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Design and characterization of biodegradable polymer-clay nanocomposites prepared by solution mixing technique

ABSTRACT

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This paper discusses about preparation of biodegradable polymer /clay nanocomposites based on organically modified montmorillonite clay; i.e. cloisite 10A and biodegradable polymer chitosan by solution mixing technique and their characterization. The nanocomposites were successfully prepared and their structures were characterized by powder x-ray diffraction (XRD), particle size analyzer (Beckman coulter), scanning electron microscopy (SEM), and fourier transmission infra red spectroscopy (FT-IR) techniques. The intensity distributions and average size and polydispersity index of particles were confirmed from particle size analysis. The XRD results revealed the information on the degree of hybrid structure generated and crystal size. The surface topography of polymer nanocomposites and their shapes were determined from SEM. These SEM results confirmed the exfoliation of polymer between the clay layers. From both XRD and particle size analysis results, it is revealed that the average diameters of the prepared nanocomposites were found to be within 300-500nm. So these nanoformulations are expected to be beneficial for controlled drug delivery system.

Keywords: *Chitosan; Cloisite 10A; Nanocomposite; Biodegradable polymers; XRD.*

INTRODUCTION

Recently, the preparation and application of novel biodegradable polymer nanocomposites as controlled drug delivery vehicles have attracted much attention due to their unique structure and properties like biocompatibility. Montmorillonite clay and hydroxyapatites have been used for the preparation of these nanocomposites [1, 2]. The biodegradable polymer nanocomposites provide improved mechanical properties, swelling behavior, drug loading efficiency and controlled release behavior as compared to simple polymer matrices.

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Cloisite 10A is organically modified montmorillonite clay. Montmorillonite is based on complex colloidal magnesium aluminum silicate. It is a member of the smectite family. Montmorillonite clays and their modified forms find wide range of applications, in various areas of science, like drug delivery systems due to their wide availability in nature. Montmorillonite has been extensively applied for prolonged release of drugs as it can retain large amounts of drug due to its high cation exchange capacity [3-8].

Chitosan is a natural amino-polysaccharide having unique structures, properties, and highly sophisticated functions. Chitosan and its modified forms offer wide ranging applications in biomedical and other industrial areas. Chitosan, derived from chitin is a copolymer of glucosamine and N-acetyl glucosamine units has gained an increased attention in biomedical and pharmaceutical purposes due to their biocompatibility, non-toxicity, biodegradability muco adhesive properties etc.[9-12].

The focus of this paper is to design novel polymer nanocomposite materials; so that these could be useful as novel drug delivery devices.

EXPERIMENTAL

Materials

Chitosan (86% deacetylation,) was commercially obtained from Research-Lab Fine Chem. Industries, Maharashtra State, India. Cloisite 10A was purchased from Southern Clay Products, USA. Other reagents and chemicals were obtained from Deepa industries ltd, Aurangabad, India. All chemicals were used as received, without further purification.

Preparation method of cloisite 10A-chitosan nanocomposites by solution mixing technique

Firstly, Cloisite 10A suspension was prepared by adding double distilled water under vigorous stirring for 24 hours and kept for another 24 hours for swelling. Then chitosan solution is prepared by dissolving it in 1 % (w/v) acetic acid to prepare 0.5 % (w/v) solution. After that chitosan solution was added slowly into the prepared cloisite 10A suspensions under stirring for 12 hour at 60 °C. The resulting mixture was precipitated with 1

mol/l NaOH. The formed nanocomposites were washed with double distilled water until they became neutral. The formed nanocomposites were dried at 50 °C and made them to powders. The weight ratios of chitosan/cloisite 10A in different nanocomposites were 100:1, 50:1, 20:1, 10:1, and 5:1 [13].

Evaluation of prepared nanocomposites

The nanocomposites were evaluated by powder x-ray diffraction (XRD), particle size analyzer (Beckman coulter), scanning electron microscopy (SEM), and fourier transmission infra red spectroscopy (FT-IR) techniques.

- **FT-IR spectroscopy**

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. This technique when coupled with intensity measurements is used for quantitative analysis. The important advantages of infrared spectroscopy over the other usual methods of structural analysis (X-ray diffraction, electron spin resonance, etc.) are that it provides information about the structure of a molecule quickly, without tiresome evaluation methods. FT-IR is based upon the simple fact that a chemical substance shows selective absorption in the infrared region giving rise to absorption bands called an IR absorption spectrum, over a wide wavelength range. Various bands will be present in the IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus an IR spectrum of a chemical substance is a fingerprint for its identification. IR spectrum of polymer nanocomposite shows the presence of both nanomaterials and polymers (depending upon the polymer chain) at various frequencies.

The infrared absorption spectra of the polymer, clay, and the formulated nanocomposites were obtained using a FT-IR spectrophotometer (PerkinElmer Spectrum Version 10.03.02).

- **Particle size analysis**

Particle size analyzer (LS230, Beckman Coulter, USA) provides the intensity of distributions, average diameter, and polydispersity index of particles in the nanocomposites.

- **Morphology**

The surface morphologies of the films were obtained using a scanning electron microscope (SEM).

- **X-Ray Diffraction study (XRD)**

The X-ray diffraction (XRD) analysis was performed using a powder diffractometer with Cu target and $K\alpha$ ($\lambda=0.154056\text{nm}$) at 40 kV with a slow scan of 0.3 degree/s in 2θ range 10-50 degree at room temperature.

The crystallite size of the nanocomposite was determined from the XRD study by the Scherrer Equation.

$$t = K * \lambda / B * \cos\theta$$

Where

t = thickness of crystallite

K = constant dependent on crystallite shape (0.89)

λ = x-ray wavelength (usually 1.54056 Å)

B = FWHM (full width at half max) or integral breadth

$$= (2\theta \text{ High}) - (2\theta \text{ Low})$$

So, B is the difference in angles at half max, and

θ = Bragg angle

X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensified peaks whereas the nanocomposites of amorphous polymer show sharp and highly intensified peaks.

RESULTS AND DISCUSSION

FT-IR spectroscopy

The objective of FT-IR analysis was to study the interaction between chitosan, cloisite 10 and prepared nanocomposites. The FT-IR spectra of chitosan, clay and the nanocomposites are shown in Figure 1.

In the spectra of chitosan, the broad band near 3500 cm^{-1} corresponded to the amine and hydroxyl groups; the peak at 2950 cm^{-1} is caused by -OH stretching. The peaks observed at 1080 cm^{-1} and 1042 cm^{-1} are the hydroxyl groups (characteristic peak of -CH-OH in cyclic alcohols, C-O stretch) and the primary hydroxyl group (characteristic peak of -CH₂-OH in primary alcohols, C-O stretch).

In the FT-IR spectra of cloisite 10A, sharp band at 3550 cm^{-1} corresponds to N-H stretching where as peaks at 2900 cm^{-1} and 2950 cm^{-1} corresponds to aliphatic C-H stretching. The peaks observed at 1590 cm^{-1} corresponds to N-H bending vibration and peak between 1000 cm^{-1} to 1100 cm^{-1} correspond to C-H stretching vibration.

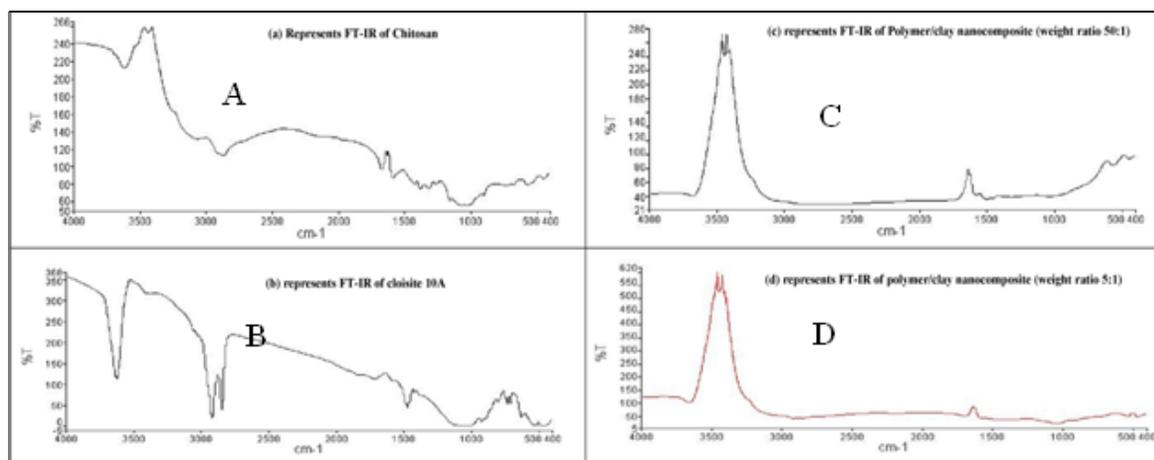


Fig. 1. FT-IR spectra of cloisite(A), cloisite 10A(B), Polymer/clay nanocomposite (weight ratio 50:1) (C) and polymer/clay nanocomposite (weight ratio 5:1) (D).

Particle size analysis

Particle size analyzer provides the intensity distributions and average size and polydispersity index of particles. The average particle diameter of the nanocomposite was found to be 218.6 nm, where as polydispersity index of particles was found to be 0.175. From the intensity of distribution table, it is found that the diameters of 10% particles are below 31.70 nm, 50% particles are below 116.90 nm, 90% particles are below 442.20 nm (Figure 2).

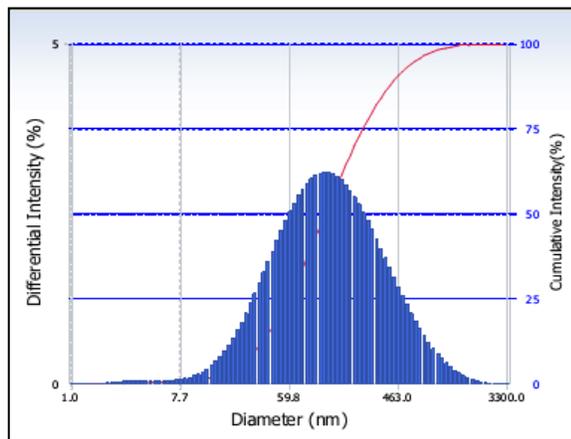


Fig. 2. represents particle distributions in nanocomposite formulation

X-ray Diffraction study (XRD)

XRD patterns of cloisite 10A- chitosan nanocomposite are shown in Figure 3. The patterns cloisite 10A- chitosan nanocomposites showed diffraction peaks at $2\theta = 19.00, 20.00$. The XRD result confirms the formation of nanocomposites.

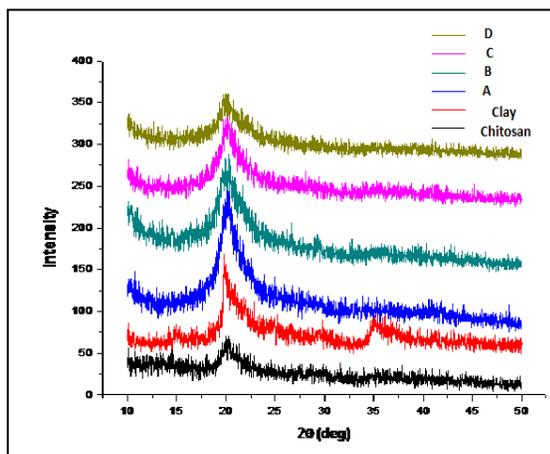


Fig. 3. represents XRD images for Chitosan, cloisite 10A and nanocomposite powder

Morphology

The surface morphologies of the prepared composites were examined using a scanning electron microscope (SEM). The SEM observation showed that chitosan is well embedded in clay layers, suggesting good exfoliation of polymer. The nanostructured composite formation between clay and polymer was identified by SEM analysis (Figure 4).

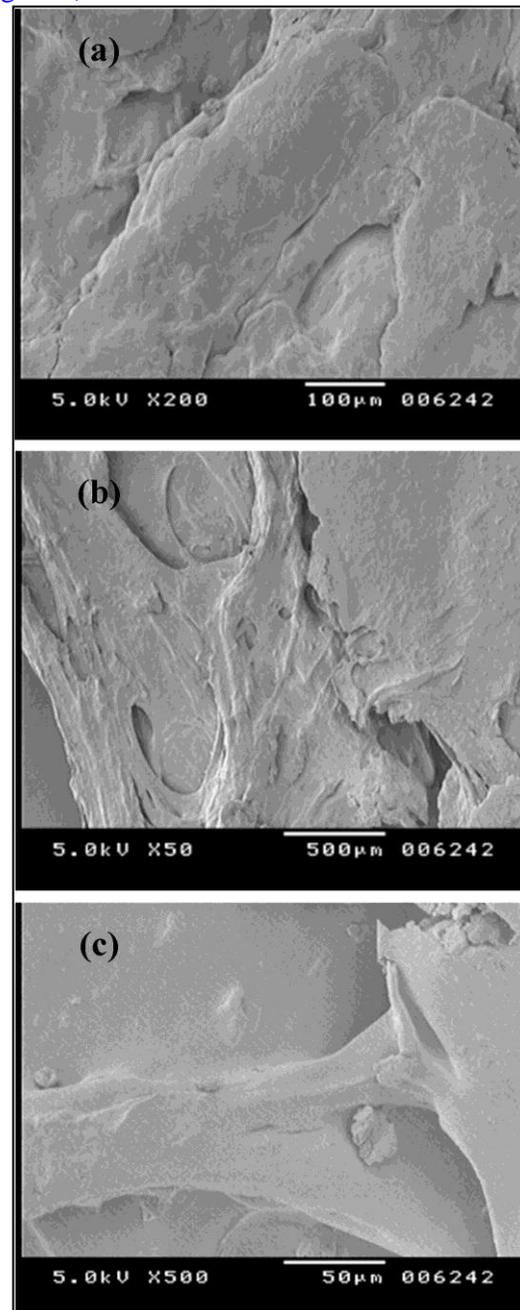


Fig. 4. (a), (b) and (c) represents a typical SEM image of the prepared polymer-clay nanocomposite at different magnifications.

CONCLUSIONS

Chitosan-cloisite 10A nanocomposites were successfully prepared by solution mixing technique. The mechanisms of nanocomposite formation, crystallite size, crystallinity, morphology were studied. XRD and FTIR investigations showed an intermolecular interaction between clay and polymer. The average diameters of particles in the nanocomposites were found to be around 300nm from both XRD and particle size analyzer. This study provides a platform for further research on the polymer-clay nanocomposites for drug delivery and biomedical applications.

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