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Nanocomposites Based on Natural Biodegradable Materials: Effect of Post-Preparative γ-Irradiation on the Swelling Properties

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ABSTRACT

Nanocomposites were prepared by in situ intercalative polymerization of acrylamide/acrylic acid in presence of fuller's earth. Agro- and food industry wastes, sugarcane bagasse and chitin, respectively were used as reinforcing/adsorbent materials. Effect of γ-radiation on adsorption characteristics of nanocomposites was evaluated by the comparison of swelling and erosion measurements of the exposed and unexposed samples. Low doses of γ-radiation improved the characteristics as adsorbents. Better results were obtained for the nanocomposites with polyacrylic acid matrix.

KEYWORDS

Nanocomposites; Sugarcane Bagasse; Chitin; Polyacrylamide; Polyacrylic Acid

1. Introduction

Renewable resource based biodegradable eco-friendly natural polymers are excellent candidates for various applications owing to increased worldwide concern about sustainability issues [1,2]. However, their application as the components of nanocomposites is limited because of dominant hydrophilic character, fast degradation rate and, in some cases, unsatisfactory mechanical properties, particularly under wet environment. This can be significantly improved by blending with synthetic polymers. An emerging area of nanotechnology is being explored for application into the environmental remediation strategies. Lee and Tiwari critically evaluated the role of organo-modified or inorgano-organo-clay or the clay based nano-materials/composites in this context [3]. Layered nanohybrids are heterostructured materials composed of two-dimensional inorganic host and intercalating inorganic-organic-, bio-, or polymer guests have been extensively explored to create new multifunctional hybrid systems [4]. The emphasis for future work is on advanced clay-based nanomaterials for use in new approaches to sustainable energy, green environment, and human health [5].

Ionizing irradiation is a promising technique for improvement in the properties of existing and advanced synthetic/hybrid materials. Effect of γ irradiation on poly (vinyl alcohol) and bacterial cellulose composites used as packaging materials was studied by swelling measurements [6]. Irradiation of cellulose acetate caused a reduction in the values of molar mass, hydrodynamic volume, real and ideal chain dimensions and its characteristic ratio [7]. Pesticide adsorption capacity of cellulose fibre was improved by high-energy irradiation-initiated grafting of glycidyl methacrylate [8].

Adsorption of radioactive species onto economy and easy to dispose materials has attracted attention of several scientists. Hacıoğlu and co-workers proposed ethylene propylene diene terpolymer (EPDM) to be relatively radiation resistant and a candidate polymer for usage in radioactive waste management [9]. Pyrolysis residues, bentonite and fly ash exhibited appreciable adsorption of radio antimony (^{122}Sb and ^{124}Sb) [10]. Yildiz and co-workers

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suggested clay and zeolites to be good sorbents in radioactive waste management [11]. Balarama Krishna *et al*. reported efficiency of immobilized moss as a biosorbent for removal of ^{137}Cs and ^{90}Sr from actual low-level radioactive waste solutions, which was efficient even after three cycles of reuse [12]. Selvakumar *et al*. studied silver nanoparticles containing carbonized yeast for adsorption of few long-lived active radionuclides [13]. Recently an attapulgite/iron oxide nanocomposite was investigated as a suitable sorbent for nuclear waste management [14]. Curti and co-workers found that mobility of $^{79}SeIV$ released from radioactive waste could be greatly decreased through uptake on the pyrite surface followed by transformation into a sparingly soluble reduced form [15]. The chitin-based sorbents of animal and fungal origin adsorb U and transuranium elements. Some of them are manufactured commercially in a form suitable for high flow-rates [16].

In the present study vinyl monomers, viz., acrylamide and acrylic acid were intercalatively polymerized in presence of fuller's earth (FE) to prepare nanocomposites with polyacrylamide (PAAm) and polyacrylic acid (PAA) matrices respectively under microwave irradiation. Biodegradable agricultural and marine wastes, namely sugar cane bagasse (SCB) and chitin (CH), besides functioning as adsorbents, acted also as reinforcing fillers. FE is composed of the layered silicates, montmorillonite being the major component. All of the four components of respective nanocomposites thus prepared, *i.e*., SCB, CH, FE and PAAm or PAA are well known to possess good adsorption characteristics for organic chemicals and metal ions. γ-radiation could have been used as the energy source in this preparation but it generally requires high doses. Our interest was to study the effect of low doses of γ-radiation on improving the adsorption behaviour. It was intended that if radiation does not exert a significant deteriorating influence, these materials could be used for radioactive waste management as well.

2. Experimental

Nanocomposites were prepared from SCB, CH and FE by in situ intercalative polymerization of the vinylic monomers, namely acrylamide (AAm) or acrylic acid (AA). The emulsion of finely ground SCB in NaOH and emulsion of CH in acetic acid were thoroughly mixed under magnetic stirring with finely powdered FE; AA or AAm; potassium per sulphate (KPS)—a free radical initiator; and N, N'-methylene bisacrylamide (MBA) a cross linker. This mixture was irradiated in a domestic microwave oven. The resulting solid mass was extracted with water to eliminate loosely bound material, and then dried in an air oven. The nanocomposite samples with polyacrylamide matrix (NCPAAm) and polyacrylic acid matrix (NCPAA) were exposed to low doses of γ-radiation from ^{60}Co radiation source. Percent swelling and percent erosion of the irradiated samples were measured using conventional gravimetric procedure.

$$\%\ Swelling = \frac{m_s - m_o}{m_o} \times 100 \quad (1)$$

$$\%Erosion = \frac{m_o - m_d}{m_o} \times 100 \quad (2)$$

Where m_o and m_s are the masses of the original and water swollen samples respectively; and m_d the mass of sample dried after immersing it in deionized water for 24 h.

3. Results and Discussion

Nanocomposites NCPAAm and NCPAA were prepared from low cost inorganic and renewable organic materials, by in situ intercalative polymerization of the monomers AAm or AA respectively by microwave irradiation, with a view to develop a cost effective method. SCB comprises of cellulose, hemicelluloses and lignin. Lignin is soluble in aqueous solution of NaOH but it was not separated from the reaction mixture during the preparation to: 1) facilitate the binding of matrix; 2) provide extra functionality for adsorption, and 3) introduce a little hydrophobicity to the matrix for prevention of fast microbial degradation. NCPAAm and NCPAA samples immersed in deionized water were stable against biodegradation even for 3 months, whereas moulds grew within a week on SCB or CH in wet condition. However, upon inoculation with Aspergillus, growth of mycelia was visible to unaided eyes over the nanocomposite samples also in seven days, which indicated possibility of their biodegradation. It was interesting to observe when a NCPAAm sample (about 1 g) was immersed in 200 mL of concentrated methyl orange (MO) solution (0.3 g/L), sample adsorbed the dye gradually and the solution became nearly colourless in 15 days. This sample, with MO adsorbed on it, was left as such for another 15 days; it slowly turned black in colour. It was examined for the growth of microbes but no fungal or microbial growth could be detected. It was inferred from UV-visible absorption spectral measurement that black color was due to the degradation of dye.

3.1. Characterization of NCPAAm and NCPAA

The FTIR spectrum of NCPAA is presented in **Figure 1** along with the spectra of its constituents. FTIR spectral analysis is a very powerful tool for the study of interactions of functional groups even for a multicomponent system. The FTIR spectrum of the nanocomposite NCPAAm is depicted in **Figure 2** (along with the spectrum of an irradiated sample).

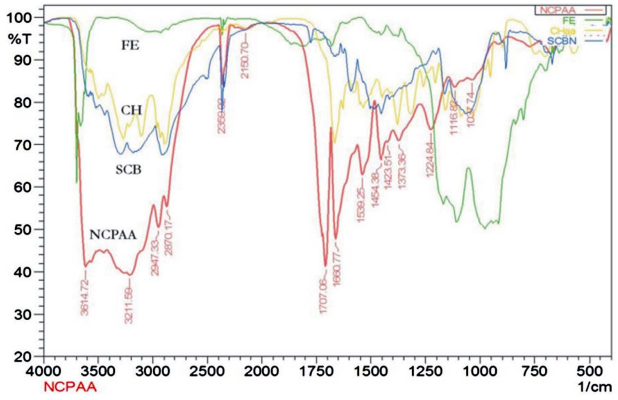

Figure 1. FTIR spectra of NCPAA and its constituents.

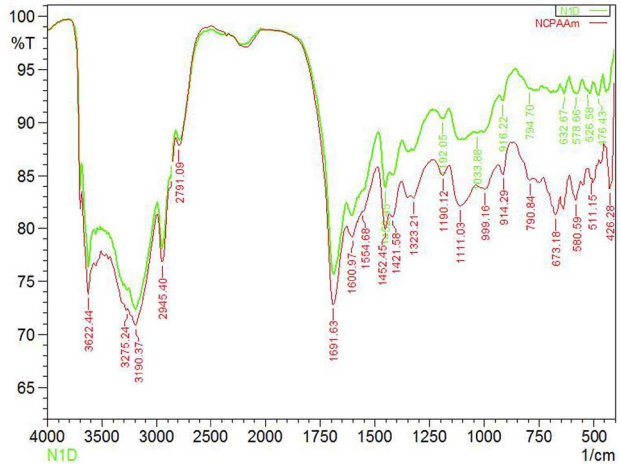

Figure 2. FTIR spectra of NCPAAm (red line: Unexposed) and N1D (green line: sample exposed to *γ*-radiation).

The absorption band due to FE (at 3696 and 3665 cm^{-1}) was clearly visible above 3610 cm^{-1} in both the nanocomposites. Decrease in intensity and slight broadening suggested the disruption of layered structure by intercalative polymerization of monomers between the clay interlayers. For NCPAA a very broad and intense band in 2800 - 3700 cm^{-1} range was observed which included absorptions from *ν*OH of cellulose, lignin and chitin; and also PAA. Similarly in NCPAAm a broad band centered at 3190 cm^{-1} appeared due to overlapping absorptions from *ν*OH and *ν*NH of SCB, CH and PAAm. The typical $\nu_{as}CH_2$ and ν_sCH_2 appeared around 2900 cm^{-1}. A very strong and broad band in 1650 - 1800 cm^{-1} range, was ascribed to the amide I and II vibrations of CH and PAAm in NCPAAm and COOH groups of NCPAA respectively. This band also included absorptions from *δ*OH and δ NH_2 of SCB and CH. The intensity of this band led to infer that it might have included absorption from carbonyl groups also because it is possible that microwave heating induced oxidation of hydroxyl groups of SCB and CH. Similar phenomenon was reported by Briones and co-workers that under the influence of microwave heating lignocellulosic residues showed strong absorption bands at 1730 cm^{-1} (C = O stretching). They attributed a higher content of carbonyl groups in the MW treated products to the fact that microwave activation induced more intensive oxidation of hydroxyl groups into carbonyl groups [2]. The spectral region below 1500 cm^{-1} showed a very complex series of overlapping absorption bands, originating from the various components of the nanocomposites.

SEM images of the fractured surfaces of nanocomposites with various magnifications are shown in **Figure 3**. Inhomogeneous morphology with irregular pores of 5 to 1000 µm diameter are visible at low magnification. A few fibres of SCB of 5 to 500 µm length are visible on the surface of nanocomposite at lower magnification. The CH flakes and SCB microfibrils coated with PAA or PAAm appeared as bright areas and the dark areas represented fuller's earth. At magnification of 4000 no pores were visible, which suggested that CH and SCB were completely embedded in the polymeric matrix intercalated within FE.

The XRD patterns of NCPAAm, NCPAA and FE in 2Θ range of 0˚ to 80˚ are depicted in **Figure 4**. The XRD pattern of NCPAAm exhibited very weak signals corresponding to those of FE. However, the prominent peaks of FE below 10˚ reduced to a shoulder and that at 26.55˚ also appeared with a decreased intensity. The d-spacing of the signal at 27˚ calculated by Bragg's equation increased from 3.3543 Å to 3.3814 Å in NCPAAm. The decreased intensity and increased width indicated the presence of disordered or exfoliated regions. The XRD pattern of NCPAA showed the featureless diffraction pattern except for a weak signal at 27˚. This type of pattern is generally associated with the exfoliated structure, as a consequence of disrupted coherent layer stacking. Hence it was inferred that intercalation of the polymer chains increased the interlayer spacing of clay (FE) and introduced the amorphous nature. These results proved

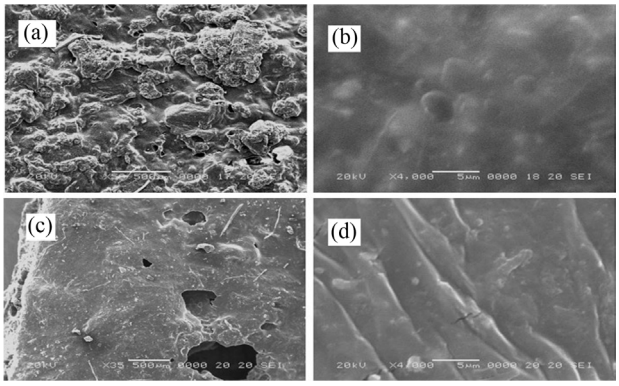

Figure 3. SEM of Fractured surfaces of nanocomposites: NCPAAm—magnifications (a) × 50 (b) × 4000 and NCPAA magnifications (c) × 35 (d) × 4000.

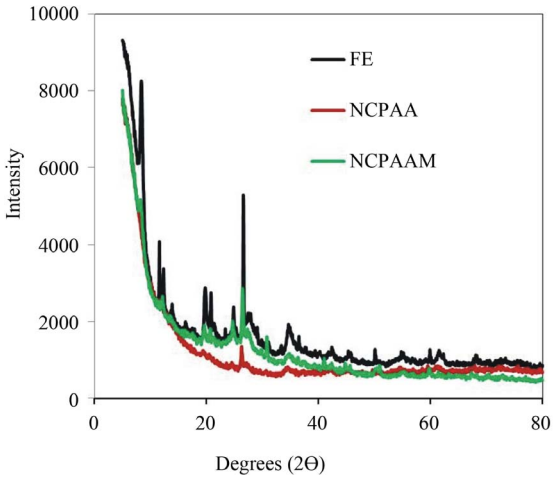

Figure 4. XRD patterns of fuller's earth, NCPAA and NCPAAm.

nanocomposite nature of the samples, since the polymer nanocomposites are materials in which nanoscopic inorganic particles, typically 10 - 100 Å in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the performance properties of the polymer.

3.2. Effect of *γ*-Irradiation

The properties required for a good adsorbent for dissolved substances are: extensive surface area and release of minimum amount of leachates, which could be evaluated by measurement of the percent swelling and percent erosion, respectively. In the present study, the nanocomposites were exposed to low radiation doses (0.25 - 1 kGy) and the results are depicted in **Table 1**, **Figures 5** and **6**.

A perusal of these data showed that erosion of NCPAAm increased upon irradiation, whereas there was no significant influence on swelling behaviour. Irradiated NCPAA samples exhibited increase in swelling capacity and decrease in percent erosion in water. It has been reported that for chitosan (partially deacetylated chitin) the main chain scission predominated over crosslinking under *γ*-irradiation [17,18]. Usually the main chain scission promotes the adsorption capacity. It was reported on the basis of study of degradation by irradiation that reduction in molecular weight led to a significant increase in the amount of fat bound by 1 g of chitosan [19]. One may expect a linear or regular trend for influence on the properties of a material on exposure to increasing doses of radiation. However, the irregular trend observed in the present study could be explained as follows. Exposure to radiation is expected to induce degradation of polymeric chains and also formation of crosslinks through the intermediacy of free radicals. Cross linking should prevent erosion of the matrix but with consequent decrease in

Table 1. Percent erosion of *γ*-ray exposed nanocomposite samples.

S. No.	Exposure dose kGy	Sample code*	Erosion %	Sample code*	Erosion %
1	0.00	N1	1.42	N2	10.68
2	0.25	N1A	2.36	N2A	03.51
3	0.50	N1B	2.80	N2B	06.71
4	0.75	N1C	4.63	N2C	04.33
5	1.00	N1D	5.50	N2D	05.65

*N1 and N2 denote NCPAAm and NCPAA samples respectively.

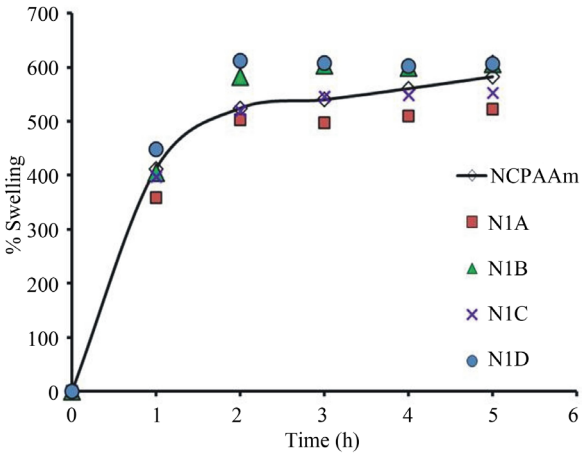

Figure 5. Swelling kinetics of NCPAAm and *γ*-ray exposed samples.

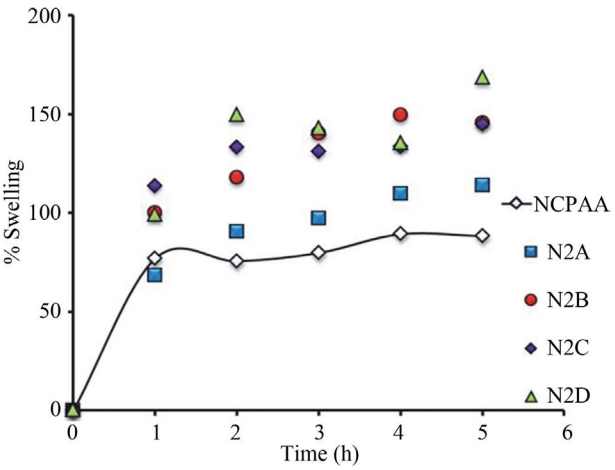

Figure 6. Swelling kinetics of NCPAA and *γ*-ray exposed samples.

swelling. The partial degradation of one or more of the matrix components would result in the formation micropores and consequent increase the surface area, whereby swelling would be enhanced. Nevertheless, with a multicomponent system comprising of biopolymers SCB and CH and interpenetrating network of PAAm or PAA, a partially degraded fragment of one component instead of being separated and lost away, could become attached

to other component by second order radical reactions. Further, due to presence of lignin (a component of SCB) physical crosslinks by assemblage of hydrophobic moieties also existed and the samples did not behave like typical hydrogels.

A comparison of FTIR spectra of irradiated samples with those of the original samples (**Figures 2** and **7**) indicated that there was almost negligible effect of γ-radiation in low doses on the average composition of nanocomposites especially for NCPAAm (**Figure 2**), *i.e.*, the interaction of functional groups in polyacrylamide matrix was not promoted by γ-radiation. A slight change was observed for NCPAA (**Figure 7**). A broad absorption band at 1743 cm^{-1} in the original sample become narrower in N2D. This broad band incorporated absorption from various functional groups of the constituents, viz. OH (SCB), -COOH (PAA), NH_2 and $CONH_2$ (CH). Narrowing of this band suggested that there was extensive interaction between these functional groups to form ester (-COO) and amide (-CONH-) linkages. These linkages crosslinked different constituents, consequently the matrix became more compact and the water molecules adsorbed on various constituents were expelled out. This led to decreased erosion. The crosslinks enhanced the surface area of embedded voids, which resulted in increased swelling capacity.

These experiments were carried out with samples cut from the hard, disc shaped product obtained on MW irradiation of reaction mixture in a beaker. When this product was cut into smaller pieces, the sides fractured and very small fragments detached from the main body which amounted to the erosion. Hence, more experiments were carried out with the entire disc shaped block and results are presented in **Figure 8**. The radiation dose was increased and swelling and erosion were measured for the longer duration. It was appreciated that the erosion was negligible and swelling of irradiated samples enhanced when compared to the virgin sample.

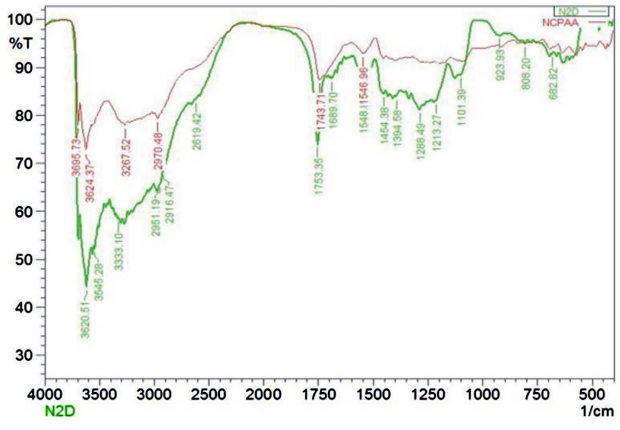

Figure 7. FTIR spectra of NCPAA (red line: Unexposed) and N2D (green line: sample exposed to γ-radiation).

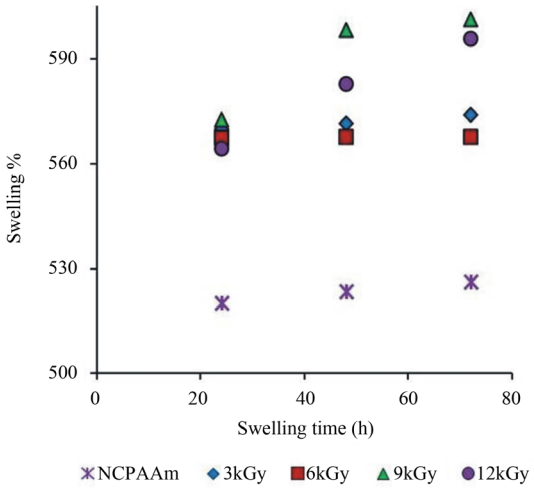

Figure 8. Effect of radiation dose on swelling of NCPAAm.

4. Conclusion

Agricultural waste sugarcane bagasse (SCB) and marine industry waste chitin (CH) were incorporated into nanocomposites comprising of organic-inorganic matrix, *i.e.*, synthetic vinylic polymers (PAA and PAAm) and fuller's earth with a view to prepare eco-friendly adsorbents for treatment of polluted water. Effect of γ-irradiation for improvement in the quality of these materials, viz. enhanced adsorption and minimization of leachate formation was studied. The preliminary investigation showed quite encouraging results. The materials were found to be sufficiently resistant to radiation and their properties as adsorbents were improved.

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