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Swelling and Mechanical Properties of Polyelectrolyte Hydrogels: Effect of Crosslinker

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Abstract

One of the fundamental approaches in controlling the swelling and mechanical characteristics of hydrogels involves modification of polymer network system through crosslinking. In this study, the crosslinking density in poly(acrylic acid) (PAA) hydrogels has been varied with a goal to investigate how certain swelling parameters and mechanical properties of polyelectrolyte hydrogels get influenced by their network structure; in specific, the stiffness of the bulk network of the hydrogel. PAA hydrogels were successfully prepared via UV polymerization using variable concentration of the cross-linker (0.02, 0.04, and 0.06 mol% with respect to monomer), *N*,*N*'-methylenebisacrylamide. After equilibrium swelling of the synthesized gels in water, all the polyelectrolyte hydrogels showed significant water absorption with their equilibrium water content in the range of 83-90%. The mechanical parameters of the prepared PAA gels were then determined from tensile tests. The PAA hydrogel synthesized from the highest crosslinker content was found to exhibit the highest elastic modulus of about 34 kPa. The extent of stress introduced inside the bulk hydrogel during crosslinking was also evident from their thermogravimetric studies, which showed a distinct pattern. The significant capacity for both water absorption and extensibility of the synthesized PAA hydrogels gives an indication of their potential in stress-bearing applications, especially biological ones.

Keywords: Hydrogel, swelling, crosslinking, polymer network, mechanical behavior

I. Introduction

Gels are three-dimensional polymer network which swell by absorbing solvents and can retain them within their interstices. Due to their sensitivity to various stimuli, such as pH[1], temperature[2], light[3], and electric and magnetic fields[4], they have been the topic of research in recent times. Among them, superabsorbent hydrogels are of immense interest as they are environmentally compatible, allow use of ubiquitous stimulus like water and are processible into smart composites with inorganic components. As soft materials, they have been incorporated as sensors or actuators in aqueous systems[5-8] and biomimetic materials-tissue engineering scaffolds[9-10] for self-healing applications. Superabsorbent properties have been shown by hydrogels synthesized from acrylic acid and its derivatives as monomers. Poly(acrylic acid) (PAA) is a polyelectrolyte with anionic carboxylic group as the repeating unit. During gelation, the self-assembly of polymer chains is dictated by hydrophobic association among the vinyl chains, and hydrogen bonding and ionic interaction among the carboxyl groups. The groups being readily ionizable, the protonation-deprotonation equilibrium controls the conformation of polymer network. Since the $_{p}K_{a}$ value of PAA-based hydrogels ranges from 4.5 to 5.0, the ionization of the carboxylic acid group functionality causes them to swell extensively at pH 7.4[11]. Apparently, gel network structure has significant effect on their swelling kinetics[12-14]. There are several approaches to design the polymer network comprising polymers of different nature and sometimes the way they are allowed to have interaction with each other[15-16]. Crosslinking is a precondition of gelation and is usually accomplished via covalent bond formation as well as by other secondary forces like hydrogen bonding. Crosslinking either way has been used to address the issue of low mechanical strength in highly absorbent gels based on acrylic and acrylamide monomers. Enhancement of mechanical properties without any compromise of the swelling ability of gel is sometimes a concern, though desirable. This has been possible to achieve by introducing secondary crosslinking points utilizing supramolecular interaction. For instance, self-healing high strength PAA hydrogel has been synthesized by crosslinking the polymer chains with Fe^{3+} ions which significantly ensures sacrificial energy dissipation[17]. The self-healing ability of PAA has also been attempted to improve by enhancing dynamic hydrophobic association with micellar units. Synthesis of composite PAA hydrogel utilizing triple physical crosslinking by coordination, hydrogen and electrostatic interaction is demonstrated[18]. Dually crosslinked polyampholyte gels are reported with better mechanical properties even by at the cost of the swelling properties[19]. Conformational changes of polymer chains can bring out events like intramolecular cyclization to affect swelling and mechanical properties[20]. Under applied stress, the interaction among the immobilized charges on the chains of PAA is supposed to change and thus swelling abilities are redefined.

The biocompatible nature and self-healing ability are important features of PAA for *in situ* applications. Conductive polymers like polyaniline (PAni), polypyrrole (PPy), and poly(3,4-ethylene dioxythiophene) (PEDOT) even though have been investigated for this purpose, their mechanical properties are not sufficient for *in situ* stress

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bearing applications. In this regard, the intrinsic conductivity of PAA gels may provide additional advantage if it can be systematically controlled with the tensile strength. The self-healing properties of PAA hydrogels were enhanced by introducing dynamic crosslinking sites[21-22]. The concern of poor mechanical strength of PAA has been well addressed in their fabrication as composite dual or multinetwork hydrogel with different natural and synthetic polymers[23-26]. An ideal combinatory approach to improve both mechanical properties and self-healing abilities should involve the study of various interaction in the gel network and the factors that have influence upon them.To our knowledge, no such investigation has yet been conducted to have the fundamental understanding regarding failure of this polyelectrolyte gel. The direct effect of pH on the swelling characteristics of PAA hydrogels, however, has been thoroughly addressed to date[27-29]. There is ambiguity whether a crosslinker only itself can influence the swelling and mechanical properties. If it is possible to modify the gel network to an extent by tuning the network with crosslinkers, sufficient mechanical properties can be achieved even in its most swollen condition.

In this work, PAA hydrogels were synthesized by photopolymerization using *N, N*'-methylenebisacrylamide and α-ketoglutaric acid as crosslinking agent and photo initiator, respectively. Our aim is to present a fundamental view of the failure properties of PAA hydrogels under tensile stress and to justify conventional approaches used for facilitated energy dissipation during deformation. The swelling properties of PAA hydrogels were studied by assessing water content and gel fraction individually. Mechanical characteristics have been assessed in terms of Young's (elastic) modulus, fracture stress and strain to decipher the effect of the crosslinking density; i.e. stiffness of the polymer on the properties.

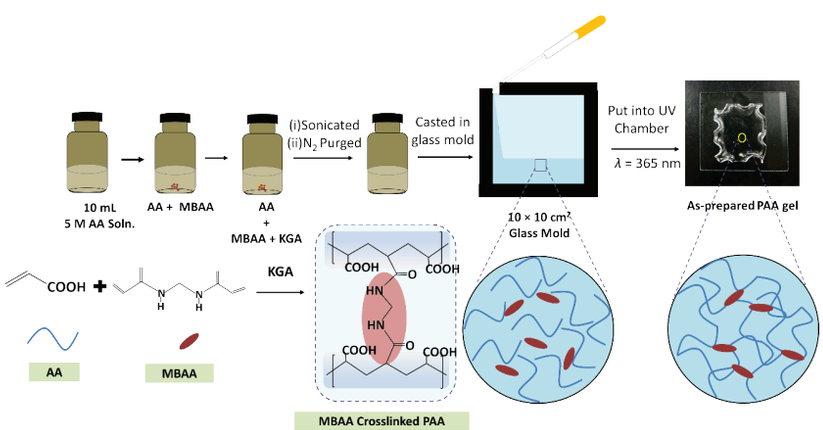
II. Materials and Methods

Materials

Pure (~99%) acrylic acid (AA) (MW ~72.04 g/mol), stabilized with 0.02% hydroquinonemonomethyl ether (inhibitor) was obtained from Sisco Research Laboratories Pvt. Ltd., New Mumbai, India. *N,N*'-methylenebisacrylamide (MBAA) and α-ketoglutaric acid (KGA) were obtained from Sigma-Aldrich, China. All materials were used as received, without any further purification and stored in the refrigerator before use. All the aqueous solutions were prepared with double-distilled deionized (DI) water (conductivity ~0.055 μS.cm^{-1} at 25.0°C) obtained from HPLC grade water purification system (BOECO, Germany).

Fabrication of PAA Hydrogel Film

PAA hydrogels were obtained by free radical copolymerization of AA monomers with varying concentrations of 0.02, 0.04, and 0.06 mol% with respect to the monomer concentration, AA. All the gels in this work were synthesized using the same monomer concentration, i.e. 5 M. Pre-calculated amount of MBAA was weighed and added directly to the monomer aqueous solution for synthesis of the PAA gel of each composition. Photoinitiator, KGA was also added similarly to the gel precursor solution at a concentration of 0.01 mol% with respect to the AA concentration. The precursor mixture was then sonicated followed by nitrogen gas bubbling to remove any dissolved oxygen. The purged solution was then injected carefully into a premade glass mold of dimension 10 cm×10 cm×0.1 cm and separated by silicone spacer of thickness 1 mm, carefully ensuring the absence of any air bubble in the precursor solution inside the mold. The mold containing the gel precursor solution was then introduced into a UV chamber with four UV lamps (λ = 365 nm) as the photon source with an intensity of ~15 mW/cm^2 each. The distance of the lamps from the sample was maintained as 10 cm. Irradiation of the samples was carried out for approximately 15 hours. Transparent, thin and soft hydrogels thus obtained were labeled as (PAA X-Y-Z), where X denotes the molar concentration of monomer AA (labeled as 5) in the precursor solution, Y labeled as 2, 4, or 6 denotes the 0.02, 0.04, or 0.06 mol% concentration, respectively, of crosslinker MBAA (with respect to AA), and Z is the mol% concentration of initiator KGA (labeled as 1; with respect to AA). Schematic representation of the whole protocol has been shown in **Scheme 1**.



Scheme 1. An illustration showing the preparation protocol of PAA hydrogels

Characterization

Swelling Properties

The as-prepared PAA gels of thickness 0.1 cm with different extent of crosslinking were cut into several pieces of two different shapes: rectangular with dimension 10 mm×10 mm and circular with diameter 1.2 cm. Each of the cut pieces of gels was then kept in 20 mL of DI-water in a container and allowed for swelling. The DI water was preheated at different temperatures, namely 30, 40, 50, 60, and 70 °C for studying the effect of temperature on the swelling. The swollen weight of each gel was measured at different times and the equilibrium swelling was ensured when a constant weight of the gel pieces was obtained. The weight of each gel sample was recorded before and after swelling (surface-adhered water was removed by wiping). Swelling ratio of the different gel samples was then calculated from their length and width for rectangular shaped gels and from, diameter and thickness for circular shaped gel, both before and after swelling. All the synthesized PAA gel samples showed distinct size expansion while maintaining the initial shape. The effect of crosslinker concentration on the water absorption capacity was observed for PAA 5-4-1 and PAA 5-6-1 hydrogels by calculating the degree of swelling (Eq.1) as follow-

$$\text{Degree of Swelling} = \frac{x_t}{x_0} \qquad \text{(Eq. 1)}$$

where x_t and x_0 are the measured values of dimension at time t and before swelling, respectively.

Water content and gel fraction of the synthesized PAA hydrogels from three different crosslinker concentrations was measured by gravimetric method. About a 5 mm×5 mm piece was cut from each swollen hydrogel. The weight of each cut sample was measured before swelling. After swelling for a constant period (48 hours), gel samples were weighted wiping off the water adhered to its surface.The gel samples were then subjected to heating on a pan preheated at about 80 °C until complete evaporation of water from the gel samples and weighed again. Eq. 2 and Eq. 3 was then used to calculate the equilibrium water content and gel fraction of the PAA hydrogels respectively.

$$\text{Equilibrium Water Content (\%)} = \frac{W_s - W_d}{W_d} \times 100 \qquad \text{(Eq. 2)}$$

$$\text{Gel Fraction (\%)} = \frac{W_d'}{W_d} \times 100 \qquad \text{(Eq. 3)}$$

where W_s and W_d are the weight of the hydrogel at swollen and initial dry states, respectively. W_d' indicates the constant weight of dry hydrogels. Both swelling and gel fraction experiments were repeated three times and the results are expressed.

Thermal Stability

Thermogravimetric analyses as mean standard deviation of the synthesized swollen hydrogel samples were carried out in the presence of O_2 using a thermogravimetric analyzer (TGA/DTA 7200), Hitachi, Japan. For this, samples were prepared by cutting a small homogeneous portion of the swollen gel and wiping out the water adhered to the surface. The gel samples were then heated from 30 to 550 °C on aluminum pans at a constant heating rate of 10 °C/min. Approximately 3–5 mg of sample was taken on an aluminum pan for each measurement.

Mechanical Properties

The tensile strength and Young's (elastic) modulus of three PAA gels were determined using a Universal Testing Machine (Test Resources, 100P250-12 System). Equilibrium swollen hydrogel samples at room temperature were taken for this purpose and cut into rectangular shape with a gauge length of 40 mm and width of 10 mm with scissors carefully, preventing unwanted fracture close to the clamping region and avoiding grip slippage. Both ends of the rectangular shaped samples were then clamped and subjected to tensile stretching using a crosshead speed of 100 mm/min, and the tensile stress-strain curves were recorded. Three runs were recorded for each sample. About five portions taken from different regions of the swollen gels were subjected to the test for any sample in order to have precision in collected data.

III. Results and Discussion

Synthesis of the PAA Hydrogels

PAA hydrogels were successfully synthesized using free radical mechanism in three different concentrations. The hydroxyl free radicals generated from water reacted with C=C double bond of AA and MBAA[30-31]. The free radicals of AA participated are polymerized into PAA while MBAA free radicals connected their long chain to form stable 3D network of hydrogels. After the irradiation is completed, the glass mold was allowed to approach room temperature, followed by their carefully separation from the glass slides with the help of a plastic spatula. Transparent and soft hydrogel film without any significant deformation was obtained (**Fig. 1(a)**). The dry gel was highly stiff with sticky surface. Samples for swelling experiments are being cut at definite shapes from the dry gel (**Fig. 1(b)**). The as-synthesized PAA gels were then immersed in an ample amount of distilled water for equilibrium swelling. Gels were preserved in DI water for swelling and mechanical characterization. The water was changed at a regular interval of 2 days until the characterizations in order to remove the unreacted monomer and sol fraction of the polymer.

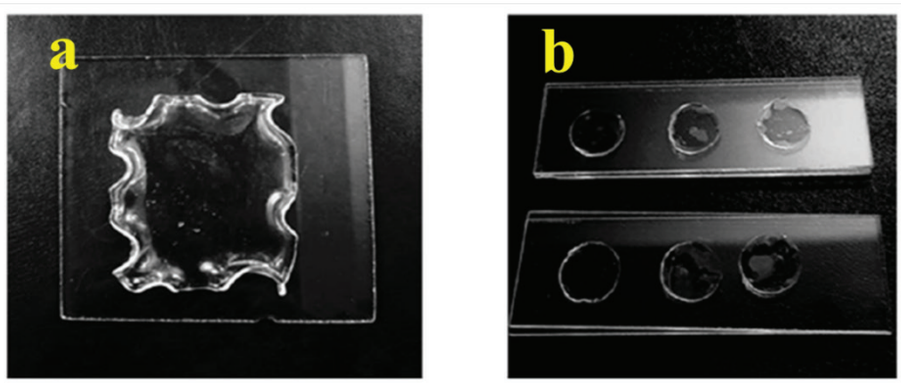


Fig. 1.(**a**) Hydrogel after removing from the glass mold and (**b**) homogeneous gel samples cut from the synthesized gel

Thermogravimetric Analysis

Thermograms of the PAA hydrogels provided information about both the structure of the hydrogel network and also their ability to absorb water (**Fig. 2 (left)**. Mass loss occurs in three consecutive steps, among which the first one is more prominent. Up to around 100 °C, the weight loss due to the loss of both free and bound water is more prominent for PAA 5-2-1, i.e. the gel sample with the lowest crosslinker concentration. The mass retained by this gel after the 1st step of weight loss was approximately 10% of the initial weight, indicating an equilibrium water content of ~90%. The water content of PAA 5-4-1 and PAA 5-6-1 hydrogels on equilibrium swelling were found to be ~89% and ~83%, respectively. The thermal profiles of the gels were studied in an oxygen atmosphere that ensured complete degradation of the polymer shown by the horizontal abscissa and zero residual weight.

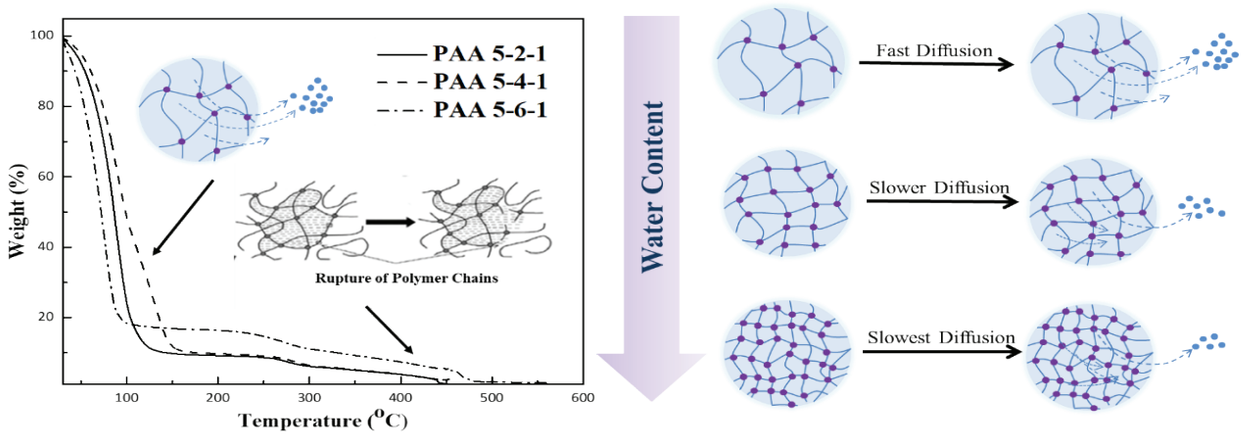


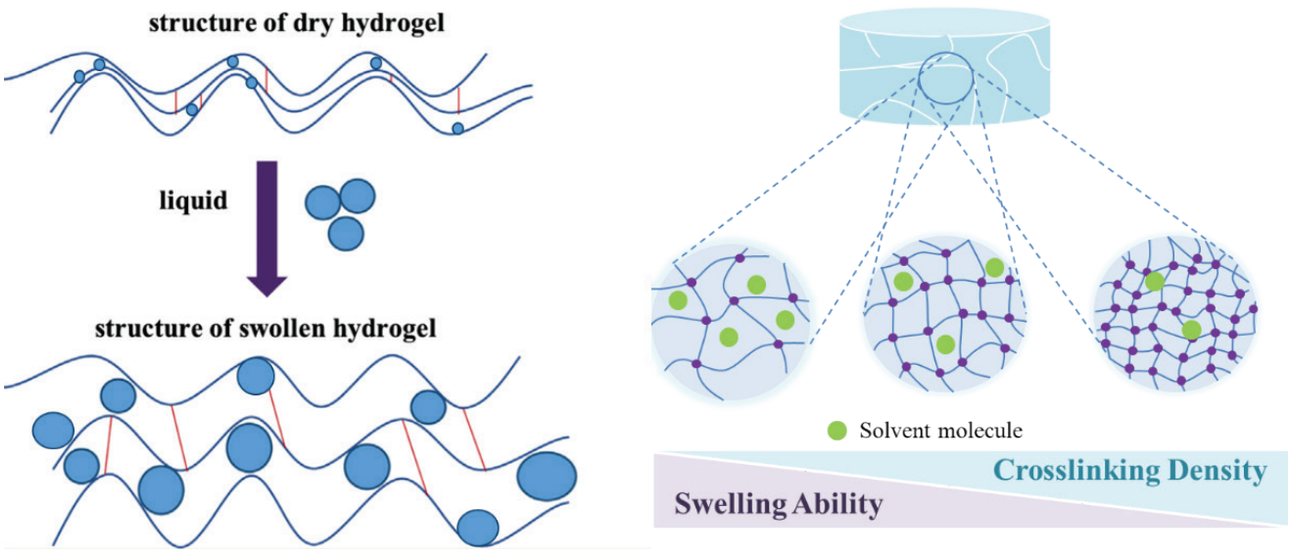
Fig. 2. Thermograms of PAA hydrogels (left) and a schematic illustration of diffusion of water from hydrogel networks of different crosslinking upon heating (right)

This observation is consistent with the theoretical aspects of the network structure of hydrogel. Hydrogels with higher crosslinker concentrations tend to have more densely located crosslinks, resulted in smaller mesh size of the polymer network (**Fig. 2 (right)**). This type of network permits the rapid initial penetration of water despite their low threshold capacity of retaining water. On the contrary, gels with larger mesh size allows sufficient penetration of water. In **Fig.1, (a)**, the second step of mass loss occurs up to 300 °C. The endothermic effect observed in this range is due to the formation of polymer anhydride by eliminating water bonded with carboxyl groups[32].The onset temperature of this dehydration step is found to be 264.2, 262.7, and 238.2 ºC for the compositions PAA 5-2-1, PAA 5-4-1, and PAA 5-6-1, respectively. The variation of onset temperatures is consistent with the polydispersity of AA chains in the gel network. Gels with higher crosslinker concentrations, i.e. PAA 5-4-1 and PAA 5-6-1, start to crosslink intermolecularly at lower temperatures. This is because the polymer chains between two consecutive crosslinking points in such networks are readily available to each other to form anhydrides. The mass loss became slower from 300 ºC and then became sharp again nearer to 450 ºC. The continuous dehydration persists in the first instants[33-34], however, ended up with the decomposition of anhydride chains[35]. The stress induced during the crosslinking process surges upon the thermal agitation,

causing the chain connectivity to be ruptured. However, the rupturing events occurs first at the crosslinking points, then to the bond connecting the repeating units of monomers. At sparsely distributed crosslinking points, most of the polymer chains show the tendency to remain as dangled chains. At higher temperatures, uncoiling of the polymer chains makes up an additional contribution to the flexibility of polymer chains. The chains are then more tolerant to heat induced pressure and are prone to complete degradation at higher temperature ca. ~550 °C.

Swelling Studies

The results of the swelling experiments demonstrated that crosslinking during the polymerization significantly affects swelling capacities of superabsorbent PAA gels. As the concentration of monomers are similar in every composition, mesh sizes were entirely controlled by the extent of crosslinking. Water molecules penetrating in as-prepared hydrogel tend to hydrate the polar groups first, in this case the carboxyl group. When the whole network became swollen, hydrophobic groups are exposed. The osmotic drive of the polymer chains allows imbibition of additional water to the network. Crosslinking produces an elastic network retraction force. **Scheme 2** illustrates the prepared hydrogels PAA 5-2-1, PAA 5-4-1 and PAA 5-6-1 containing different amounts of crosslinker.



Scheme 2. A pictorial representation of swelling of gel network (left) and increased difficulty in the diffusion of water towards the gel network with increasing crosslinking (right)

Three fundamental trends are evident from the overall swelling study which are in good agreement with the literature[36-38], however, few exceptions are noticeable. At the beginning of swelling, the swelling ratio increases dramatically and with time it tends to be slower (**Fig. 3 (a)**). In addition, both the rate of swelling and the swelling ratio (**Fig. 3 (c) and (d)**) are higher at elevated temperatures, as shown by the steep rise of the curve and also the extent of swelling after a specific time interval (**Fig. 3 (a) and (b)**. The equilibrium swelling ratio is affected by the network structure, more specifically by the crosslinking density of the polymer network. Hydrogels containing low crosslinking content are found to show higher initial swelling ratios than those having high crosslinking content.

When the gel is left in water for a significant time, it is likely for the water molecules to penetrate through the surface first. Swelling becomes possible because of a balance between the elasticity and hydrophilicity of the polymer network chains. During swelling, when the elastic tension of the polymer chains reaches a threshold, total dissolution is prevented. The portion of water that are retained by the gel network by hydrogen bonding (in this case) are commonly regarded as free water or freezable water.

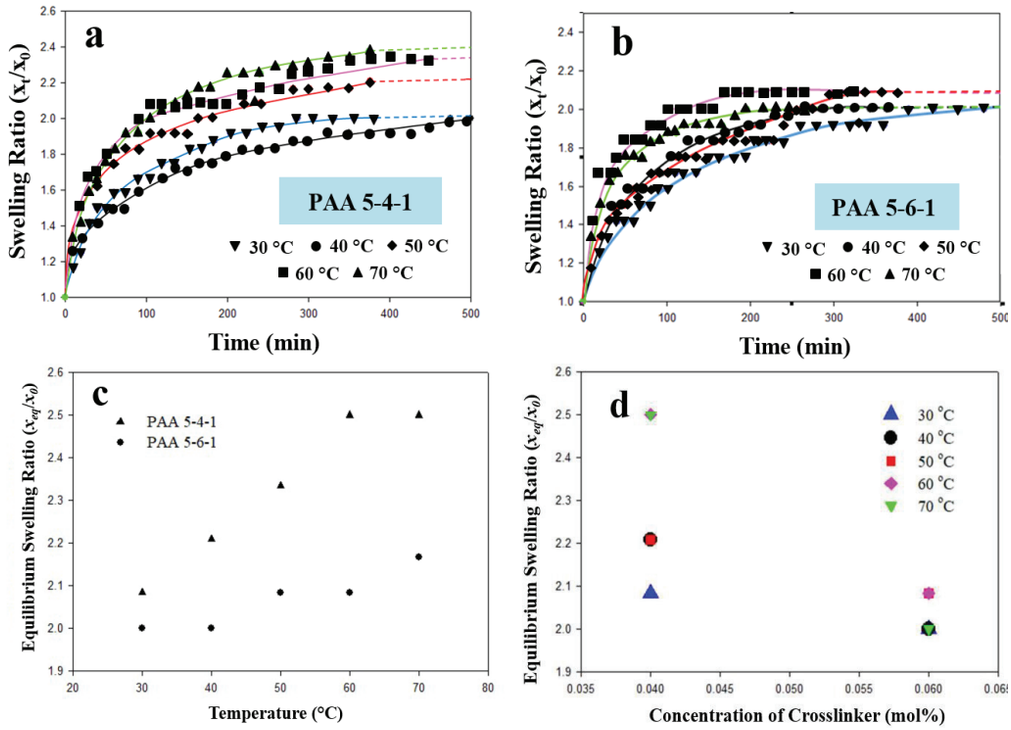


Fig. 3. Swelling ratio with time for (**a**) PAA 5-4-1 and (**b**) PAA 5-6-1. Variation of equilibrium swelling ratio with (**c**) temperature and (**d**) concentration of crosslinker

The process of losing water becomes too fast at elevated temperatures as the thermal energy is sufficient to affect a number of consequential events, e.g. the disentanglement of interpenetrated polymeric chains, destruction of hydrogen bonding or other weak hydrophobic interaction between polymer molecules, the extent of chain mobility, or the translational energy of the water molecule[39]. The extent of swelling is suppressed to some degree in the presence of densely located crosslinking in the polymer network. The decrease in equilibrium swelling ratio can be mainly attributed to the high crosslinking ratio in a unit volume. The mesh size influences the diffusivity of the network and the time scales taken to reach equilibrium for any solute diffusing through it. Dense network of polymers leads to the insufficient interaction of carboxyl groups with the excess amount of water resulting in a shorter time period required to reach the swelling equilibrium. Swelling of PAA hydrogels can also be explained as the prominence in hydrogen bond formation. As the hydrophilic groups increase, the tendency of hydrogen bond formation increases.

The results of the swelling ratio or water retention capacity of the synthesized PAA hydrogels were consistent with the value of their degree of swelling. Polymer chains in hydrogels that are chemically crosslinked or irreversibly bonded with each other possess a certain level of extensibility and flexibility. Shorter chains produced by high crosslinking density of the polymer network reaches to the maximum extensibility quickly by absorbing a small fraction of free water compared to those found in the gel network of low crosslinking density. The way the hydrogels expel water from the network is also analogous to the way they absorb water; the rate of expelling water being faster for the highly crosslinked gels compared to loosely crosslinked ones. Swelling induced deformation can be explained by gel strength, a parameter usually interlinked with the shear modulus of a swollen polymer. By reducing the amount of crosslinking agent, the gel volume can be increased. In reality, swelling of PAA along with other superabsorbent polymers are found to occur under pressure. The polymers with low gel strength tend to deform easily upon swelling, leading to undesirable gel blocking. When a superabsorbent polymer swells, the swollen particles deform and eliminate the gap between particles. Swelling parameters like equilibrium water content (EWC) and gel fraction are helpful to get the explanation. Gels with low cross-linking have low gel fraction thus exhibit high degree of swelling. However, such assumption may be misleading for polyelectrolyte hydrogels, as their swelling is controlled by conformation of polymer chains. At higher pH, the electrostatic repulsion became significant due to the deprotonation of COOH groups. The observation in our case is in good agreement with the approximation stated above. The variation of EWC and gel fraction with crosslinker concentration is shown in **Fig. 4**.

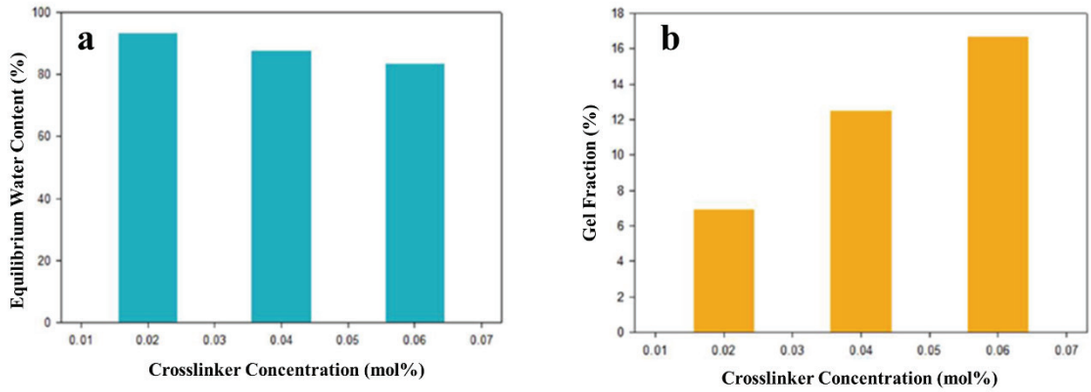


Fig. 4. Variation of (**a**) EWC and (**b**) gel fraction with varyingin feed concentration of crosslinker w.r.t. monomer

Mechanical Properties

The purpose of carrying out tensile tests was to investigate the effect of crosslinker density on the mechanical performance and differentiating the hydrogel networks in terms of strength from their distinct response upon tensile force. All the gels, irrespective of the crosslinking composition, shows elastic behavior up to small ranges of stress followed by a broad plastic deformation region and a sudden rupture upon elongation. Among them, PAA 5-6-1 and PAA 5-4-1 were found to exhibit high modulus of elasticity within a little proportional limit correspondingly with higher stiffness and lesser extensibility. Accordingly, earlier fracture of the gels is observed due to higher initial elastic modulus. It has been found that highly stretchable hydrogels are those that have well established supramolecular interactions such as hydrogen bonds, coordination bonds, electrostatic interaction, etc. within a long range of the polymer mechanisms. Crosslinking imposes arbitrary stress to the polymeric network that prevents the deformation of the gel even during swelling. When shear force is applied on the polymer, the polymer chains get mobilized by flowing over each other through a sliding mechanism. During that movement, the chain structure relieves that stress to which they are subjected to by dissipating the energy to nearer crosslinking domains. The energy is consumed in the process of overcoming the hydrophobic and other van der Waals interactions associated with physical or chemical entanglement. The energy dissipation is continued until the polymer chains approach their highest extensibility.

When crosslinking is accomplished via formation of irreversible bonding, the prolonged stress induced sliding phenomena causes the bonds to rupture with time because of lacking efficient energy dissipation mechanisms[40]. The significant rupture of bonding is anticipated from the onset of plastic deformation region when the polymers are disentangled, realigned, or form new bonds. This is the moment when polymer chains possess lesser extensibility causing them to fail to slide and align at the directions they are being stretched. Higher crosslinking density also decreases the percentage elongation at break. The different types of energy dissipation mechanisms exhibited by hydrogels is schematically represented in **Fig.5**.

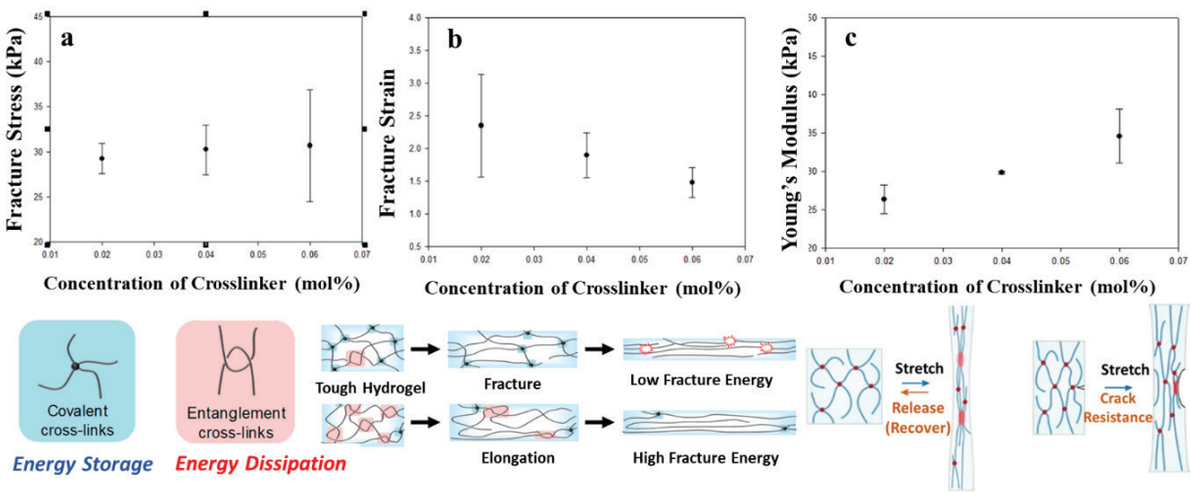


Fig 5.(**a**) Average fracture stress, (**b**) fracture strain, and (**c**) Young's modulus obtained for PAA hydrogels from three different in feed crosslinker concentrations

At the fracture point, the material physically separates, i.e. the produced strain reaches its maximum value under stress. Among the gel samples used in this work, nearly large deformation has been shown by PAA 5-4-1 and PAA 5-2-1 samples. Although PAA 5-4-1 and PAA 5-6-1 failed to depict the actual scenario, i.e. they should have shown the highest amount of fracture stress in this case, the strain values are found to follow the reverse trend in agreement.The values of fracture stress, fracture strain, and Young's modulus for all the PAA hydrogel samples are presented in **Table 1** below. The result is quite consistent; the polymer chains possess a significant amount of extensibility which can be accountable to the variation in crosslinking points in their network. Crosslinking imparts additional strength to the network by joining the polymer chains with a stable orientation; the more the crosslinker, the more would have been the force required per unit area, i.e. stress to cause the fracture. The mode of fracture is highly dependent on the mechanism of crack propagation, it can be assumed that cracks in gel samples with low crosslinking density, i.e. PAA 5-2-1 are stable (i.e. resist extension without an increase in applied stress) whereas for PAA 5-6-1 they are unstable. That means quick crack propagation, once started, continues spontaneously without an increase in stress level resulting in catastrophic deformation.

Table 1. Calculated values of fracture stress, fracture strain, and Young's modulus of the PAA hydrogel samples obtained from tensile testing

Gel Sample	Fracture Stress (kPa)	Fracture Strain	Youngs Modulus (kPa)
PAA 5-2-1	29.2 ± 2.9	2.3 ± 4.8	26.3 ± 3.2
PAA 5-4-1	30.2 ± 4.8	1.9 ± 0.6	29.9 ± 0.2
PAA 5-6-1	30.7 ± 8.7	1.5 ± 0.4	34.6 ± 6.2

A low value of initial elastic modulus also becomes remarkably interpretive during the swelling of the network for all the compositions. During swelling, the orientation hardening occurs at an earlier strain range. This result indicates that the solvent present in the polymer network causes the extension of the molecular chain, thereby resulting in the decrease in the extensibility.

IV. Conclusion

This work outlined successful synthesis of PAA hydrogels via free radical polymerization using MBAA of three different concentrations as the chemical crosslinker. The variation of some fundamental characteristics of the synthesized gels, e.g. the thermal stability, swelling behaviour, and mechanical properties were studied to understand the impact of network structure on such fundamental properties of hydrogel. Among the synthesized gels, PAA 5-6-1 and PAA 5-4-1 showed lower values of swelling rate as well as equilibrium swelling ratio, however both were higher for the gel PAA 5-2-1, i.e. the one with the lowest crosslinker concentration. Moreover, loosely crosslinked gels were characterized with greater thermal stability. The result was a clear indication of the influence of crosslinking on the thermal and swelling properties of hydrogels. Additionally, the fracture strain, i.e. extensibility of the gel was also found to differ with the extent and type of crosslinking. Highly crosslinked PAA gels are highly stiff, characterized with their higher Young's Modulus, but they tend to have lower extensibility. The extent of ionic interaction among the ionic groups in the monomer may vary at high concentrations. As the mechanisms explored so far, this would have an impact on the swelling as well as mechanical properties of the hydrogels. The aspect, however, was not explored in this study. However, it implies that through the correct optimization of gel network with suitable monomer and crosslinker concentration, the method of fabrication, and proper combination tuning of swelling and mechanical properties may be possible to achieve even from single network poly(acrylic acid) gel.

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