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SYNTHESIS AND CHARACTERIZATION OF CHITOSAN -GRAFT - METHACRYLONITRILE COMPOSITE

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ABSTRACT

Chitosan was grafted with methacrylonitrile (MAN) through oxidative-radical copolymerization using ammonium persulfate (APS) in acidic medium. The grafting conditions were extensively studied by varying grafting parameters. All the findings have been discussed and proposed a plausible mechanism for the graft copolymerization. Evidence of graft copolymerization was obtained by FTIR spectroscopy, e.g., the appearance of nitrile in the spectrum of chitosan-graft-polymethacrylonitrile. The synthetic conditions were systematically optimized through studying the influential factors including temperature, as well as concen-trations of initiator, Chitosan-g- methacrylonitrile composite can be best adsorbent for metal extraction and dyes extraction. It can use in analytical chemistry would be attractive not only in terms of product cost and environmental safety but also from a materials science point of view.The representative chitosan-graft- methacrylonitrile was characterized using FTIR, DSC, XRD and Scanning electron microscopy taking chitosan as reference.

KEYWORDS: *Chitosan, Composite, acrylonitrile,* methacrylonitrile.

INTRODUCTION

Highly swelling polymers, which is, superabsorbent composites are hydrophilic three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight Po (1994). They are widely used in various applications such as drug delivery, hygienic, foods, cosmetics and agriculture (Zhou et al., 2011; Huixia et al., 2010; Raghavendra et al., 2010; Hoffman, 2002; Peppas and Harland, 1990; Kost, 1995). This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from

6000 tons in 1983 to 450000.

Abbreviations: AN, Acrylonitrile; **AA,** acrylic acid; **APS,** ammonium persulfate; **SEM,** scanning electron microscopy; **DSC,** Differanational Scanning Colourimentry analysis; **MBA,** methylenebisacrylami **FTIR,** fourier transform infrared

Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and characterization of superab-sorbent composites is the main goal of the several research groups in the world. Because of their exceptional properties, that is, biocompatibility, biodegradability, renewability and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent composites. Graft copolymerization of vinyl monomers onto polysaccharides is an efficient rout to preparation of composites. Vinyl graft copoly-merization onto polysaccharides and proteins is a well-known method for synthesis of natural-based superab-sorbent composites.[1-3]

The first industrial superabsorbent composite, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method Fanta (1996). The composite forming ability through graft copolymerization of vinyl monomers onto polysaccharides such as starch, chitosan, sodium alginate, carrageenan and cellulose has been well documented, (Sokker et al., 2001; Yu et al., 2006; Lin et al., 2010).Because of the presence of certain functional groups along the polymer chains, composites are often sensitive to the conditions of the surrounding environment, which are referred to as “intelligent materials” or “smart materials”. For example, the water uptake of these materials may be sensitive to temperature, pH or ionic strength of the swelling solutions or even to the presence of a magnetic field or ultraviolet light. These smart composites are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems and controlled release systems.[4-6]

Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin, (Roberts, 1992). It is a basic polymer, having amine side groups. Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan composites Zhang et al. (2007). When anionic monomer such as acrylic acid in present acrylonitrile monomer is grafted onto chitosan (in

the presence of a divinyl crosslinking agent monomer), an ampholytic composite containing both cationic and anionic charges is prepared. So, by introducing anionic charges ($-COO^-$) onto chitosan, a composite with swelling ability at various pH is prepared. In this study, we evaluate the synthesis and characterization of chitosan-g-poly(acrylic acid-co-acrylonitrile) composite as a new natural-based polymer with pH-responsiveness properties. In this composite, AN is as a co-monomer (as seen from the title of the paper) and used mainly for increasing the hydrophilicity and improving the swelling rate of the resulted network.[7-10]

MATERIALS AND METHODS

Chitosan (from Sigma AldrichMol wt. 22742 Da and degree of deacetylation of 75%), Acrylic acid (AA, Merck) and methacrylonitrile(MAN, Merck) were used after vacuum

Synthesis of Composite

A general procedure for chemically crosslinking graft copoly-merization of MAN onto chitosan backbones was conducted as follows. Chitosan was dissolved in degassed, distilled water containing 2 wt% of acetic acid. In general, (0.5 to 1.0 g) of chitosan was dissolved in 50.0 ml of the acetic acid solution. The reactor was placed in a water bath preset at 60°C. Then, APS (0.1 gm in 5 ml H_2O) was added to the chitosan solution and stirred for 10 min at 60°C. Following this, MAN (3 gm) were added to the chitosan solution.

MBA (0.01 to 0.13 g in 5 ml H_2O) as a crosslinker was added to the reaction mixture after the addition of monomer and the mixture was continuously stirred for 60 min under argon atmosphere. After 60 min, the reaction product was allowed to be cooled to ambient temperature. To separate the polymethacrylonitrile (PMAN) homopolymer, 0.50 g of the crude product was poured into 50 mL of dimethylformamide (DMF) and stirred gently at 30°C for 24 h. After centrifuging and decanting the supernatant (PMAN in DMF), the chitosan-graft-polymethacrylonitrile was precipitated in methanol, thoroughly washed with methanol, and dried at 50°C to reach a constant weight.

The resulting composite was neutralized to pH 8 by addition of 1 N NaOH solution. Then, methanol (500 ml) was added to the gel product, while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2×50 ml) and dried at 50°C.

Grafting parameters

% Grafting efficiency (%Gr) are Grafting parameters of grating copolymerization reaction.

$$\%Gr = \frac{W3}{W2} \times 100$$

Where, W2, and W3 are weight of the total product (i.e., copolymer and homopolymer), and pure graft copolymer(after solvent extraction), respectively.

Swelling Study of Composite

A composite sample (0.10 g) was put into a weighed tea bag and immersed in 100 ml distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen composite was allowed to drain by removing the tea bag from water and hanging until no drop drained (20 min). The bag was then weighed to determine the weight of the swollen composite. The absorbency (equilibrium swelling) was calculated using the following equation.

$$\text{Equilibrium swelling ratio} = \frac{\text{weight of equilibrated swollen composite material}}{\text{weight of dry composite material before swelling}}$$

So, swelling ratio (absorbency) was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was ±3%.

pH stimuli study of composites

Swelling Study of composite's

Buffer solution of pH3, 5, 9 and 11 was prepared by using respective buffer tablets. Dry weight of composite were measured and inserted into respective buffer solution and then weight of composite was measured after 2 hours at room tem and swelling ratio of following composite's solution are observed.[11-12]

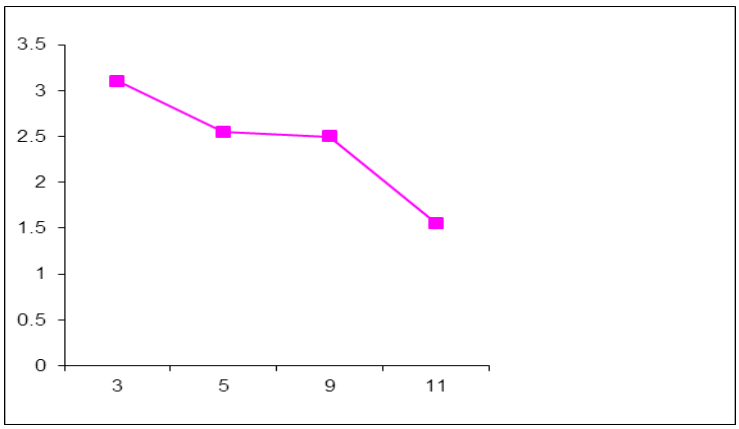

Fig : 1: Swelling behavior of composite with change in pH

pH-dependent swelling of the composite

To investigate the sensitivity of the hydrolyzed composite to pH, firstly the equilibrium swelling (ultimate absorbency) of the composite was studied at various pHs. No additional 3, 5, 9 and 11 .No additional ions(through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength . Therefore, stock NaOH (pH 11.0) and HCl (pH 3.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. The two sharp swelling capacity changes can be attributed to high repulsion of $–NH_3^+$ groups in acidic media and $–COO^-$groups in basic media. Remarkable decreasing in equilibrium swelling is observed(composite collapsing). Around pH 5, the carboxylic acid component comes into action as well. Since the pKa of the weak polyacid is about 6.4, its ionization occurring above this value, may favor enhanced absorbency. But under pH 6.4, at a certain pH range 4–6, the majority of the base and acid groups are as non-ionized forms, so hydrogen bonding between amine and carboxylic acid (and probable carboxamide groups) may lead to a kind of crosslinking followed by a decreased swelling. A similar observation is recently reported in the case of an interpenetrating network composed of poly(N-isopropylacrylamide)–poly(acrylic acid).[13-15] Athigher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Again, a screening effect of the counter ions (Na+) limits the swelling at pH 8–11 and opposed the swelling at pH> 12, so that the composite totally collapses at pH 13.Such behavior has been reported for copolymeric composites from acrylic acid (the anionic constituent) and methacryl amidopropyltrimethyl ammonium chloride (the cationic constituent). In this system, a combination of attractive or repulsive electrostatic interactions and hydrogen bonding are the main reasons for existence of several phases observed in various environmental conditions.[16-19]

The product obtained is characterized by IR, DSC and SEM analysis.

RESULTS AND DISCUSSION

IR Spectral Characterization

A possible mechanism of the polymerization of acrylic acid and acrylonitrile onto chitosan in the presence of MBA is shown in Scheme 1. For identification of the composite, infrared spectroscopy and SEM were used. The FTIR spectra of pure chitosan and superabsorbent composite based on chitosan. Chitosan-g-MAN are shown in Figure 1. In Figure 1(a), a broad

band at 2995cm^{-1} corresponds to the associated –OH stretching vibrations of the hydroxyl groups and the peak at 1718 cm^{-1} corresponds to the N-H deformation bending of chitosan. The superabsorbent composite product comprises a chitosan backbone with side chains that having corboxylate and amide functional groups that are evidenced by new peaks at 1550 and 2097 cm^{-1} corresponds, respectively. The very intense characteristic band at 1665 cm^{-1} is due to C O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1449 cm^{-1} which is related to the symmetric stretching mode of the carboxylate anion.[21-22]

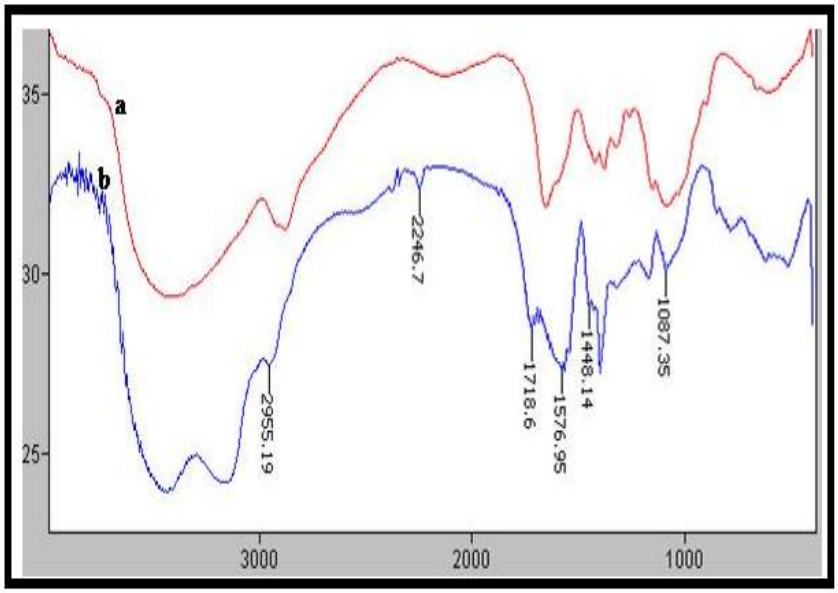

Fig. 2 – IR Spectra of a) Chitosan B)Chitosan-g- methacrylonitrile

Scanning Electron Microscopy

One of the most important properties that must be considered is the Composite microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 2 shows an SEM micrograph of the polymeric composites obtained from the fracture surface. The composite has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymer.

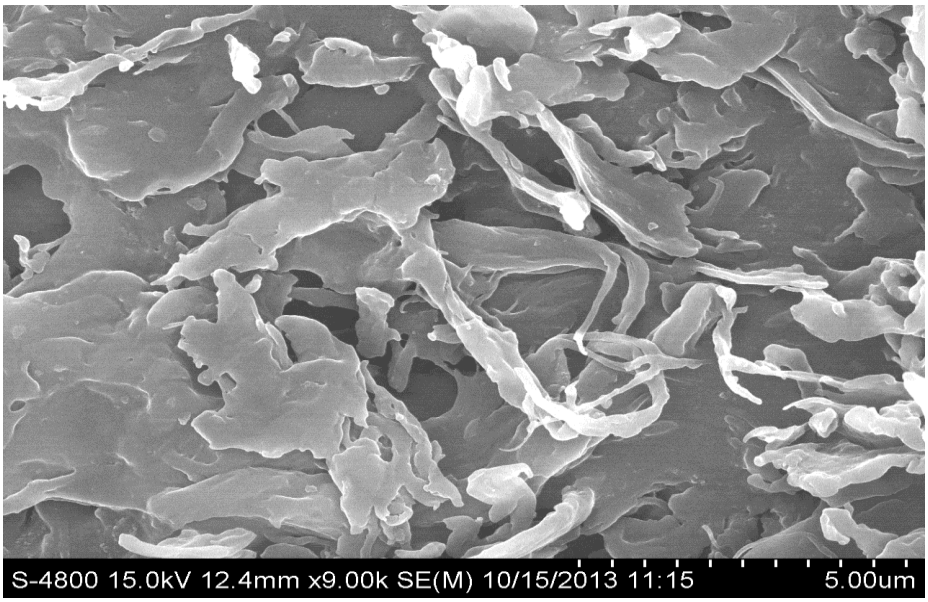

Fig: 3 SEM image of Chitosan-g-MAN composite

Differential Scanning Colourimentry

Differential scanning Colourimentry (DSC) is the best analytical technique to find the polymer crystallinity, which measures the physical nature of the sample, i.e., to check it is heated, cooled or under isothermal conditions. In this technique a sample would heat or cool at linear intervals of temperature and measure the particular temperature and energy accompanied with any one of the range of thermal events. It is observed from DSC plot that chitosan undergoes dehydration at lower temperature as compare to Chito-aa-am composite. However loss of water from composite is steady and periodically which shows that dehydration pattern is regular in case of composite.[23-26]

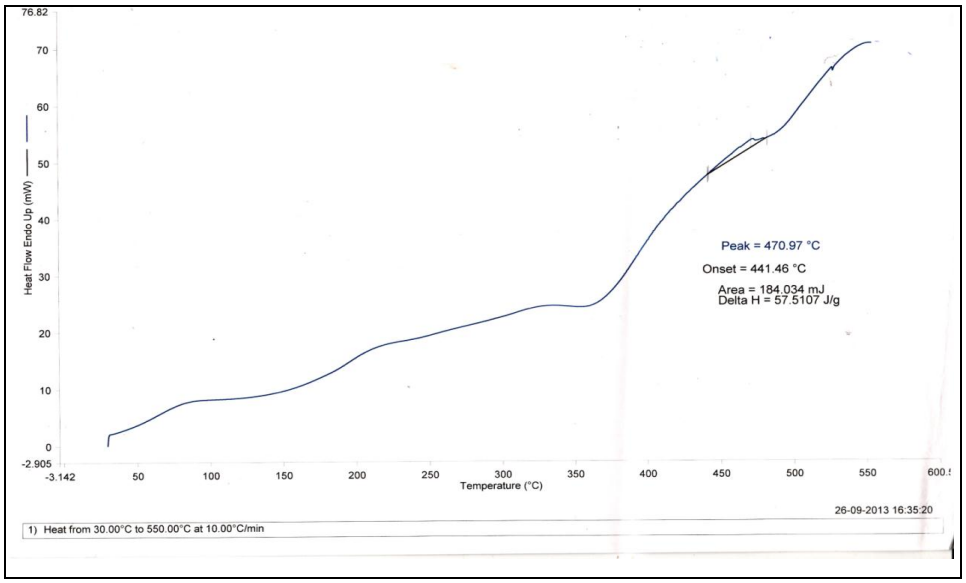

Fig 4 DSC of Chitosan-g-poly MAN

XRD of Chitosan –g- MAN- Powder X-ray diffraction is a more suitable technique than electron microscopy for solids identification, and as such it was used in our crystallization assays to confirm the electron microscopic results. Fig. 5 shows the XRD patterns of crystals grown on the grafted CHI-g-MAN .It can be seen that the strongest diffraction intensity is the broad peak around 2θ = 17–23◦ due to the substrate chitosan.

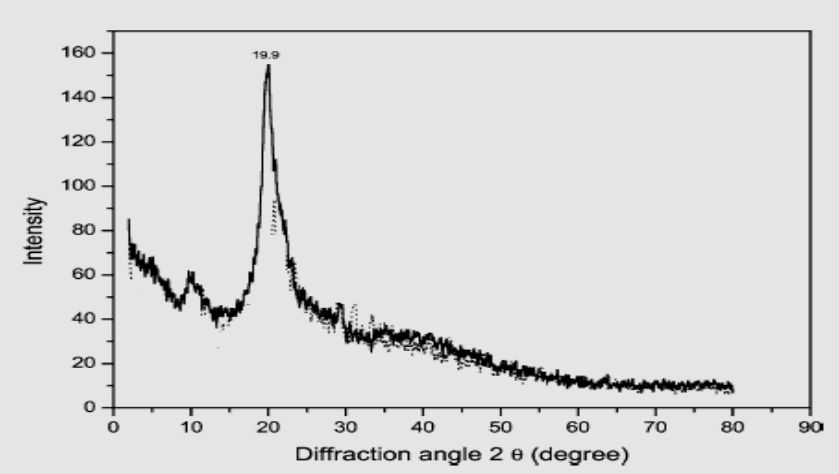

Fig. 5 : XRD of Composite Chito-g-MAN

CONCLUSION

Chitosan-g- methacrylonitrile composite, were synthesized through grafting of methacrylonitrile monomers onto chitosan using ammonium persulfate (APS) as an initiator and methylene bis acrylamide (MBA) as a crosslinking agent under an inert atmosphere. Swelling capacity of the composite was found to affect by monomers and crosslinker concentrations which maximum at pH-5. It also exhibited ampholytic nature of pH-responsiveness in swelling behavior. We investigated their swelling in different salt solutions and in media with a wide range of pHs. This composite polyampholytic network intelligently. Infrared analysis indicates presences of –OH from chitosan backbone in the grafting which is indicating by broad band 2995 cm^{-1}. DSC indicates crystalline nature of Composite (Chito-g-MAN). SEM indicates porous structure and support permeation of water molecule in composite, inversion supports the applicability of such smart material in drug delivery, biomedical material and analytical chemistry. Also the swelling study of gels reveals that the gels are have variable swelling behavior at different pH solutions. The gels used in present investigation have polyamphophilic network which intelligently gives response to pH change. Thus these gels may be considered as excellent advanced material for sustainable development in field of analytical chemistry. All the experimental data supports pH dependent behavior of the composites and it may be concluded that for swelling ratio as well

as metal and dyes extraction the composites work efficiently in low acidic solution which in turn may be related to stability, equilibrium ratio or equilibrium of composite in aqueous solution.

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