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Research Article

POLYACRYLAMIDE BASED HYDROGELS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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ABSTRACT

Hydrogels are polymeric networks those imbibe large quantity of water without dissolving themselves. Hydrogels contain water solubility groups such as –OH, -COOH, -NH2, -CONH2, and-SO3H. Polyacrylamide hydrogel is widely used in ophthalmic operations, drug treatment, food packaging products, and water purification.This review describes the various methods of synthesis of polyacrylamide based hydrogel; characterization of polyacrylamide based hydrogel by D.S.C ,S.E.M, I.R; various properties of polyacrylamide based hydrogels like swelling, mechanical, rheological; and various application of polyacrylamide based hydrogel in drug delivery, heavy metal removal, medical fields and agricultural fields.

Keywords: Polyacrylamide, Water absorbent.

1. INTRODUCTION

Hydrogels are water-swellable, three-dimensional polymeric networks. The capacity of hydrogels to absorb water is enormous and can be as much as 1000 times the mass of polymer (Huglin and Zakaria (1986); Peppas and Mikos (1986); Given and Sen (1991); Kulicke and Noltelman (1989). Hydrogels find application in food industry (as thickening agents, etc.), in pharmaceuticals (as controlled release preparations etc.), agriculture and related fields (in controlled release of moisture, fertilizers, pesticides, etc.), technical and electronic instruments (as a protector from corrosion, and short circuits, etc.), biomedicine (as artificial organs etc.), bioengineering (in biomolecular immobilization), veterinary medicine, photographic technology and as an adsorbent for removal of some unwanted agent in environmental application(Kulicke and Noltelman (1989); Roorda et al., (1986); Kost and Langer (1987).

1.1 Polyacrylamide based Hydrogel

Acrylamide based hydrogel are the most common hydrogel. These hydrogel undergo large volume transition on swelling but they lack hydrolytic stability. Their hydrolytic stability can be increased if substituted acrylamides have alkyl or hydroxy alkyl groups (Ghanshyam et al., (2000).. Polyacrylamide hydrogel is an atoxic, stable, nonresorbable sterile watery gel consisting of approximately 2.5% cross-linked polyacrylamide and nonpyrogenic water. Polyacrylamide hydrogel is widely used in ophthalmic operations, drug treatment, food packaging products, and water purification

2. Various methods of synthesis of polyacrylamide based hydrogels

2.1 Overview

Polyacrylamide is synthetic polymer derived from acrylamide monomer. Polyacrylamide is crosslinked polymer of acrylamide. In the cross-linked form, it is highly water-absorbent, forming a soft gel. Generally, polyacrylamide hydrogels results from polymerization of acrylamide with a suitable bifunctional Crosslinking agent, most commonly, N,N′-methylenebisacrylamide (bisacrylamide).

2.2 Structural features and chemistry of Polyacrylamide

Polyacrylamide (IUPAC poly (2-propenamide) or poly (1-carbamoylethylene) is a polymer (-$CH_2CHCONH_2$-) formed from acrylamide subunits that can also be readily cross-linked.

Polyacrylamide is a cross-linked polymer of acrylamide. In the cross-linked form, it is highly water-absorbent, forming a soft gel used in such applications as polyacrylamide gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent. (Note .1)

2.3 Synthesis of Polyacrylamide based Hydrogel

2.3.1 Radiation Method

A radiation technique is a widely used technique for preparation of hydrogels because a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material (Rosiak et al., (1983). Radiation technique offers unique advantages for preparing polymer and hydrogels from vinyl monomer without the addition of any chemical substances (Rosiak et al., (1988).

Dilek et al., (2002) prepared Acrylamide (AAm)/acrylic acid (AAc) hydrogels in the cylindirical by γ-irradiating binary systems of AAm/AAc with 2.6-20.0 kGy γ-rays.

. Alam et al., (2004) described that hydrogels have been synthesized from 10%, 20%, 30%, 40%, 50% and 60% aqueous solutions of acrylamide monomer by gamma radiation employing doses in the range of 0.2-30 kGy from a Co-60 source

Tuncer et al., (2007) prepared macroporous poly (acrylamide) [poly (AAm)] hydrogels by using poly (ethylene glycol) (PEG) with three different molecular weight as the pore-forming agent during the radiation induced polymerization reaction..

2.3.2 Crosslinking Method

synthetic polymers for the preparation of crosslinked structures is polyacrylamide (PAAm) (Thomas WM., (1964). Highly cross-linked polymers are generally chemically prepared from their monomers or polymers in the presence of cross-linking agents.(Note 2)

Marcos et al., (2005) prepared novel superabsorbent hydrogels were manufactured using chemically modified cashew gum (CGMA) and acrylamide (AAm) as reactants. Zolfaghari et al., (2006) prepared nanocomposite type of hydrogels (NC gels) by crosslinking the polyacrylamide/montmorillonite (Na-MMT) clay aqueous solutions with chromium (III).

Camelia et al., (2007) synthesized a polyacrylamide-based hydrogels by simultaneous polymerization/crosslinking method.

2.3.3 Free radical Polymerization Method

Hydrogels are usually prepared by freeradical copolymerization of acrylamide (AAm)-based monomers with a chemical cross-linker such as N,N -methylenebis (acrylamide) (BAAm) in an aqueous solution (Oguz and Wilhelm, (2007).

Bajpayi and Dubey, (2004), developed a pH sensitive terepolymeric hydrogel system based on acrylamide, methacrylamide, and acrylic acid by free radical polymerization.

3.1 Fourier transform-Infrared Spectroscopy (FT-I.R) of Polyacrylamide based Hydrogel

In view of the increasing importance, the structure and conformation of polyacrylamide (PAAm) based hydrogels have received considerable attention in thel last two decades; Vibrational spectroscopy is potentially useful tool for structural analysis and deriving conformational variations for polyacrylamide (PAAm) based hydrogelsThe FTIR spectra of PAAm hydrogel (Figure 8), shows significantly lesser amount of hydroxyl groups as compared to hydrolyzed PAAm, and the amide band has also shifted in the lower side possibly due to hydrogen bonding. The bands at 3080 and 2975cm^{-1} corresponding to =CH2 and =CH- disappear.(Note.3)

3.2 Thermal studies of Polyacrylamide based hydrogel

Differential scanning calorimeter (DSC) is an effective tool for studying the cure kinetics and it also helps in establishing cure mechanism (Kudela et al., (1985 . In the initial phase of cross-linking reaction and at lower temperature rapid hydrolysis occurred which was endothermic in nature, but at higher temperature curing reaction was favoured. Isothermal cure kinetics revealed that curing reaction was n ' 'order type and followed third order kinetics. The study also indicates that with the degree of conversion 0 .25-0.26. both curing and hydrolysis occurs simultaneously but at higher conversions curing reaction proceedes alone. (Singhal et al., (2002).(Note. 4)

3.3 Morphological studies of Polyacrylamide based hydrogel by Scanning Electron Microscopy (S.E.M)

.Tuncer et al., (2007) prepared macroporous poly (acrylamide) [poly (AAm)] hydrogels by using poly (ethylene glycol) (PEG) with three different molecular weight as the pore-forming agent during the radiation induced polymerization reaction. n. The cross-sectional SEM micropictures of the freeze dried traditional and PEG-modified hydrogels are exhibited in Fig.. (Note.5)

Scanning electron microscopy experiments, together with swelling ratio studies, reveal that the PEG-modified hydrogels are characterized by an open structure with more pores and higher swelling ratio, but lower mechanical strength, compared the conventional hydrogel (Tuncer et al., (2006). Figure . Shows the SEM photos of the surface structure of the conventional and PEG modified hydrogels. (Note.6)

3.4 Fluorescence Monitoring of Polyacrylamide based Hydrogel

Among the various types of hydrogels polyacrylamide (PAAm) gel is most suitable for optical studies because it remains optically transparent for a wide range of concentrations of the monomer and the cross-linker. While in such a gel most of the molecules move freely and hence a fluorescent probe molecule experiences a solution-like environment, movement of a minute fraction of the probe molecules is markedly restricted (Dickson, et al., (1996**)**. (Note.7)

.. Figure 13 depicts the absorption spectrum of 4-AP in 5% PAA gel. It is readily seen that the absorption spectrum is remarkably similar to that of 4-AP in water20 with the characteristic peaks at around 255, 302, and 362nm except for the slight blue shift by 8nmingel compared to water.

4. Properties of polyacrylamide based hydrogel

4.1 Swelling Properties

The most important property of hydrogels based on acrylamide is its ability to imbibe water while elasticity of stretched network opposes osmotic swelling. Swelling of hydrogel can be expressed in weight, volume and length units and weight fraction of water (Wf) in a hydrogel is given as:

$$Wf = \frac{(\text{Weight of wet hydrogel} - \text{Weight of dry hydrogel})}{\text{Weight of Wet hydrogel}}$$

$$Dsw = \frac{(\text{Weight of wet hydrogel})}{(\text{Weight of dry hydrogel})}$$

For practical purposes, volume swelling unit is swelling ratio (Rsw) defined as:

$$Rsw = Dsw \times \frac{d0}{dsw} \times \frac{\text{Volume of wet hydrogel}}{\text{Volume of wet hydrogel}}$$

Where d0 and dsw are densities of dry gel and swollen gels, respectively.

Eylem and Tuncer, (2007) synthesized poly(acrylamide-co-acrylic acid) [P(AAm-co-AAc)] hydrogels by free-radical crosslinking copolymerization of acrylamide (AAm) monomer at fixed amount.

4.2 Mechanical Properties

Valles et al., (2003) investigated the equilibrium swelling and the plateau elastic modulus of a family of hydrogels made by the polymerization of acrylamide with itaconic acid or method.

Lin et al., (2004) studied the mechanical properties of a polyacrylamide gel with reversible DNA crosslink's.

4.3 Rheological Properties

Shevchenko et al., (2003) studied the rheological properties of hydrogels of polyacrylamide-based polyelectrolytes ..

Kundu et al., (2008) described a cavitation rheology technique to characterize the network mechanics of polyacrylamide hydrogel materials, a common material used in many biological applications

4.4 Equilibrium Properties

Equilibrium properties of polyacrylamide hydrogels are studied a function of volume change transition by water absorption or desorption. It was observed that under certain condition hydrogel undergo a discontinuous volume phase transition (Tanaka et al., (1981). Henmei and Haruma, (2007) studied the forming process and characteristics of monodispersed hydrogel microspheres of poly(acrylamide–methacrylic acid) with sharp pH–volume transition.

5. Application of polyacrylamide based hydrogel

5.1 Drug delivery

Controlled drug delivery is gaining importance over the conventional methods of drug administration because of its inherent benefits. Self-regulated release from the delivery vehicle may enhance drug potency with a sustained action. Makarand et al., (2000) describes a novel hydrogel blend of polyacrylamide with chitosan for controlled delivery of antibiotics**.** Anionic hydrogels are used in the design of intelligent controlled release devices for site-specific drug delivery of therapeutic proteins to the large intestine.(Satish et al., 2006)

Rosangela et al., (2008) reported that the blends formed by electrochemical polymerization of polypyrrole (PPy) into polyacrylamide (PAAm)

hydrogels were used as devices for controlled drug release.

5.2 Heavy Metal Removal

Hydrogels of two important biopolymers (dextrin and starch) with different acrylamide monomers viz., acrylamide, N-isopropyl acrylamide and 2-acrylamido-2-methylpropanesulfonic acid and crosslinked with N,N-methylene bisacrylamide were used as sorbents for three transition metal ions. Effect of functionalization of hydrogels by partial hydrolysis with 0.5 M NaOH on metal ion uptake has also been studied, and it results in appreciable uptake of Cu^{2+} ions and Fe^{2+} ions but in total rejection of Cr^{6+} ions These results are of interest for the development of hydrogel-based technologies for water purification and metal ions separation and enrichment (Chauhan et al., (2006).

5.3 Medical Fields

A hydrogel for use as a prosthetic device for supplementing, augmenting or replacing cartilage in the intra-articular cavity of a joint and for treatment or prevention of arthritis. The hydrogel may be a polyacrylamide hydrogel obtained by combining acrylamide and methylene bis-acrylamide (Petersen, Jens. (2007).

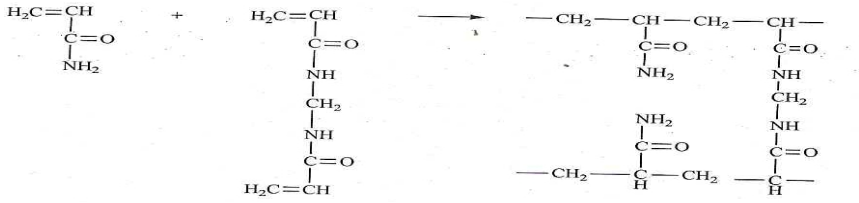
Jens Petersen., (2007) described a bio-stable hydrogel for use in the treatment and prevention of incontinence and vesicouretal reflux.

6. CONCLUSION

Polyacrylamide based hydrogel are the most common hydrogel. Polyacrylamide hydrogel is an atoxic, stable, nonresorbable sterile watery gel consisting of approximately 2.5% cross-linked polyacrylamide and nonpyrogenic water. From this review it is concluded. Among the various method used for synthesis of acrylamide based hydrogel the radiation method has advantages over others, especially with respect to a clean environment and higher production rate It is also concluded from this review that Hydrogels based on Polyacrylamide are widely used hydrogels which have variety of applications in drug delivery devices artificial muscles, seperation of chemical system, sensors, artificial corneas, eye capillary drains, plastic surgery an biomaterials. Hydrogels based polyacrylamide played an important role in environmental management. Hydrogels based on polyacrylamide has widely used for removal of heavy metal ions from water system and protect the environment from harmful effect caused by heavy metal. Hydrogels based on polacrylamide have wide potential for used as superadsorbent, sanitary materials as specific sorbents separation and enrichment technologies. Graft copolymer of hydroxyethylcellulose and hydroxypropylcellulose with AAm have been reported as strong flocculants against effluents of tannery, electroplating, spinning mils and brewries. Graft copolymers of starch and cellulosics like carboxymethylcellulose with AAm are efficient flocculants and these combine both efficiency of AAm and shear stability of polyaccharides.

Finally it is concluded that hydrogels based on Polyacrylamide is very useful hydrogel which have variety of application in drug delivery, heavy metal removal, medical fields, agricultural fields and industrial fields.

(Example of note 1)



, N'-methylenebisacrylamide Representative segment of cross-linked polyacrylamide

Fig . Polymerization of acrylamide

(Example of note 2)

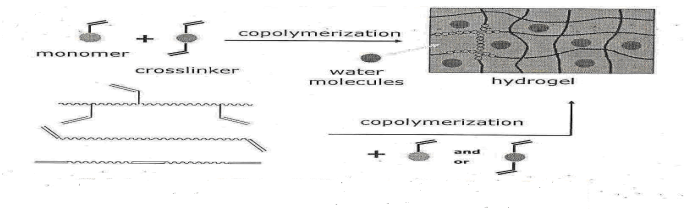


Fig. Hydrogels by Crosslinking Method

(Example of note 3)

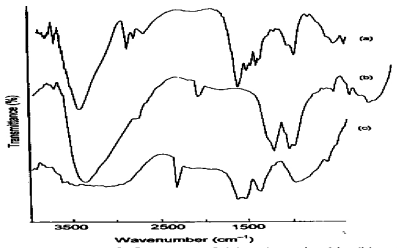


Fig. FT-IR Spectrum of (a) polyacrylamide (b) polyacrylamide hydrogel and (c) hydrolyzed polyacrylamide

(Example of note 4)

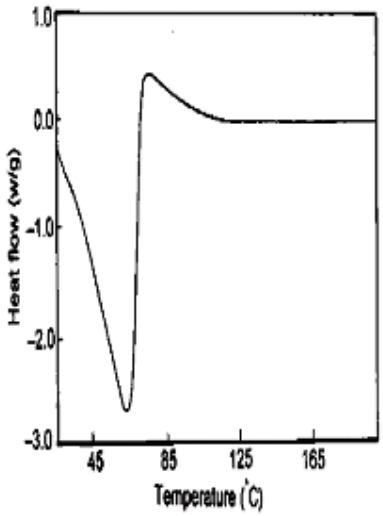


Fig. Dynamic D.S.C scan of freshly preparation of Polyacrylamide hydrogel

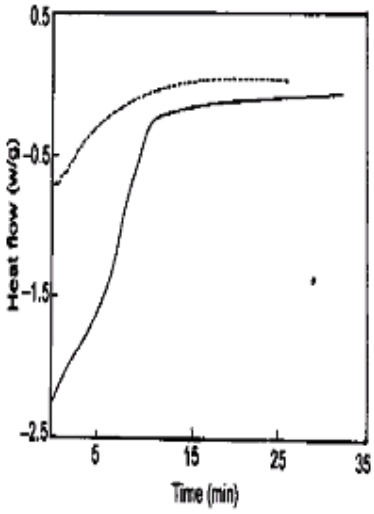


Fig. Isothermal D.S.C scan of freshly mixed reaction mixture for preparation of Polyacrylamide hydrogel

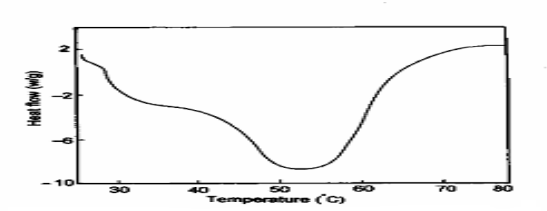


Fig. Dynamic D.S.C scan of freshly reaction for preparation of hydrolyzed Polyacrylamide

(Example of note 5)

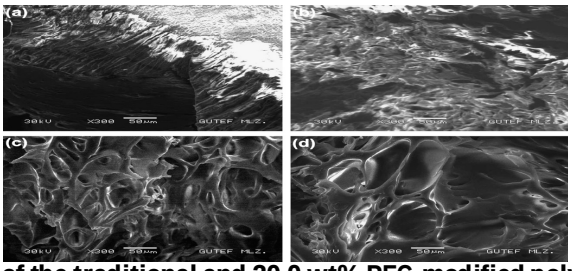


Fig. SEM micrographs of the traditional and 20.0 wt% PEG-modified poly(AAm) hydrogels: (a) poly(AAm), (b) PEG-4000 modified poly(AAm), (c) PEG-6000 modified poly(AAm) and (c) PEG-10000 modified poly(AAm)

(Example of note 6)

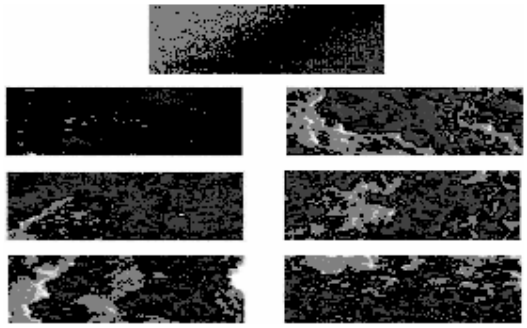


Fig. SEM micrographs of the conventional and PEG-modified PAAm hydrogels. (a) the conventional PAAm hydrogel, (b) 4.8 wt% PEG-4000-modified PAAm, (c) 20.0 wt% PEG-4000-modi-fied PAAm, (d) 4.8 wt% PEG-6000-modified PAAm, (e) 20.0 wt% PEG-6000-modified PAAm, (f)4.8 wt% PEG-10 000-modified PAAm, (g) 20.0 wt% PEG-modified PAAm

(Example of note 7)

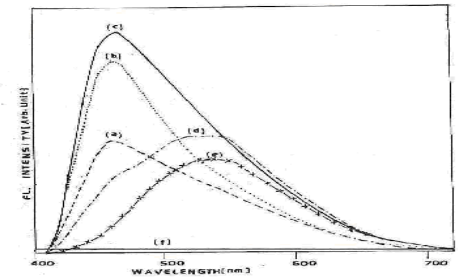


Fig. Emission spectra of 8×10^{-5} 4-aminopthalamide in 5% polyacrylamide gel excited at (a) 300nm ( ). (b) 325 nm(...). (c) 350 nm (-) (d) 375 nm (- · -) and (e) 400 nm (*) and (f) emission spectrum of the reference gel excited at 300 nm (-)

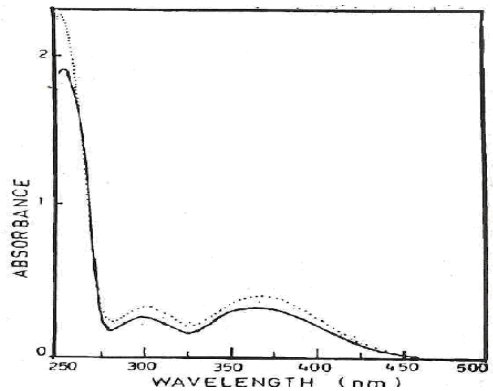


Fig . Absorption spectra of 8×10^{-5} 4-aminopthalamide in (a) water (...) and (b) 5% polyacrylamide gel (-)

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