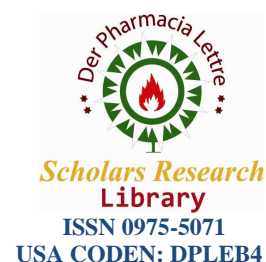




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f- Multiwalled carbon nanotube-grafted –Chitosan/Polyvinylpyrrolidone blends: Preparation and characterization

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ABSTRACT

In this study, we have prepared the blends using chitosan, polyvinyl pyrrolidone and functionalized carbon nanotube and the blends were prepared in the presence and the absence of crosslinking agent. Chitosan blend films were prepared by casting the respective polymer solutions. The glutaraldehyde was used as a cross-linking agent. Chitosan grafted with functionalized multiwalled carbon nanotube with PVP (f-MWCNT-g-Chitosan/PVP) and the same blend was cross-linked in the presence of glutaraldehyde (f-MWCNT-g-Chitosan/PVP/GLU) was prepared via solution casting method and physicochemically characterized. Cross-linking with glutaraldehyde improves thermal properties and decreases elongation of the films. The cross-linkages in the f-MWCNT-g-chitosan/PVP scaffold in the presence and absence of crosslinking agent were observed by FT-IR spectroscopy. The prepared scaffold was subjected to various spectral studies. The literature suggests that the f-MWCNT grafted with Chitosan/PVP composites are promising biomaterials for tissue engineering applications.

Keywords: Chitosan, Carbon nanotube, Blends, Crosslinking agent.

INTRODUCTION

During the past 20 years, a substantial amount of work has been reported on chitosan and its potential use in various bioapplications. Chitosan is derived from naturally occurring sources, which is the exoskeleton of insects, crustaceans and fungi that has been shown to be biocompatible and biodegradable[1]. Chitosan is a polysaccharide primarily formed by the repeating units of β -(1 \rightarrow 4)-2-amino-2-deoxy-d-glucose (or d-glucosamine). This polycationic biopolymer is generally obtained by alkaline deacetylation of chitin, which is the main component of the exoskeleton of crustaceans, such as shrimps [2]. In fact, chitosan is the preferred form of chitin as it can be dissolved very easily in different solvents to form solution.

Chitosan is mainly used in pharmaceutical and biomedical industries along with photographic production, cements and wastewater treatment [3]. Although the chemical modification of chitosan improves its properties, it is possible to maintain some interesting characteristics such as mucoadhesivity, biocompatibility, and biodegradability [4]. Unlike the natural polymers derived from costly mammalian proteins, chitosan evokes minimal foreign-body response and fibrous encapsulation, and has unlimited material sources and excellent reproducibility[5-8].

Chitosan has reactive functional groups that allow modifications of chitosan to produce various useful forms for tissue engineering applications [9]. Physical and chemical modifications were done mainly to overcome certain drawbacks of chitosan. The most commonly used chemical modifications employed are the cross-linking, grafting of a new functional group and acetylation. Glutaraldehyde (GLU) is a highly reactive dialdehydes reagent that has been widely used as a fixative and crosslinker in biological assays. Through coupling reaction of the aldehyde groups at the two separate terminals with the amino groups of proteins, the oligomeric proteins can be crosslinked via a mild aldehyde–ammonia condensation reaction [11-12]. Crosslinking of chitosan with the bifunctional glutaraldehyde agent [13].

The crosslinking reaction occurs between primary amino groups and aldehyde groups, resulting in the formation of Schiff bases. The complex reaction mechanism modifies the structure and functionality of chitosan, improving its chemical resistance. In addition, chitosan can be easily modified into various forms like films, fibers, beads, sponges and more complex shapes for orthopedic treatment. Chitosan with CNT will be promising biomaterials for bone tissue engineering due to high mechanical strength and electrical conductivity of CNT [14].

The results suggest that CNT-based hybrids have unique properties, leading to advanced catalytic systems, highly efficient fuel cells, tunable electronic or optoelectronic devices, and ultrasensitive chemical sensors/biosensors [15]. So far, the CNT based carrying materials have been developed significantly. A lot of works have reported the intracellular transporting of biomolecules by CNT based carrying materials [16].

Polyvinylpyrrolidone (PVP) has attracted considerable interest due to its hydrophilicity, lubricity, anti-adhesive property and excellent biocompatibility. Moreover, PVP and chitosan can form a homogeneous phase due to the strong hydrogen binding forces between two kinds of molecules [17]. Poly(vinylpyrrolidone) (PVP) is a vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring [18].

In recent years, biomedical applications of CNTs have attracted much attention and the CNTs have been used as drug delivery vehicles, gene vectors or composite materials for tissue scaffolds [19]. With its carbon composition, high aspect ratio, electrical and physical properties, there has been growing interest in using carbon nanotubes for biomedical applications.

In the present study, we employed multi-walled carbon nanotubes (MWCNTs) as a filler to be incorporated into a Chitosan/PVP (0.2:2:1), to increase their dispersion and compatibility in the matrix and PVP is used here to improve the film forming nature of chitosan and the same blend was cross-linked in the presence of glutaraldehyde (f-MWCNT-g-Chitosan/PVP/GLU) to improve their mechanical strength and thermal properties. The prepared blend samples were characterized and then the results were investigated.

MATERIALS AND METHODS

Materials

Chitosan was kind gift from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Multiwalled carbon nanotube (outer diameter 20 nm, inner diameter 5 nm, number of walls- 5-15, length 50 μ m) was purchased from Nano beach, Polyvinylpyrrolidone is purchased from SD Fine Chemicals.

Methods

Functionalization and purification of Carbon nanotube (CNTs)

Functionalization of the CNTs were carried out by the procedure describe by An et al 2007 [20].

Preparation of f-MWCNT-g-Chitosan /PVP

About 2g of Chitosan was weighed and dissolved in 2% Acetic acid. Simultaneously 1 g of (PVP) and (0.2g of f-MWCNT) was dispersed in minimum amount of deionized water. The dispersed PVP and f-MWCNT was slowly added to the chitosan suspension and then the mixture was stirred in magnetic stirrer for 2 hours then poured into the petriplates and dried *Figure 1a*.

Preparation of f-MWCNT-g-Chitosan /PVP with Glutaraldehyde

About 2g of Chitosan was weighed and dissolved in 2% Acetic acid. Simultaneously 1 g of (PVP) and (0.2g of f-MWCNT) was dispersed in minimum amount of deionized water. The dispersed PVP and f-MWCNT was slowly added to the chitosan suspension and finally 15ml of Glutaraldehyde was added slowly and then the mixture was stirred in magnetic stirrer for 2 hours then poured into the petriplates and dried *Figure 1b*.

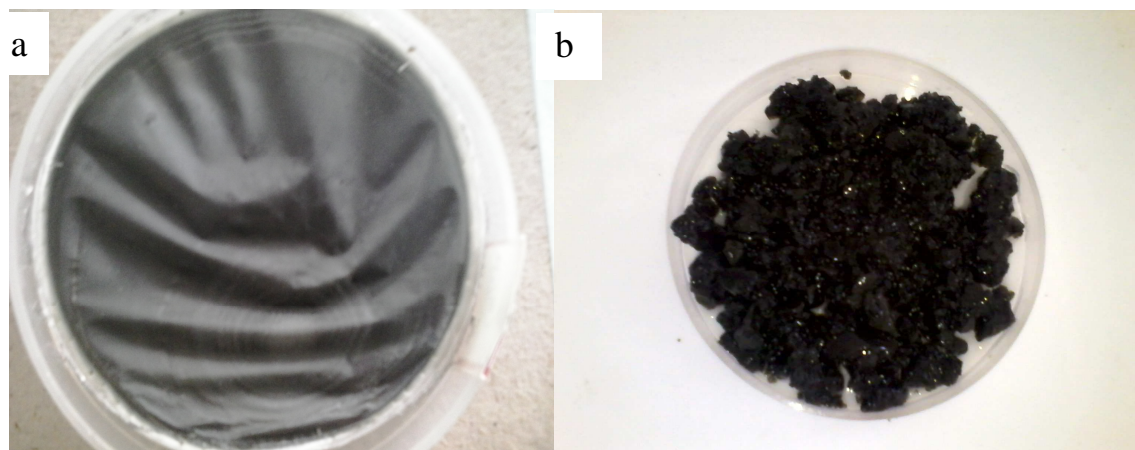


Fig.1: (1a) f-MWCNT-g-Chitosan /PVP ;(1b) f-MWCNT-g-Chitosan /PVP with GLU

Characterization

The FT-IR spectra of f-MWCNT-g-Chitosan /PVP Scaffold prepared in (0.2:2:1) ratio and f-MWCNT-g-Chitosan /PVP with Glutaraldehyde in (0.2:2:1) ratio were recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Alpha Bruker FTIR Spectrophotometer. The X-ray diffraction patterns of the above prepared sample were tested by an X-ray scattering D8 ADVANCE Diffractometer using Ni filter Cu K α radiation source ($\lambda=0.154\text{nm}$), set at scan rate = $10^\circ\text{C}/\text{min}$, using a voltage of 40kV and a current of 30 mA . The TGA study of the prepared samples was carried out using SDT Q600 V8.0 Build 95 instrument at a heating rate of 10°C per minute in nitrogen atmosphere. The weight losses at different stages were analyzed. The differential scanning calorimeter (DSC) was used to examine the thermal property of the blends. The measurements were performed with NETZSCH DSC 200 PC in a pan Al, pierced lid in the N $_2$ atmosphere at a heating rate of $10^\circ\text{ K}/\text{min}$. The results were recorded and analyzed.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

FTIR spectroscopy is an appropriate technique to establish the variations introduced by different treatments on the chemical structure of the isolated samples. In *Figure 2(a)* The FT-IR spectrum of the (f-Multiwalled Carbon Nanotube-Grafted-Chitosan/Polyvinylpyrrolidone) contains characteristic peaks. The FT-IR spectrum of f-MWCNT-Grafted -Chitosan/PVP depicted a strong absorbance at 1540.04 cm^{-1} (corresponds to the amide group), indicating that the $-\text{COOH}$ groups of f-MWCNT reacts with the NH_2 of Chitosan and converts it to amide group. This unique band frequency clearly indicates the formation of grafting between Chitosan and f-MWCNT. The peak obtained at 1288.74 cm^{-1} corresponding OH bending and the OH stretching frequency was observed at 3650 cm^{-1} . The peak at 1648.08 cm^{-1} corresponds to the carbonyl group involving Hydrogen bonding. Asymmetric C-H stretching is seen at the region 2922.17 cm^{-1} .and a small peak at 1412.81 cm^{-1} is due to C-H bending. *Figure 2(b)* Shows the IR spectra of f-MWCNT-g-Chitosan /PVP with GLU contains characteristic peaks. A little broad peak is observed at 3302.43 cm^{-1} corresponds to OH stretching frequency. Asymmetric C-H stretching is seen at the region 2942.25 cm^{-1} and symmetric C-H stretching is also seen at the region 2870.39 cm^{-1} . F-MWCNT-g-Chitosan /PVP with GLU depicted a strong absorbance at 1649.45 cm^{-1} which corresponds to C=N. The intensity of band at is also increased due to the formation of C=N imine bonds in GLU cross-linked with chitosan through Schiff base reaction between amino group of chitosan and aldehyde group of GLU. After modification with glutaraldehyde the intensity of peak increased from 1540.04 cm^{-1} to 1563.48 cm^{-1} due to ethylenic C=C bond from Chitosan-GLU Crosslinking chain overlapped with N-H of Chitosan. A new peak was seen at the region of 1317.25 cm^{-1} is due to OH bending. A little broad peak is observed at 3302.43 cm^{-1} corresponds to OH stretching frequency and a small peak at 1412.81 cm^{-1} is due to C-H bending. From the IR spectra it clearly shows that the grafting has been takes place between f-MWCNT and Chitosan and change in the peak intensity and shifting of peak wavelengths were seen after adding the crosslinking agent to the polymeric blend.

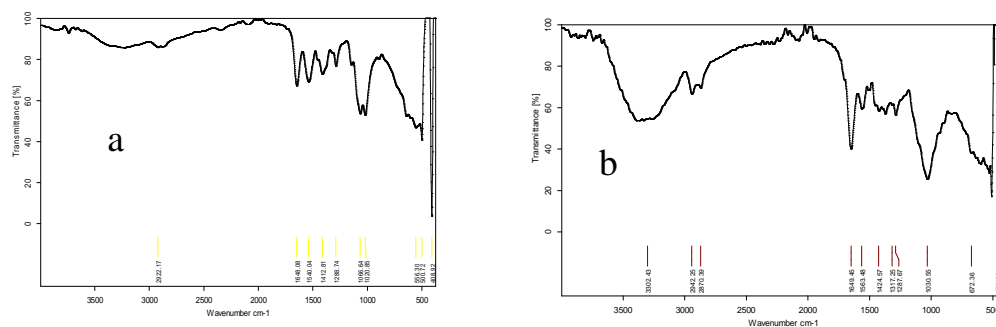


Fig. 2: FT-IR spectra of (a) f-MWCNT-g-Chitosan /PVP; (b) f-MWCNT-g-Chitosan /PVP with GLU

X-ray diffraction studies (XRD)

Figure 3(a) represent the XRD spectra of the f-MWCNT-Grafted –Chitosan/PVP which shows little sharp peaks at various 2θ values such as, 12° , 19° , 22° and a slight shoulder peak were observed at range of 42° which confirm the presence of MWCNT. Figure 3(b) represent the XRD spectra of the f-MWCNT-Grafted –Chitosan/PVP with Glutaraldehyde which shows little sharp peaks at various 2θ values such as, 16° and a slight shoulder peak were observed at range of 42° . From Fig 3(b) the peaks conclude the poor crystallinity state or amorphous forms were introduced after the addition of cross-linking agent to the polymeric blend.

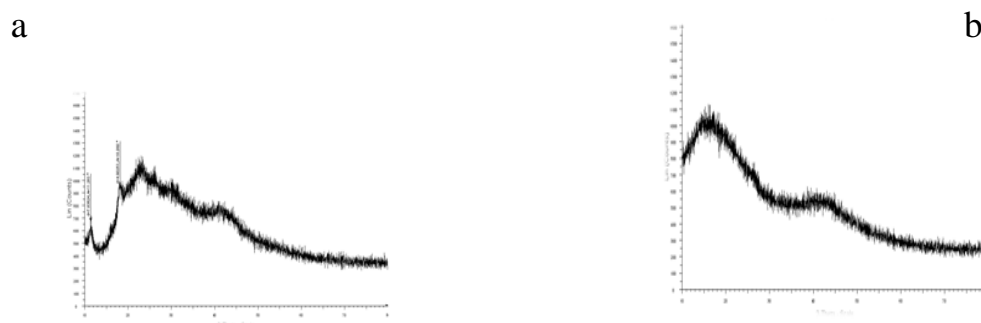


Fig. 3: XRD Pattern of (a) f-MWCNT-g-Chitosan/PVP; (b) f-MWCNT-g-Chitosan /PVP with GLU

Thermogravimetric Analysis (TGA)

The thermal stability of the scaffold (f-MWCNT-Grafted–Chitosan/PVP) was assessed by TGA thermogram curves. The TGA thermogram curve of f-MWCNT-g-chitosan /PVP (0.2:2:1) was represented in Figure 4(a). Around 80% of the sample gets disintegrated in the temperature range of 620°C . The residual temperature of the sample was found to be around 790°C . At the end of the experiment, 24.77 % of the sample remained as a residue. Figure 4(b) shows the TGA thermogram of f-MWCNT-g-Chitosan /PVP with GLU Around 80% of the sample gets disintegrated in the temperature range of 780°C . The residual temperature of the sample was found to be around 790°C . At the end of the experiment, 33.7 % of the sample remained as a residue. From the amount of blend which is remained as a residue at the end of experiment it was observed that the prepared f-MWCNT-g-chitosan /PVP with glutaraldehyde was found to be thermally more stable when compared to f-MWCNT-g-chitosan /PVP .

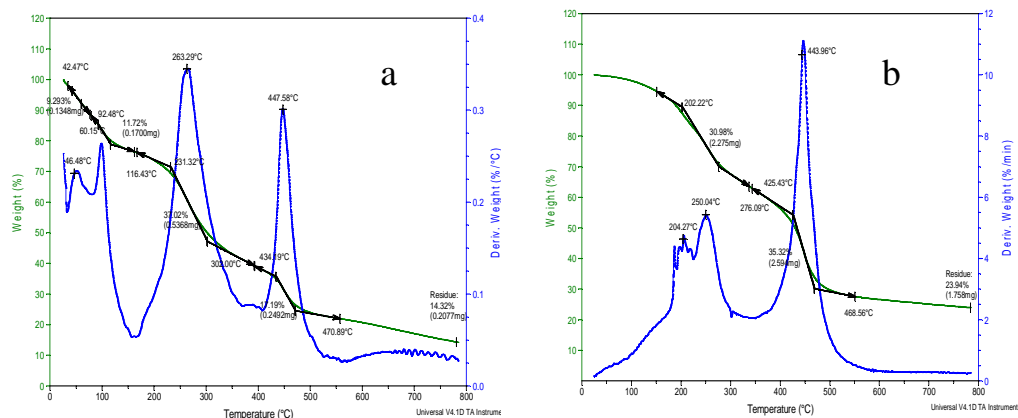


Fig. 4: TGA thermogram of (a) f-MWCNT-g-Chitosan/PVP; (b) f-MWCNT-g-Chitosan/PVP with GLU

Differential Scanning Calorimetry (DSC):

DSC helps in finding the glass transition temperature of polymers, polymer blends and polymer composites. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change, while the melting temperature (T_m) and crystallization temperature (T_c) were taken as the maximum of endothermic peak and the minimum of exothermic peak, respectively. Figure 5(a) Represents the DSC curve of f-MWCNT-g-Chitosan/PVP blend. The glass transition temperature of the blend was observed at 200°C. The DSC curve showed an exothermic peak at 289.44°C (T_m) showing the melting of the sample at this temperature and an endothermic peak at 95.10°C (T_c) shows the crystallization of the sample at a lower temperature. For f-MWCNT-g-Chitosan/PVP with GLU in Figure 5(b) the T_g value was increased to 260 °C and the T_m and T_c values are 259.52°C, 210.49°C respectively. The observed single glass transition temperature confirms the good miscibility of the blends.

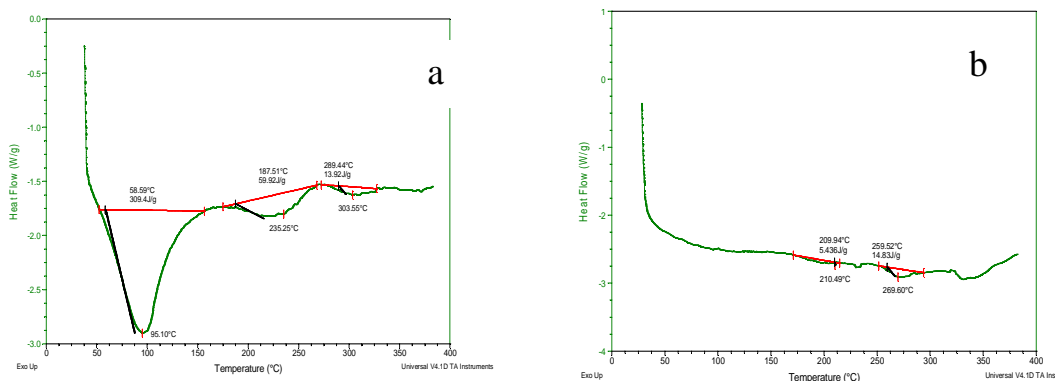


Fig.5: DSC Thermal Studies of (a) f-MWCNT-g-Chitosan/PVP; (b) f-MWCNT-g-Chitosan/PVP with GLU

CONCLUSION

In the present study, we attempted to prepare blends using f-MWCNT, Chitosan and PVP in presence and absence of cross-linking agent. The results obtained highlight that the addition of crosslinking agent to the polymer blend solution increases the thermal stability which was clearly seen in TGA and DSC and IR spectra clearly shows the grafting has been takes place between f-MWCNT and Chitosan and change in the peak intensity and shifting of peak is seen after adding the crosslinking agent. In XRD amorphous nature of the sample is improved more after adding the crosslinking agent is seen clearly. Carbon nanotube (CNT) organic polymer hybrids have important potential applications in the immobilization of therapeutic biomolecules. So the prepared polymer blends will have great potential application in both water treatment and biomedical applications.

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