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Synthesis and Characterization of Poly (N-tert-amylacrylamide –co-Acrylamide/Maleic acid) Silver Nanocomposite Hydrogel

KEYWORDS: nanoparticles, hydrogel, swelling, Silver nanocomposite

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ABSTRACT *A series of Poly (N-tert-amylacrylamide -co –Acrylamide/Maleic acid) Silver Nanocomposite Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinker at 60^{0}C. . The swelling behavior of the Ag NC Hydrogels was studied by Gravimetric method and degree of swelling was increased by increasing the amount of MA. The SEM/EDX and XRD images indicate (Ag NP) Silver nanoparticles are in the polymer matrix.*

Introduction:
Hydrogels represent polymeric networks capable of absorbing large quantities of water, but remain insoluble due to chemical or physical crosslinks between individual polymeric chains [1] . When fully hydrated, can contain over 95% water, therefore they are in effect parcels of water that can be easily handled .Their ability to absorb water is due to the presence of hydrophilic groups such as -OH,-CONH , -$CONH_2$,-COOH,-SO_3H etc. Hydrogels can be divided into two categories based on the chemical or physical nature of the crosslink junctions. Chemically crosslinked networks have permanent junctions, while physical networks have transient junctions that arise from either polymer chain entanglements or physical interactions such as ionic interactions, hydrogen bonds, or hydrophobic interactions They are also classified as non-ionic and ionic materials in which the ionic type comprises of anionic (–

COO^-, $–SO_3^{-)}$ or cationic pendants ($–NR_3^+$). Due to specific properties like swelling in water, biocompatibility, absorbing water easily or hydrophilicity, and non-toxicity , hydrogels can be used in various fields of biomedical, catalytic, optical, pharmaceutics and environment (2-4). Recent trends demonstrate that the macroscopic gels are becoming most promising as templates/nano reactors for *in situ* synthesis of smaller size nanoparticles and this strategy has brought up a new concept in hybrid or composite systems in chemistry and engineering science (5-7). A promising antimicrobial coating of Poly (2-hydroxylethyl acrylate) (PHEA) and Poly(ethylenimine) (PEI) networks loaded with Ag nanoparticles, modified with Poly(ehyleneglycol) (PEG) was reported for biomedical and daily-life applications(8). Noteworthy, the hydrogel template methodology is that one can control the size and morphology of the nanoparticles by varying the amount of monomer, cross-linker, and functionality of gel networks. Owing to the fascinating properties of the stimuli-sensitive hydrogels, which can sense the environmental changes and induce structural changes by themselves, it is certain that they offer many future applications such as suitable materials for the design of intelligent biomaterials and self-regulated drug delivery systems. A study by Saravanan *et al.*(9) has shown that Poly(acrylamide) hydrogels are effective for the production of nano-sized silver particles (~4 nm). The combination of metal nanoparticles (silver) with smart polymeric architectures seems to be a promising route to the design of novel materials. Thus herein, we explored the feasibility of precisely producing silver nanoparticles in hydrogel networks and they were characterized by their structural characteristics, swelling behavior, SEM,. EDX and XRD studies

Experimental
Materials
N-tert- amylacrylamide (NTA) was prepared by the reaction of acrylonitrile and Amyl alcohol. The Acrylamide (AM), ammonium persulfate (APS).N',N',-Methylene bis acrylamide (MBA) and Maleic acid (MA) were purchased from Aldrich. Silver nano particles are also purchased from Aldrich.

Preparation of Hydrogels
Nanocomposite Hydrogels were prepared by Free-radical cross linking copolymerization. Monomers NTA (0.5g) ,AM (0.5g) and MA (0.10,0.30, 0.50 and 0.70) were charged into the reaction vessel , followed by addition of APS (0.005g) as initiator and MBA(0.045) as crosslinker in methanol water mixture at room temperature. They were purged with nitrogen for 15 min, and then heated at 60 ^{0}C in thermostatic water bath and the polymerization was conducted for 1 day. After the reaction, the extracted hydrogels were dried in vacuum oven at 50 ^{0}C to constant weight for further use .

Swelling behavior
Swelling experiments were carried out with a view of evaluation the swelling capacity of the hydrogels under investigation in double distilled water. When a hydrogel is brought into contact with water, water diffuses and the hydrogel swells. The swelling behavior of the hydrogels was determined by applying in the following equation

Ds % = [(Ws-Wd/Wd)] X 100
Where **(Ds%)** is the degree of swelling most commonly described as swelling ratio which is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time. **Ws** is the weight of the swollen gel at a given time and **Wd** is the weight of the dry gel. The swelling behavior of the hydrogels was carried out in water at room temperature and is depicted in the Figure -1.The swelling is driven by repulsion of hydrophilic groups such as NH_2 , C=0 NH_2 and COO^- inside the network and osmotic pressure difference between the gels and the external solution. As the concentration of MA increases the swelling behavior also increases due to the additional osmotic pressure developed which expand the gel network further.

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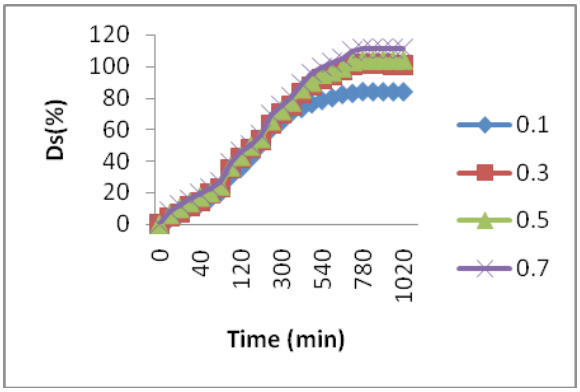

Figure 1: Swelling behavior of Hydrogels

SEM / EDX Analysis

The Micro structure of Hydrogels were studied by Scanning electron Microscopy The scanning electron micrograph of copolymeric-silver nanocomposite hydrogel was shown in figure 2.which shows the formation of defined nanostructures in the hydrogel networks.

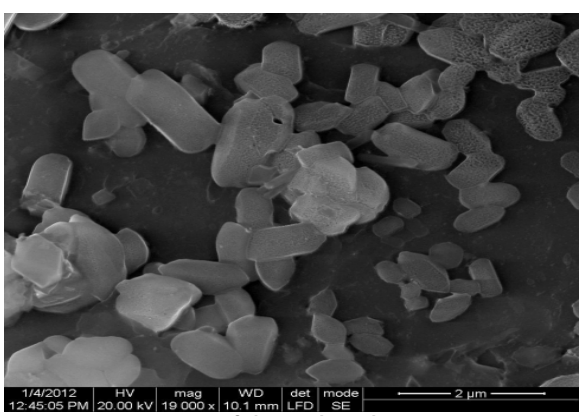

Figure 2: SEM image of the Hydrogel

Energy dispersive X-ray spectrum (EDX)

An elemental analysis of the particles was implemented by a SEM equipped with an energy dispersive X-ray spectrum (EDX), which can provide a rapid qualitative and quantitative analysis of the elemental composition.The EDX analysis showed that the incorporation of AgNPs in the Hydrogel matrix.

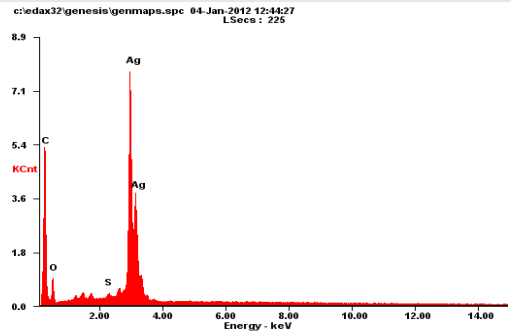

Figure3: Energy dispersive X-ray spectrum

XRD Studies

To get information on unit cell dimensions X-ray powder diffraction (XRD) patterns were collected using a Philips X-Pert automatic diffractometer operating at 40 kV and 40 mA in theta–theta configuration, secondary monochromator with Cu Ka radiation (k = 1.5418 A °) and a PIXcel solid state detector. The samples were mounted on a zero background silicon wafer fixed in a generic sample holder.The diffractogram of copolymeric hydrogel-silver nanocomposites are assigned to diffractions at 2θ values of about 20,38 and44 plane of face centered cubic (fcc) structure of silver nanoparticles. Sharp and intense peaks represent the highly crystalline silver nanostructures formed in copolymeric nanocomposites and the broad peak represents that the hydrogel is more amorphous and thereby the water diffuses more rapidly.

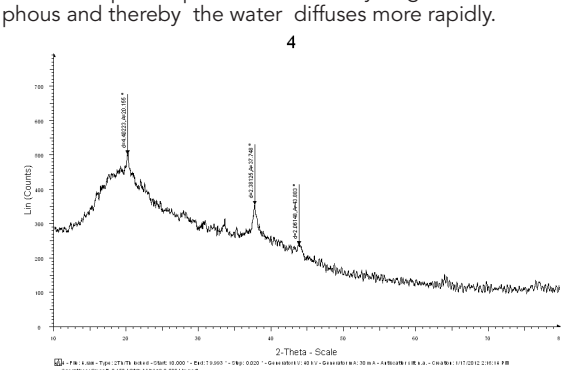

Figure 4:XRD pattern of Silver Nanocomposite Hydrogel

Conclusion

Copolymeric silver nanocomposite hydrogels were successfully synthesized by free radical polymerization. The swelling behavior of the resulting hydrogels shows that the swelling capacity increases as the concentration of MA increases. SEM, EDX and XRD data reveals the incorporation of silver Nanoparticles in the hydrogel matrix.

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