

Nanocomposite of PVC with CNT



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Abstract Poly(vinyl chloride) (PVC) with various advantages such as good chemically stability, biocompatibility and relatively low price could be one of the widely used polymers in industries. However, low electrical and thermal conductivity and poor mechanical strength have been the main problems of PVC limiting its practical applications so far. Over the past decade, to enhance electrical and thermal conductivity and mechanical strength of PVC, a lot of research has been carried out using various nanofillers. Carbon nanotubes (CNTs) with high modulus (1 TPa), high strength (stronger than steel), high thermal stability (2800 °C in vacuum), excellent electrical conductivity (higher than copper), and high thermal conductivity (higher than diamond) are excellent candidates for PVC-based nanocomposites preparation as nanofillers. Recently, PVC/CNTs nanocomposites have received considerable attention as an interesting and important research area, worldwide. But, further research on optimization of the PVC/CNTs nanocomposites properties is necessary to find their future applications for practical uses. Current progresses in development of PVC/CNTs nanocomposites are being reviewed, in this chapter.

Keywords Poly(vinyl chloride) · Carbon nanotubes · Composite · Nanocomposite · Nanofiller

1 Introduction

For many years, combination of two or more materials to create new materials with improved properties has been a common procedure. Composites as a combination of two or more materials provide characteristics that not achievable by either material alone. Compared to the traditional materials, composites are lighter, stronger and less expensive. Therefore, today, composites have become increasingly necessary in a wide variety of structural applications [1, 2]. Composites are fabricated by matrix

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materials and fillers, in which the former surrounds the latter. The fillers impart their special characteristics to the matrices. With rapid development of composites, polymers with good processibility have replaced many of the conventional matrices of composites [2].

Polymers with distinct characteristics including simplicity of manufacture, light weight, and ductility are commonly employed in various applications. Low electrical conductivity, poor mechanical strength and low thermal stability are the main problem of polymers that limit their practical applications. Therefore, improving electrical, mechanical and thermal properties of polymers using fillers including fibers, platelets, or particles has recently received much attention. Even with minimal level of fillers, improvements in characteristics of polymers could often be obtained [1, 2].

In recent decades, polymer nanocomposites (PNCs), made up of nanofillers embedded in polymer matrices, have received much attention by researchers and industries. The PNCs properties depend on their interfacial characteristics beside properties of their individual elements. Large interface area between the nanofiller and the polymer matrix is a key issue for PNCs. According to the theoretical assumptions, the objective of PNCs is to create large interface between nanofillers and polymer macromolecules. In comparison to traditional polymer composites containing microfillers, the larger interface between nanofillers and polymer macromolecules results in remarkable properties in PNCs [3]. These properties can also be related to the properties of nanofillers (size, shape, and surface area), and polymers (molecular weight, chemistry, and architecture), and fabrication procedure (concentration of nanofillers, nanofillers/polymer interaction, and nanofillers dispersion in polymers). In addition, the nanofillers can impart their functionality to the polymer matrices including thermal, electrical and mechanical properties. Importantly, PNCs retain the polymers' desirable features, such as processability and low mass density [4]. For example, incorporation of nanofillers to rubber matrix of car tires can boost mechanical strength, wear resistance, and traction with preserving low cost and weight [5]. PNCs have features that make them suitable for a variety of applications, including land and air transportation vehicles (automotive and aerospace sectors), as well as sports equipment. PNCs also have good barrier, permeability, and selectivity properties, making them good candidates for gas separation and water and wastewater treatment as well as food packaging [6–12]. For example, blending fumed silica as nanofiller with poly(4-methyl-2-pentyne) (PMP) results in significant increase in both n-butane/methane selectivity and n-butane permeability, two properties that are frequently in competition [13]. On the other hands, incorporation of nanofillers into polymer matrices can contribute functional features, particularly optical and electrical capabilities. For example, addition of silver nanowires, carbon nanomaterials, or other conductive nanofillers into insulating polymer matrices can increase their electrical conductivity [14–17].

Polyvinyl chloride (PVC) as a widely-used polymer is inevitable for our modern daily life. Various applications of PVC include packaging, bottles, electrical cables insulation, plastic cards, pipes, clothing, inflatable products and etc. The PVC properties can be tuned by using fillers for different applications, such as clay, glass, calcium carbonate bamboo, pine flour, and wood fibers. Carbon Black (CB) can be

used effectively as PVC filler [18]. As reported in literature, elongation at break of the CB-PVC composite decreases with increasing CB amount, but tensile strength of the CB-PVC composite increases with increasing CB amount until 15 wt%, then decreases. Nanostructured materials (nanofillers) are frequently used as PVC reinforcing agents [19]. Han Wang et al. reported fabrication of the PVC nanocomposites containing multilayer graphene (MLG) with improved glass transition temperature and tensile modulus [20]. Sajini et al. reported fabrication of PVC nanocomposites filled with graphene with high thermal stability and mechanical strength [21].

Carbon nanotubes (CNTs) with unique characteristics including high thermal stability (2800 °C in vacuum), high modulus (about 1 TPa), high strength (100 times stronger than steel), excellent electrical conductivity (1000 times higher than copper), high thermal conductivity (2 times than diamond), high aspect ratio and high flexibility are excellent candidates for PVC-based nanocomposites preparation as nanofillers. However, van der Waal interactions between CNTs prevent their widespread usage as PVC nanofillers, because CNTs with inert surface tend to aggregate in the polymer matrix. Uniform CNTs dispersion in the polymer matrices can improve PNCs characteristics, significantly. Hence, to avoid CNTs agglomeration and improve their dispersion within organic solvents and polymer matrices, CNTs functionalization with specific functional groups is of great importance. CNTs functionalization can modify CNTs physical and chemical properties, resulting in fabrication of CNTs-based PNCs with improved properties and performance for various applications [22–26].

Current progresses in preparation and characterization of PVC/CNTs PNCs are being reviewed, in this chapter.

2 CNT-Based PNCs Preparation

Uniform CNTs dispersion in polymer matrices is a critical issue in PNCs preparation. The polymer/CNTs properties can be improved by several factors including CNTs distribution and orientation in the polymeric matrices, surface adhesion between the both components (CNTs and polymers) and manufacturing processes. Solution mixing, melt mixing, and in-situ polymerization are some techniques which can be used to make CNT-based PNCs [27–29].

2.1 Solution Mixing

The simplest and most widely used technique for CNT/PNCs preparation is called solution mixing or solvent molding. This method involves CNTs dispersion in PVC solution by energetic agitation, controlled solvent evaporation and casting CNTs/PVC nanocomposite films on substrates surface. Upon solvent evaporating, PVC chains may reassemble and wrap CNTs as nanofillers. Agitation can be performed

by shear mixing, refluxing, magnetic stirring, and sonication as the most commonly used methods [30]. It is well known that simple magnetic stirring is ineffective in completely dispersing intact CNTs in solvents, and the use of high-speed shear mixing or ultrasonication is more effective in formation of the CNTs dispersion. Dispersion, emulsification, comminution, and activation of nanomaterials in solvents are all common uses of sonication. As reported in literature, sonication as a high-speed agitator or mixer is useful in dispersing aggregated and entangled CNTs in solvents for PVC-based PNCs preparation [31]. Although sonication can be used to break CNTs aggregation in solutions, sonication of raw CNTs is not usually enough due to re-aggregation of CNTs after stopping sonication. Surface modification of CNTs that is accomplished by adding functional groups to the CNTs surface is another method to create desired and permanent CNTs dispersion. In some cases, the functional groups of CNTs and the polymer matrices may be incompatible. Although solution mixing method has a number of advantages, for the extensive use of this method, the effective removal of solvents used during the procedure remains as a significant problem. In other words, high solvents cost and their disposal have negative effects on scaling-up of this method [32, 33].

2.2 *Melt Mixing*

Melt mixing is one of the most efficient and environmental-friendly methods of PNCs production. This method involves heating a mixture of polymer and nanofiller (CNTs) to generate a viscous liquid. In other words, this method consists of CNTs dispersing in molten polymer matrix by mechanical shearing action [34–40]. In this method, a shear mixer improves the CNTs dispersion in the molten polymeric matrix using extrusion or injection. High temperature shear mixer can also be used to automatically disperse CNTs into polymer matrix [41]. Compared to the solution mixing method, one of the challenges of the melt mixing method is the lower CNTs dispersion in the polymer matrix due to the higher viscosity of the dispersion media (molten polymeric matrix) [42]. Melt mixing is performed in the presence of an inert gas including argon, nitrogen, or neon. Melt mixing is an environmental-friendly method due to the absence of organic solvents and is compatible with current industrial processes including injection and extrusion molding. Therefore, the melt mixing method has become more popular, due to its potential in industrial applications for mass production and also its cost-effectiveness. Poor dispersion of nanofillers in the polymer matrices, specifically in higher nanofiller loadings is also the main disadvantage of this method which can be afforded by the CNTs functionalization. Crushing and shortening of nanofillers (CNTs) is another disadvantage of this method due to strong shear forces applied for the nanofillers dispersing that can affect negatively PNCs properties [34–40].

2.3 *In Situ-Polymerization*

In situ-polymerization has been used extensively in the last decades for PNCs preparation with excellent dispersion and distribution of nanofillers in polymeric matrices. This method involves nanofillers mixing in a monomer (or monomers) or a monomer (or monomers) solution, and then polymerization in the presence of the dispersed nanofillers. Both thermoplastic and thermosetting polymers can be processed using this method. As reported in literature [43–46], in the resulting PNCs fabricated by this method, covalent linkages between the nanofillers and the polymer matrices occur. To avoid the nanofillers aggregation during the polymerization, grafting offers an excellent possibility for direct covalent linking of the polymer matrices and nanofillers. Polymers can either be grafted to or from the nanofillers surface. However, using this procedure noncovalent nanocomposites can also be obtained. In comparison to the melt mixing method, high level of nanofillers dispersion can be achieved, because this method allows for direct integration of well-dispersed nanofillers in bulk polymeric matrix. One of the advantages of this approach is grafting of the polymer molecules onto the CNTs walls, resulting in improved dispersion of CNTs in polymer matrices [43–46].

3 Carbon Nanotubes

Carbon nanotubes (CNTs) as a member of carbon nanomaterials family, discovered by Iijima [47], in 1991, have been widely considered during the last decade as the century material [48–50]. Because of their unique one-dimensional tubular structure and outstanding mechanical, thermal and electrical properties, CNTs have attracted enormous scientific attention and their various applications specially in PNCs preparation have been continuously under further investigation. Other extraordinary chemical and physical properties of CNTs include high specific surface area, high aspect ratio (length to diameter ratio), high mechanical stiffness, ease of functionalization, high flexibility, low mass density, frictionless surface and effective π - π interactions with aromatic compounds. CNTs consist of one, two or several carbon sheets with thickness of one-atom of carbon as graphene sheets which are rolled in hollow cylindrical structure with diameter of less than 100 nm and length of more than several micrometers [51, 52]. There are three CNTs types: single walled (SWCNTs), double walled (DWCNTs) (two layers of rolled graphene sheets) and multi walled (MWCNTs) (multiple layers of rolled graphene sheets) as shown in Fig. 1. CNTs diameters typically range 0.4–3 nm for the SWCNTs, 1–3 nm for the DWCNTs and 2–100 nm for the MWCNTs, with length ranging from 1 to 50 μ m [53–55]. Strong covalent bonds hold the carbon atoms in graphene sheet structure and Van der Waals forces (π -stacking) hold graphene sheets together in DWCNTs and MWCNTs structures. Therefore, CNTs have the highest strength-to-weight ratio among the other nanomaterials [56]. CNTs mass density is very low and their aspect ratio is over than

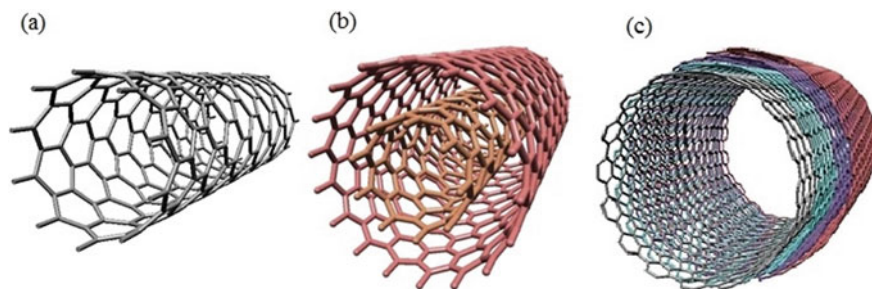


Fig. 1 A schematic of **a** SWCNT, **b** DWCNT and **c** MWCNT

1000. According to the experimental results, tensile modulus and tensile strength of CNTs are remarkably high. As different factors such as CNTs length and diameter can affect their electrical properties, CNTs can be conductive or semi-conductive. CNTs provide freely movement of electrons through their long-hollow cylindrical structure. Hence, CNTs can be more conductive than copper [57, 58].

At present, the main methods of CNTs synthesis are arc discharge [59], electric laser ablation [60], and chemical vapor decomposition (CVD) [61, 62]. The last method due to its relatively low growth temperature, and high purity and yield is the most promising method for possible scale-up [63]. CNTs purification is an essential issue that to be addressed because as-prepared CNTs at low growth temperature usually contain metallic or carbonaceous impurities. Chemical oxidation as a common method has been developed for increasing CNTs purity [64]. Open end or closed end CNTs can be obtained depending on the synthetic procedure. In general, synthesis of CNTs is a striking challenge, because walls number, dimensions (diameter and length) and alignment (chiral, armchair or zig-zag) of CNTs should be controlled [65].

There are several methods for CNTs functionalization including non-covalent and covalent functionalization and oxidation (defect functionalization) [53, 66]. Covalent modification is an effective method but deteriorates the intrinsic properties of CNTs. For the first time, Smalley and co-workers [67] were successfully cut and functionalized SWCNTs with carboxylic groups, under ultrasonic waves using strong acid [25, 26, 68].

4 PVC-Based PNCs

Polyvinyl chloride (PVC) is one of the most commonly used polymeric materials because of its superior chemical, mechanical, and thermal properties, and also its relatively low cost compared to other polymers. PVC is soluble in a wide range of solvents, including tetrahydrofuran (THF) [69], N,N dimethyl acetamide (DMAc) [70], dimethylformamide (DMF) [71], and N-Methylpyrrolidone (NMP) [72]. PVC

can be generated via three methods, commercially. PVC generated by suspensions polymerization, emulsion polymerization, and bulk or mass polymerization is named as SPVC, EPVC, and MPVC, respectively. Surfactants are used to disseminate vinyl chloride monomer in water during emulsion polymerization [25, 73–75]. PVC was first commercially produced via emulsion polymerization in the early 1930s in Germany. PVC's heat processing and stability were enhanced for the first time in 1932, with discovering plasticizers and stabilizers [76].

PVC is an important commercial polymer that can be used in variety of industrial fields [77]. In particular, PVC is one of the most common polymers used in production of PNCs due to its properties including widely developed processing, relatively low cost, high environmental resistance, and ability to be modified [78–80]. The limitation of PVC is mainly related to its relatively high glass transition temperature (T_g), which results from the strong polar interactions between the PVC molecules due to the presence of chlorine atoms [81, 82]. T_g of a polymer is widely dependent on its molecular structure and molecular weight [83]. However, specific plasticizers, which are inserted into the polymeric macromolecular structure, can usually reduce the T_g value of PVC [84]. Although several studies have been conducted on the effects of nanofillers on the PVC nanocomposites properties, only a few of them have addressed the effect of nanofillers on thermal properties of this polymer in its glassy state [85, 86]. Incorporation of very small amount of CNTs with outstanding properties into PVC matrix can improve thermal, mechanical, and electrical properties of PVC for various engineering applications. Also, CNTs with excellent transport properties can improve separation properties of PVC membranes [73, 74, 87]. General properties of PVC are presented in Table 1.

Table 1 General properties of PVC

Properties	Value
Density	1380 kg/m ³
Elongation at break	20–40%
Glass transition temperature	87 °C
Tensile strength	50–80 MPa
Young's modulus	2900–3300 MPa
Melting point	212 °C
Heat transfer coefficient	0.16 W/m.K
Specific heat	0.9 kJ/kg.K

5 Effect of CNTs on the PVC-Based PNCs

5.1 Mechanical Properties

Mechanical properties of CNTs are outstanding. CNTs with Young's modulus of 270–950 GPa and tensile strength of 11–63 GPa are the stiffest and strongest materials yet discovered. These excellent mechanical properties are due to the covalent sp^2 bonds between carbon atoms in the CNTs structure. In the axial direction, CNTs are very strong. CNTs are at least 30 times stronger than Kevlar (used in bulletproof vests) and 117 times stronger than steel. CNTs with high aspect ratio (length to diameter ratio), excellent spring-like flexibility, and extraordinary mechanical properties can be used as polymer reinforcement agent, effectively. Preparation of the CNTs-based PNCs with improved mechanical properties is now a challenge, because homogenous dispersion of CNTs in polymeric matrices is difficult due to the agglomeration tendency of CNTs. Therefore, one of the most concerns in the CNTs-based PNCs field is how to enhance the CNTs dispersibility in polymer matrices. The CNTs functionalization has significant effect on reaching the CNTs-based PNCs with optimum mechanical properties. By enhancing the interaction between CNTs and polymers, controlling the CNTs amount and adjusting the CNTs orientation in the polymeric matrix, mechanical properties of the CNTs-based PNCs can be improved. On the other hands, poor CNTs dispersion in polymer matrix results in poor stress transfer [2].

There are three approaches to improve the CNTs dispersity in polymer matrices including mechanical mixing, sonication and covalent or non-covalent functionalization of CNTs. Sonication is a common method to achieve good dispersion of CNTs in polymer matrix. Although covalent functionalization of CNTs introduces structural defects to the CNTs surface, the stress transfer from the polymer matrix to CNTs can be greatly improved by this functionalization. Covalent functionalization of CNTs can be achieved by oxidation or in-situ polymerization that in this method monomers react with oxygen-congaing functional groups on CNTs to introduce polymer chains on CNTs wall. In general, in situ-polymerization technique is scalable for large-scale production of the CNTs-based PNCs [2].

Aljaafari et al. [88] reported fabrication of two groups of PVC-based PNCs loaded with different CNTs contents. Their results demonstrated that CNTs have lower electrical and mechanical percolation threshold than other nanofillers like carbon nano powder (CNP). It was found that with incorporation of 1 wt.% CNTs in PVC matrix, elastic modulus increases 2.3 times greater than with incorporation of 2 wt.% CNP. The T_g value was slightly changed with addition of either nanofillers. It was found that the interfacial effect cannot be ignored when the interaction between polymer and CNTs is strong.

Mechanical properties of the CNT/PVC PNCs containing 0.5 wt.% CNTs were investigated by Yazdani et al. [89]. It was found that failure strain of the fabricated PNCs is affected by CNTs, significantly. In the presence of CNTs, failure

strain reduces, up to 60%, regardless of the dispersion quality of CNTs. The PVC-based PNCs were also synthesized by Blake et al. [90]. It was found that strength, Young's modulus and toughness of the fabricated PNCs are improved as the functions of nanofiller content. Shi et al. [91] grafted poly n-butyl methacrylate (PBMA) onto CNTs to improve the CNTs dispersion in PVC matrix. It was found that the grafted PBMA-CNTs are better dispersed in PVC matrix and the load transfer efficiency from the polymer matrix to the CNTs is improved. Also, it was found that even at lower CNTs content, Young's modulus, storage modulus, tensile strength, yield stress, toughness, and ultimate strain of the fabricated PNCs are significantly improved. The load transfer from PVC to the CNTs is also improved due to the strong miscibility between PVC and PBMA. Pan et al. [92] fabricated the PVC/CNTs PNCs, using the modified CNTs covalently and non-covalently with N-epoxypropyl PPTA (PPTA-ECH). It was found that compared with the neat PVC, mechanical properties of the fabricated PNCs are significantly improved. The physicochemical features of PVC/CNTs functionalized with riboflavin (RIB) were investigated by Abdolmaleki et al. [93]. It was found that the PNC containing 12 wt.% RIB-CNTs exhibits better mechanical and thermal behavior compared to the other CNTs contents. Katarzyna et al. [94] investigated the improved dispersion of CNTs in the PVC matrix using methyl oleate and oleic acid. The results showed that the obtained samples demonstrate lower agglomeration rate of the modified CNTs with their higher stability in the PVC matrix.

5.2 Thermal Properties

For a single CNT, longitudinal thermal conductivity is about 2800–6000 W/m.K, at room temperature. Thermal conductivity of CNTs with aspect ratio in the order of 10^3 , is higher than those of graphite and carbon fibers and is comparable to diamond. Theoretical studies predicted ultrahigh thermal conductivity values for CNTs (3000 W/m K for MWCNTs and 6000 W/m K for SWCNTs), while, smaller thermal conductivity values have been obtained by experimental measurements (3218 W/m K for SWNTs and 15–1500 W/m K for MWNTs) [95, 96]. The CNTs structure such as morphology, size and dispersion ability have significant effects on the CNTs thermal conductivity. CNTs along their length have high thermal conductivity, but across their width have poor thermal conductivity. Therefore, it is required that CNTs to be aligned through thickness of a PNC layer to conduct heat from one face to other face of the PNC layer. Carbon-based conductors such as CNTs can be replaced with copper wire with a weight reduction of up to 90%. PVC is thermally weak and decomposed at 140 °C, thus incorporating CNTs as a reinforcing material into PVC matrix can improve its thermal stability. It was shown that the thermal and electrical transfer mechanism of CNTs-based PNCs is better than composites filled with metallic particles [13]. A combination of insulating polymer matrix with low content of conductive CNTs is expected to develop thermally and electrically conductive composites [5, 14]. It was

shown that thermal conductivity of a polymer matrix containing a segregated structure of conductive filler is higher than that of a polymeric matrix containing a random distribution of filler. Mamunya et al. [97] investigated the concentration dependence of CNTs/PVC PNCs thermal conductivity. Due to the high CNTs anisotropy and presence of segregated CNTs structure within the PVC matrix, an ultra-low value of electrical percolation threshold (0.05 vol.%) was obtained. It was found that, at higher CNTs contents, an improved thermal conductivity can be obtained.

5.3 Electrical Properties

As reported in literature, CNTs have high electrical conductivity (10^2 – 10^6 S/cm for SWCNTs and 10^3 – 10^5 S/cm for MWCNTs) [96, 98]. CNTs conduct electricity by vibration of covalent bonds holding carbon atoms together. Since each carbon atom in the CNTs structure has four electrons and only three electrons are used to form the covalent bonds, there is one remaining electron in outer shell that is highly mobile and available for electrical conduction. Therefore, this intrinsic high conductivity of CNTs makes them as logical choices for tuning the polymers electrical conductive properties. Estabraq et al. investigated electrical properties of PVC/CNTs PNCs. The PNCs were prepared by THF as solvent, followed by the film casting. It was found that with increasing the amount of CNTs, electrical conductivity of the fabricated PNCs increases [99]. As reported in literature, PNCs containing small amounts of CNTs have better electrical and thermal properties than PNCs filled with metallic particles [99]. Broaza et al. found that with uniform dispersion of CNTs in the PVC matrix, electrical conductivity of the PVC/CNTs PNCs increases [100]. Mamunya et al. investigated electrical behavior of the PVC/CNT PNCs by the percolation theory. It was found that electrical conductivity of the PVC/CNT PNCs depends on the CNTs content enabling to reveal the ultra-low percolation threshold value which is 0.05 vol.% [97].

5.4 Permeation Behavior

Polymer nanocomposite membranes (PNMs) with improved properties and performance than polymeric membranes have attracted enormous interest for various separation applications, in recent years. This improvement could be obtained by incorporation of inorganic nanomaterials including metal organic framework (MOF), carbon nanomaterials (for example carbon nanotubes (CNTs)), carbon molecular sieve (CMS), silica, zeolite, and titanium oxide (TiO_2) as nanofillers into polymer matrices. These membranes combine advantages of both polymeric and inorganic membranes and compensate their disadvantages [101–110]. CNTs with unique structure and extraordinary chemical and physical properties have attracted considerable attention as a new type of nanofillers for novel PNMs fabrication. CNTs can be

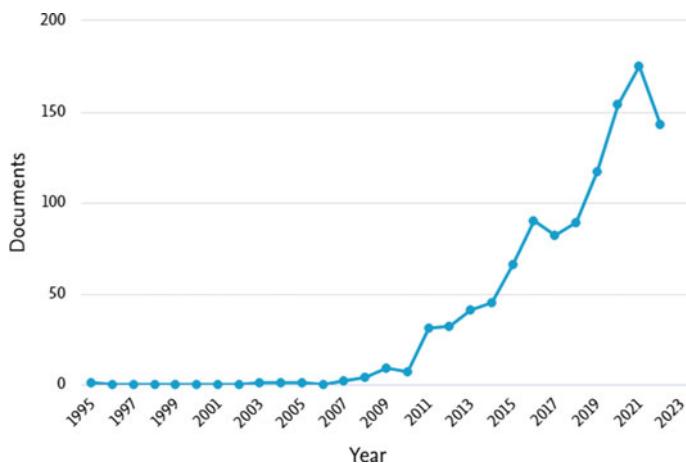


Fig. 2 Publications number in the field of “CNTs”, “PVC” and “membranes”, over time (Reprinted from Scopus)

incorporated with polymeric membranes by embedding into the polymer matrix or modification of the membrane surface. The potential advantages of CNTs incorporation in polymer matrices are improved membrane performance (rejection and permeability), increased membrane mechanical strength, reducing fouling tendency, and controlling pore size and etc. [102, 111–115].

Figure 2 shows the increasing number of publications on the topic of CNTs/PVC PNMs in the recent years.

CNTs with outstanding properties including high mechanical strength and chemical and thermal stability, ease of functionalization, large surface area, high aspect ratio, and fast water transport rate (3–4 orders of magnitude faster than the rate predicted by the Hagen–Poiseuille equation) that is due to the molecular ordering phenomena and atomic-scale CNTs walls smoothness could be used for development of high performance PNMs in water purification and desalination applications [116–118]. The enhanced antifouling properties of the PNMs containing CNTs have been related to the hydrophilic functional groups [119–121].

Haghighat and Vatanpour reported fabrication of PVC nanofiltration nanocomposite membranes containing polypyrrole-functionalized CNTs (PPy-MWCNTs). It was found that flux recovery ratio and antifouling capabilities of the prepared nanocomposite membranes increase during BSA filtration. In the presence of 0.25 wt.% PPy-MWCNTs, pure water flux (PWF) increased from roughly 59.7 LMH for the neat membrane to 75.2 LMH for the optimized nanocomposite membrane. Furthermore, the fabricated membranes showed effective rejection of BSA and Reactive Blue 50 dye (higher than 95%). It was found that hydrophilicity of the fabricated nanocomposite membranes increases by increasing the PPy-MWCNTs content, due to the presence of amine groups on the membrane surface which facilitates hydrogen bonds formation with water molecules. The results showed that adding the optimum

amount of PPy-MWCNTs to the casting solution can enhance the mean pore radius and porosity of the fabricated membrane. In comparison to the neat PVC membrane, all of the modified nanocomposite membranes exhibited better antifouling properties [122]. Rajabi et al. reported fabrication of PVC/MWCNTs nanocomposite membranes for gas separation application. The membranes were prepared using both raw and functionalized MWCNTs. The functionalized CNTs showed better gas separation performance (higher CO₂/CH₄ selectivity). The CNTs incorporation into the PVC matrix improved mechanical properties (tensile module) of the fabricated membranes, significantly [123]. Zhao et al. reported fabrication of PVC/SWCNTs ultrafiltration nanocomposite membranes with enhanced antibacterial properties. It was found that surface roughness of the nanocomposite membranes enhances after being blended with SWCNTs. The surface hydrophilicity of the fabricated nanocomposite membranes was also improved. As a result, the membranes permeation flux increased. However, the inclusion of SWCNTs significantly resulted in diminished membrane elongation and mechanical properties [124]. Vatanpour & Haghghat fabricated PVC nanofiltration nanocomposite membranes incorporated with MWCNTs/triethylenetetramine (TETA) as nanofiller. It was found that formation of hydrogen bonds between the functional groups of MWCNTs and water molecules increases hydrophilicity and permeability of the fabricated membranes. Compared with the neat membrane, fouling rate of the nanocomposite membranes was significantly reduced. BSA, Lanazol Blue 3R dye and their combination rejection of the nanocomposite membranes was also enhanced compared to the neat membranes [125]. Hosseini et al. reported fabrication of PVC/MWCNTs nanocomposite cation exchange membranes. The effect of MWCNTs content as additive on electrochemical properties of the prepared membranes was investigated. The membrane water content was originally raised by increasing the MWCNTs content up to 4 wt.%, but subsequently began to decline with increasing the additive content. Ion exchange capability was reduced when the loading ratio of MWCNTs in the casting solution increased. For monovalent ionic solutions, increasing the MWCNTs content up to 4 wt.% decreased the membrane permselectivity and transport number, and then increased with increasing the MWCNTs content. The membrane permselectivity and transport number were enhanced for bivalent ionic solutions by increasing the MWCNTs content up to 8%, but subsequently significantly decreased with increasing the additive content. The increased MWCNTs content improved the monovalent ionic flux. The ionic flux for bivalent ions was also improved first by increasing the MWCNTs content up to 2 wt.%, then decreased by increasing the MWCNTs content from 2 to 8 wt.%. With increasing the MWCNTs content, the bivalent ionic flux showed an increasing trend. The increased MWCNTs content reduced the membrane electrical resistance [126]. Masoumi et al. reported fabrication of PVC nanocomposite membranes containing pristine and modified MWCNTs. To achieve well-dispersion of MWCNTs within the membranes, MWCNTs was carboxylated. It was found that at the presence of pristine and modified MWCNTs, the number of pores on the membranes surface increases and the pore size distribution curves shift towards smaller pores. With increasing the pristine and modified

MWCNTs content up to 0.3 wt. %, tensile strength, PWF, hydrophilicity, and abrasion resistance of the membranes increased and then decreased due to the MWCNTs agglomeration. It was found that, at the same content of the pristine and modified MWCNTs, the modified MWCNTs show more significant effect on the membrane performance in humic acid (HA) removal. For the PVC membrane containing 0.3 wt. % modified MWCNT, HA rejection reached 96.88%. On the other hands, with increasing the modified MWCNTs content, antifouling properties of the fabricate membranes improved [127]. In other work, Masoumi et al. used functionalized MWCNTs (F-MWCNTs) to modify polyvinylidene fluoride (PVDF)/PVC blend ultrafiltration nanocomposite membranes fabricated via solution blending method. Influence of the F-MWCNTs content (0–1%) on performance and properties of the F-MWCNTs/PVDF/PVC nanocomposite membranes was studied. It was found that with increasing the F-MWCNTs content, hydrophilicity of the membranes was improved. Also, performance and antifouling properties of the prepared membranes were improved in the presence of F-MWCNTs. Maximum permeate flux and dextran rejection were achieved by incorporation of 0.3–0.5 wt.% of the F-MWCNTs [128]. Garudachari et al. reported fabrication of PVC nanocomposite membranes containing 0.01, 0.25, and 0.5 wt. % CNTs by immersion precipitation method. A reduced surface roughness and an improved macrovoid structure with increasing the CNTs content were observed [129].

6 Conclusion

PVC with superior chemical, mechanical, and thermal properties, and also its relatively low cost compared to other polymers can be one of the most commonly used polymeric materials in industries. However, low electrical and thermal conductivity and poor mechanical strength have been the main drawbacks of PVC limiting its practical applications so far. Over the past decade, a lot of research has been carried out using various nanofillers to enhance electrical and thermal conductivity and mechanical strength of PVC. CNTs with superior mechanical, thermal and electrical properties are excellent candidates for PVC-based PNCs preparation as nanofillers. Solution mixing, melt mixing, and in-situ polymerization are some techniques which can be used to make PVC/CNT PNCs, effectively. The PVC/CNTs PNCs properties can be improved by several factors including CNTs dispersion in the PVC matrix, surface adhesion between CNTs and PVC and manufacturing processes. As a drawback, uniform dispersion of CNTs in polymer matrices is a critical issue in PNCs preparation. There are three approaches to improve the CNTs dispersity in polymer matrices including mechanical mixing, sonication and covalent or non-covalent functionalization of CNTs. Finally, although, PVC/CNTs PNCs have received considerable attention as an interesting and important research area, worldwide, further research is needed to be performed regarding CNTs/PVC PNCs to optimize their properties and commercialize their practical applications in very near future.

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