

Effect of Crosslinking on the Network Parameters, Swelling and Mechanical Properties of PVA-Borax and Poly (AM-co-HEMA) Double Network (DN) Hydrogels

AKANSHA DIXIT, DIBYENDU S. BAG^{*}, DHIRENDRA KUMAR SHARMA^a,
HARJEET SINGH AND N. ESWARA PRASAD

*Defence Materials and Stores Research and Development Establishment
DMSRDE P. O., G. T. Road, Kanpur-208013, INDIA*

^a*Department of Chemistry, Bundelkhand University, Jhansi-284128, INDIA*

ABSTRACT

Crosslinking is one of the most important factors affecting the major characteristics of polymer and hydrogel materials. Now-a-days, double network (DN) hydrogels have attracted special attention for their high strength and stretchability. In this investigation, we report the effect of crosslinker concentration on the DN hydrogels which are consisting of poly(vinyl alcohol)-borax as the first network and poly(acrylamide-co-2-hydroxyethyl methacrylate) as the second network synthesized by in-situ crosslinking polymerization process using N, N'-methylenebisacrylamide (MBA) as crosslinker. Various properties of the DN hydrogels such as degree of swelling, swelling kinetics, gel fraction and network parameters (crosslink density, average molar mass between crosslinks, mesh size etc.) were studied. The polymer-solvent interaction parameter (χ) and polymer volume fraction in swollen state (V_p) were also calculated using Flory-Rehner Theory. We observed that the degree of swelling was increased with increasing crosslinker concentration up to 0.1 wt% of monomers. But above this concentration, it was decreased with crosslinker concentration. The gel fractions as well as mechanical properties were increased with increasing MBA crosslinker concentration.

KEYWORDS : *Double network hydrogels, Crosslinker effect, Network parameters, Swelling kinetics, Mechanical properties*

1. INTRODUCTION

Hydrogels are three dimensional hydrophilic polymer networks which remain in swollen state by absorbing large amount of water [1-3]. These materials may be called smart (or intelligent) materials if they can reversibly change any of their properties by external stimuli (such as temperature, light, pressure, chemical triggering, electric and magnetic field etc.) [4-8]. Such novel class of materials have attracted great attention of scientists due to their potential application in scaffolds and tissue engineering, drug delivery systems, smart windows, actuators and sensors etc. [9-12]. It is well established that crosslinking plays important role on the properties and performance of polymers [13]. It decreases the viscosity and improves the strength, toughness and glass transition of polymers. It also affects the hydrogel structures and properties such as mesh size, degree of swelling, gel fraction, and other properties [14].

A large number of applications of hydrogels are often severely limited by their low mechanical strength especially in their swollen state and they are unsuitable for applications under load. Therefore, many new and novel approaches have been adopted to develop mechanically tough and stretchable hydrogels. A few of such notable approaches include topological hydrogels [15], hybrid hydrogels [16-17], nanocomposite hydrogels [18-20] and double network (DN) hydrogels [21-23]. Among these, 'DN hydrogels' is a promising approach to synthesis mechanically strong and tough hydrogels in which a polymer network is obtained by polymerization of monomer(s) and a crosslinker in the presence of another polymer network [24-25]. First network is mostly loosely

crosslinked structure (e.g., ionic or physical crosslinking) which has a high young modulus and the second network may be highly crosslinked (e.g., chemical crosslinking) which dissipates the fracture energy and prevents crack development [26-28]. The DN hydrogels exhibited excellent mechanical strength with high water content (20% to 90%) [29]. Several possible reasons have been proposed for the high strength of DN hydrogels which include the engagement and interaction between the networks via physical crosslinking, molecular association and chemical crosslinking [30-37]. The presence of hydrogen bonding between networks also contributes to the mechanical properties of DN hydrogels [30-33]. We have also recently reported a strong and stretchable DN hydrogel system in which the first network was composed of poly (vinyl alcohol) and borax with a defined molecular weight and structure, and the second network was a crosslinked copolymer of acrylamide (AM) and 2-hydroxyethyl methacrylate [33]. Although hydrogen bonding and double crosslinking can explain the anomalous high strength of DN hydrogels, the DN hydrogels became strong when the second component was polymerized without the presence of any crosslinker rather than with crosslinker [34]. Some recent reports also described the dominant parameters for the improvement of mechanical properties which are inter-molecular and intra-molecular interaction including hydrogen bonding [36-37]. On the other hand, it was also reported that the fracture toughness was increased because the first network generated a crosslinking with second network during polymerization of second network [38]. In the present work, we have investigated the effect of crosslinker concentration (i.e., the crosslink density) on

the DN hydrogels consisting of PVA-borax as the first and P(AM-co-HEMA) as the second network.

2. EXPERIMENTAL

2.1 Materials

Poly (vinyl alcohol) (PVA) (88% hydrolyzed, $\overline{M}_w = 22000 \text{ g mol}^{-1}$) (Across Organics, USA) and di-sodium tetraborate (Borax) (98%, Qualigens, India) were used directly as received. The monomers, acrylamide (Kochlight Laboratories, UK) and 2-hydroxyethyl methacrylate (HEMA) (97%, Lancaster, England) were used directly as received. The crosslinker, N, N'-methylenebisacrylamide (MBA) (LR, Aldrich, USA) was recrystallized from ethanol and dried under vacuum before use. The initiator, ammonium persulfate (APS) (AR, SD Fine Chem, India) and accelerator, N, N, N', N'-tetramethylethylenediamine (TMEDA) (98%, Lancaster, UK) were also used as received.

2.2 Synthesis of Double Network Hydrogels

In order to understand the effect of crosslinker concentration, the DN hydrogels were synthesized by varying amount of crosslinker for the second

network of AM and HEMA while keeping other content constant including the first network of PVA-borax (Table 1). The DN hydrogels were prepared through in-situ crosslinking polymerization of acrylamide and 2-hydroxyethyl methacrylate using N, N'-methylenebisacrylamide (MBA) as a crosslinker, ammonium persulfate (APS) as an initiator and N,N,N',N'-tetramethylethylenediamine (TMEDA) as an accelerator varying the MBA concentration in the presence of double strand complex network of poly (vinyl alcohol)-borax system at room temperature (25°C).

For the synthesis of a double network hydrogel sample, 5 gm of AM, 5 gm of HEMA and crosslinker(MBA) were added into 30ml of PVA-borax solution/gel and shaken well. Then 0.1 gm APS initiator was added into it and dissolved followed by 0.02 ml TMEDA accelerator was added to the reaction mixture and shaken well and quickly poured into Teflon mould of dumbbell-shaped cavity where in-situ crosslinking polymerization formed the DN hydrogels. The sample specimen was taken out of mould after polymerization was complete at room temperature (25 °C) for 24 hours (Fig.1). Similarly other samples were prepared taking different amount of MBA crosslinker (0.02 wt%, 0.05 wt%, 0.07 wt% , 0.1 wt%,

TABLE 1. Synthesis of Double Network (DN) Hydrogels^{a,b}

Sl. No.	Sample Code	Crosslinker amount (wt % of (total monomer)	Amount of AM/HEMA (gm/gm)	Degree of Equilibrium swelling
1.	GVC-0	0	1:1	240.2
2.	GVC-1	0.02	1:1	341.2
3.	GVC-2	0.05	1:1	437.9
4.	GVC-3	0.07	1:1	542.2
5.	GVC-4	0.10	1:1	624.9
6.	GVC-5	0.50	1:1	419.7
7.	GVC-6	1.00	1:1	414.2
8.	GVC-7	1.50	1:1	307.8

a. First network: 25 ml of 4wt% aqueous solution of PVA and 5 ml of 4 wt% of borax solution.

b. Second network: monomer mixture 10 gm (5gm AM and 5gm HEMA), crosslinker (MBA) concentration was varied and initiator was taken as 1wt% of total monomer. Time of the polymerization was 24 hours.

0.5 wt%, 1.0 wt% and 1.5 wt% of total monomer). Samples were studied for their swelling characteristics and tested for their mechanical properties for the study of effect of crosslinker concentration.

2.3 Characterization

2.3.1 FTIR Analysis

FTIR spectroscopy is an effective analytical technique for detecting functional groups and characterizing bonding information in hydrogels. Hence, the synthesized double network hydrogels were characterized by FTIR analysis. FTIR spectra of the samples were recorded on a Perkin Elmer (Spectrum 100 Series) spectrophotometer using KBr pellets.

2.3.2 Study of Swelling Properties of the DN Hydrogels

The swelling property of the DN hydrogels was measured by the gravimetric measurement at room temperature^[39]. When a dry sample was poured in distilled water, the sample started swelling due to uptake of water. After a fixed interval of time (one hour), the hydrogel sample was taken out from water, blotted with filter paper to eliminate excess of water from the surface and weighed until constant weight was achieved.

Degree of Swelling of the DN Hydrogels

The % degree of swelling was calculated using the following equation:

$$\% \text{ Degree of Swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

Where, W_s = weight of a swollen hydrogel with respect to swelling time, t and W_d = weight of the dry hydrogel sample taken for swelling study.

Equilibrium Degree of Swelling of the DN Hydrogels

The equilibrium water content is the maximum amount of water absorbed by a hydrogel and this stage is known as fully swollen state. The equilibrium swelling is calculated with the help of the following equation:

Equilibrium Degree of

$$\text{Swelling (\%)} = \frac{W_e - W_d}{W_d} \times 100 \quad (2)$$

Where, W_e is weight of a swollen hydrogel sample after equilibrium swelling was achieved and W_d is the weight of the dry sample.

Rate of Swelling of the DN Hydrogels

Change of swelling (volume or weight) per unit of time is called "swelling rate" of the hydrogel and is calculated using the following equation:

$$S_R = \frac{W_{t+\Delta t} - W_t}{\Delta t} \quad (3)$$

Where, $W_{t+\Delta t}$ is the weight of swollen hydrogel after swelling time $t + \Delta t$ and W_t represents the weight of swollen hydrogel after swelling for time, t .

2.3.3 Swelling Kinetics of the DN Hydrogels

The 'kinetics' of swelling of hydrogels is theoretically generalized and experimentally studied for the first time by the Tanaka and Colleagues^[40]. A dry hydrogel is poured into the distilled water, the weight of the hydrogel is increased with time due to uptake of water and finally it attains equilibrium when no further increase of weight of the hydrogel is observed. Thus the weight of a hydrogel was measured at regular time intervals. The water absorbed by a hydrogel at a particular time, 't' is calculated by the difference of weight of the swollen hydrogel sample (W_s) and that of the dry sample (W_o). The difference ($W_s - W_o$) is equal to M_t . The water uptake (or degree of swelling), S_w is equal to the ratio of this difference of weight to the weight of dry hydrogel sample and it is an exponential function of time (t)^[41]. Thus,

$$S_w = \frac{W_s - W_o}{W_o} = \frac{M_t}{W_o} \quad (4)$$

$$S_w = Kt^n \quad (5)$$

$$\text{So, } \log S_w = \log K + n \log t \quad (6)$$

Where, the swelling characteristic constant is 'K' and transport exponent is 'n'. The value of 'K' and 'n' are determined from the logarithm plot of S_w versus time (t), where the value of 'K' is obtained from the intercept and 'n' is from slope. These parameters are dependent on polymer network-solvent system.

2.3.4 Study of Gel Fraction

To determine the gel fraction, the synthesized hydrogels were purified by the soxhlet extraction using deionised water as a solvent for 48 hrs to remove unreacted non-crosslinked species. The hydrogel samples after extraction was subsequently dried until a constant weight was achieved. The gel fraction was thus calculated using the following equation [42]:

$$\text{Gel fraction} = \frac{W_d}{W_p} \quad (7)$$

Where, W_d and W_p are the weight of a dried hydrogel sample after extraction and before extraction, respectively.

2.3.5 Determination of Crosslink Density and other Network Parameters

The crosslink density (CLD) of the double network hydrogel was determined with the help of Flory-Rehner Equation [43]. The mesh size of the double network is usually determined in terms of average molecular weight between networks. Average molar mass between networks (M_c) is calculated by the following equation:

$$M_c = \frac{V_m \rho (V_p^{1/3} - \frac{V_p}{2})}{\ln(1 - V_p) + V_p + \chi V_p^2} \quad (8)$$

Here, ρ is the density of dry hydrogel sample, V_m is the molar volume of solvent (water), V_p is the volume fraction of the polymer and χ is the polymer-solvent interaction parameter. At the equilibrium swelling, V_p and χ were calculated using the following equations:

$$V_p = \frac{1/\rho}{(q_w/0.99) + (1/\rho)} \quad (9)$$

$$\chi = \frac{V_p}{3} + 0.5 \quad (10)$$

The crosslink density (CLD) in the double network hydrogels was calculated [44-45].

CLD is represented as ρ_c which is given below:

$$\rho_c = \frac{M_o}{M_c} \quad (11)$$

Where, M_o is the molar mass of the repeating units which is calculated using the following equation:

$$M_o = \frac{M_{AM}n_{AM} + M_{HEMA}n_{HEMA} + M_{PVAn}n_{PVA}}{n_{AM} + n_{HEMA} + n_{PVA}} \quad (12)$$

Here, n is the number of moles of a monomer component and M is the molecular weight of the same monomer component.

The mesh size (ξ in \AA) of the swollen double network gels was calculated from the following equation [46]:

$$\xi = \sqrt{\frac{2C_n}{\rho_c}} l_m^{1/3} \quad (13)$$

The C_n is Flory's characteristic ratio taken from literature and the ' l ' is the C-C bond length, which was assumed as 1.54\AA [47].

2.4.6 Measurement of Mechanical Properties

Tensile stress-strain measurement of the swollen hydrogels was carried out using an Instron Universal Testing Machine (Model 3369) with the dumbbell-shaped specimens according to ASTM specification (D638-99). Three specimens were tested for each sample and the data is presented as the mean of obtained values. The cross head speed of the instrument was 50 mm/ min and a given preload was 0.3N. The sample length between jaws was 40 to 60 mm, thickness was 5 mm and the width was 7.2 mm. The stress at break (σ_{break}), strain at break (δ_{break}) and the elastic modulus were determined from the stress-strain measurements with the help of following equations[48-49]:

$$\text{Tensile Strength (TS)} = \frac{\text{Load taken to break hydrogel sample (N)}}{\text{Cross-sectional area (m}^2\text{)}} \quad (14)$$

$$\text{Elastic Modulus} = \frac{\text{Stress at break}}{\text{Strain at break}} \quad (15)$$

3. RESULTS AND DISCUSSION

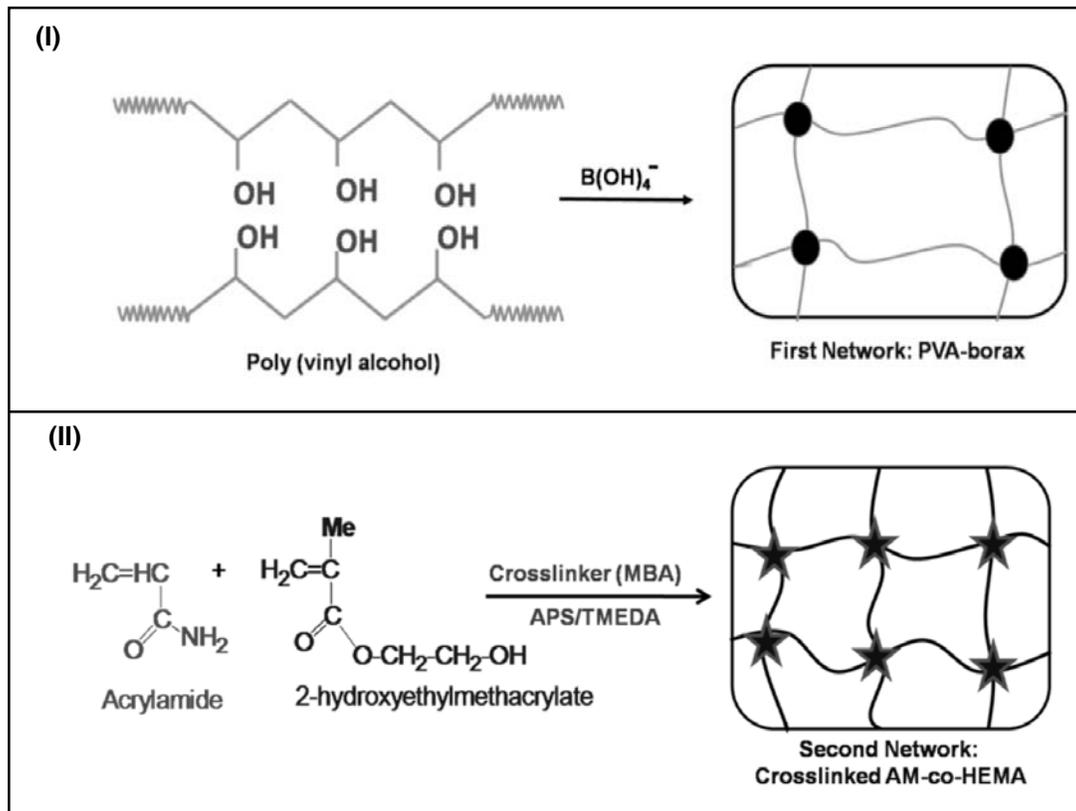
3.1 Synthesis of Double Network (DN) Hydrogels

The double network hydrogels of PVA-borax as the first network and crosslinked P(AM-co-HEMA) as the second network were

synthesized by in-situ crosslinking polymerization process varying the crosslinker (MBA) concentration from 0.02 to 1.5 wt% of total monomer. Poly(vinyl alcohol) is well known for the formation of “di-ol” complex with four hydroxyl (–OH) groups and one borate ion. Hence PVA-borax forms a reversible crosslinked structure as the first network (Fig. 1). The second network of acrylamide and HEMA was synthesized using MBA as a crosslinker, APS as initiator and TMEDA as accelerator. The amount of crosslinker was varied to study its effect on the network parameters, swelling and mechanical properties of DN hydrogels (Table 1).

3.2 FTIR Spectroscopy

The FTIR spectra of DN hydrogels obtained varying amount of bis MBA are shown in Fig. 2 and Fig. S1. A broad and large peak is observed around 3200–3600 cm^{-1} which is attributed to the stretching vibration of O–H groups which is present in PVA and HEMA units. For GVC-4 sample (AM/HEMA=50/50), amide and ester carbonyl peaks are appeared at 1655 cm^{-1} and 1738 cm^{-1} respectively. The sharp peak at 1738 cm^{-1} is due to C=O group of ester of HEMA unit. The OC–O appears at 1279 cm^{-1} . The C=O stretching (amide I band) and N–H in-plane bending (amide II band) and



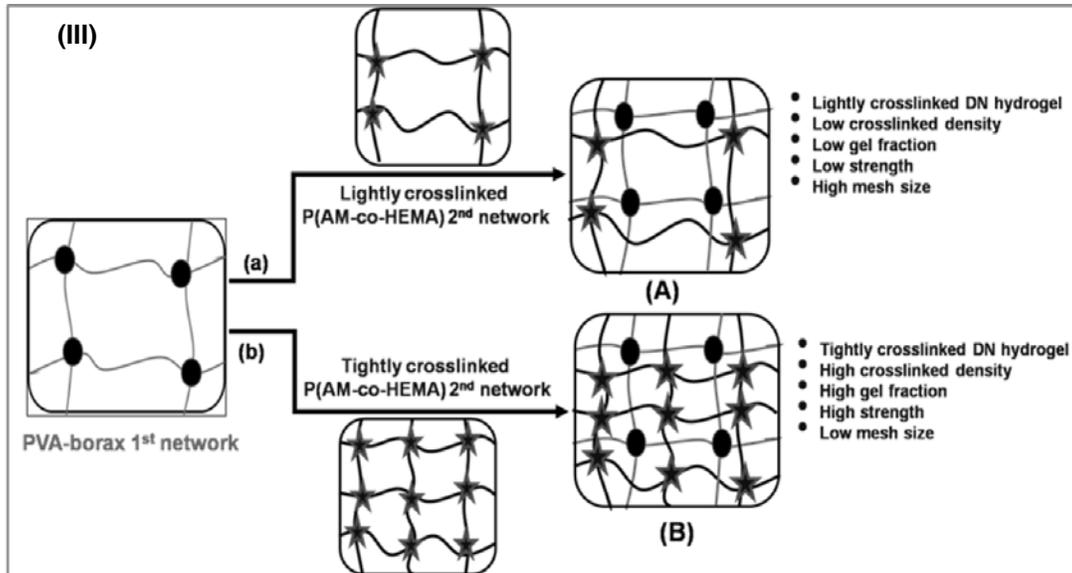


Fig. 1. Schematic representation of synthesis of DN hydrogel: (I) formation of first network of poly(vinyl alcohol) with borax, (II) second network of acrylamide and 2-hydroxyethyl methacrylate with variation of MBA crosslinker and (III) schematic representation of DN hydrogels obtained by in-situ crosslinking polymerization process (Two cases are shown: lightly and tightly crosslinked network)

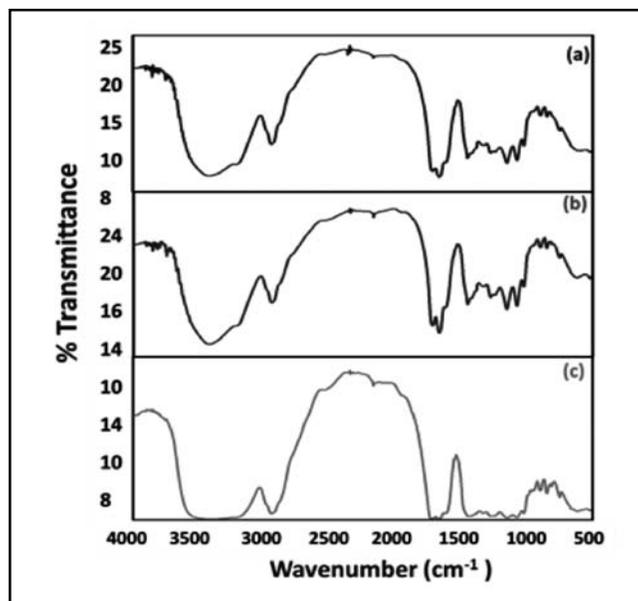


Fig. S1. FTIR spectra of the double network hydrogel samples: (a) GVC-2, (b) GVC-5 and (c) GVC-7

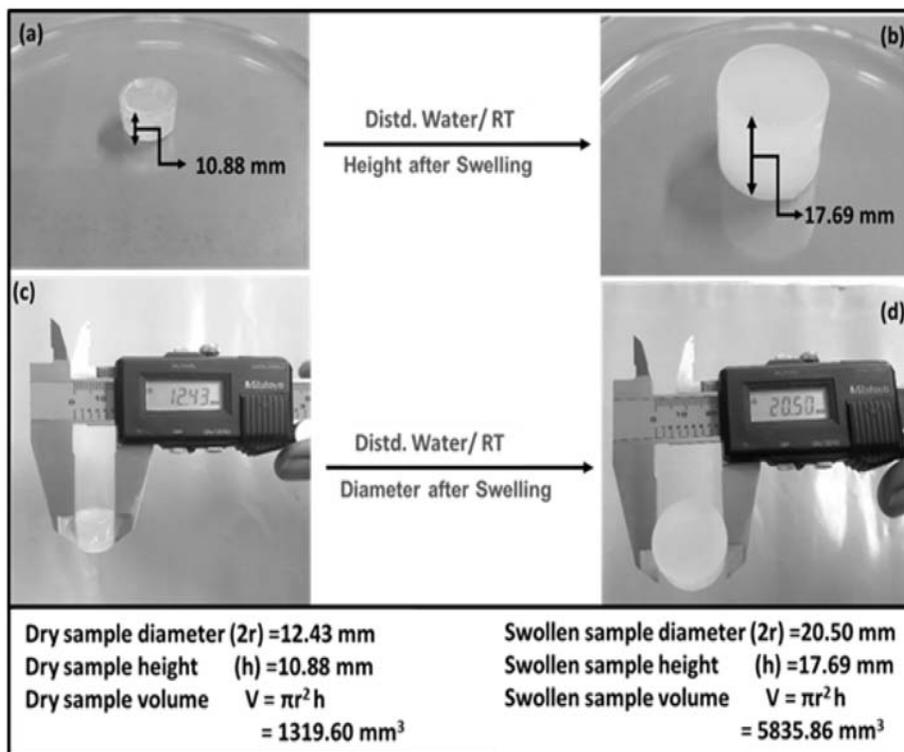


Fig. S2. (a) A dry hydrogel GVC-4 sample (height was 10.88 mm), (b) the sample after swelling (the height was increased to 17.69 mm), (c) the same sample having diameter 12.43 mm and (d) after swelling the diameter became 20.50 mm

band) of $-\text{CONH}_2$ group of acrylamide unit appear at 1655 cm^{-1} and 1535 cm^{-1} [33, 38] respectively. However, these peaks are almost merged together in most of the samples because of the presence of AM and HEMA in same ratio. There are enormous possibility of forming hydrogen bonding because of the presence of amide ($-\text{CONH}_2$), ester ($-\text{COO}-$) and hydroxyl ($-\text{OH}$) functional groups in the DN hydrogels. A new peak at 1610 cm^{-1} is observed to appear. The appearance of this peak of amide at lower energy certainly indicates the hydrogen bonding [33].

If at all the carbonyl ($\text{C}=\text{O}$) group of ester is H-bonded, the obvious appearance of such a peak at lower frequency would merged in this region with other peaks. The peak of N-H *trans* stretching of amide of AM unit is merged with the hydroxyl band. The peak at 2944 cm^{-1} is appeared due to the C-H stretching of methyl ($-\text{CH}_3$) group and alkyl ($-\text{CH}_2-$) chains. The crosslinking between PVA and borax due to complexation is observed by the characteristic peaks of borax and borate which appear at 1462 cm^{-1} and 1330 cm^{-1} (asymmetric stretching relaxation of B-O-C) and 625 cm^{-1} (bending of B-O-B linkage within borate networks) [50-51].

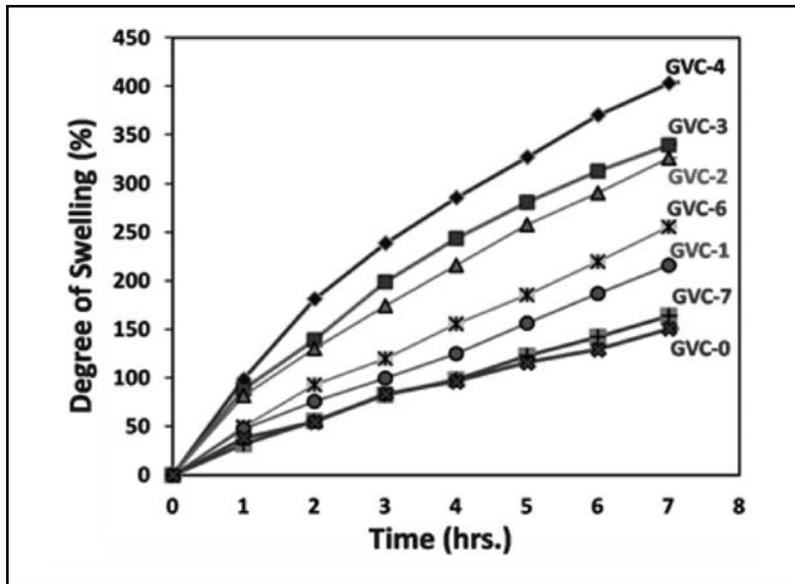


Fig. S3. Plot of initial degree of swelling versus to time (only up to 7 hrs) for the DN hydrogels

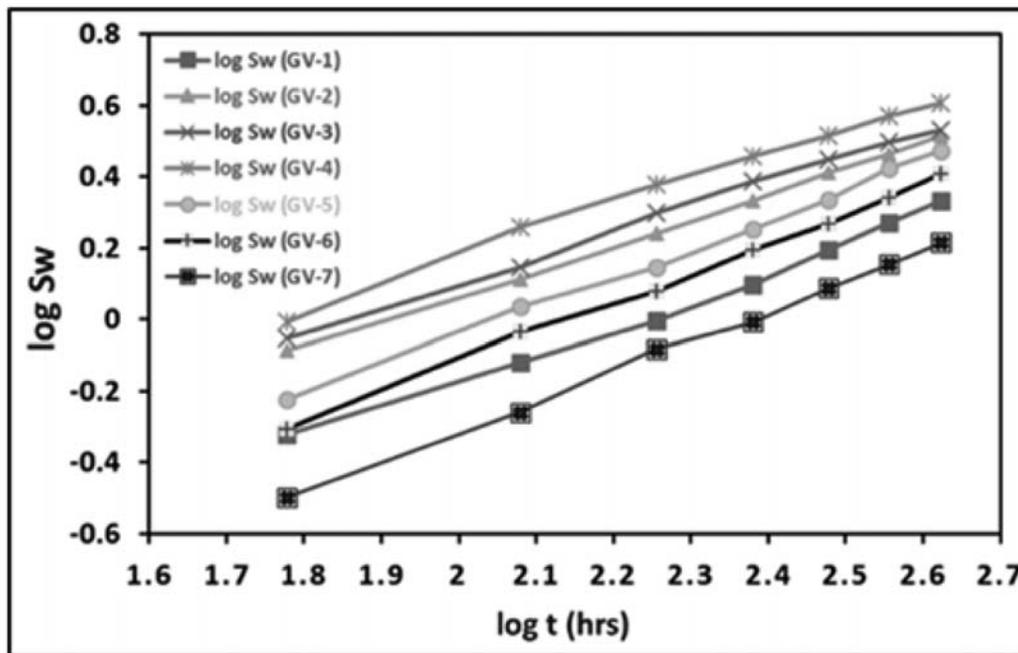


Fig. S4. Log plot of S_w versus time (t) for DN hydrogels obtained with different amount of MBA crosslinker

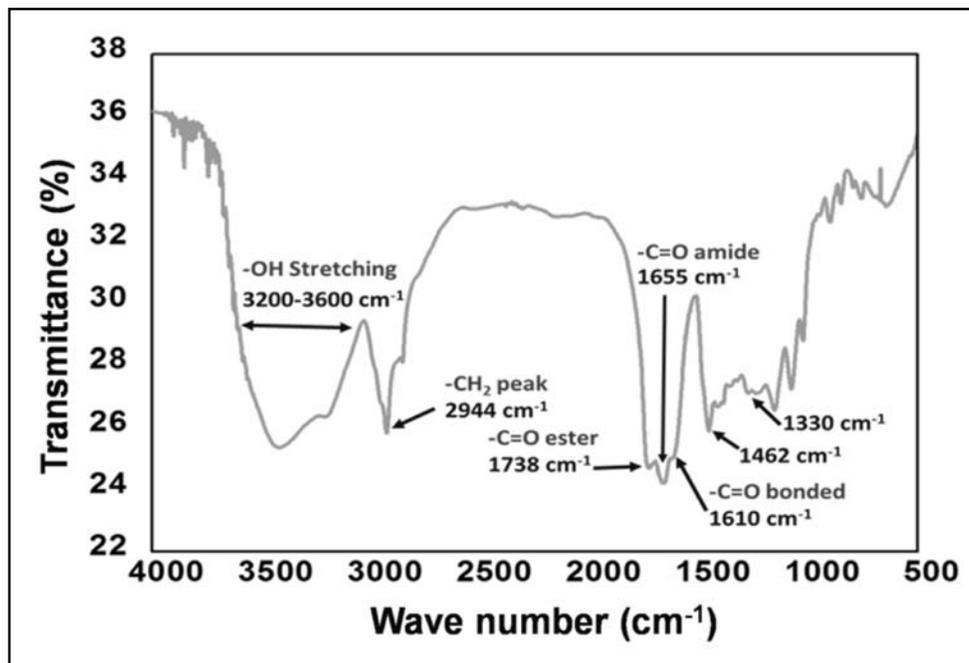


Fig. 2. FTIR spectrum of a double network hydrogel sample (GVC-4) obtained using 0.1 wt % crosslinker concentration

3.3 Swelling Properties of DN Hydrogels

To investigate the swelling behavior of synthesized DN hydrogels firstly a dry cylindrical sample was taken and its height and diameter were measured with the help of vernier scale. The hydrogel sample was having 10.88 mm height and 12.43 mm diameter (Fig. S2). The cylindrical dry sample was then poured into distilled water at room temperature. After 72 hours, the sample absorbed maximum amount water and attended equilibrium swelling. The diameter of swollen hydrogel sample was measured to be 20.50 mm and the height 17.69 mm. Thus there was an increase in volume due to swelling from 1319.60 mm³ to 5835.86 mm³ which indicated the increment of 342.24 % volume.

3.3.1 Effect of Crosslinker Concentration on Swelling Properties

The study of effect of crosslinker concentration on the swelling properties of DN hydrogel was carried out quantitatively by gravimetric method. The weight of a swollen hydrogel sample was taken at 1 hr interval and after removing the surface water by gently wiping with filter paper. It is carried out until no change of weight of the swollen hydrogel sample was observed. A plot of degree of swelling vs time is shown in Fig. 3 (a). The minimum time taken to attain optimum swelling for a sample is considered as the time of equilibrium degree of swelling.

The equilibrium degree of swelling is the optimum weight of a hydrogel and no further

increment in weight of the hydrogel was observed. It is measured from the plot. The equilibrium degree of swelling is plotted against the crosslinker concentration [Fig. 3 (b)]. Swelling was increased with the amount of crosslinker (MBA) and maximum swelling of 624% was observed for GVC-4 sample which was prepared with 0.1 wt% MBA. However,

further increase of MBA concentration caused to decrease of swelling of hydrogels because at higher concentration of crosslinker, the network became highly crosslinked, so pore size was also started to decrease accordingly. The minimum swelling of 287% was observed at maximum amount of crosslinker concentration i.e., 1.5 wt% (GVC-7).

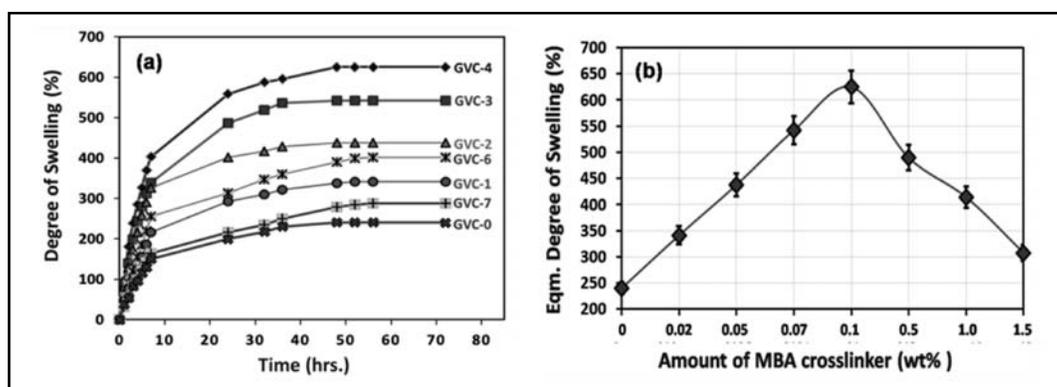


Fig. 3. (a) The plot of degree of swelling (%) with respect to time (GVC-5 was not shown because of its overlapping with other curves) and (b) variation of equilibrium degree of swelling with respect to crosslinker concentration

Initially, swelling was increased with increasing MBA concentration upto 0.1wt%. It apparently contradicts the fact that with increasing crosslinker concentration crosslink density would increase resulting tighter hydrogel structure and lowering of hydrogel swelling^[13]. But in case of using N,N'-methylenebisacrylamide (MBA) which is a hydrophilic monomer, its chemical nature also plays significant role on the swelling of hydrogels. The initial increase of swelling of such hydrogels is a result of such hydrophilic nature of MBA^[52]. It is also reported that swelling increased with increasing poly(vinyl alcohol) contents in chitosan/PVA hydrogels as a result of increasing hydrophilic hydroxyl

group concentration in the same order^[13]. Thus the results obtained in our study corroborated with the reported results.

Beyond 0.1 wt% MBA concentration, swelling was started decreasing which is due to increasing crosslink density in the DN hydrogels. The increasing crosslink density lowers the average molecular weight between crosslinks and it curtails the free volume accessible to the penetrate water molecules. Also at higher amount of MBA, the hydrogel network chains become very inflexible and rigid. Thus the swelling decreased with increasing concentration of crosslinker beyond 0.1 wt% of MBA.

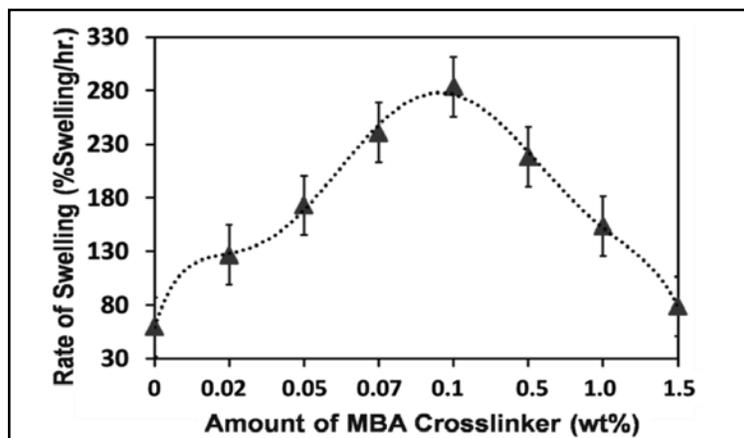


Fig. 4. Rate of swelling with respect to amount of MBA crosslinker

3.3.2 Effect of Crosslinker Concentration on the Rate of Swelling

In this investigation, the crosslinker concentration was slowly increased for the P(AM-co-HEMA) second network of the DN hydrogels (PVA-Borax first network was kept constant). The rate of water absorption is one of the important indices to know the performance of hydrogel materials to absorb water in speed. Again the rate water absorption is relatively fast at the early stage of swelling and then gradually decreased until it reached a stable state. So it was measured from the early swelling behavior of the hydrogels using Eq. 3. The initial degree of swelling was plotted against time (only upto 7 hrs.) (Fig. S3). It may also be calculated from the slope of each plot. The plot of rate of swelling (% swelling/hr) versus crosslinker concentration is shown in Fig. 4.

Rate of swelling of a hydrogel is affected by numerous factors such as molecular nature, surface structure, porosity, size and shape of particles. It is observed that rate of swelling

initially increased with the crosslinker concentration which may be because of the hydrophilic nature of MBA crosslinker [52]. On the other hand, with the increase of crosslinker concentration, the network structure becomes tighten due to increase in crosslink density which decreases free volume available for the penetrated water molecules. As a result of these two opposite effect, the rate of swelling attained an optimum value at 0.1 wt% MBA concentration (GVC-4). On the other hand, further increase of MBA crosslinker concentration, rate of swelling was decreased beyond it due to formation of more rigid crosslinked structure of the DN hydrogels.

3.4 Swelling Kinetics

To study the swelling kinetics, a cylindrical hydrogel sample was poured into distilled water at 25 °C. The water molecules were started diffusion into the material and the sample was started to increase its volume (weight) with time by uptake of water which was measured gravimetrically until and the swollen hydrogel

attained equilibrium swelling state. Eq. 6 was used to study the swelling kinetics of the double crosslinked hydrogels reported here. The logarithm plot of water uptake (S_w) versus time is shown in Fig. S4. The values of swelling characteristic constant, 'K' and diffusional exponent, 'n' were determined from the intercept and slope of the plot and are given in Table 2.

The mode of water transport into hydrogel network is governed by chemical nature, structure, porosity and surface characteristics of hydrogel materials. The diffusion exponent (n) indicates such water diffusion into hydrogels. If the value, $n \leq 0.5$, it is called Fickian swelling (or diffusion controlled swelling) and the rate of solvent diffusion is slower than the rate of the

relaxation of the polymer chains. When $n=1.0$, it is non-Fickian swelling (or relaxation controlled swelling) in which the rate of solvent diffusion is more than the rate chain relaxation. Again, in a case where the rates of diffusion of solvent molecules into polymer network and relaxation of polymer chains are comparable, it is called anomalous diffusion and the value of 'n' lies between 0.5 and 1.0. The values of 'n' obtained for all the DN hydrogels reported here lie within this range representing non-Fickian anomalous swelling behavior of the DN hydrogels (Table 2). The absolute values of 'K' and 'n' were decreased with increasing the concentration of MBA crosslinker up to 0.1wt% whereas above this concentration the values were started to increase and saturated (Fig. 5). So this 0.1wt% MBA concentration in this DN

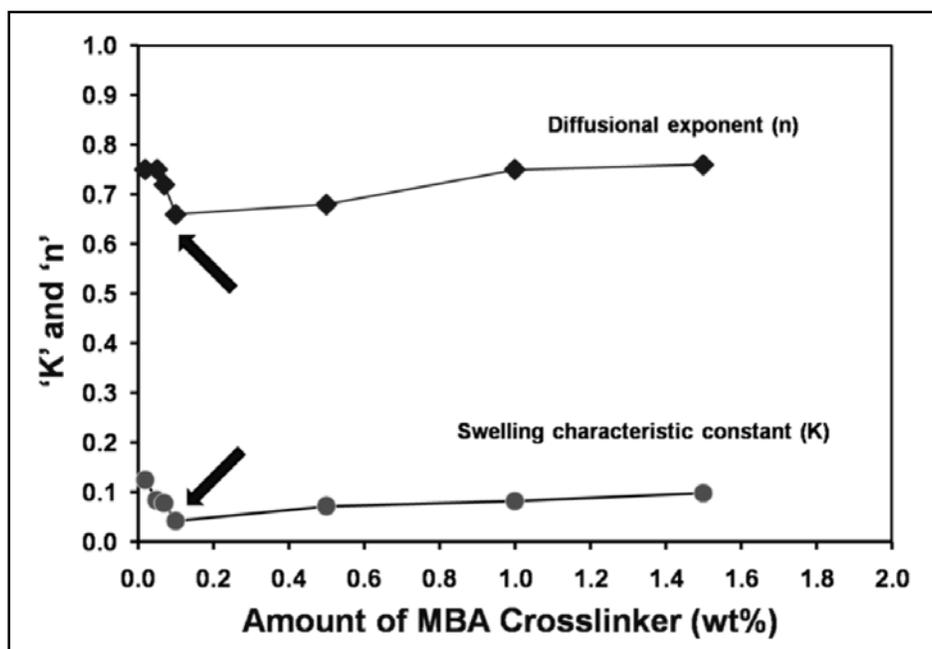


Fig. 5. Variation of swelling characteristic constant and diffusional exponent with the concentration of MBA crosslinker

TABLE 2. Characteristics Parameters of Swelling Kinetics of DN Hydrogels

Sl. No.	Sample Code	Gel Fraction (G ₁) (%)	Characteristic constant 'K'	Log K	Diffusional Exponent 'n'
1.	GVC-1	86.24	0.125	-0.90309	0.75
2.	GVC-2	87.12	0.084	-1.07572	0.75
3.	GVC-3	87.87	0.078	-1.10791	0.72
4.	GVC-4	88.10	0.042	-1.37675	0.68
5.	GVC-5	90.23	0.072	-1.14267	0.70
6.	GVC-6	91.87	0.082	-1.08619	0.75
7.	GVC-7	92.56	0.098	-1.00877	0.76

hydrogel system may be considered as the critical MBA crosslinker concentration for swelling where the values of diffusional exponent (n) is 0.68 and swelling characteristics constant (K) is 0.042. This may be because of the hydrophilic effect of MBA crosslinker along with

its crosslinking effect. However, it is to mention here that the diffusional exponent remained almost the same for the same DN hydrogel system with 0.1wt% MBA concentration although the composition of the second network (AM and HEMA) was varied [33].

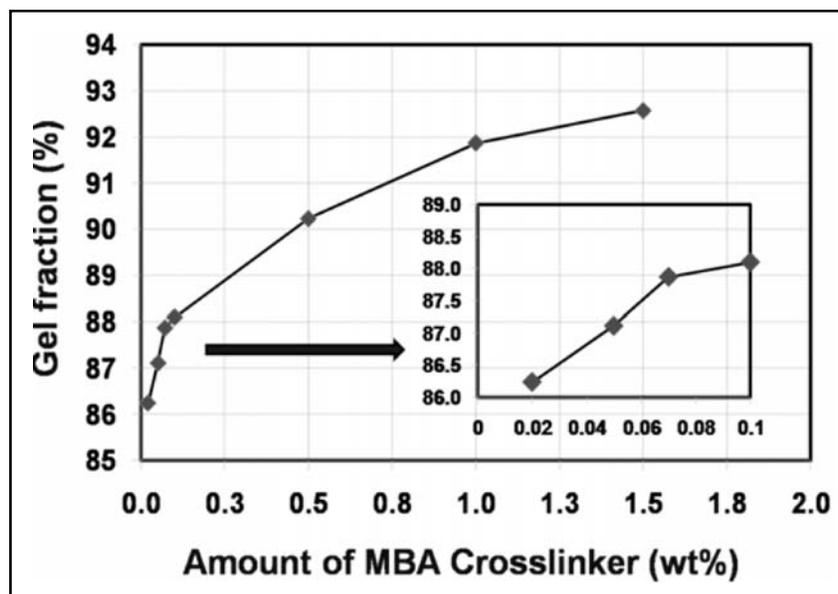


Fig. 6. Variation of gel fraction (%) with crosslinker concentration

3.5 Gel Fraction (G_f)

Sol-gel fraction analysis of the DN hydrogels obtained with different crosslinker concentration was carried out to determine the uncrosslinked and crosslinked fraction of the polymers. The gel fraction (%) is plot against the crosslinker concentration (Fig. 6). It was observed that gel fraction (G_f) increased with the increase of concentration of MBA in the composition of DN hydrogels. As more crosslinker is taken, the more polymer chains are interlinked chemically which leads to the increase of gel fraction. This is obvious and similar results were also reported [53].

3.6 Network Parameters

It is well established that the nature and concentration of crosslinker highly influence the polymer network parameters, swelling characteristics and mechanical properties [54-56]. In general, the crosslinker concentration is directly related to the density of crosslinks in the hydrogels. Hydrogels obtained with low crosslinker concentration may have low crosslink density and hence high swelling capacity. On the other hand, hydrogels formed at high crosslinker concentration should possess high crosslink density which causes a decrease in the distance between crosslink points and thereby lowering the swelling capacity.

In this investigation, the swelling of hydrogels was increased initially with crosslinker concentration up to 0.1wt% MBA which is because of the hydrophilic nature of the MBA crosslinker. However, after this MBA concentration swelling was started to decrease because of the crosslinking effect. The network parameters for the hydrogels

were measured based on the hydrogel swelling as described in Section 2.3.5. The results are given in Table 3. The networks parameters like the crosslink density (CLD), average molecular weight between crosslinks (M_c), mesh size (ξ) and polymer-water interaction parameter (χ) were calculated based on the experimental findings of swelling measurements (Table 3). The polymer volume fraction (V_p) was calculated with the help of swelling ratio (q_w) and polymer density (ρ) using Eq. 9. The polymer-water interaction parameter (χ) was calculated using V_p with the help of Eq. 10. The M_c was calculated with using V_p , χ , V_m and ρ with the help of Eq. 8.

The plots of network parameters like CLD, average molar mass between crosslinks and mesh size with respect to crosslinker concentrations are shown in Fig. 7. It is clear that with increasing amount of MBA from 0.02 wt% to 0.1 wt% (from sample GVC-1 to GVC-4), average molecular weight between crosslinks (M_c) as well as mesh size (ξ) were increased. This effect is accompanied with the decrease in crosslink density (ρ_c) as a result of increasing swelling ratio in this direction because of hydrophilic MBA crosslinker [Fig.10]. However, with further increase in crosslinker concentration beyond 0.1 wt%, the crosslinking effect was predominated, thus crosslink density was increased; whereas, M_c and ξ were decreased accordingly from 0.1 wt% to 1.5 wt% crosslinker concentration (from sample GVC-4 to GVC-7). This is because of the fact that swelling ratio was started to decrease and volume fraction was increased due to high crosslink density and rigid structures in the same direction of increase of crosslinker concentration.

TABLE 3. Network Parameters of DN Hydrogels

Sample Code	Polymer density (ρ) (gm/cc)	Swelling ratio (q_w)	Volume fraction in swollen hydrogel (V_p)	Polymer-water interaction parameter (χ)	Average molar mass between crosslinks (M_c)	Crosslink Density (CLD)	Mesh Size (ζ) \AA
GVC-1	0.9927	4.412	0.22617754	0.575393	815.7737	0.174723	19.01178
GVC-2	1.1103	5.379	0.16917282	0.556391	2299.7409	0.061983	53.59145
GVC-3	1.2013	6.422	0.13196045	0.543987	5419.1063	0.026305	126.27662
GVC-4	1.2846	6.249	0.10978694	0.536596	10255.8901	0.013901	238.94786
GVC-5	1.1536	5.197	0.16976300	0.556588	2363.3198	0.060386	55.008912
GVC-6	0.929	5.142	0.20467278	0.568224	1051.5758	0.135887	24.445155
GVC-7	0.8683	4.078	0.27036186	0.590121	399.9050	0.357782	9.2844209

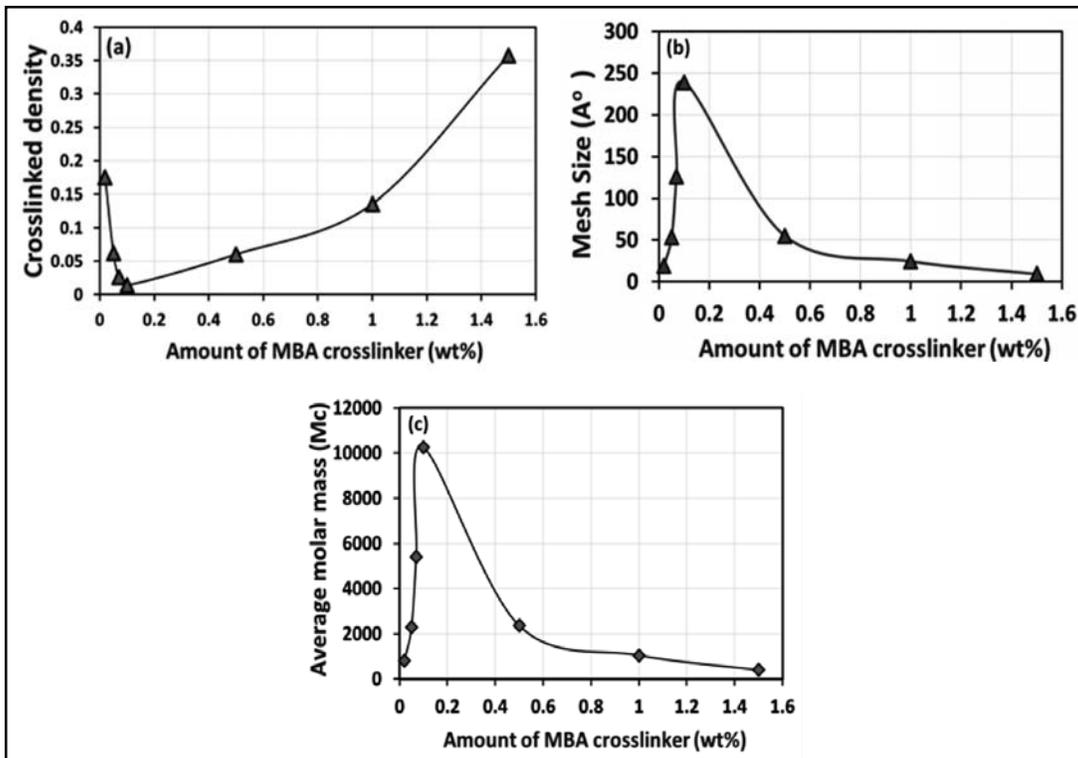


Fig. 7. Plots of different network parameters versus amount of crosslinker: (a) crosslink density, (b) mesh size and (c) average molar mass between crosslinks

The χ parameter is used as an indicator to understand the interaction between polymer and solvent. It was reported that the greater the values χ , weaker is the interaction of polymer and solvent. The values of χ decreased with increase of MBA concentration up to 0.1 wt% in the DN hydrogels. This lowering of value indicates the favorable interaction. This is thus supports the effect of hydrophilic nature of the chains because of MBA and strong interaction between polymer and solvent [57-59]. The variation of the interaction parameter with content of MBA is the evidence that χ is crosslinker

concentration dependent parameter and all other network parameters are interconnected.

3.7 Mechanical Properties of DN Hydrogels

It is well known that the crosslinking increases the mechanical properties of polymers^[60-61]. The mechanical properties of hydrogels were measured and the results are given in Table 4. These indicate that the mechanical properties are highly dependent on the crosslinker concentration which is obvious^[60-61]. Hydrogel strength and modulus were controlled by

TABLE 4. The mechanical properties of DN hydrogels obtained with different crosslinker concentration

Sample Code	Conc. MBA (wt%)	Stress (kPa)	Strain (%)	Modulus (kPa)
GVC-3	0.07	32.6	112	29.1
GVC-4	0.10	57.5	148	38.8
GVC-5	0.50	99.5	252	39.3
GVC-6	1.00	149.3	271	54.9
GVC-7	1.50	180.3	278	64.7

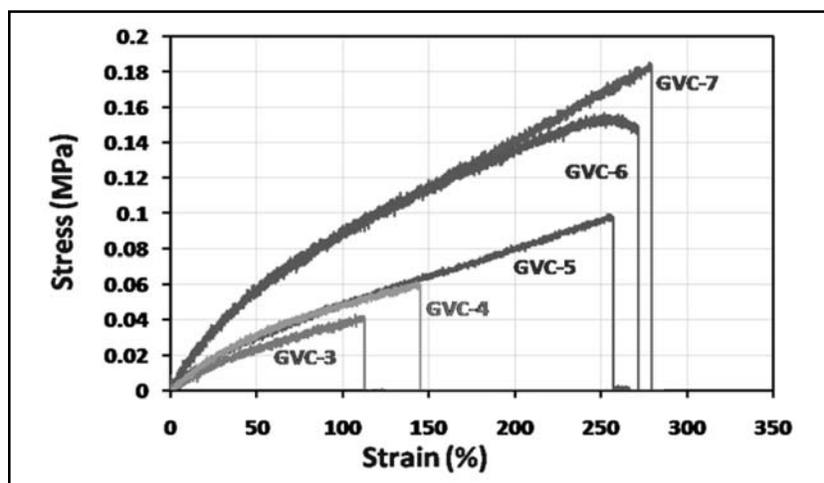


Fig. 8. Stress-strain curves of DN hydrogels obtained at different crosslinker concentration

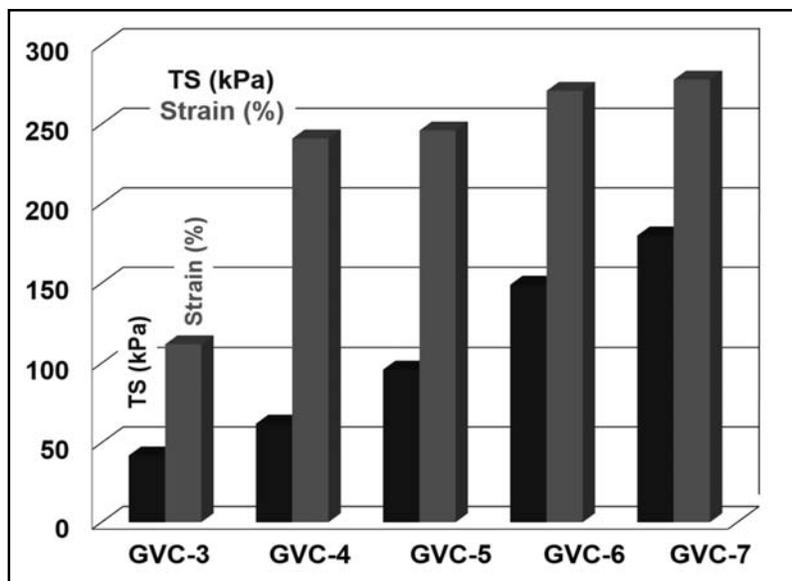


Fig. 9. Variation of tensile strength (kPa) and strain (%) with MBA crosslinker concentration

varying crosslinker length^[60]. A higher MBA content generally led to a stronger and harder poly(acrylic acid-co-methyl methacrylate) hydrogels^[61]. At the same time, swelling capacity was decreased as the MBA concentration increased between 0.5% and 2%, and remaining constant beyond this range^[61]. The tensile strengths of various DN hydrogels obtained with different amount of crosslinker concentration are shown in Fig. 9. As the crosslinker concentration was increased, the crosslink density was increased and as a result of it the tensile strength of the hydrogels was also increased.

4. CONCLUSION

The effect of MBA crosslinker concentration on the properties of double network (DN) hydrogels composed of P(AM-co-HEMA) as the second network and poly(vinyl alcohol)-

borax complex as the first network was investigated. The swelling capacity increased at the very early stage with increasing crosslinker concentration up to 0.1wt% because of the hydrophilic nature of the crosslinker, N, N'-methylene bisacrylamide (MBA). However, beyond this concentration of 0.1wt% MBA, swelling capacity decreased as the MBA concentration was increased because of the crosslinking effect. DN hydrogels formed at high crosslinker concentration possess high crosslink density which causes a decrease in the distance between crosslink points, mesh size and thereby lowering the swelling capacity. All the network parameters such as crosslink density (CLD), molar mass between two crosslinks (M_c), mesh size(ξ), polymer-solvent interaction parameter(χ) and polymer volume fraction in swollen state (V_p) were varied with

different crosslinker concentration. Such hydrogels exhibited non-Fickian anomalous swelling behavior. Diffusional exponents (n) of such hydrogels were observed to be between 0.5 and 1.0. The diffusional exponent (n) and also swelling characteristics constant (K) were also observed to be minimum at 0.1wt% MBA concentration. This MBA concentration in this DN hydrogel system may be considered as the critical crosslinker concentration for hydrogel swelling. However, the gel fraction and mechanical properties of the DN hydrogels increased throughout with the increase of crosslinker concentration of the DN hydrogels.

Supporting Information

Supporting information may be found in the online version of this article.

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