Preparation and characterization of f- multi walled carbon nanotube- blended with Alginate for the application of effluent water treatment

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Abstract— In this study, we have prepared the blends using alginate, polyvinyl pyrrolidone and functionalized carbon nanotube and the blends were prepared in the presence and the absence of crosslinking agent. Alginate blend films were prepared by casting the respective polymer solutions. The glutaraldehyde was used as a cross-linking agent. Alginate grafted with functionalized multiwalled carbon nanotube with PVP (f-MWCNT-g-Alginate/PVP) and the same blend was cross-linked in the presence of glutaraldehyde (f-MWCNT-g-Alginate/PVP/GLU) was prepared via solution casting method and physiochemically characterized. Cross-linking with glutaraldehyde improves thermal properties and decreases elongation of the films. The cross-linkages in the f-MWCNT-g-alginat/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 Alginate/PVP composites are promising biomaterials for water treatment applications.

Index Terms— Alginate, Carbon nanotube, Blends, Crosslinking agent.

I. INTRODUCTION

During the past 20 years, a substantial amount of work has been reported on alginate and its potential use in various bioapplications. Alginate 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]. In fact, alginate is the preferred form of chitin as it can be dissolved very easily in different solvents to form solution.

Alginate is mainly used in pharmaceutical and biomedical industries along with photographic production, cements and wastewater treatment [2]. Although the chemical modification of alginate improves its properties, it is possible to maintain some interesting characteristics such as mucoadhesivity, biocompatibility, and biodegradability[3]. Unlike the natural polymers derived from costly mammalian proteins, alginate evokes minimal foreign-body response and fibrous encapsulation, and has unlimited material sources and excellent reproducibility[4-8].

The cross linking 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 alginate, improving its chemical resistance. In addition, alginate can be easily modified into various forms like films, fibers, beads, sponges and more complex shapes for orthopedic treatment. Alginewith CNT will be promising biomaterials for bone tissue engineering due to high mechanical strength and electrical conductivity of CNT [9].

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 [10]. So far, the CNT based carrying materials have been developed significantly. A lot of work have reported the intracellular transporting of biomolecules by CNT based carrying materials [11]. Polyvinylpyrrolidone (PVP) has attracted considerable interest due to its hydrophilicity, lubricity, anti-adhesive property and excellent biocompatibility. Moreover, PVP and alginate can form a homogeneous phase due to the strong hydrogen binding forces between two kinds of molecules [12]. Poly(vinylpyrrolidone) (PVP) is a vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring [13].

In the present study, we employed multi-walled carbon nanotubes (MWCNTs) as a filler to be incorporated into a Alginate/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 alginate and the same blend was cross-linked in the presence of glutaraldehyde (f-MWCNT-g-Alginate/PVP/GLU) to improve their mechanical strength and thermal properties. The prepared blend samples were characterized and then the results were investigated.

II. MATERIALS AND METHODS

A. Materials

Alginate 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 50μm) was purchased from Nano beach, Polyvinylpyrrolidone is purchased from SD Fine Chemicals.

B. Methods

1) Preparation of f-MWCNT-g-Alginate /PVP

About 2g of Alginate was weighed and dissolved in 2% Acetic acid. Simultaneously 1 g g (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 alginate suspension and final the mixture was stirred in magnetic stirrer for 2 hours then poured into the petriplates and dried.

2) Preparation of f-MWCNT-g-Alginate /PVP with Glutaraldehyde

About 2g of Alginate was weighed and dissolved in 2% Acetic acid. Simultaneously 1g 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 alginate 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.

a) (1a) f-MWCNT-g-Alginate /PVP

b) (1b)f-MWCNT-g-Alginate /PVP with GLU

(1) Characterization

The FT-IR spectra off-MWCNT-g-Alginate /PVP Scaffold prepared in (0.2:2.1) ratio and f-MWCNT-g-Alginate /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 Kα radiation source (λ=0.154nm), set at scan rate = 10˚C/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/min, using a voltage of 40kV and a current of 30 mA.

III. RESULTS AND DISCUSSION

A. FT-IR Spectrometry

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–Alginate/Polyvinylpyrrolidone) contains characteristic peaks. The FT-IR spectrum of f-MWCNT-Grafted –Alginate/PVP depicted a strong absorbance at 1540.04 cm⁻¹ (corresponds to the amide group), indicating that the –COOH groups of f-MWCNT reacts with the NH₂ of Alginate and converts it to amide group. This unique band frequency clearly indicates the formation of grafting between Alginateand 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-Alginate /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-Alginate /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 alginate through Schiff base reaction between amino group of alginate 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 Alginate-GLU Crosslinking chain overlapped with N-H of Alginate. 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 Alginate and change in the peak intensity and adding the crosslinking agent to the polymeric blend.
Fig. 2: FT-IR spectra of (a) f-MWCNT-g-Alginate /PVP; (b) f-MWCNT-g-Alginate /PVP with GLU

IV. X-RAY DIFFRACTION STUDIES (XRD)

Figure 3(a) represent the XRD spectra of the f-MWCNT-Grafted –Alginate/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 –Alginate/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 3b) 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-Alginate/PVP; (b) f-MWCNT-g-Alginate /PVP with GL.

V. THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermal stability of the scaffold (f-MWCNT-Grafted–Alginate/PVP) was assessed by TGA thermogram curves. The TGA thermo gram curve of f-MWCNT-g-alginate /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.

Fig: TGA thermo gram of a) f-MWCNT-g-Alginate /PVP(b) f-MWCNT-g-Alginate /PVP with GLU.

A. Thermogravimetric Analysis (TGA)

In the present study, we attempted to prepare blends using f-MWCNT, Alginate 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 IR spectra clearly shows the grafting has been taken place between f-MWCNT and Alginate 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 treatments.

V. CONCLUSION

In the present study, we attempted to prepare blends using f-MWCNT, Alginate 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 IR spectra clearly shows the grafting has been taken place between f-MWCNT and Alginate 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 treatments.

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