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PREPARATION OF HYDROGELS BASED ON PVA-ACRYLIC ACID USING N,N-METHYLENEBISACRYLAMIDE AS CROSSLINKING AGENT

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A transparent hydrogel based on PVA-acrylic acid using N,N-methylenebisacrylamide as crosslinking agent was prepared. Effects of deionised water, distilled water, tap water, aqueous solution of NaCl and NaOH were examined. Degree of swelling was maximum in deionized water, in aqueous NaCl it became minimum whereas it increased in alkaline medium. Increment in degree of swelling was due to the formation of carboxyl anions ($-COO^-$) in the polymer network leading to the development of strong electrostatic forces. Dry hydrogel was white polymeric material insoluble in most of the organic solvents. Decomposition started after 170°C. The refractive index of hydrogel was 1.332-1.345.

Key words: Transparent hydrogel, Degree of swelling, Crosslink density

Introduction

Hydrogels are becoming familiar day by day due to their mechanical and biomedical characteristics. Survey of literature provides many references about the synthesis and uses of hydrogels (Wichterle and Lim 1960; Gregonis *et al* 1978; Huglin *et al* 1982; Lee 1983; Khan and Amin 1988; Andreopoules 1989). They have been successfully prepared from polyvinyl alcohol (PVA), methacrylic acid, hydroxyethyl methacrylate and acrylamide. Hydrogels prepared from PVA are very important because of their low toxicity, good biocompatibility, rubbery or elastic nature and high degree of swelling in water. Amongst the network characteristics of the hydrogels, crosslink density is the main factor to maintain its behaviour. The crosslink density of hydrogel may be modified by the concentration as well as structure of crosslinking agent (Peppas and Merrile 1977; Peppas and Merrile 1977; Hyon *et al* 1989; Urushizaki *et al* 1990).

This paper deals with the preparation of PVA-acrylic acid based hydrogels. The main aim of this work is to study swelling properties in deionized water, distilled water, tap water and aqueous sodium chloride. The influence of alkali and crosslinking agent on degree of swelling is also undertaken.

Material and Methods

Acrylic acid (E.Merck) was distilled and fraction boiling at 141°C was collected. Pollyvinyl alcohol (GH-17, Gohsenol product) N,N-methylenebisacrylamide (E.Merck), sorbitan monostearate (Span-60) of Fluka were used without further purification. Cyclohexane and other organic solvents were distilled before use.

Preparation of hydrogel. Hydrogel was prepared by the reverse phase suspension polymerization technique in a five necked Quickfit flask fitted with a stirrer, thermometer, condenser, two inlets fitted with two way adapter. Required quantity of cyclohexane was added in the reaction flask already containing Span-60. The temperature of reaction flask was maintained at 68-70°C. Stirring was started to dissolve Span-60 and then acrylic acid, PVA (10% solution in water) N,N-methylenebisacrylamide (MBAM) and ammonium persulfate in required quantities were added simultaneously in steps within half an hour. After about 20 min gel formation started and at the end of the reaction (after 2 h.) cyclohexane/H_20 were distilled off. The gel was removed from the flask and washed with distilled water to remove any unreacted material or short chain fragments to make it neutral. The neutral stage was checked using pH paper. The swollen gel was left to dry to constant weight at 60°C in an oven and then kept in dessicator under vacuum throughout the studies.

I R spectrum of the dried gel was recorded to identify the attachment of PVA, acrylic acid, MBAM from the appearance of characteristic absorption bands which were not present in the spectra of PVA, acrylic acid and MBAM.

Swelling of dried gel was followed by immersing in deionized water, distilled water, tap water and aqueous solution of sodium chloride at room temperature for 24 h.

Results and Discussion

Tables 1-4 include the data regarding the preparation of hydrogels based on PVA-acrylic acid.

Hydrogels were characterised by yield, solubility and I R spectral studies. The polymeric material obtained in the

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absence of PVA was 99% (12.0g) whereas in the presence of different quantity of PVA, the yield varied from 80 to 96% (10.1-12.1g). It showed that acrylic acid, PVA, MBAM and Span 60 participated in the reaction resulting in the formation of a polymeric material called gel. The dry gel (Polymeric material) was insoluble in water and in most of the organic solvents like alcohol, DMF, DMSO, THF, toluene, acetone, ethyl acetate, cyclohexane, ether, ethyl acetate, cyclohexane, ether, dioxane, methylene chloride, CCI_4 etc. On the other hand PVA and polyacrylic acid were soluble in water. The product obtained in the absence of MBAM was also soluble in water. These results indicated that MBAM crosslink growing polymer chains of acrylic acid and PVA resulted in the product whose insolubility was enhanced in their solvents. Due to crosslinking effect a transparent hydrogel was obtained which on drying remained a transparent white polymeric material. These results supported the cause of variation in the yield. For further identification, IR spectral studies were also undertaken. The I R spectra of the product samples also provided evidences to support above results. In fact, the spectra of the polymer were simpler than monomer itself. This was due to the fact that the degree of freedom of vibration was restricted in the polymer. However, the general pattern of the spectra of polymer and monomers remained the same. As a rule the spectra of resultįng product (dry gel) should show the addition of commutative behaviour of acrylic acid, PVA and N,N`-methyl- enebisacrylamide. In the I R spectra of the product (Sample no.2) the absorption resulting from vibrations which typical of the following groups were observed: O-H stretching frequency 3400 cm^{-1}, C-O frequency of the C-OH group as PVA a secondary alcohol, 1100 cm^{-1}, C-O stretching 1715 cm^{-1}. An absorption at 2260 cm^{-1} was also observed showing the presence of nitrogen in the product.

Keeping the concentration of acrylic acid, Span-60, crosslinker and initiator constant, the polymeric gel as prepared at differnt concentrations of PVA in the absence and presence of sodium hydroxide. The results illustrated in Tables 1-3. In Fig 1, yield (g) was plotted against feeded PVA (%). It show that in the absence and presence of alkali the rate of formation of polymeric gel increased with increasing concentration of PVA but it droped when the concentration reached to 15%. In the presence of 2.5-10% PVA, yield ranged 10.8-12.1g whereas on addition of 15-40% PVA yield droped to 11.8-10.1g though not on higher side. On the other hand in the presence of alkali the rate of formation of polymeric gel enhanced. It increased with increasing concentration of NaOH as indicated from the results shown in Tables 2-3. When 3.3g NaOH was added at 2.5-10% PVA yield ranged 12.2-14.4g whereas 15-40% PVA gave 13.6-10.2g gel. Similarly on addition of 5g NaOH yield ranged 13.8-15.5g at 2.5-10% PVA whereas it became 13.9-10.6g at 15-40% PVA. In brief alkaline treatment developed the negatively charged carboxyl groups ($-COO^-$) which set up an electrostatic repulsion and expanded the polymeric network (Flory 1953) resulting in increase of the rate of formation of hydrogel.

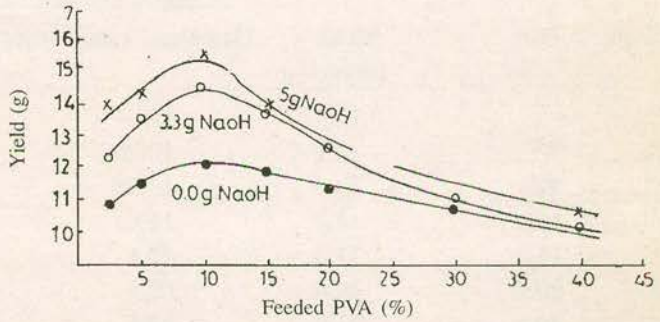

Fig 1. Plot of yield (g) vs feeded PVA (%) for the preparation of hydrogels based on PVA-acrylic acid using N,Ń-methylenebisacrylamide as crosslinking agent.

Table 1

Preparation of hydrogels based on PVA-acrylic acid using N,Ń-methylenebisacrylamide (MBAM) as crosslinking agent*

			degree of swelling of gel after 24 h (g/g)				
S.No.	PVA %	Yield (dry gel)g	Deionised water	Distilled water	Tap water	1% aqueous NaCl	Refractive index
1.	-	12.0	38.5	28.1	7.1	4.0	-
2.	2.5	10.8	54.3	49.1	4.8	3.1	1.335
3.	5.0	11.5	73.1	69.6	7.8	4.1	1.345
4.	10.0	12.1	130.7	118.1	9.3	4.7	1.345
5.	15.0	11.8	154.3	140.0	9.5	5.0	1.345
6.	20.0	11.3	165.4	153.9	14.5	6.0	1.345
7.	30.0	10.7	148.9	140.3	5.2	3.2	1.345
8.	40.0	10.1	140.9	132.4	3.5	2.6	1.345

* acrylic acid; 12g, MBAM; 0.09g, span-60; 0.48g, initiator; 0.03g, cyclohexane; 70ml.

The swelling of dry gel was followed by immersion in deionized water, distilled water, tap water and 1% aqueous solution of NaCl at room temperature (29-30°C). The degree of swelling was calculated using the following equation,

$$\text{Degree of swelling} = \frac{W_s - W_d}{W_d}$$

where W_s was weight of the swollen gel and W_d was the weight of the dry gel.

Table 1 includes the results of the effect of PVA concentration on the swelling uptake in the absence of NaOH. Keeping for 24 h at room temperature with an increased concentration of PVA, there was a regular increase in degree of swelling up to 20% PVA then for higher concentration (>20%), the degree of swelling decreased. In Fig 2, degree of swelling was plotted against feeded PVA (%). These curves indicated that deionized water gave highest degree of swelling whereas it was lowest in aqueous NaCl. It was due to the formation of carboxyl anions in the polymer network leading to the development of strong electrostatic forces. These electrostatic forces helped in expanding the polymer network (Flory 1953). This strong electrostatic network was affected by dissolved CO_2 in distilled water and Na+ (Cations) in tap water and aqueous NaCl. Due to the presence of various ions present in tap water and aqueous NaCl, the network began narrowed and did not accept excess of water. It might be due to the absorption of various ions including cations (Na+) on the surface of gel. When saponified maizestarch-g-acrylonitrile was kept in aqueous sodium chloride (0.25-2%), the absorbancy dropped from 175 to 34g H_2O g^{-1}. Sodium chloride was adsorbed on the surface of saponified polymer and closed the pores which resulted in decrease in absorbancy (Khan *et al* 1999). Similar results were also obtained from the studies of poly (Methacrylic acid) gels crosslinked with divinyl benzene (Katchalsky *et al* 1952) and 1,4 butanediol dimethyl acrylate (Andreopoulos

Table 2

Effect of sodium hydroxide (3.3g) on the preparation of hydrogels based on PVA-acrylic acid using N,N′-methylenebisacrylamide (MBAM) as crosslinking agent*

			degree of swelling of gel after 24 h (g/g)				
S.No.	PVA %	Yield (drygel) g	Deionised water	Distilled water	Tap water	1% aqueous NaCl	Refractive index
1.	-	11.5	124.4	105.9	33.3	13.7	-
2.	2.5	12.2	105.0	91.2	75.2	24.6	1.332
3.	5.0	13.5	140.8	121.6	88.5	25.8	1.332
4.	10.0	14.4	147.2	131.9	95.4	26.1	1.335
5.	15.0	13.6	97.1	84.7	65.9	20.6	1.335
6.	20.0	12.6	65.9	54.3	52.9	18.4	1.340
7.	30.0	11.0	57.8	48.9	39.1	16.2	1.340
8.	40.0	10.2	53.1	45.6	34.7	13.8	1.345

* acrylic acid; 12g, MBAM; 0.09g, Span-60; 0.48, initiator; 0.03g, cyclohexane; 70ml.

Table 3

Effect of sodium hydroxide (5g) on the preparation of hydrogels based on PVA-acrylic acid using N,N′-methylenebisacrylamide (MBAM) as crosslinking agent*

			degree of swelling of gel after 24 h (g/g)				
S.No.	PVA %	Yield (dry gel) g	Deionised water	Distilled water	Tap water	1% aqueous NaCl	Refractive index
1.	-	10.2	168.3	146.6	107.6	27.8	1.332
2.	2.5	13.8	130.2	113.8	91.0	91.3	1.332
3.	5.0	14.3	181.6	162.7	114.2	36.4	1.332
4.	10.0	15.5	221.4	200.5	129.9	39.0	1.335
5.	15.0	13.9	154.9	137.4	102.0	26.4	1.340
6.	20.0	12.8	131.5	116.5	68.9	24.1	1.345
7.	30.0	11.8	79.9	66.2	49.6	20.8	1.345
8.	40.0	10.6	65.8	53.8	28.8	16.2	1.345

*acrylic acid; 12g, MBAM; 0.09g, Span-60; 0.48g, initiator; 0.03g, cyclohexane; 70ml.

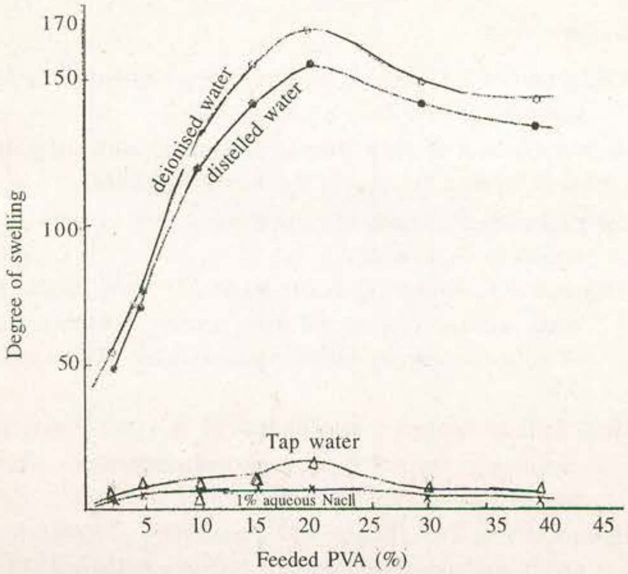

Fig 2. Plots of degree of swelling vs feeded PVA (%) in deionized water (o), distilled water (o), tap water (Δ) and 1% aqueous NaCl (x).

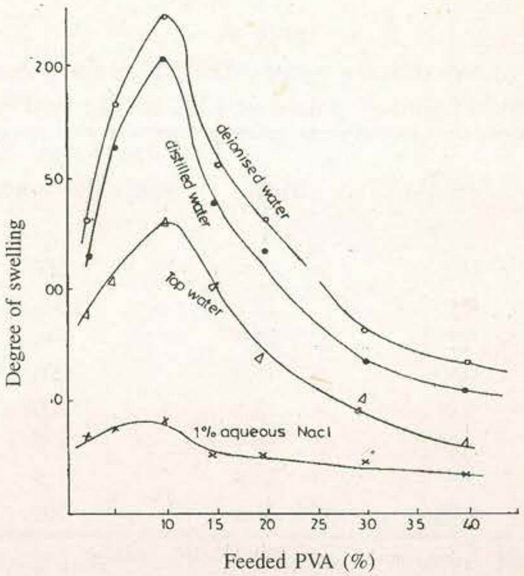

Fig 4. Effects of NaOH (5g) on degree of swelling in deionized water (o), distilled water (o), tap water (Δ) and 1% aqueous NaCl (x).

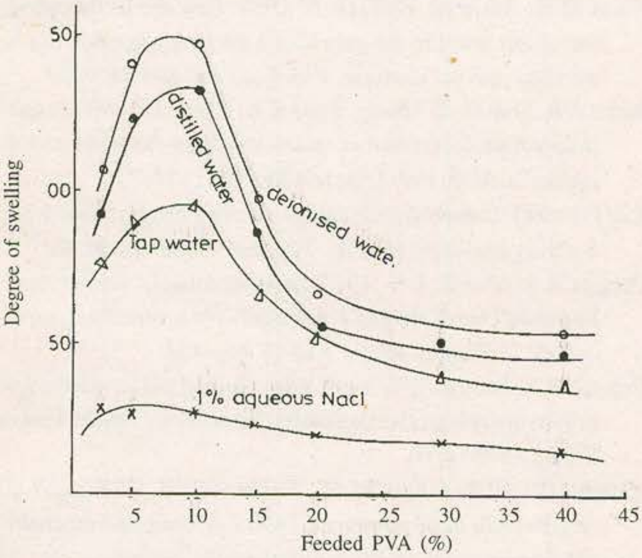

Fig 3. Effects of NaOH (3.3g) on degree of swelling in deionized water (o), distilled water (o), tap water (Δ) and 1% aqueous NaCl (x).

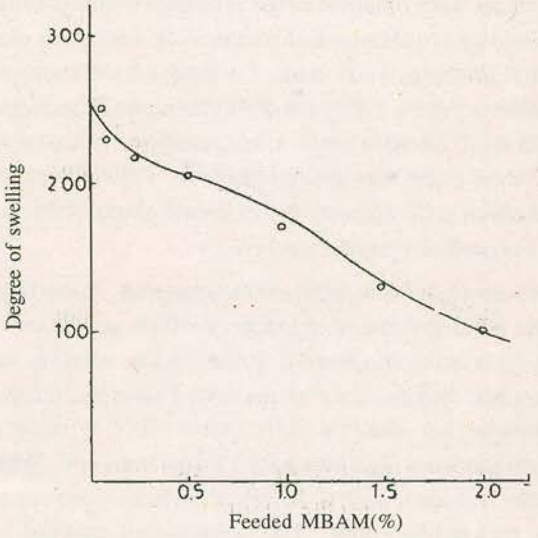

Fig 5. Effect of crosslinking agent (MBAM) on degree of swelling in deionized water.

1989). In brief, CO_2 and impurities present in tap water affects on the magnitude of electrostatic network.

Tables 2-3 include the data of the effect of PVA concentration on the degree of swelling in the presence of NaOH (3.3 and 5g) kept for 24 h at room temperature. These results indicate that degree of swelling increased with an increase in concentration of PVA. Increment in degree of swelling dropped when concentration of PVA reached to 10%. It occurred in both concentrations (3.3 and 5g). The addition of alkali (NaOH) enhanced the degree of swelling of gel. In Figs 3 and 4 degree of swelling was plotted against feeded PVA (%). From these curves it is obvious that the degree of swelling was highest in deionized water and lowest in aqueous NaCl. The addition of sodium hydroxide caused more negatively charged carboxyl groups which set up an electrostatic repulsion tending expand the polymeric network (Flory 1953). In brief degree of swelling in different vehicles in the presence or absence of alkali may be explained in the following order:

deionized water>distilled water>tap water>aqueous NaCl

In Fig 5, degree of swelling plotted against concentration of feeded NBAM (%). The degree of swelling increased with decreasing concentration of crosslinking agent. Degree of swelling influenced not only by the crosslinking agent concentration but also by its chemical structure. Short chaincrosslinking agent gave reduced crosslinking efficiency. Results in Table 4 also show that rate of formation of gel in-

Table 4

Effect of crosslinking agent (MBAM) on the preparation of hydrogels based on PVA-acrylic acid*

S.No.	MBAM %	Yield g	degree of swelling in distilled water g/g
1.	0.05	13.4	248
2.	0.10	14.2	228
3.	0.25	14.6	216
4.	0.50	15.0	206
5.	0.75	15.5	200
6.	1.00	15.7	170
7.	1.50	15.9	128
8.	2.00	16.5	100

*PVA; 1.2g, Acrylic acid; 12g, span-60; 0.48g, Initiator; 0.03g, cyclohexane; 70 ml, NaOH; 5.0g

creased with increase in concentration of crosslinking agent. Similar results were obtained in the preparation and swelling of polymeric hydrogels based on methacrylic acid using multifunctional methylacrylate ester, 1,4-butanediol dimethylacrylate (Andreopoulos 1989) and divinyl benzene (Katchalsky *et al* 1952) as crosslinking agent. 1,4-butanediol dimethyl acrylate has longer chain than divinyl benzene. Divinyl benzene has short chain which shows lower crosslinking efficiency than 1,4-butanediol dimethylacrylate.

Hydrogels are white transparent swollen material. In dry form, it is white solid polymeric substances which powdered on crushing. It is insoluble in most of the organic solvents and swells in water. Dry gel remains unaffected when heated up to 170°C showing 8% loss in weight. After 170°C it begins to decompose and turns light pink with 3% loss in weight. When temperature reaches to 200°C the colour of decomposed material turns into reddish pink. The decomposed material not swell in any organic solvent and in water. It might be due to the intermolecular and intramolecular rearrangement of -COO groups. The refractive index of hydrogel at room temperature (30+1°C) is 1.332-1.345.

References

Andreopoulos A G 1989 Hydrophilic polymer networks for agricultural uses. *Eur Polym J* **25** 977.

Andreopoulos A G 1989 Preparation and swelling of polymeric hydrogels. *J Appld Polymer Sci* **37** 2121.

Flory P J 1953 *Principles of polymer chemistry*. Cornell University Press, Ithacany.

Gregonis D E, Russell G A, Andrade J D 1978 Effect of water and tacticity on the glass transition temperature of poly (2-hydroxy ethyl methacrylate). *Polymer* **19** 1279.

Huglin M B, Yahya I B, Zakaria M B 1982 Purity of crosslinkers for polymeric hydrogel preparation. *Polymer* **23** 340.

Hyon S H, Che W A, Ikada 1989 Preparation of transparent poly (vinyl alcohol) hydrogel. *Polymer bulletin* **22** 119.

Katchalsky A, Lifson S, Eisenberg 1952 Equation of swelling for polyelectrolyte gels. *J Polymer Sci* **8** 476.

Khan M H, Amin M, Zulfiqar M 1988 Release of theophylline from dried hydrogels based on hydroxyethyl methacrylate and acrylamide. *Pak J Sci Ind Res* **31** 385.

Khan A R, Shabih-ul-Hasan, Syed K A, Ahmed K 1999 Preparation of graft copolymer maize starchacrylonitrile and its saponification. *Pak J Sci Ind Res* **42** (2) 74-77.

Lee P I 1983 Dimensional changes during drug release from a glassy hydrogel matrix. *Polymer Commun* **24** 45.

Peppas N A, Merrile E W 1977 Development of semicrystalline poly (vinyl alcohol) hydrogels for biomedical application. *J Biomed Mater Res* **11** 423-434.

Peppas N A, Merrile E W 1977 Crosslinked poly (vinyl alcohol) hydrogels as swollen elastic networks. *J Appld Polym Sci* **21** 1763-1770.

Urushizaki F, Yamaguchi H, Nakamura K, Numajiri S, Sugibayashi K, Morimoto Y 1990 Swelling and mechanical properties of poly (vinyl alcohol) hydrogels. *Int Aj Pharm* **58** 135-142.

Wichterle O, Lim D 1960 Hydrophilic gels for biological use. *Nature* **185** 117.