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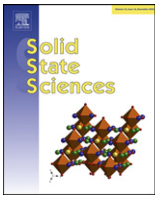

Surfactant dispersed multi-walled carbon nanotube/polyetherimide nanocomposite membrane

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ABSTRACT

Carbon nanotube based nanocomposite membranes have been fabricated through solution casting by embedding multi-walled carbon nanotubes (MWCNTs) within polyetherimide (PEI) polymer host matrix. In order to achieve fine dispersion of nanotubes and facilitate strong interfacial adhesion with the polymer matrix, the nanotubes were first treated with surfactants of different charges, namely anionic sodium dodecyl chloride, cationic cetyl trimethyl ammonium chloride and non-ionic Triton X100, prior to the dispersion in the PEI dope solution. Dispersion of MWCNTs in N-methyl-2-pyrrolidone solvent showed that the agglomeration and entanglement of the nanotubes were greatly reduced upon the addition of Triton X100. Scanning electron microscopy and atomic force microscopy examination has evidenced the compatibility of Triton X100 dispersed MWCNTs with the polymer matrix in which a promising dispersion and adhesion has been observed at the MWCNT-PEI interface. The increase in both thermal stability and mechanical strength of the resulting Triton X100 dispersed MWCNT/PEI nanocomposite indicated the improved interaction between MWCNTs and PEI. This study demonstrated the role of Triton X100 in facilitating the synergetic effects of MWCNTs and PEI where the resulting composite membrane is anticipated to have potential application in membrane based gas separation.

1. Introduction

The field of carbon nanotubes (CNTs) research has attracted a great deal of worldwide attention driven by their remarkable potential and unique properties which lead to many promising applications. A great focus is devoted to their exceptional thermal, electrical and mechanical properties which facilitate the viability of this material to be served as compatible filler for the development of a new generation of nanostructured CNT-based composite material. The current interests in this area have exceptionally blossomed within the past decade and the most well established composite material is most probably CNT reinforced polymer nanocomposites [1–4]. A substantial improvement in the desired properties can be achieved through the synergetic effects resulted from the intimately mixed polymer matrix and the CNT fillers in which the resulting materials possess the unique combination of physical and mechanical properties and as multifunctional systems with great potential that are not present in conventional polymer matrix composite. In fact, CNT-based polymer composites have spurred enormous interest in the community of materials primarily due to their potential to demonstrate remarkable increase in strength and thermal stability when compared to other conventional and typical carbon black or silica-based polymer composite [5,6].

In order to obtain a hybrid system with excellent and superior properties, several parameters have to be taken into account during the fabrication process, including the size of the filler particles, the degree of dispersion in the matrix, as well as the degree of adhesion with the polymer chains [7,8]. The full compatibility of the CNT filler with evenly distributed particle size and the polymer matrix will in turn result in high quality and homogeneously dispersed CNT-polymer nanocomposite [9]. Furthermore, the strong interfacial interaction will give rise to an effective load transfer from the polymer matrix to the CNTs. To exploit the utility of CNTs for this purpose, uniform dispersion of CNTs in the polymer matrix is required. Unfortunately, the use of CNTs in this application has been largely limited by their poor processability and dispersibility [10–13]. Besides the presence of intrinsic van der Waals force, their high surface area and aspect ratio of CNTs have rendered to the formation of highly stabilized bundles which in turn resulting in the formation of tight bundles and hollow ropes. In addition to that, the relatively smooth CNT surfaces which lack of interfacial bonding have also restricted the effective load transfer [14,15].

There have been several ways to produce CNT-polymer nanocomposites. The most commonly used is probably through polymer

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solution casting which possesses few advantages over the in-situ polymerization and melt processing. Preparation through polymer solution casting allows the use of polymers which were previously not suitable for in-situ polymerization [16,17]. During the polymer dissolving and agitating process, the most crucial part is the dispersion of CNT agglomerations before the evaporation stage. However, the economical scale up of CNT nanocomposite manufacturing remains hurdle as it is usually difficult to achieve homogeneous dispersion of CNTs throughout the polymer matrix. To date, the efforts made towards the controlling of CNT aggregation remain as a challenge. The existing challenges of poor dispersion and interfacial bonding in the CNT-polymer matrix are being addressed with some forms of improvement through the modification of CNT surfaces in order to create stronger CNT array–polymer interface adhesion.

A surface modification of CNTs is generally classified in chemical and physical means. The former is known to be an effective method as it allows high quality dispersions to be obtained at high CNT loading in polymer matrix but unfortunately it always leads to remarkable damages and distortion to the structure of CNTs due to the oxidation or surface interaction [18,19]. The latter modification is therefore becoming an attractive mean of CNT surface modification. The surface modification of CNTs is carried out using third phase dispersing agent such as surfactants, with the assistance of sonication for a period of time to debundle the CNTs [20–22]. Unlike the harsh reaction condition experienced by the chemical modification, this physical modification is relatively mild and only involves the non-covalent bonding without disturbing the overall structure of the graphite sheets, hence maintaining the pristine properties of the CNTs. CNTs subjected to ultrasonication appeared shorter due to the sonication-induced nanotube cutting and the tips opening of the CNTs. At the same time, the surfactant molecules are uniformly built up on the tube walls. After the adsorption of surfactant molecules on the nanotube surface, ultrasonication for minutes or hours may helps the surfactant to disperse the nanotube bundles by steric or electrostatic repulsion. A recent report [23] has also underlined the ability of the surfactant coated nanotubes to maintain high quality dispersions at concentration approaching 1 mg/mL with reasonably large populations of individual single-walled carbon nanotubes (SWCNTs).

According to Shvartzman [24], mechanical exfoliation of the bundles prior to surface treatment must occur in order to obtain individual CNTs. The stabilization of aqueous suspension of CNTs using surfactants gives rise to the introduction of surface charges onto the CNTs depends on the nature of surfactant, which is either cationic, anionic or non-ionic properties. A considerable amount of works related to the dispersion of CNTs with different types of surfactants have been carried out [25–27]. In most of the cases, ultrasonication has been applied to disperse the highly entangled carbon nanotubes. In particular, the utilization of anionic sodium dodecyl chloride (SDS) as stabilizer has been widely studied due to its excellent CNT stabilization and separation capabilities. Yu et al. [25] have demonstrated the dispersion of MWCNTs in aqueous SDS solution. The surfactant molecules were found adsorbed on the surface of nanotubes and hence prevent the re-aggregation by electrostatic repulsion for several months. In a recent study by Karousis et al. [26], aqueous SDS has been applied to induce a stable aqueous colloidal dispersion of MWCNTs and significant solubility of the modified MWCNTs in polar solvent was also observed. Non-ionic surfactant such as Triton X350 has also been used to functionalize CNTs in aqueous solution as it was found to interact strongly with graphite surfaces [11].

Although a vast number of papers dealing with dispersion of CNTs using surfactants have been published to date, the selection of suitable surfactant to disperse the as-grown CNTs prior to the preparation of CNT-polymer nanocomposite has been scarcely reported. It is an important aspect of consideration as the proper choice of the surfactant is essential to ensure an effective surface wrapping of CNTs. The influence of the surfactant molecules is closely related to their ionic and non-ionic characteristics. To address the current issue, the objective of this work is to prepare a surfactant dispersed MWCNTs hence to evaluate the effects of varying types of surfactant on the dispersion property of the CNTs. The surfactant dispersed MWCNTs were subsequently used as the nanofiller for the realization of CNTs based polyetherimide (PEI) membrane through polymer solution casting. The purpose of varying the type of surfactant is to investigate the dispersion behaviour rendered by the surfactants and hence correlate to the physical properties of the resulting nanocomposite.

2. Experimental

2.1. Materials

MWCNTs were prepared by catalytic decomposition of acetylene. The commercial available alumina hydrate powder purchased from Fluka was used as the support of metallic acetate (Fe/Co) catalyst for the synthesis of MWCNTs. In the catalytic processes, nitrogen was passed through the quartz tube as the furnace was heated to reach 700 °C. The as-grown MWCNTs were collected as loosely aggregated fluffy black powders.

The surfactants possessing different charges, namely anionic sodium dodecyl chloride (SDS) purchased from Merck, cationic cetyl trimethyl ammonium chloride (CTAB) purchased from Fluka and non-ionic Triton X100 supplied by J.T. Baker were used as dispersing agent of MWCNTs. PEI was used as polymer material, supplied by General Electric Co. (USA) under the trade name 'Ultem 1000'. N-methyl-2-pyrrolidone (NMP) supplied by Sigma Aldrich was used as solvents for PEI.

2.2. Dispersion of MWCNTs

The concentration of each type of surfactant in aqueous solution was fixed at 1 wt%. All solutions were prepared by mixing 0.5 g of MWCNTs with 100 cm^3 of aqueous surfactant solution. After sonication for 60 min, the surfactant treated MWCNT was filtered from the solution in order to remove excess surfactants. The samples were then dried overnight in oven at 60 °C.

2.3. Preparation of MWCNT/PEI nanocomposites

To fabricate MWCNT/PEI nanocomposite, the surfactant dispersed MWCNTs were blended with PEI in NMP to obtain a polymer concentration of 25 wt%. The temperature and stirring speed were controlled so that the PEI dissolved completely to form a yellowish clear solution. Appropriate amount of surfactant dispersed MWCNTs was added to obtain a fixed CNT loading of 1 wt % in the resulting polymer composite to avoid agglomeration of CNTs that likely to occur at high concentration. The mixture was then stirred to obtain a homogeneous suspension. Flat sheet membranes were prepared according to the dry/wet phase separation process. The polymer solution was cast on a clean glass plate using a simple pneumatically-controlled membrane casting system under a fixed casting speed. The membranes were then immersed in water that acts as coagulation medium to allow wet phase inversion process. The resulting MWCNTs/PEI flat sheet membranes, with thickness of 200 μm, were left in water immersion for overnight to enable complete solvent exchange before drying in atmosphere for 24 h.