Digest Journal of Nanomaterials and Biostructures Vol. 9, No. 1, January - March 2014, p. 237 - 244

INSIGHT ONTO SURFACE MODIFIED MWCNTs INFLUENCE IN TAILORING POLY(VINYL)ALCOHOL FILM PROPERTIES

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The effect of the surface modified multi-walled carbon nanotubes (MWCNTs) presence in bulk poly(vinyl)alcohol (PVA) polymer was studied. The MWCNTs-PVA film was prepared using simple wet casting method and the effect from different loading amount of surface modified MWCNTs was investigated. The interaction between the MWCNTs and PVA which characterized using total organic carbon (TOC) analysis showing the decreases of the polymer solubility in aqueous, whereas the elasticity of MWCNTs-PVA film is significantly increasing on addition of MWCNTs, as evaluated via tensile analyzer. The nucleating effect of MWCNTs in polymer matrix, resulting in the limitation of polymer solubility consequently stabilizing MWCNTs-PVA film shape and form in aqueous. Surface modified MWCNTs was effectively contributed to the better interfacial compatibility with the polymer matrices thus providing the controllable solubility of PVA composite in aqueous.

(Received November 9, 2013; Accepted February 10, 2014)

Keywords: MWCNTs; Polymer solubility; Polymer elasticity

1. Introduction

Poly(vinyl)alcohol, (PVA), which derived from poly(vinyl)acetate is one of the highly water-soluble polymeric material. PVA has been identified as a free toxic and non-carcinogenic type of synthetic polymer, thus their demand were growing greatly [1, 2]. The use of PVA as a potential material for the biological immobilization support has risen in numerous areas especially in the biomedical and biotechnology engineering, Yet, the high solubility properties of PVA in water, somehow is not favorable as reported by Scardaci *et al*, (2007) explaining that the PVA dissolution will affect its application [3]. The usage of PVA itself in the biological immobilization support will cause the leaching of the biological elements, as the dissolution of PVA in aqueous taken place. Concerning to the PVA applications in this multi-displinary area, tailoring of the PVA dissolution characteristic is vital for a new scope of PVA utility.

Hassan *et al*., (1998) explained that the solubility of PVA is depending on these three main factors, which are the degree of hydrolysis, molecular weight, and degree of saponification, which also was explained as the tendency to form hydrogen bond in aqueous solution [4]. Among of these three main factor ascribed above, we are going to manipulate the solubility properties of PVA by altering the degree of saponification, throughout the incorporation of nanofiller. In this study, an excellent mechanical strength yet small-size scale nanomaterials, known as carbon nanotubes (CNTs) was incorporated into PVA via wet casting method. However, the MWCNTs are always in a pack of bundles and agglomerated, due to the strong van der Waals forces within the tubules [5,6,7]. Multi-walled carbon nanotubes (MWCNTs) can works well as polymer reinforce material after it has undergone surface modification process, which is the way to promote the debundling of MWCNTs agglomerated floss [8]. The surface modification of the MWCNTs

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through functionalization process using mixture of H_2SO_4/HNO_3 were carried out [9,10]. The effect from the presence of MWCNTs as nanofiller on the polymer dissolution will be determined.

2. Materials and methods

PVA with an average molecular weight (Mw) of 180,000 was purchased from Sigma Aldrich. While, multi-walled carbon nanotubes (MWCNTs) were directly synthesized via catalytic chemical vapor deposition (CCVD), with the MWCNTs diameter size is within 10-30 nm. The surface modification of MWCNTs by oxidation method using mineral acid was done, in order to get an excellent MWCNTs dispersion and distribution within the polymer matrix. For the MWCNTs surface modification process, the acid mixture of 6 M H_2SO_4/HNO_3 with the ratio of 1:3 volumes per volume was prepared. Then, 0.1g of MWCNTs was weighed and then was added into 20 mL of the prepared acid mixture solution and sonicated using Branson ultrasonic water bath for 3 hours, to supply sufficient vibrating energy in assisting the debundling of MWCNTs pack floss bundles. The surface modified MWCNTs were collected and washed thoroughly with distilled water until approximately pH 7 was obtained [11].

2.1 Preparation of MWCNTs-PVA film

The preparation of the MWCNTs-PVA film involved the integration of the surface modified MWCNTs which has been prepared earlier, into the PVA matrix and then followed by the evaporation process of the mixture solution [12]. This technique is known as the wet casting preparation method.

For better understanding on the polymer changes characteristic upon MWCNTs integration, a solely PVA film was prepared as a standard. Three grams of PVA beads were weighed out and then were dissolved in distilled water at 90°C, with continuous stirring for 1 hour. The dissolved PVA solution was poured into a Petri dish, which act as the molding for the dissolved polymer to harden. While for the preparation of the MWCNTs-PVA film, firstly, the dispersed form of surface modified MWCNTs in distilled water is prepared. The MWCNTs was weighed out and sonicated in 10 ml of distilled water for 15 minutes. The dissolved of PVA solution was then mixed together with the MWCNTs solution prepared. Finally, the mixed polymer solution was dried at ambient temperature and the film formation took nearly 3 to 4 hours. In this study, the MWCNTs-PVA film was prepared in different MWCNTs loading content of 0.3 % (w/w), 0.6% (w/w) and 1.0 % (w/w) to the PVA amount, respectively.

For the characterization of the filler-polymer interaction, Transmission Electron Microscopy (TEM) model JEOL EM-2100 was used to get the insight on the MWCNTs incorporation in the MWCNTs-PVA film. The mechanical and elasticity properties of the MWCNTs-PVA film were measured using the tensile analyzer model Instron TENSILON/H-500BP. While, the solubility and the water retention behavior of the respected PVA and MWCNTs-PVA film were investigated using Total Organic Carbon (TOC) analyzer model Shimadzu VE-1.

3. Results and discussion

3.1 Tensile study

The physico-mechanical characteristic of the prepared polymer film was carried out using tensile analyzer. This is done by measuring continuously the force developed as the polymer sample is elongated at constant rate of extension [13]. The size of the sample film prepared for the tensile testing was made into 50 cm in length and 10 cm in width. The mechanical testing was performed at the speed of 5mm/min at room temperature and the tensile strength and Young modulus of PVA and MWCNTs-PVA film were calculated. MWCNTs-PVA film incorporated with MWCNTs showed remarkable improvement on the tensile strength as compared to the solely PVA film, as contributed from the strong formation bond between the MWCNTs and the PVA polymer matrix [14].

Results from the stress-strain curves of MWCNTs-PVA have shown an overview of mechanical properties of the composite. The stress value for the MWCNTs-PVA film were increased from 6, 15 and 40 kN at 0.3, 0.6 and 1.0 % w/w loading of MWCNTs, respectively. The elongation at break for MWCNTs-PVA film stretched less compared to the solely PVA film, due to the stress transfer effect. Results obtained clearly showed that the presence of MWCNTs has significantly controlled the elongation of the MWCNTs-PVA film as the external force were applied on, while the solely PVA film are stretched freely, thus bring to easily ripped with further force applied. The presence of MWCNTs was found to bridge the micro cracks in the polymer matrix when external force is applied continuously and thus enhanced the strength of the MWCNTs-PVA film.

The result on the tensile tests for each type of the film was shown in Table 1. It is revealed that the mechanical strength of MWCNTs-PVA film is increases with only 0.3 wt% content loading of MWCNTs, and the strength are kept on rises as the amount of the MWCNTs loading were increased from 0.6 wt% until 1.0 wt%.

Table 1: Physico-mechanical measurement PVA and MWCNTs-PVA film

MWCNTs loading	**0 wt%**	**0.3 wt%**	**0.6 wt%**	**1.0 wt%**
Tensile strength (MPa)	33	60	167	470
Tensile elongation (cm)	1.3	1.0	0.9	0.85
Tensile modulus (kN)	4	6	15	40

3.2 Morphological study

Figure 1 shows TEM micrographs of MWCNTs-PVA film. The TEM micrographs depicted the defect structure on the sidewall of MWCNTs as resulted from surface modification by the acid used. The defect site of MWCNTs sidewall was filled up with the PVA matrix, since the defected site creates an opening for the PVA to be bonded to MWCNTs surface. This finding was supported with Bower *et al*., (1999) where it shows that surface modified MWCNTs has better performance in having chemically interaction with the polymer matrix [15].

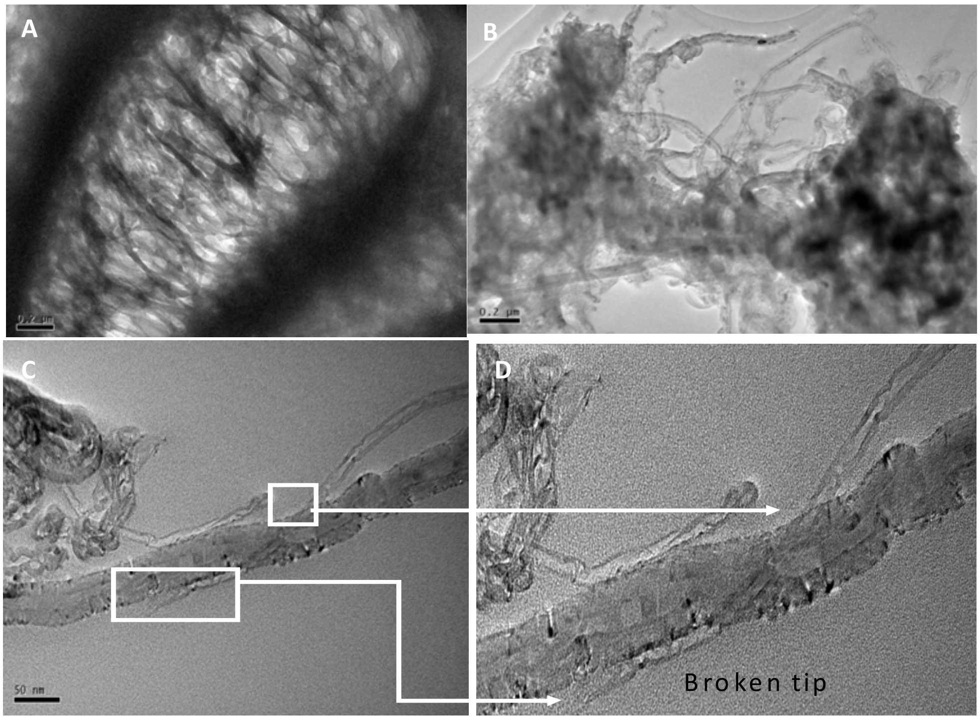


Fig. 1. (A) MWCNTs-PVA mixture (B) MWCNTs floss in PVA matrix (C) Pull out effect on MWCNTs-PVA mixture (D) Defect site of MWCNTs-PVA mixture.

TEM micrograph in Figure 2 showed one of the end-cap of MWCNTs single tubule was successfully opened inside the bulk PVA. The uncapping of the MWCNTs end-tip was being initiated by the acid mixture used in the surface modification process. The opening of the end-cap has created the route for the polymer matrix to be filled into the hollow tube of the MWCNTs, to provide strong interaction between both of the inner and outer wall of carbon nanotubes structure [16].

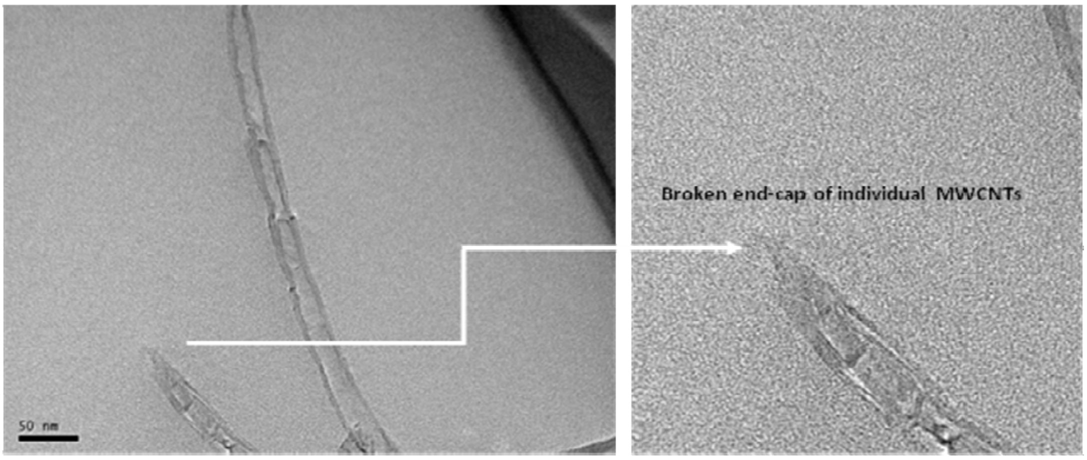


Fig. 2. Uncapping of MWCNTs end-tip

A part from the uncapping of the MWCNTs end-tip, there are another interesting finding how the single layer of MWCNTs walls being pulled out. Figure 1 (c), depicted a single layer of MWCNTs inner-wall was being pulled out from the multiple layer of its wall. We found that the layer of MWCNTs walls could be separated from the others when the force between the layer and polymer matrix exceeded the van der Waals force of the layers. Based on the previous work by Harris (1999), it is assumed that most MWCNTs have a “Russian doll’ layer structure, instead of “Swiss roll” structure [17]. Figure 3 depicted the schematic illustration on the differences of these two types of layered structure model of MWCNTs.

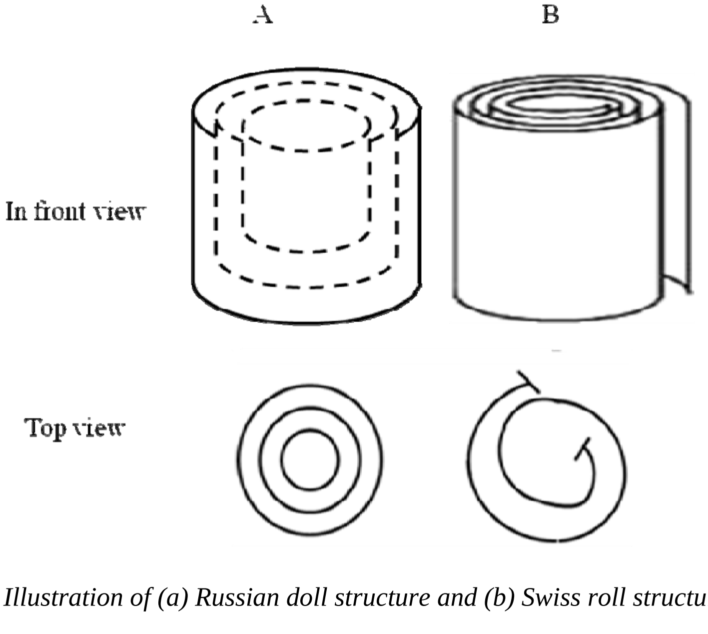


Fig. 3. Illustration of (a) Russian doll structure and (b) Swiss roll structure

For "Russian doll" structure model, each constituent tubule is only bonded to its neighbours by the Van Der Waals forces. However, since the MWCNTs were being incorporated with polymer matrix, there might be a strong bonding exists between the outermost layer of MWCNTs wall and the polymer matrix. Thus, when the energy comes in the form of electron beam and hit the polymer sample, the polymer part was ripped out. Due to the strong polymer bonding towards the outermost layer of MWCNTs wall, the outermost layer wall of MWCNTs is pulled away from the inner layer (Figure 1 (c)). Otherwise, for "Swiss roll" structure model, the whole layer of MWCNTs definitely will be opened and will looks like ribbon or flat graphene sheet if the interaction of polymer matrix with the MWCNTs wall exceeded the Van der Waals force.

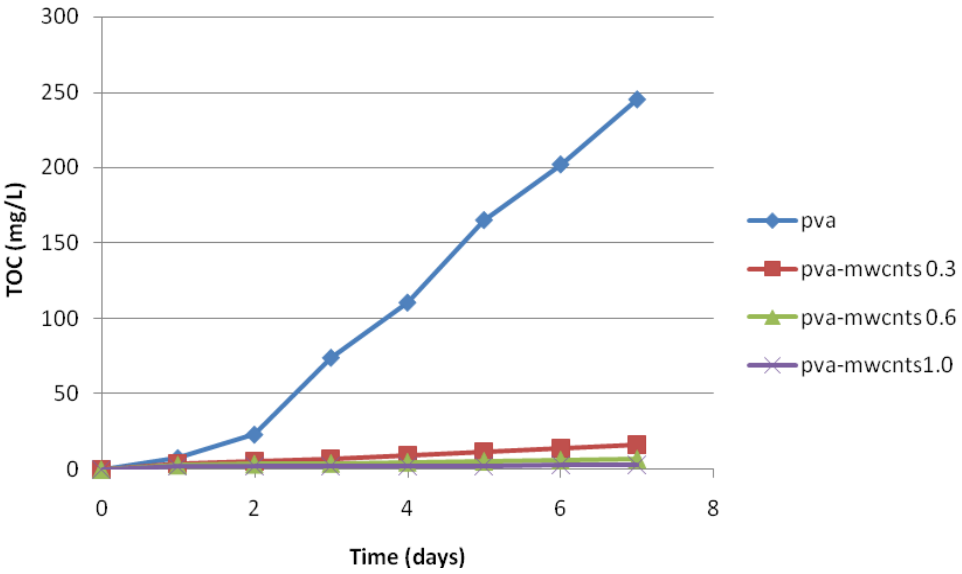
Through the TEM analysis, the MWCNTs were found retained inside the polymer networks. This observable fact suggested that the strong chemical bonding interaction between the PVA and MWCNTs has held them tightly thus reduced the degree of saponification of the polymer in the aqueous solution.

3.3 Polymer leaching analysis

Total organic carbon (TOC) were use to measure percentage of the leached out of carbon composition from the respected samples. TOC concentration is defined as the amount of organic carbon detected which leached out from the soluble PVA film. The solubility of PVA was expressed by the TOC concentration, as the TOC concentration is directly proportionate to the polymer solubility.

The TOC data recorded that the TOC concentration of solely PVA sample in water is 240 ppm, thus confirmed the dissolution of PVA is nearly 100% resulted by the interaction of the hydroxyls groups of PVA network and water. Meanwhile the TOC concentration for MWCNTs-PVA film was at 2 ppm at 1.0 wt% content loading of MWCNTs, equivalent to 0.8% leached out carbon. The extreme reduction of the TOC values signifies the enhancement in the water retention of polymeric structure upon the addition of surface modified MWCNTs into the PVA network.

In addition, the percentage of MWCNTs content loading was studied as to determine the optimum amount of surface modified MWCNTs in controlling the solubility properties of MWCNTs-PVA film fabricated. Result on the MWCNTs content loading toward the effect on solubility properties of PVA was shown in Graph 1.



Graph 1: Effect of surface modified MWCNTs content loading on the TOC concentration.

It is shown that the TOC concentration value was affected by the content loading of MWCNTs. At 0.6 wt % MWCNTs loading, the recorded TOC concentration is at 6 ppm. While, for the MWCNTs lowest loading (0.3 wt %), the TOC concentration value was at 16 ppm.

On the other hand, the swelling ability of PVA composite in aqueous is one of the desired properties of PVA to be tested. However, the swelling properties of PVA are affected by the amount of foreign particles presence. The presence of 0.3 wt % and 0.6 wt % of MWCNTs in polymer matrix however did not restrict the swelling properties of the PVA. With higher MWCNTs loading content (1.0 wt %), the MWCNTs-PVA film would loss the elasticity characteristic thus restricted to swell. Swelling measurement of MWCNTs-PVA film was tested by immersing the MWCNTs-PVA film into the water for 5 hours. The swelling of the polymer sheet with the initial size of 0.5cm x 0.5cm was measured and recorded. Result obtained was shown in the Table 2.

Table 2: Swelling measurement of MWCNTs-PVA film

Sample	**MWCNTs-PVA 0.3 wt%**	**MWCNTs-PVA 0.6 wt%**	**MWCNTs-PVA 1.0 wt%**
Initial film size	0.5cm x 0.5cm	0.5cm x 0.5cm	0.5cm x 0.5cm
Final film size	2.2cm x 2.2cm	1.7cm x 1.7cm	0.6cm x 0.6cm

Results showed the MWCNTs-PVA swollen properties were decreased with the increment of the MWCNTs in the polymer blending. The MWCNTs-PVA with 0.6 wt % of MWCNTs loading showed the best criteria as polymer immobilization matrices with intermediate swelling behavior among them. The optimum loading of MWCNTs allow the PVA chains to swell, yet avoiding them from dissolve into the water. The inter-molecular hydrogen bonding by O-H groups in the PVA has reacted with the MWCNTs thus removed the hydrogen atom to form strong cross-linking bonding between MWCNTs and polymer network. There are two different types of hydrogen bond occurred in the polymer composite and they are competing with each other in the aqueous solution. The first hydrogen bonding is the inter-molecular hydrogen bonding between the O-H groups in the PVA molecules. Second is hydrogen bond between water molecules and the O-H groups in the PVA molecules. If the entire strength of the hydrogen bonding between water molecules and PVA exceeds the strength of hydrogen bonding between the hydroxyl groups in PVA chains, then PVA will likely dissolve in water.

However, the competition between these two types of hydrogen bond can be controlled by the amount loading of MWCNTs into the PVA matrix. By having the MWCNTs in the polymer blending, the strength of the hydrogen bond between the hydroxyl groups in PVA molecules were greater, since the hydroxyl group in water molecules cannot be bonded to the hydroxyl groups in PVA, thus stabilized the polymer structure when surrounded in the aqueous solution, rather than dissolve into the water. In addition, according to Ramaraj (2006) this may be due to both of the PVA chain and polymer filler, which containing hydroxyl groups that can possibly form strong hydrogen bonds between them [18].

The presence of MWCNTs in the PVA network has created filler cross-linked within the polymer, thus prevent the PVA from dissolve. In addition, the elasticity properties of PVA has also provided excellent grip for MWCNTs to nucleate and cross-linked to polymer [19]. The surface modified MWCNTs helped to establish a good interaction between the MWCNTs and PVA molecules. However, the loading of MWCNTs into the polymer matrices give effect on polymer swelling behavior. When the percent of the MWCNTs is low, the interaction among the MWCNTs themselves is weaker than between the PVA molecule and the MWCNTs, so that the MWCNTs can homogenously disperse in the PVA matrix. Nevertheless, when the MWCNTs loading were increased, the distances between two individual MWCNTs are more closer, exhibit the Van der

Waals interactions and the tendency of the MWCNTs to agglomerate is increased [20], thus caused less interaction with polymer matrix and polymer/filler distribution quality will be reduced.

4. Conclusion

The fabrication of PVA film composited with MWCNTs was successfully prepared by the simple wet casting method. The MWCNTs work effectively as polymer nanofiller for PVA molecules chain reinforcement in aqueous solution, via inhibiting the hydrogen bonding formation between water molecules and PVA molecules chain. The strong interaction exists between the surface modified MWCNTs and PVA raised the stability of the film in the water. The presence of MWCNTs at the optimum amount gave improvement on the polymer mechanical properties which will lead to the better performance as enzyme carrier and support application in the future. The amount of MWCNTs loading should be monitored in order to get the polymer composite film at the specific mechanical properties as desired.

Acknowledgement

We would like to thank the Ministry of Higher Education (MOHE), Malaysia for the financial support under the FRGS fund (vot number 78318) and Ministry of Science and Innovation (MOSTI) for National Science Fund (NSF) scholarship. Thanks are also due to the Department of Chemistry, Faculty of Science and the Fundamental Science Institute of Ibnu Sina (IIS), Universiti Teknologi Malaysia (UTM) Johor Bahru.

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