Research Paper Chemistry

Synthesis and Characterization of Poly(N-tert-amylacrylamide-co-Acrylamide/Sodium acrylate) Gold Nanocomposite Hydrogels

E.Kayalvizhy Research and Development Centre, Bharathiar University, Coimbatore - 641 004, Tamil Nadu, India.

P.Pazhanisamy Department of Chemistry, Sir Theagaraya College, Chennai – 600 021, Tamil Nadu. India.

ABSTRACT

In the present study, a series of Poly (N-tert-amylacrylamide –co –acrylamide / Sodium acrylate) gold 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. The amount of N-tert-amylacrylamide (NTA) and Acrylamide (AM) monomers are fixed (50:50) and the amount of Sodium Acrylate (AcNa) ionic monomer was varied from 0.1g to 0.5g. The swelling ehaviour of Nanocomposite Hydrogels studied by Gravimetric method and degree of swelling was increased by increasing the amount of Sodium acrylate. The surface morphology was studied by SEM analysis and it indicates the formation spherical shaped gold nanoparticle in the polymer matrix.

KEYWORDS Hydrogels, N-tert-amylacrylamide, Acrylamide, Sodium acrylate.

1. Introduction

Hydrogels represent polymeric networks capable of absorbing large quantities of water, but remain insoluble due to chemical or physical crosslink between individual polymeric chains [1-4]. Recently, there is a great deal of interest concerning the production of nanoparticles in the hydrogel networks since they have enormous valuable applications in bio-related fields [5-9]. Indeed the design and development of nanoparticles and nanostructural materials have opened a new era for constructing well designed nanostructures that have been considered as a novel class of materials for catalytic, optical, electronic and biomedical application.

Polymer nanocomposite containing metal nanoparticles can be prepared by several methods. Methods used for preparation comprise mechanical mixing of a polymer with metal nanoparticles[10-12], the in situ polymerisation of a monomer in the presence of metal nanoparticles and the in situ reduction of metal salts or in a polymer [13-15]

In this work, we have synthesized gold nanocomposite hydrogel by in situ polymerisation of N-tert-amylacrylamide, Acrylamide and Sodium acrylate (AcNa) using ammonium persulphate as free radical initiator and N,N' – methylenebisacrylamide (MBA) as cross linker. Swelling behavior and swelling kinetics of the obtained hydrogels were evaluated. Distribution of gold nanoparticles within the polymer matrix was studied through their characterization using SEM analysis.

2. Experimental

Materials

Acrylamide (AM, Merck) was recrystallized from acetone/ethanol mixture. Ammonium persulphate (APS), Acrylic acid and Sodium hydroxide were supplied from Aldrich. The crosslinker N,N'-methylene-bis-acrylamide(MBA) was used as received.

Acrylonitrile

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over andhydrous CaCl2. The acrylonitrile was then distilled in an atmosphere of Nitrogen at reduced pressure. It was then collected in a clean dry amber colour bottle and kept in the refrigerator at 5°C.

Preparation of N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene.

Preparation of sodium acrylate (AcNa)

Sodium acrylate was prepared by neutralizing the acrylic acid using Sodium hydroxide

Preparation of Gold Nanoparticles(GNP)

1.0mM of $HAuCl_4$ was added to 1% solution of trisodium citrate dehydrate and heated. The gold sol gradually forms as the citrate reduces the gold (III). Remove from heat when the solution has turned deep red colour [6].

Preparation of Gold Nanocomposite Hyrogels - Poly (N-tert-amylacrylamide - co - Acrylamide / Sodium acrylate) Gold Nanocomposite Hydrogels

The hydrogel were prepared by free radical copolymerisation of NTA, AM and Ac Na in the presence of MBA as crosslinker and APS for initiating the polymerisation system. Aqueous solution containing a weighed amount of NTA, AM, MBA, APS and certain amounts of AcNa (0.00, 0.10, 0.30, 0.50g) were dissolved in methanol – water (3:1) mixture and final volume was made 10mLin a polymerization tube. A solution containing 10mg of gold nanoparticle was added with constant stirring. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60^0C and the polymerization was conducted for 1 day. The prepared hydrogels were air-dried followed by vacuum drying.

Characterization

FTIR Spectral Analysis

FTIR Spectral Analysis of the monomer N-tert-amylacrylamide (NTA) and the Gold Nanocomposite hydrogels were recorded using Schimadzu

Swelling and Diffusion

The swelling behaviour of dried hydrogels were carried out by immersion in doubly distilled water at 25 ± 0.1 °C in a water bath. The water absorbed was determined by weighing the samples, after wiping, at various time intervals. Swollen gels weighed by an electronic balance.

Scanning Electron microscope (SEM)
Images for the Gold Nanoparticle and Gold Nanocomposite hydrogels were recorded using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. SEM/EDAX was used to study the internal or cross morphology of the nanocomposite hydrogel. Before the measurements, the swollen nanocomposite hydrogel at 22^{0}C was firstly freeze-dried and then fractured and sputter coated with gold.

X-ray Diffraction (XRD)
XRD patterns of Gold nanocomposite hydrogel was measured using Riga-ku DMAX-2000 X-ray diffractometer with the Cu Ka radiation at a scanning rate of 2s-1 in 2 ranging from 10 to 80. The sample for XRD was supported on glass substrates.

3. Results and Discussion
The concept of producing nanoparticles in the networks of hydrogel systems was recognised as an important approach due to its direct applicability in various biomedical applications. That is why, a number of composite systems were evaluated [3].

Preparation of Monomer - N-tert-amylacrylamide
The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene. The white crystals have a M. Pt.91°C (Lit.91-92^{0}C) and the yield was -87%.

^{1}H-NMR(CDCl$_3$),δ(ppm) :
^{1}H-NMR spectra of the monomer N-tert-amylacrylamide are shown in Figure 1. The peaks observed at 0.78 ppm for-CH_3, 1.2ppm for-$(CH_3)_2$, 1.7 ppm for- CH_2, 5.49 ppm for =CH vinyl proton, 6.1 ppm for vinyl =CH_2 proton and 7.2 ppm for NH.

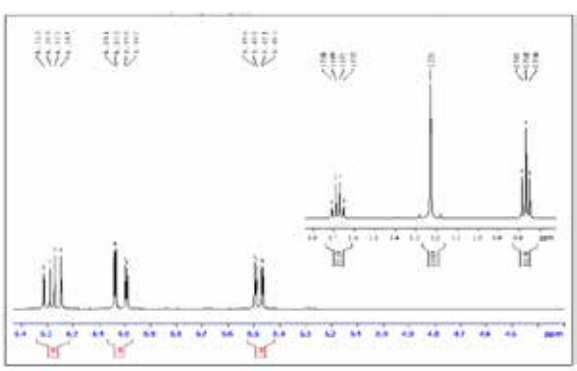


Fig.1. ^{1}H-NMR spectra N-tert-amylacrylamide
^{13}C-NMR(CDCl$_3$), δ(ppm)

13C-NMR spectra of the monomer N-tert-amylacrylamide are shown in Figure 2. The characteristic group peak assignments are : δ 163.90 (CH2 = C (H)-CO-NH..), δ 132.93 (CH2 =C(H)-CO-NH…), δ 123.87(CH2=C (H)-CO-NH..), δ 52.82(-CO-NH-C(CH3)-CH2), δ 31.87(-CO-NH-C(CH3)2-CH2-CH3), δ 26.19(-CO-NH-C(CH3)2-CH2-CH3), δ 8.26(-C(CH3)2-CH2-CH3)

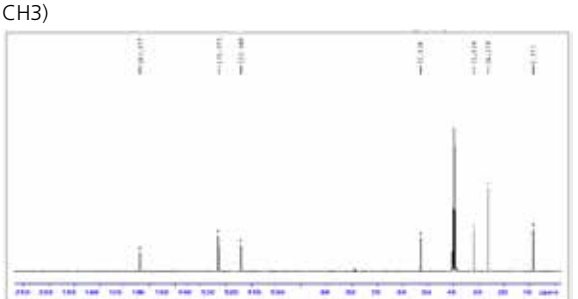


Fig.2. ^{13}C-NMR spectra of N-tert-amylacrylamide

Preparation of Gold nanoparticles (GNP)
To characterize the surface morphology of gold nanoparticle SEM and energy dispersive X-ray (EDAX) were recorded. Figure 3 shows the SEM images and indicates the GNP are spherical in shape. EDAX of gold nanoparticle (Figure 5) was used to evaluate their elemental composition. Energy Dispersive Analysis X-ray confirms GNP in the matrix

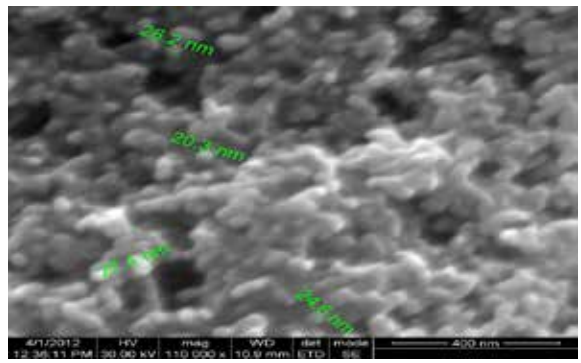
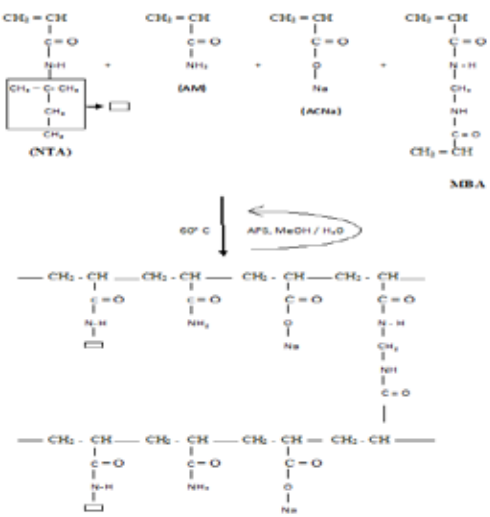


Fig.3 .SEM image Gold nanoparticles

Synthesis of Poly (NTA-co-AM/Ac Na) Gold Nanocomposite Hydrogels
The gold nanocomposite hyrogels were prepared by in situ free radical copolymerisation of NTA, Am and AcNa using APS initiator and MBA cross linker. The aqueous containing gold nanoparticle was added during the polymerisation.



Scheme: Poly (NTA-co-AAm/AcNa) Gold Nanocomposite Hydrogel

Characterization
FTIR Spectra
The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. Figure 4 shows the FT-IR spectra of the gold nanocomposite hydrogel and the spectral values are illustrated in Table 1.

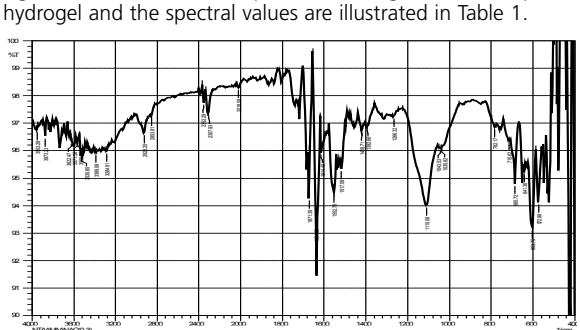


Fig.4. FT-IR Spectra of Gold Nanocomposite Hydrogel

Table: 1. Interpretation of Infrared Spectra of Gold Nanocomposite Hydrogel

3489 cm-1	N-H of NTA as well as NH stretching of AM
3284 cm-1	Vinyl –CH stretching
2923 cm-1	Methyl –CH sym stretching (strong)
1671 & 1735 cm-1	C=O of NTA and Am
1110.08 cm-1	C-O stretching
1631 & 1614.49 cm-1	C=C stretching & conjugation of NTA
1266.32 cm-1	C-C stretching
1517.08 & 782.17 cm-1	-CH2 bending & wagging
1392.66 & 1552.76 cm-1	COO- group of AcNa
1418 cm-1	C-N stretching of amide

Swelling Behavior

Swelling experiments were carried out with a view of evaluation of the swelling capacity of the hydrogels under investigation in distilled water. Results of these experiments indicated that the increase in weight of the swollen hydrogels is directly related to the duration of swelling. The swelling behaviour observed could be associated with absorption mechanism, which, in turn, is determined by the diffusion process.

Swelling measurements

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. The percentage swelling (or mass swelling) is the most important parameter about swelling studies. The percentage swelling (%S) was calculated from the following equation

$$\%\, S = \frac{M_t - M_0}{M_0} \times 100 \quad \text{-------(1)}$$

Where M_t is the mass of the swollen gel at time t, and M_0 is the mass of dry gel at time 0. Figure 5 shows the effect of varying content of AcNa in the presence of gold nanoparticle on the swelling characteristics of the hydrogel.

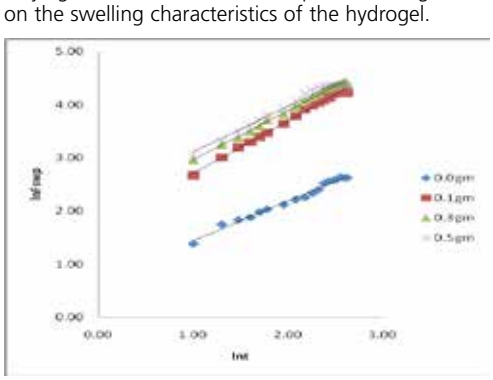


Fig.5. Swelling Behavior of GNP Hydrogels

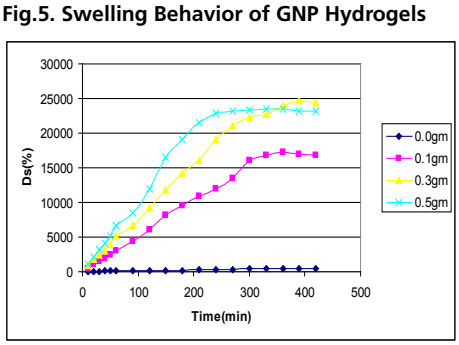


Fig.6. Swelling kinetics curves of GNP hydrogels at Room Temp.

It can be seen that percentage swelling increases with time until a certain point, when it becomes constant. This value of percentage swelling may be named "equilibrium" or "percentage" swelling. The values of equilibrium swelling of NTA-AM/AcNa) Gold Nanocomposite Hydrogels are given in Table 2.

Table.2. Equilibrium swelling of poly(NTA-AM/AcNa) Gold Nanocomposite Hydrogels

AcNa	0.0 g	0.1 g	0.3 g	0.5 g
Equilibrium Swelling	900	17500	24000	23000
EWC	--	0.8795	0.9144	0.9371
'n' (swelling exponent)	0.75	0.84	0.92	0.99

It was also observed that the swellability of the prepared hydrogel increases at higher concentrations of AcNa ratio in the matrix. This is expected since abundance of the hydrophilic groups of AM and AcNa causes an improvement in the swelling characteristics of the hydrogel prepared under these conditions. It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network [16 - 18]

The ionic charge content is important. AcNa contains many ionic units (COO^-). As it can be seen from the Table 2, the swelling increase is due to an increase of the anionic units. If the content of AcNa in copolymer is increased, the equilibrium swelling of Hydrogels also increased.

Equilibrium water content

The water absorbed by AcNA is quantitatively represented by the equilibrium water content (EWC) , where

$$\text{EWC} = \frac{\text{Mt} - \text{Mo}}{Mt} \quad \text{------ (2)}$$

Here M_t is the mass of the swollen gel at time t (equilibrium), and M_o is the mass of the dry gel at time 0. EWC's of all GNP hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in Table 2. All EWC values of hydrogels (0.8795 – 0.9371) were greater than the percent water content values of the body about 0.60 (or 60%). Thus, the GNP hydrogels were exhibit similarity of the fluid contents with those of living tissues. It can be said that GNP hydrogel systems cross linked by MBA can be used as a new material as a biomaterial in medicine, pharmacy, veterinary and other applications such as water absorbency.

Determination of swelling power

When a hydrogel is brought into contact with water, water diffuses into the hydrogel and the hydrogel swells. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger scale segmental motion resulting in an increased distance of separation between hydrogel chains. Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in fields of biomedical, pharmaceutical, environmental and agricultural engineering.

The swelling mechanism of the samples was determined using the following equation

$$F_{swp} = \frac{Mt - Mo}{Mo} = Kt^n \quad \text{---------- (3)}$$

In the above equation, M_t and M_o are the mass of the swollen and dry sample at time t, respectively, K is the swelling constant, and n is the swelling exponent [19 – 20]

For cylindrical shapes, n = 0.45 – 0.50 and corresponds to Fickian diffusion whereas 0.50 < n < 1.0 indicates that diffu-

sion in non-fickian type. This equation is applied to the initial stages of swelling and plots of $\ln F_{swp}$ versus ln t yields straight lines up to almost 60% increase in the mass of hydrogel.

For the hydrogels, in F_{swp} versus ln t plots were drawn using the kinetics of swelling and some representative results are shown in Figure 6. The swelling exponents 'n' were calculated from the slopes of the lines and are listed in Table 2.

In Table 2, it is shown that the values of the diffusion exponent range generally between 0.75 and 0.99. Average of swelling exponents is 0.874. In the experiments, the number to determine type of diffusion (n) was found to be generally over 0.50. Hence the diffusion of water into GNP hydrogel systems had a non-Fickian character. In this diffusion, diffusion and relaxation are said to be isochronal effective[16].

Scanning Electron microscope (SEM)

The Surface Morphology of Gold Nanocomposite hydrogels (Fig 10) were studied by SEM analysis. The image indicates the GNPs are spherical in shape. Gold Nanocomposite hydrogels have the particle size between 28 to 35 nm and distributed uniformly throughout the polymer matrix.

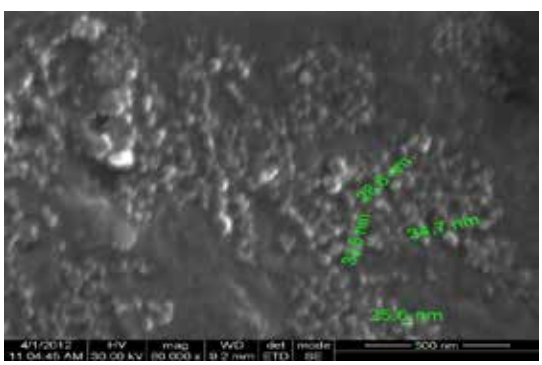


Fig.7. SEM image of GNP Hydrogel

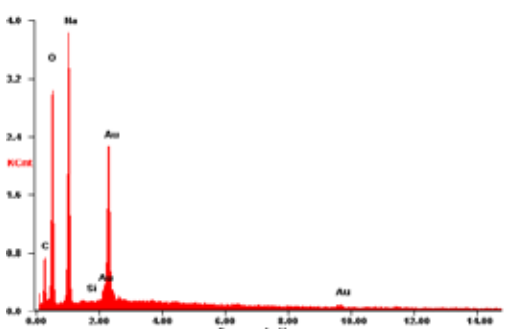


Fig. 8. EDAX spectrum of GNP Hydrogel

SEM/EDAX micro analysis was employed to determine the constitution of the gold nanoparticles dispersed in the hydrogel matrix. The surface/cross sectional micrographs of the gold nanocomposite hydrogel are illustrated in Figure 7and 8. Energy dispersive analysis x-ray confirms the presence of gold nanoparticles in the hydrogel polymer matrix.

The representative EDAX spectrum showing well-resolved peaks for gold, carbon, oxygen and sodium which are the elements present in the gold nanocomposite hydrogel. The observation of silicon in the EDAX spectra is due to the thinness of gold layers

X-ray Diffraction (XRD)

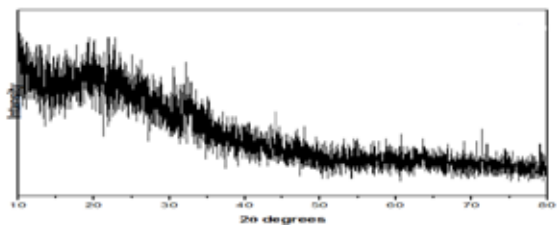


Fig.9. X-ray diffraction pattern of gold nanocomposite hydrogel

X-ray diffraction pattern shows the nanocomposite material is more amorphous and less crystalline in nature

Conclusion

Gold nanocomposites hydrogels with the ability to absorb many hundred times their dry weight of water have received considerable attention. Such materials are widely used as absorbents in medical, chemical, and agricultural applications. The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. Gold Nanoparticles are prepared by reducing Hydrogen tetrachloro aurate using sodium citrate as reducing and capping agent. Surface Morphology was confirmed by SEM analysis. Particle size of the GNPs is between 20 - 27nm. Gold Nanoparticles are Spherical in shape. Poly (N-tert-amylacrylamide - co - Acrylamide / Sodium acrylate) Gold Nanocomposite Hydrogel are prepared by in-situ free radical copolymerization of N-tert-amylacrylamide , AM and Ac Na in the presence of MBA as crosslinker and APS as initiator. The SEM analysis indicates the GNPs are spherical in shape and distributed uniformly throughout the polymer matrix. Particle size of Gold Nanocomposite hydrogels are between 25 – 35 nm .Energy dispersive analysis x-ray (EDAX) Spectrum of all the synthesized hydrogels are showing well-resolved peaks for gold, carbon, nitrogen, oxygen and sodium which are the elements present in the gold nanocomposite hydrogel. X-ray diffraction pattern shows the nanocomposite material is more amorphous and less crystalline in nature. The swelling behaviours such as percentage of swelling, equilibrium swelling and equilibrium water content of Gold nanocomposite hydrogels have been calculated. The swellability of the prepared hydrogel increases at higher concentrations of AcNa in the matrix. Because abundance of the hydrophilic groups of AMand AcNa causes an improvement in the swelling characteristics of the hydrogel prepared. The GNP Hydrogels follow non-Fickian character.

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