Polyaspartic Acid Based Superabsorbent Gels with Different Cross-Linkers- A Comparative Study

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Abstract: Two cross-linkers with different functional groups amide (N,N- Methylenebisacrylamide (NMBA)) and esters (Ethylene Glycol Dimethylacrylate (EGDMA)) have been selected for comparative study for cross-linking polyaspartic acid (PAsp) and acrylic acid (AA). Thus, resulting in formation of different polymers with PAsp and acrylic acid in different ratios and cross-linked with different cross-linkers. Polymers with maximum PAsp have shown best superabsorbent properties. The developed polymers have been analysed for their swelling behaviour in different physiological solution like glucose, saline, and water. Varying swelling behaviour has been observed under highly alkaline and acidic conditions. Best absorbing characteristics, as indicated by the swelling behaviour have been observed with EGDMA as cross-linker. The swelling behaviour confirms that the synthesized polymers have superabsorbent characteristics. The structure of the polymers has been studied by FTIR (Fourier Transform Infrared spectroscopy), NMR (Nuclear Magnetic Resonance Spectroscopy) and CHN analysis. The surface morphology has further supported the results. These results can be exploited for their use in wound dressings with superabsorbent polymers.

Keywords: Polyaspartic acid (PAsp)(polyamides); Crosslinking; Gels; Swelling; Superabsorbent polymers (SAP)

I. Introduction

Absorbing materials have observed continuous transition through decades and each decade gave different absorbing materials having their own specific absorption capacity. The early absorbing materials used were cellulosic or fibre based product like Whatman filter paper, tissue paper, wood pulp fluff, cotton ball with maximum water absorption capacity of 1890 wt %.¹ The water absorption capacity achieved was only 20 times their weight and the prominent disadvantage was that they lose most of the fluids absorbed by them when squeezed. This drawback was overcome by development of new class of speciality absorbents as superabsorbent polymers.

Superabsorbent polymers are class of hydrogel which can absorb and retain large amount of liquid relative to their own mass due to the three dimensional network of the hydrophilic polymers. Superabsorbent polymers (SAP) developed are ultra high absorbing material (hydrogel) and can hold as high as 100-10000 % (10-1000g/g) of water.¹ The cross linked polymer network enhances the absorption capacity of SAP to 500 times without dissolving and losing its integrity. The absorbing and swelling capacity is dependent on the type of cross-linkers and degree of cross-linking. The highly cross linked polymer exhibits low absorption capacity whereas the low cross linked polymer dissolves in liquid. Therefore, optimum cross linkers are used to develop superabsorbent polymers so that they exhibit high absorption capacity. These superabsorbent polymers with high absorption and gel strength find application in various fields like wound dressings, agriculture, wound care management, environment industry and diaper industry.²⁻⁵

Polyaspartic acid (PAsp) has been known for its biodegradability, biocompatibility and high water absorbent properties, thus it has been studied actively in recent years. ⁶ PAsp has been known as a polyelectrolyte which can take up water.^{7,8} To develop PAsp as a material with wider application it should possess certain exceptional properties. PAsp suffers from the defect of poor wet strength, resulting from high charge density.^{9,10} The properties have been improved by developing interpenetrating and semi-interpenetrating polymer.¹¹⁻¹⁸ Few publications covering the use of PAsp with hylauronic acid and poly(N-isopropylacrylamide) have been developed as pH sensitive materials.¹³⁻¹⁵ Some work on semi-IPN was initiated with PAsp and acrylic acid also.^{11,17,18} Zhao, et al have exploited the use of NMBA as cross-linker and potassium persulphate as initiator.¹¹ In continuation to these studies it is important to understand how different cross-linkers affect the swelling properties of the PAsp and acrylic acid based polymer system. For comparative study EGDMA based polymers were synthesized and compared with NMBA as cross-linker to have an understanding of the structure-property relationship of the developed polymer system. The results of this study can open up an area of developing polymers with different absorbing properties which can then be exploited.

Thus, this paper presents the results of comparative study of two cross-linkers with amide and ester functional groups.

II. Experimental

Materials: L-Aspartic acid and sodium hydroxide pellets (NaOH) were obtained from Merck Specialities Private Limited (Mumbai, India). Acrylic acid was purchased from Sigma Aldrich Chemical Corporation (St. Louis, USA). O-phosphoric acid for preparing the PAsp was purchased from Spectrochem Private Limited (Mumbai). Cross-linkers N,N'-Methylenebisacrylamide (NMBA) and Ethylene Glycol Dimethacrylate (EGDMA) were procured from Polysciences Inc. (Warrington, PA). Initiator ammonium peroxodisulphate (NH₄)₂S₂O₈ was purchased from Spectrochem Private Limited (Mumbai).

Method:

Synthesis of Polysuccinimide (PSI) and PAsp: L-Aspartic acid powder (5g) and 85% of o-phosphoric acid (2.18ml) were taken in a round bottom flask. The reaction mixture was heated for 3h at 200^oC under vacuum using rotary evaporator (Buchi type). Yellow powder of Polysuccinimide (PSI) was obtained which was then hydrolysed by adding sodium hydroxide (NaOH) solution prepared by dissolving 3.75g NaOH in 25ml deionised water. The NaOH solution was gradually added with continuous stirring by using magnetic stirrer to the PSI on an ice bath. To this mixture 35% HCl solution is added drop wise till it becomes neutral. This neutral solution was precipitated by adding saturated methanol solution (methanol in NaCl) and then filtered using vacuum filtration. The precipitate obtained is polyaspartic acid (PAsp).¹¹

Synthesis of polymer gels of PAsp and PAA: Acrylic acid was neutralized by adding with NaOH solution (26g NaOH in 100ml of deionised water) drop wise using a dropping funnel. During addition of NaOH, the mixture was stirred on a magnetic stirrer to make a homogeneous mixture. The concentration of sodium hydroxide used results in 70% neutralization of the acrylic acid.¹⁹

Different volumes of aqueous polyaspartic acid (PAsp) and neutralised acrylic acid (as mentioned in Table 1) were taken and mixed for 10-15 minutes. In this study different ratios of acrylic acid and PAsp were used keeping the cross-linker and initiator concentration constant.

SET.	PAsp (%)	Acrylic acid (AA) (%)	Mass Ratio of PAsp: AA	Initiator (g)	Cross-Linker (Moles)
1	10	50	1:5	0.01	0.05
2	20	40	1:2	0.01	0.05
3	30	30	1:1	0.01	0.05

TABLE 1 Different Mass Ratios of Polyaspartic acid and Acrylic acid Studied

The table shows the decreasing mass ratio of acrylic acid with relative increase in polyaspartic acid and with 40% water in all the systems studied. To this cross linkers NMBA and EGDMA are added calculated in moles, followed by initiator ammonium peroxodisulphate. The mixture was heated to 80^{0} - 100^{0} C for 30 minutes. The product obtained was analyzed for their swelling behaviour.

The initiator concentration and cross-linker was established to give the best absorbent properties. The chemical structures of the cross-linkers used are given below in Figure 1.

FIGURE 1 Structure of Cross-Linkers



Analysis

Measurement of Molecular weight of Polyaspartic acid: Molecular weight of PAsp was determined by using GPC and it was found to be 2,15,692. A homopolymer has been prepared with polydispersity index Mw/Mn equal to 3.12.

Swelling in various Physiological Fluids: The swelling ratios of the various polymers were studied in various physiological fluids. The different physiological fluids used were water, saline and glucose solution. The solutions prepared were:

a) *Saline Solution*: Sodium chloride (NaCl) solution was prepared by dissolving 9g per litre NaCl

- b) *Water*: Conductivity of water was measured using conductivity meter. The conductivity was analysed to be 0.023 μS/cm and pH of water was neutral.
- c) *Glucose solution*: 50g of glucose was dissolved in 100ml deionised water.

The tea bags used in the method were made using mesh made of nonwoven polypropylene with dimensions of 15cm by 15cm. The polymer samples was dried and weighed. Around 0.15g of sample was taken and weighed accurately. The sample of known weight was then placed in tea bag and this tea bag was weighed then immersed in different solutions. Three readings of each sample were taken. An average of three readings has been reported.

The swelling ratio was calculated as:

Swelling ratio
$$\left(\frac{Wt}{Wt}\right) = Wt - W0 - Wn/W0$$

Where, Wt is the weight of tea bag in grams including swollen polymer; W0 is the weight of dry sample in grams (g) and Wn is the weight of wet polypropylene mesh in grams (g).

The swelling ratio was calculated at different time intervals (0.5 h, 1h, 2h, 3h, 4h and 24h.)

Swelling studies under different pH: Buffer solution with of pH values 2, 4, 7, 8 and 10 were made by using NaOH and HCl. The pH values were checked by a pH meter by Decibel (accuracy = ± 1 mv). These were used to study the pH sensitivity of various polymers formed by using different cross linkers. The pH-sensitive properties of the polymers were studied in terms of swelling ratio by using tea bag method as discussed above.

The same tea bag method was repeated for calculating swelling ratio of various SAPs at different interval of time (0.5h, 1h, 2h, 3h, 4h and 24h).

IR Analysis: FTIR spectrometer, Spectrum RX1 from Perkin Elmer, at the University Scientific Instrumentation Centre, University of Delhi was used to carry out IR analysis. The dried samples were ground into fine powder and then mixed with potassium bromide (KBr) powder. The mixed samples were compressed into pellets. The pellets were scanned from 4000 to 550 cm⁻¹.

NMR Analysis: The NMR spectra of the various samples were carried out in D_2O . 300MHz NMR Spectrophotometer, Brucker NMR Spectrophotometer at Indian Institute of Technology, Delhi was used for the study.

SEM Analysis: SEM analysis was carried out on gold coated samples of SAP. Analysis of gold coated samples was carried out using Carl Zeiss SEM Analyser, Model EVO-18. The magnification used for the study was 250X and the scale was 10µm.

III. Results And Discussion

Neutralised acrylic acid is used to prepare the SAP samples with polyaspartic acid. Acrylic acid monomer is usually neutralised by alkali (NaOH) owing to high activity of acrylic acid over sodium acrylate. This neutralisation degree of acrylic acid has been reported to affect the swelling capacity of SAP and at an optimum value of degree of neutralisation is 65-70% the swelling capacity as reported [19]. The best swelling is observed due to maximum repulsion between the $-COO^{-}$ and $-COO^{-}Na^{+}$ groups, thus resulting in breaking of cross-links. Above 65-70% degree of neutralization the swelling decreases due to further increase in electrostatic repulsion between $-COO^{-}$ and $-COO^{-}Na^{+}$. Due to increase in repulsion, the cross -links in the polymer further decreases thereby decreasing the water entrapping capability. Similarly, when degree of neutralisation is lower, the cross-linking is higher and swelling is lower. Thus an optimum degree of neutralization is required to obtain good swelling.

Swelling in various Physiological Fluids:

The swelling capacities of the polymers were studied in different physiological fluids- water, saline solution and glucose solution. The observations and results of the swelling in different physiological fluids are discussed below:

Water: The trend in the absorption observed in water with different cross-linkers, NMBA and EGDMA are shown in the graph below (Figure. 2).



The swelling studies have shown that the increased concentration of polyaspartic acid and lower concentration of acrylic acid have better swelling capacity than the ratios in which more of acrylic acid is used for both the cross-linkers studied. However, with EGDMA better results have been observed in case of 24 h swelling studies than NMBA in case of all the ratios studied. Trends have also been observed in the swelling behaviours at various time intervals. In case of NMBA the swelling characteristics have shown a smooth increasing trend with initial absorption being higher in all the ratios studied. But in case of EGDMA as a cross-linker difference in swelling characteristics have been observed. The initial absorption is lower but a continuous increase in absorption has been observed in case of lower concentration of acrylic acid and higher concentration of polyaspartic acid.

Saline Solution: The swelling characteristics of the polymers in saline solution have shown different results. The overall absorption of saline is lower than absorption observed in case of water. The low concentration of acrylic acid and greater concentration of polyaspartic acid have shown increased absorption after 24h of exposure in saline solution as compared to high concentration of acrylic acid and lower concentration of polyaspartic acid for both the cross-linkers studied. Figure 3 shows the trends of absorption in saline solution.



FIGURE 3 Absorption in Saline

The trends in absorption of saline in case of NMBA and EGDMA have shown that the initial absorption of saline is better in case of EGDMA than NMBA. But with time although a constant increase has been observed but not much change in absorption has been observed in case of both the cross-linkers studied. EGDMA has shown better overall absorption of saline solution than NMBA, except in case of maximum polyaspartic acid wherein NMBA has shown better results.

As observed in case of water absorption studies minimum absorption has been observed in case of 1:2 ratio of the polyaspartic acid: acrylic acid.

Glucose solution: The results of glucose absorption and the trend observed are shown in Figure 4.



The results have shown that the absorption of glucose increases with time for all the concentrations of the polyaspartic acid and acrylic acid studied with both cross-linkers. EGDMA has given better results than NMBA, although the initial absorption is better in NMBA in case of lower concentration of polyaspartic acid. In the 24 h absorption studies best results have been observed with EGDMA in case of polymers with low concentration of acrylic acid and high concentration of polyaspartic acid. However with high acrylic acid ratio NMBA has given better results. The initial absorption is low in case of EGDMA but with time the absorption increases. Exponential trend have been observed in case of EGDMA but constant increasing trend has been observed in case of NMBA.

Thus the studies on swelling in different physiological fluids concludes that EGDMA has given better absorption for both water and glucose showing an exponential increase especially in case of polymers with low concentration of acrylic acid and high concentration of polyaspartic acid. However, in case of saline solution absorption not much difference has been observed in case of both the cross- linkers used. Initial absorption has been better in case of EGDMA as a cross-linker.

Swelling at different pH

Swelling at pH 2: In case of pH 2 (Figure 5) the cross-linker EGDMA has given better results than NMBA. Initially the results of absorption have shown almost similar results for all the ratios of polyaspartic acid and acrylic acid studied.



FIGURE 5 Absorption at pH2

The absorption values have shown slight improvement in case of equal ratios of acrylic acid and polyaspartic acid. Continuous increase in absorption has been observed with time for both the cross-linkers studied. But with time the increase in absorption is less in case of samples with equal ratios of polyaspartic acid:acrylic acid and maximum for higher ratios of acrylic acid. For 24h absorption studies maximum absorption has been observed for EGDMA for higher ratios of acrylic acid. The absorption keeps on decreasing with decreasing ratios of acrylic acid in case of EGDMA. However, in case of 24h absorption studies with NMBA changing trends have been observed. Better results have been observed with equal ratios of polyaspartic acid and acrylic acid.

Swelling at pH-4: The results are shown in Figure 6.



FIGURE 6 Absorption at pH4.

At pH 4, best results have been observed with both the cross-linkers with equal ratios of polyaspartic acid and acrylic acid. The results of initial absorption have shown that with 1: 1 ratio of polyaspartic acid and acrylic acid the absorption is low as compared to other ratios studied in case of EGDMA. EGDMA and NMBA have shown almost comparative results with higher ratio of polyaspartic acid and acrylic acid for initial as well as 24h absorption. However, different trend has been observed with 1:5 and 1:2 ratios of polyaspartic acid and acrylic acid where in NMBA has given better results of absorption in case of the initial as well as for 24h.

Swelling at pH 8: At pH 8 exponential increases in the results of absorption has been observed in case EGDMA as compared to NMBA for all the ratios studied. The results of initial as well as 24h absorption have been observed in case of higher ratios of acrylic acid in case EGDMA as the cross-linker (Figure 7).



Swelling at pH 10: The trends in the swelling properties at pH10 are shown in Figure 8 below.



FIGURE 8 Absorption at pH10.

Similar increase in absorption results have been observed with EGDMA at pH 10. As compared to pH 8 better results have been observed with NMBA. The results of initial absorption are better in case of NMBA. But with the increase of time the absorption increase in case of EGDMA. The lowest absorption has been observed in

case of 1:2 ratio of polyaspartic acid to acrylic acid with EGDMA as the cross-linker, while with NMBA continuous increase in absorption has been observed with decreasing ratio of acrylic acid.

The effect of cross-linkers on the absorption is depicted in Figure 9 below. For pH 7 the results of water absorption have been considered.



FIGURE9 Effect of cross-linkers on absorption at varying pH

EGDMA has shown increased absorption under alkaline conditions (pH 8) relative to NMBA where the absorption is slightly lower. Thus this study shows for application under alkaline conditions a polymer of polyaspartic acid with acrylic acid and EGDMA based superabsorbent can be a material of better choice than NMBA. In acidic medium, NMBA shows more swelling as compared to EGDMA due to more -CONH- which gets protonated and gives more repulsion. In basic medium, EGDMA shows more swelling than NMBA due to -COO- group present which gives more repulsion when OH⁻ interacts. One such area where it can find application is in highly exudating wounds, which are alkaline in nature where EGDMA based superabsorbent can be materials of better choice.

Both NMBA and EGDMA based polymers possess different functional groups. Each functional group has its own importance. The NMBA-polymers has -CONH- (Polyaspartic acid) and -COO⁻ (acrylic acid) functional groups where as EGDMA-SAP has -CONH- (Polyaspartic acid) and -COO⁻ (EGDMA and acrylic acid). In acidic medium, the NMBA shows more swelling as compared to EGDMA due to more of -CONH-group which gets protonated and gives more repulsion. In basic medium, the EGDMA shows more swelling than NMBA due to -COO- group present which gives more repulsion when OH⁻ interacts.

The presence of these functional groups is further confirmed by the IR and NMR studies discussed below.

FTIR Spectroscopy: IR studies have been presented for the polymer with maximum concentration of polyaspartic acid. Figure 10 gives the IR of the sample prepared with NMBA.



The IR studies confirms the presence of certain groups like the C-O-C symmetric stretching which is being formed by reaction of polyaspartic acid with the cross linkers or the monomer. The -COOH of the polymer reacts with the cross-linker having ethylene group. The asymmetric stretching of carboxylate anion is due to the presence of acrylic acid as sodium salt. The –NH stretching further supports the presence of -NH group in the polyaspartic acid as well as in the cross-linker. The presence of ester group is also indicated by the presence at 1320cm⁻¹ and 1088cm⁻¹. In case of EGDMA the IR spectra is shown in Figure 11. The FTIR studies are representing the bonding between the polymeric chains. The various functional groups are assigned in Table 2. The presence of -CH₂ group is also visible which is present in polyaspartic acid, EGDMA and also acrylic acid. The difference in the two is that the NMBA based polymer has the -CO-NH- linkage while EGDMA has the ester linkage.



FIGURE 11 IR spectra of EGDMA sample with 1:1 ratio of PAsp:PAA

Assigned frequencie	s for NMBA	Assigned frequencies for EGDMA		
Frequency (cm ⁻¹)	requency (cm ⁻¹) Functional Group		Functional Group	
3451.07	Intramolecular H- bonding	3437.52	Intramolecular H- bonding	
2927.51	C-H stretch in -CH ₂	2924.79	C-H stretch in CH ₂	
1409.14	C-H bend in -CH ₂	1444.09	C-H bend in CH ₂	
788.32	C-H def in -CH ₂	1559.15	Asymmetric carboxylate anion	
2519.57	Carboxylic acid (small hump)	2523.25	Carboxylic acid (small hump)	
1409.14	Asymmetric carboxylate anion	2389.84	>NH ₂ stretch	
2356.04	>NH ₂ stretch	1559.13	N-H (symmetrical bending)	
1577.09	N-H (symmetrical bending)	1056.12	Symmetric C-O-C stretch	
1068.06	Symmetric C-O-C stretch	1637.44	-C=O stretching	

These studies have been further carried out by NMR discussed below.

NMR analysis:

The ¹H NMR analysis is done in D_2O solvent and exhibit following signals shown in Figure 12 and 13. The comparative NMR spectra of all NMBA [Figure12] and EGDMA [Figure 13] based polymers show the presence of neutralized acrylic acid and polyaspartic acid used in the synthesis. As the concentration of neutralized acrylic acid decreases, the intensity of peak keeps decreasing. The NMR values at 1.5ppm and 1.4 pm for alkyl groups, i.e. R_3CH - and R_2CH_2 - respectively. The presence of polyaspartic acids is







FIGURE 13 Showing Signals with Increasing Proportion of Polyaspartic Acid in EGDMA Samples

confirmed by the peak at 2.1ppm (2H, t) and 2.3ppm (2H,t). The neutralized acrylic acid shows its presence at 5.5 (2H, t) and 5.9 (4H, quintet). The cross-linker and polyaspartic acid are linked by an ester bond showing a peak at 3.6 ppm for both NMBA and EGDMA based polymers. The peak at 2.6ppm corresponds to the $-CH_2$ - present in NMBA (-NH-CH₂-NH-). The presence of -NH- is shown by peak between 1-5ppm. The peak at 2.2ppm corresponds to CH₂ present in EGDMA (-C(=0)-CH₂-C(=O)-) [Fig.13].

SEM Analysis: The scanning electron microscopic studies have been carried for all the concentration of polyaspartic acid and acrylic studied with both NMBA and EGDMA. Figure 14 presents the micrograph of cross-linker EGDMA and Figure15 gives the results of NMBA. The porosity of the samples is increasing with the increasing concentration of polyaspartic acid as visible from the micrograph Figure 14(c).



FIGURE14 The scanning electron micrographs of samples with EGDMA as a cross-linker at 250X; **a**) EGDMA 1 with ratio 1:5 of PAsp and PAA; **b**) EGDMA 2 with ratio 1:2 of PAsp and PAA **c**) EGDMA 3 with ratio 1:1 of PAsp and PAA

On comparing Figure14 and Figure15 it can be observed that different kinds of polymers have been obtained with NMBA and EGDMA. No porosity observed when SEM is performed in case of maximum acrylic acid is cross-linked with NMBA. The increase in concentration of polyapaspartic acid has shown an increase in porosity. The difference in concentration is easily seen by the SEM image which shows the porosity in the polymer. The porosity is better with increasing concentration of polyapartic acid. The surface of the polymer is smooth when NMBA is compared to EGDMA. Increasing time has shown better improvement with EGDMA. Moreover increasing concentration of polyapartic acid also improves absorption due to increase in porosity as evident from Figure 14c and Figure 15c.

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FIGURE15 The scanning electron micrographs of samples with NMBA as a crosslinker at 250X; a) NMBA1 with ratio 1:5 of PAsp and PAA; b) NMBA 2 with ratio 1:2 PAsp and PAA and c) NMBA 3 with ratio 1:1 of PAsp and PAA

The polymers prepared by replacing acrylic acid with polyaspartic acid using different cross-linkers have shown maximum swelling capacity in water and minimum in case of saline solution for 24h absorption studies. The trend observed in different physiological fluids is as follows: Water > Glucose solution > Saline solution.

The polymers prepared comprises of carboxyl group (polar) and amide group (polar). The saline solution contains Na^+ ions which have a greater influence on a polar group but little effect on non polar group. When the polymers are placed in saline solution, resistance in swelling capacity of the polymer is observed. This is because Na^+ ions present in the saline solution gets attracted towards the acidic group .i.e. –COOH of the polymer and the –COOH group gets solvated. This ion- dipole interaction hinders the stretching of the polymeric chains. The polymers present in glucose solution shows higher swelling capacity than in saline solution. This is because of the fact that glucose gets dissolved due to H-bonding but glucose being non-polar in nature and does not affect the polymeric chains as the saline solution does as there are weak induced dipole-dipole interaction between glucose and polymeric chain.

IV. Conclusions

This study has revealed that by changing the cross-linkers polymers with better properties can be designed. Moreover tailor making of materials could be carried out to design materials as per requirements. In this study polymers prepared with EGDMA as cross-linkers has proven to be better in terms of absorbency under different physiological conditions, especially under alkaline conditions. These could find better applications for highly exudating wounds which are alkaline when infected. The functional groups present are ester and amide which has proved that both being di-functional cross-linkers ester functionality has proved much better as a superabsorbent material.

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