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Zincoxidenanocomposite Hydrogels-Synthesis and Characterisation.

KEYWORDS: Nanocomposite Hydrogel, free radical polymerization, antibacterial activity , drug delivery.

R. Krithika	P. Jeyanthi	P. Pazhanisamy
Research and Development Centre, Bharathiar University. Coimbatore, India	Department of Chemistry, Bharathi women's College, Chennai-600 108, India	Department of Chemistry, Sir Theagaraya College,hennai-600021, India

ABSTRACT *In the present study, we synthesized a set of ZincOxidenanocomposite hydrogels by free-radical copolymerization of water /Methanol medium using Azobisbutyronitrile (AIBN) as initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinker. The obtained copolymers Poly (N-tert-amylacrylamide - co - Acrylamide / Sodium acrylate) ZincOxideNanocomposite Hydrogels , Poly (N-tert-butylacrylamide - co - Acrylamide / Sodium acrylate) ZincOxideNanocomposite Hydrogels, Poly (N-Cyclohexylacrylamide - co - Acrylamide / Sodium acrylate) ZincOxideNanocomposite Hydrogels structures were characterized by FTIR . Molecular dispersion and the distribution of zincOxide nanoparticles within the polymer matrix was studied by X-ray crystallography and using SEM analysis. The swelling mechanics of Nanocomposite Hydrogels were also observed by using Gravimetric method. Swelling was investigated in USP phosphate buffer solutions of pH 2.7, 3.5, 4.2, 5.1, 6.8 with constant ionic strength.The swelling behaviour of the hydrogel differs with change in pH of the solution. Drug and protein were loaded into these Nanocomposite hydrogels and the release behaviour were recorded by UV –Vis spectroscopy.The anti-bacterial activity was studied by Well-Diffussionmethod.*

Introduction

Nanotechnology is as a fast growing field with its application in Science and Technology for the objective of developing the materials in nanoscale level. The fabriacation of zinc oxide nanocomposite hydrogels are believed to bebiosafe, and biocompatible and have been used as drug carriers. In recent years, Zinc has acquired a greater attention in the use of antimicrobial agents.

In this work, we have fabricated the ZincOxidenanocomposite hydrogel by free radical copolymerization of N-tert- amylacrylamide, Acrylamide (AM), Sodium Acrylate (Na Ac),N-tert- butylacrylamide, Acrylamide (AM) , Sodium Acrylate (Na Ac) , N-cyclohexylacrylamide, Acrylamide (AM) , Sodium Acrylate (Na Ac),using AIBN as free radical initiator and N,N' – methylenebisacrylamide (MBA) as cross linker. These polymers were characterized by FTIR and studied by SEM analysis and X-ray crystallography. The behaviour ofthe polymers with the loaded drug , protein and the release behaviouralso evaluated and measured using UV – Vis spectroscopy.

Experimental

Preparation of ZincOxideNanocomposite Hydrogels –

Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate),

Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate),

Poly (N-Cyclohexylacrylamide - co – Acrylamide- Sodiumacrylate) ZincOxideNanocomposite Hydrogels.

The Nanocomposite hydrogels were prepared by free radical copolymerization of NTA, AM,NaAc in the presence of MBA as crosslinker and AIBN for initiating the polymerisation system. Aqueous solution containing a weighed amount of NTA, AM,NaAc, MBA, AIBN were dissolved in methanol – water (3:1) mixture . A solution containing 10mg of ZincOxide nanoparticle was added with constant stirring. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 65^{0}C and the polymerization was conducted for 1 day. The prepared hydrogels were air-dried followed by vacuum drying. Similarly – Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate) ZincOxideNanocompositeHydrogels , Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate) ZincOxideNanocomposite Hydrogels.

Characterization by FTIR Spectra

. A broad peak corresponding to NH stretching of acrylamide was observed around 3461cm^{-1} , the peak 1592 cm^{-1} corresponding to C=O 1389, 1123 cm^{-1} correspond to C-N and C-H bonding respectively and there was only new band at 500 cm^{-1} specific for stretching vibration of ZnO group. The Peaks at 1217 and 1389 cm^{-1} are corresponding to [-C(CH3)3] groups of NTB.

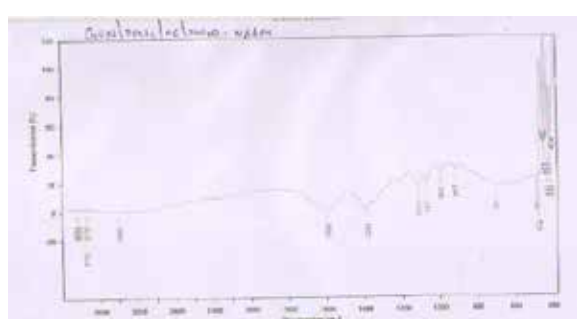

Fig 1.FTIR of Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

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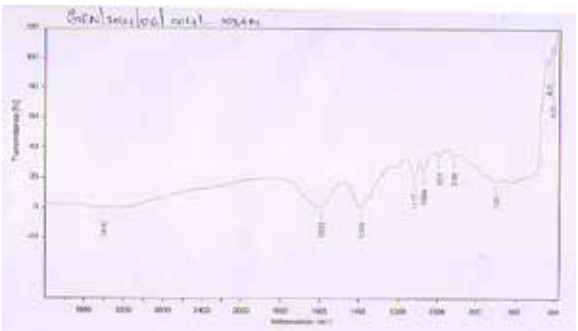


Fig 2.FTIR of Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

Fig 3.FTIR of Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

Scanning Electron microscope (SEM)

Images for the ZincOxide Nanoparticle and ZincOxideNanocomposite hydrogels were recorded using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. The morphology was studied with SEM/EDAX images. The image indicates the ZincOxidenanocomposite hydrogels are spherical in shapeand distributed uniformly throughout the polymer matrix.

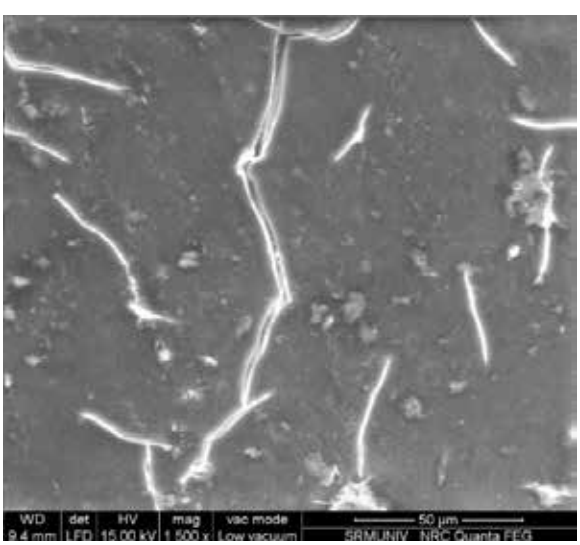


Fig 4.SEM image ofPoly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

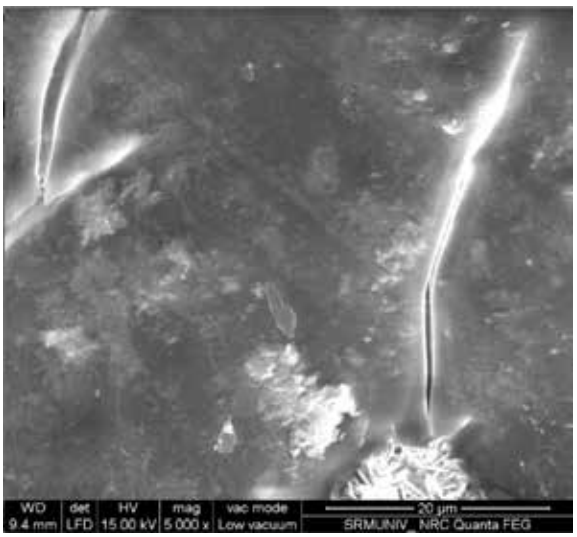


Fig 5. SEM image ofPoly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

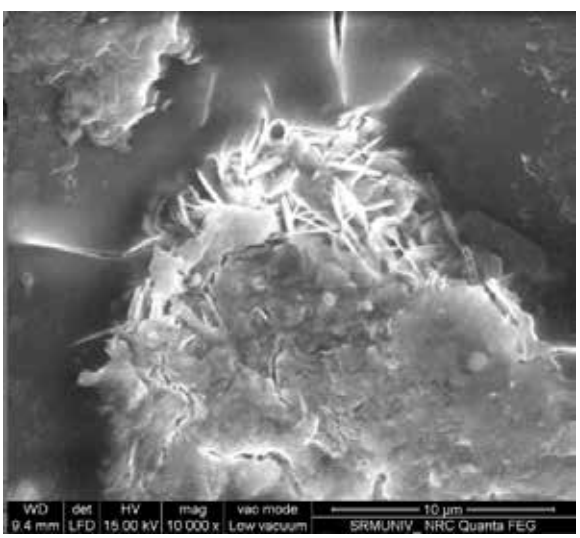
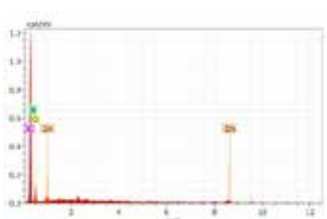


Fig 6.SEM image ofPoly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

EDAX spectrum of ZNP Hydrogel

SEM/EDAX micro analysis was employed to determine the constitution of the ZincOxide nanoparticles dispersed in the hydrogel matrix. The surface/cross sectional micrographs of the ZincOxidenanocomposite hydrogel Energy dispersive analysis X-ray confirms the presence of ZincOxide nanoparticles in the hydrogel polymer matrix. The representative EDAX spectrum showing well-resolved peaks



for Zinc, carbon, oxygen,Nitrogen.

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FIG 7.EDAX imageofPoly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

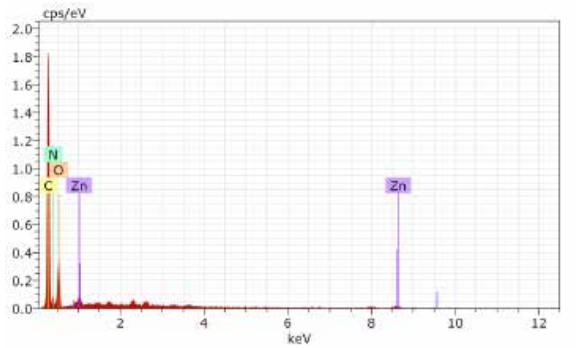

Fig 8.EDAX image ofPoly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

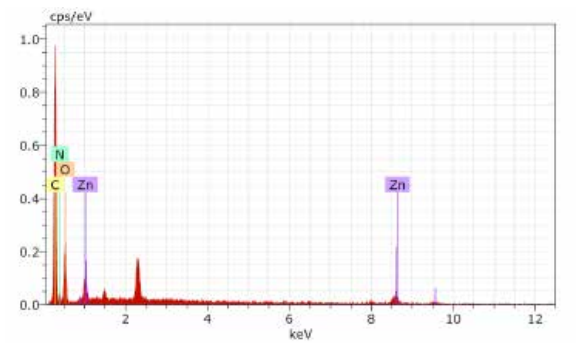

Fig 9 EDAX image ofPoly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

X-ray Diffraction (XRD)

XRD patterns of ZincOxidenanocomposite 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.

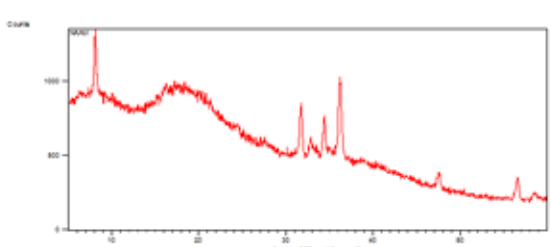

Fig 10. X-ray diffraction pattern of Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate) ZincOxide-Nanocomposite Hydrogel

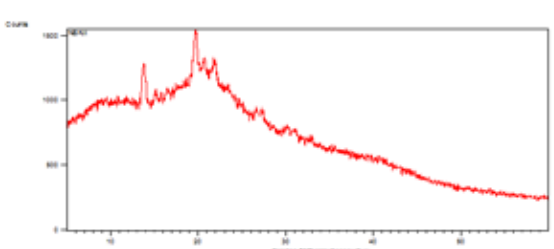

Fig 11. X-ray diffraction pattern Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxideNanocomposite Hydrogel

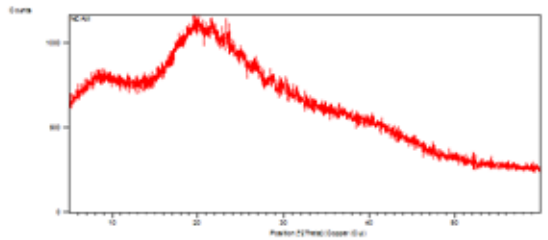

Fig 12.X-ray diffraction pattern of Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate) ZincOxideNanocomposite Hydrogel

Antibacterial Activity and antifungal activity (well diffusion method)

Antibacterial analysis was followed using standard agar well diffusion method to study the antibacterial activity of compounds. Each bacterial and fungal isolate was suspendedin Brain Heart Infusion (BHI) broth and diluted to approximately 105 colony forming unit (CFU) per mL. 5mm diameter wells were cut from the agar using a sterile cork-borer and 30 µL (5µg compound in 500 µL DMSO) of the sample solution were poured into the wells. The plates were incubated for 18 h at 37°C for bacteria and at room temperature for fungi. Antimicrobial activity was evaluated by measuring the zone of inhibition in mm against the test microorganisms. DMSO was used as solvent control.

Swelling measurements

The swelling measurement is the most important factor in the swelling studies. The percentage swelling (%S) was calculated using the following equation

$$\%S = (M_t - M_0)/M_0 \qquad \text{-------(1)}$$

Where M_t is the mass of the swollen gel at time t

M_0 is the mass of dry gel at time 0.

Swelling behavior of ZincOxidenanocomposite hydrogels in different pH

Dynamic and equilibrium swelling coefficients of ZincOxidenanocompositehydrogels were determined in different buffer solutions of pH 2.7,3.5,4.2,5.1,6.8 with ionic strength was constant. The hydrogels were soaked in different pH solutions for 8 hours. For dynamic swelling, swollen gels were dried and weighed at regular intervals of time.

Swelling behavior of Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels in different pH

Table1.

pH	2.7	3.5	4.2	5.1	6.8
DSC-NAAM	0.50	0.73	0.80	0.10	2.35
NBAM	1.85	2.75	3.10	5.83	7.4
NCAM	1.91	2.33	2.64	3.71	4.5
ESC-NAAM	0.33	0.40	0.44	0.50	0.70

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NBAM	.64	.73	.75	.85	.88
NCAM	.65	.70	.72	.78	.81

DSC-Dyanamic swelling Coefficient , ESC-Equlibrium swelling coefficient,

NAAM- Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NBAM- Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NCAM-Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

Loading and Release behavior of Drug in ZincOxide-Nanocomposite Hydrogels

50ml of 100 ppm (drug) Chloramphenicol solution was used for loading the Nanocomposite hydrogels. Dried nanocomposite hydrogels were soaked in drug solution for complete one day without exposing to direct sunlight.The swellablityofnanocomposite hydrogels were studied with the absorbance of UV-Vis spectrometer during different time intervals. Dried Hydrogelswere immersed in phosphate buffer having pH 4.2.Drug(Chloramphenicol)release was studied with the measured absorbance through different time intervals using UV-Vis spectrometer.

Table 2

SAMPLES	UV absorbance of drug loaded samples	UV absorbance of drug released samples
NAAM	0.094	0.252
NBAM	0.331	0.665
NCAM	0.112	0.317

Absorbance of loaded drug solution =1.511

NAAM- Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NBAM- Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NCAM-Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

Fig 13. Drug Loading and Release of ZincOxidenanocomposite hydrogel

Loading and Release behavior of Protein in ZincOxide-Nanocomposite Hydrogels

50ml of 100 ppm (BSA) Bovine –Serum-Albumin solution was used for loading the Nanocomposite hydrogels. The dried gels were soaked in Protein solution for a day and it was maintained away from direct sunlight .The swelling behavior was obtained by recording the absorbance using UV-Visible spectroscopy through different time intervals. Then it was dried and added to required amount of phosphate buffer of pH 4.2 and stored. The release behaviour of the hydrogels were also studied by UV-Visible spectroscopy absorbance at different time intervals.

Table 3

SAMPLES	UV absorbance of Protein loaded samples	UV absorbance of Protein released samples
NAAM	0.167	0.392
NBAM	0.390	1.320
NCAM	0.179	1.307

Absorbance of loaded Protein solution =1.842

NAAM- Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NBAM- Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

NCAM-Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels

Fig 14. Protein Loading and Release of ZincOxidenanocomposite hydrogel

Antibacterial Studies:

The antibacterial activity was studied by Well-diffussion method.Hydrogels were tested against gram positive , gram negative and fungi at various concentarations.

Table 4

Sample	Zone of inhibition (mm)	
	200mL	100mL
NCAM	14.5	10.5
NBAM	13.5	10
NAAM	1.55	0
Sample number	Zone of inhibiton (mm) Fungal(Aspergillusniger)	
	50mL	
NAAM	9	

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Fig 15.Images of antibacterial and antifungal activity.

Conclusion

ZincOxidenanocomposites hydrogels have broad spectrum of applications as absorbents in medical, chemical, and agricultural applications. X-ray diffraction studies indicatesZincOxidenanocomposite hydrogels are micro-crystalline in nature.Swelling behaviour increases with the increase in pH of the solution. The diffusion of ZincOxidenanocomposite hydrogels systems has non-Fickian character. The drug loading is effectively observed in Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels and protein loading is observed in both Poly (N-tert-butylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogels and Poly (N-Cyclohexylacrylamide - co – Acrylamide-Sodiumacrylate) ZincOxidenanocomposite hydrogels.These hydrogels are biologically active and it shows antibacterial activity effectively and the antifungal activity has been observed only in Poly (N-tert-amylacrylamide - co – Acrylamide-Sodiumacrylate)ZincOxidenanocomposite hydrogel in addition to antibacterial activity.

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