds having abundant '$\pi$-electrons' viz. napthalenes, anthracenes, porphyrins etc. or derivatives of such molecules which would further allow desirable functional groups on the surface of CNT. In the light of this approach, *in situ* thin layer wrapping of CNT with cross-linkable conducting polymer glue can plausibly enhance the dispersion stability of CNT and further improve the electrical conductivity of the composites. The *in situ* generated polymer is likely to reduce the aggregation of CNT which otherwise segregates through attraction-depletion mechanism as suggested by Demir et al. [139] in case of inorganic oxides. However, the molecular weight and thickness of the *in situ* generated polymer layer are the governing factors. Hence, intimate understanding of the interactions at molecular length scales and the associated limiting factors would enable to obtain optimal macroscopic properties.

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**Paula Moldenaers** is Full Professor at the Department of Chemical Engineering of the Katholieke Universiteit in Leuven and is Head of the Laboratory of Applied Rheology and Polymer Processing. Her research focuses on the rheology and morphology of complex fluids. Paula Moldenaers received the Annual Award of the British Society of Rheology in 1991 and the Publication Award of the Society of Rheology in 1997 (with I. Vinckier and J. Mewis) and in 2008 (with S. Reynaert, C. F. Brooks, J. Vermant and G. G. Fuller). She is a member of the Royal Flemish Academy of Belgium for Arts and Sciences.

**Suryasarathi Bose** studied at the Andhra University, Visakhapatnam, India from 1998 to 2002, where he received a bachelor's degree in Chemical Engineering. He then moved to Institute of Chemical Technology, Mumbai, to obtain his master's degree in Polymer Engineering and Science. He obtained his Ph.D. from Indian Institute of Technology Bombay working on structure and development of carbon nanotubes based polymer blends. He is now a post-doctoral researcher in the group of Applied Rheology and Polymer Processing of the Katholieke Universiteit Leuven, where he continues his work on carbon nanotubes based polymer blends.

**Rupesh Khare** studied at the Institute of Chemical Technology, Mumbai from 2002 to 2006, where he received a bachelor's degree in Chemical Technology. He is now doing his Ph.D. on polymer/CNT composites at Indian Institute of Technology Bombay.