



# Eco-friendly method for preparation of cross-linked PVA/PAA thin films and membranes thereof for water treatment

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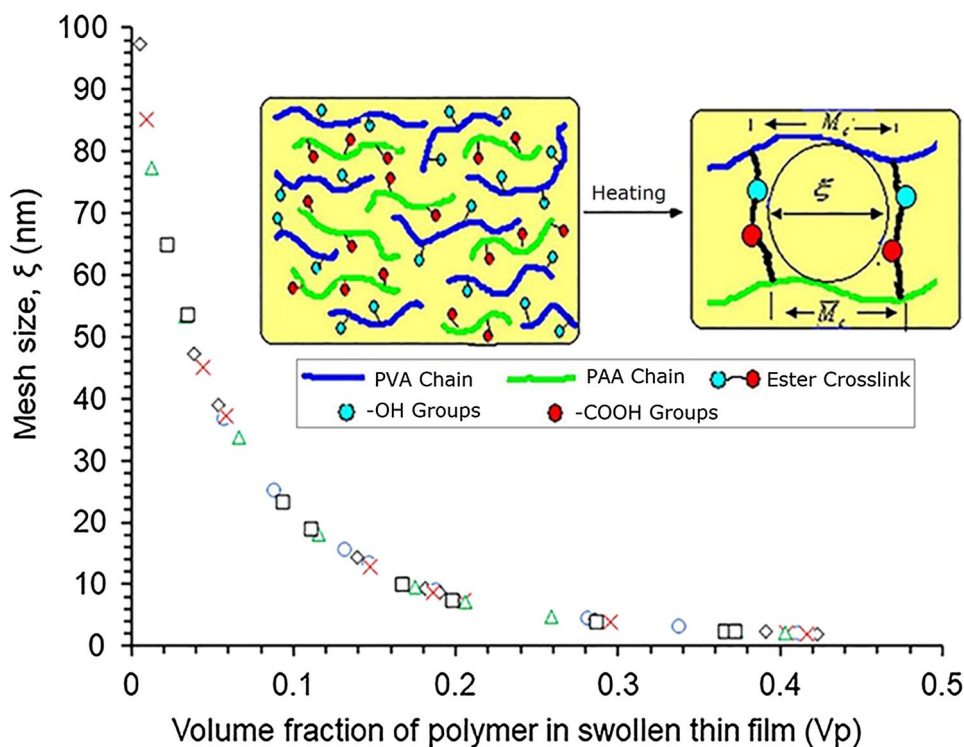
## Abstract

Making use of water-soluble polymers as films, membranes, and coatings for aqueous applications has increased over the years, owing to their environmentally benign nature and biodegradability. Interaction of solvent (i.e., water) with highly polar polymers, i.e., water-soluble polymers, results in weakening of cohesive forces between the polymer molecules and increase in the solvent–polymer interaction forces due to the formation of strong hydrogen bonds and polar–polar interactions. This, in turn, leads to the formation of highly swollen polymer gels. The present work focuses on the preparation of water-insoluble ionic thin films using water-soluble blends of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA), by adopting an environment friendly approach. For this purpose, solutions containing varied PVA and PAA contents were prepared in water, and the resulting clear solutions were cast to make films. The cross-linking of cast films were carried out at different temperatures and cross-linking durations. With increasing the cross-linking temperature, properties of the thin films, such as percentage swelling, molecular weight between cross-links, and mesh size, decreased, while cross-link density, gel content, thermal stability and  $T_g$  increased. The thin film obtained using solution containing 50% (by wt) of PAA and 50% (by wt) of PVA, and cross-linked at 140 °C, showed optimum swelling properties. Further, cation exchange membranes and thin film composite membranes were fabricated using ion exchange resin and polysulfone substrate membrane, respectively. The composite membrane cross-linked at 140 °C exhibited 95.1% rejection of  $\text{Na}_2\text{SO}_4$ . Finally, PVA–PAA/polysulfone composite nanofiltration membranes demonstrated  $\text{Na}_2\text{SO}_4/\text{NaCl}$  selectivity in the range of 2.14 to 2.6.

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## Graphical abstract



**Keywords** Cross-linking · Poly(vinyl alcohol) · Poly(acrylic acid) · Molecular weight between cross-links · Thin film · Composite membrane

## Introduction

The water-soluble polymer, poly(vinyl alcohol) (PVA), has found several applications over the years by virtue of its biocompatibility and biodegradability [1, 2], hydrophilicity, chemical resistance, gas and liquid barrier property, and film forming ability [3, 4], adhesive properties and semi-crystallinity [5, 6], as well as good thermal and mechanical properties [7]. These characteristics allow their major applications in packaging films [8], ionic membranes [9], hydrogels [10], paper coatings [11], and for drug delivery, wound dressing, fibers, and adhesives [12, 13]. However, in applications involving the presence of water, PVA suffers for its very high affinity toward water. Especially, when considering films, fibers, and membranes applications, the PVA must be essentially rendered insoluble [8, 14]. On the other hand, the hydrophilic polymer poly(acrylic acid) (PAA) is a super-absorbent that swells heavily upon absorption of water [7]. This high extent of swelling, although advantageous for some applications, can serve as a major drawback in other certain applications. It has been found that the degree of swelling can be controlled by introducing cross-links within the chemical structure of PAA or by

performing copolymerization [7]. In applications, PAA has been primarily used as anti-scaling agent and for membrane formation [15, 16], preparation of ion exchange resins [17], disposable diapers [18], and controlled release devices [19].

Interaction of water with PVA invariably results in the reduction of cohesive forces that exist between the polymer molecules, as well as enhancement in interaction forces between the solvent and the polymer. These observations can be attributed to the formation of strong hydrogen bonds [20], coupled with polar–polar interactions. As a result, formation of a highly swollen polymer gel takes place. This excessive swelling results in the gradual dissolution of the polymer, which, thus, loses its network and dimensional stability. Therefore, water-soluble polymers essentially require physicochemical modifications for the purpose of tailoring their functional ability and dimensional stability, particularly for aqueous applications. Techniques, like film formation, grafting, cross-linking and inclusion of additives, are the most prominent ways that have been employed to modify the structure of the polymers for reduction of their swelling tendencies [21]. Among the above-mentioned prominent techniques, cross-linking has been found to be the most effective in controlling the swelling of the polymers [8, 14].

Also, cross-linking technique allows selection of different cross-linkers as well as cross-linking conditions in order to produce network polymers that exhibit mechanochemical stability under certain environmental conditions. Usually, optimization of the cross-linking of water-soluble polymers involves mechanistic approaches to measure the various swelling parameters and correlate them with the resulting cross-linked polymer network [21].

PVA, PAA, and PVA–PAA films are characterized as highly hydrophilic, non-toxic, and biocompatible. PVA–PAA blends are known to form molecular level miscibility [7]. As already mentioned above, cross-linking of PVA–PAA is crucial for its successful application as fibers, films, membranes, electrochemical sensors, hydrogels for controlled drug release, wound dressing, and other biomedical applications [22–24]. Until date, several researchers have tried to prepare physically cross-linked PVA–PAA-based hydrogels by employing different techniques, such as freeze thawing. PVA–PAA film can also be transformed into chemically cross-linked structures either by employing a cross-linking agent or by heat treatment. Cross-linking of both PVA and PAA has been reported to prevent dissolution of polymers upon contact with aqueous solution, as well as to decrease the extent of swelling [25–27]. Zhang et al. have noted that the molecular level miscibility of PVA–PAA blend system is due to the formation of strong interpolymer hydrogen bonds between the –COOH– and the OH– groups [28]. During heat treatment, these groups interact and form ester linkages by elimination of water. In another study, Kumeta et al. cross-linked PVA by neutralized PAA at 200 °C. However, it was found that such high-temperature cross-linking generates ketonic groups, which results in severe brittleness of the cast film membranes [14]. Additionally, Lim et al. noted that addition of PAA into PVA has resulted in high transparency of the heat-induced cross-linked PVA–PAA film membranes. Advantageously, these membranes also demonstrated good thermal stability, water resistance, and barrier toward oxygen [8]. Jose et al. observed that in a PVA–PAA blend system, increase in the PAA content in the film led to an increase in the extent of swelling in water, along with a decrease in the blend-component-dissolution during the period of equilibrium swelling [7]. Recently, a number of published papers have emphasized on the applications of PVA–PAA as eco-friendly food packaging film [29], strain and temperature-sensing hydrogel [30], proton exchange membrane for fuel cell and water electrolyzer [22], and eco-friendly electrospun nanofibers for metal ion adsorption and controlled drug release [31, 32].

A thorough literature survey has revealed that there is a need of systematic study on the effect of temperature and time of cross-linking on the swelling characteristics of water-insoluble PVA–PAA films that are made by eco-friendly approach. In this direction, the present work reports

the preparation of PVA–PAA films, as well as composite and ion exchange membranes, using water as the solvent. The advantage of the blends of these polymers is to avoid the use of any external cross-linking agent, and it has enabled the fabrication of a membrane by a single step process, which involved simple solution coating and casting technique without the requirement of any special experimental conditions, such as humidity, inert atmosphere, and stringent solvent purity. Further to understand the swelling properties of the fabricated films and membranes, this study first focuses on the swelling parameters/properties, by taking into account the various blend ratios of PVA/PAA toward finding the volume fraction of polymer in swollen mass of cross-linked thin film. Therefore, the main aim of this study is to understand the effect of heat treatment on the swelling and water-resistant properties of cross-linked PVA–PAA thin films in cold (30 °C) and hot water (85 °C). For this purpose, the PVA–PAA films were first cross-linked by heat treatment. Here, heat treatment has been chosen for carrying out the cross-linking as it eliminates the involvement of an additional cross-linking agent. Percentage swelling, gel content, molecular weight between cross-links, mesh size, and cross-link density of the films were calculated to realize the effect of heat treatment. Finally, to demonstrate a potential application of the PVA–PAA blend, cross-linked thin film composite (TFC) membranes were fabricated by employing a coating of PVA–PAA on a base polysulfone ultrafiltration membrane to study their flux and rejection capabilities.

## Experimental

### Materials

Acrylic acid (AA) (AR grade) was purchased from Sigma Aldrich. Potassium persulfate and metabisulfite (AR grades) were procured from SD Fine Chemicals, India. PVA ( $\overline{M}_w$  86,000–98,000), with degree of hydrolysis of 99%, and PAA were obtained from CSIR-IMMT (India) as test samples. A commercial strong cation exchange resin, Indion 225, was procured from ion exchange (India). This resin possessed a particle size of – 300 to + 400 mesh (or 39  $\mu\text{m}$ ) and an ion exchange capacity (IEC) value of 4.2 meq.g<sup>-1</sup>. Milli-Q water was used for the experiment.

### Preparation of cross-linked thin films using water as solvent

A 10% (w/w) solution, containing PVA and PAA, were prepared separately in Milli-Q water. Blends of PVA–PAA [solution of 10% (w/w)] were prepared by mixing the PVA and the PAA in the weight ratios: 70:30, 60:40, 50:50, 40:60, and 30:70, under continuous stirring. Following the mixing of PVA

and PAA, entrapped air bubbles were allowed to escape from the solutions. The obtained clear PVA–PAA solutions were then cast on plastic sheets, and allowed to dry at room temperature for a period of 48 h. This was followed by scraping of the transparent PVA–PAA films from the plastic sheets. The average thickness of these physically cross-linked films was found to be  $0.15 \pm 0.05$  mm. Virgin PVA films were also prepared by maintaining the same thickness. The obtained PVA–PAA films were heat treated at temperatures of 90 to 160 °C for periods of 30 to 90 min.

## Swelling studies

Immediately after the heat treatment, the PVA–PAA cross-linked films were cut into pieces having a uniform dimension of  $1.7 \times 1.7$  cm<sup>2</sup>, followed by keeping immersed in water for a period of 7 days for complete swelling. The changes occurring in the areas of the films after swelling were measured. Also, percentage swelling values of the films were measured in hot water. For this purpose, the swollen films that were obtained after keeping in water at room temperature for 7 days were then kept immersed in hot water at a temperature of 85 °C for 7 h. Percentage swelling was calculated from the changes in the areas of the swollen films, according to Eq. 1.

$$\text{Swelling}(\%) = \frac{(A_{as} - A_{bs}) \times 100}{A_{bs}}, \quad (1)$$

where  $A_{as}$  and  $A_{bs}$  represent the areas of the films after and before swelling, respectively. The percentage gel was calculated as

$$\text{Gel}(\%) = \frac{(W_1 - W_2) \times 100}{W_1}, \quad (2)$$

where  $W_1$  is the original weight of the sample and  $W_2$  is the dry weight of the sample after swelling. Molecular weight between cross-links. The extent of swelling in a cross-linked gel will depend upon the number of effective chains per unit volume,  $V_e$ , which can be expressed as

$$V_e = \frac{\left[ \ln(1 - V_p) + V_p + \chi V_p^2 \right]}{d_r V_0 \left[ (V_p)^{\frac{1}{3}} - \frac{1}{2}(V_p) \right]}, \quad (3)$$

where  $V_p$  is the volume fraction of the polymer in the swollen mass,  $V_0$  is the molar volume of the solvent,  $d_r$  is the density of the polymer measured by gravimetric method (i.e., 1.33 g.cm<sup>-3</sup>), and  $\chi$  is the polymer–solvent interaction parameter (which is 0.494 for PVA and 0.500 for PAA) [33].  $V_e$  is related to  $\overline{M}_c$  (in g/mol) as

$$V_e = \frac{1}{M_c} - \frac{2}{M_n}, \quad (4)$$

where  $\overline{M}_n$  is the number average molecular weight of the starting polymer (i.e., 38,856 and 179,160 for PVA and PAA, respectively). Calculation of mesh size and cross-link density of the network. Mesh size ( $\xi$ ), as presented in Figure S1, was calculated as follows:

$$\xi = V_p^{-\frac{1}{3}} \left( \overline{r_0^2} \right)^{\frac{1}{2}} \quad (5)$$

where  $\left( \overline{r_0^2} \right)^{\frac{1}{2}}$  is the average end-to-end distance of the unperturbed (solvent-free) state, and can be calculated as

$$\left( \overline{r_0^2} \right)^{\frac{1}{2}} = \left( 2\overline{M}_c / M_r \right)^{\frac{1}{2}} C_n^{\frac{1}{2}} l \quad (6)$$

where  $l$  is the C–C bond length (i.e., 1.54 Å);  $M_r$  is the molecular weights of the repeating units of PVA (i.e., 44) and PAA (i.e., 72).  $C_n$  is the Flory characteristics ratio, which for PVA is 8.9 and for PAA is 6.7 [34]. The cross-link density of the IPN was calculated using Eq. 7 [35]:

$$\rho_x = \frac{1}{\nu \overline{M}_c}, \quad (7)$$

where  $\nu$  is the specific volume, which is 0.788 cm<sup>3</sup>g<sup>-1</sup> for PVA and 0.951 cm<sup>3</sup>g<sup>-1</sup> for PAA.

## Characterizations of thin films

The PVA–PAA thin cross-linked films were first subjected to thermal analysis conducted with Mettler-Toledo instruments (TGA/SDTA 851e, DSC 822e star<sup>e</sup>). The heating rate employed for the thermogravimetric analysis (TGA) was 10 °C min<sup>-1</sup>. For differential scanning calorimetry (DSC), the heating rate was maintained at 5 °C min<sup>-1</sup>. FTIR spectra were recorded using a Perkin and Elmer Spectrum GX spectrometer.

## Eco-friendly methods for membranes preparation

### Preparation of PVA–PAA cation exchange membranes and evaluation of ion exchange capacity

Six grams of a strong cation exchange resin (Indion 225) powder, having an average particle size of 17 μm, was dispersed in 100 mL of 4% (by wt) aqueous solution of PVA–PAA (containing 1:1 weight ratio of PVA:PAA) under continuous stirring to make a dope solution that possess a resin/binder weight ratio of 60/40. After thorough mixing of this binder solution, containing dispersed resin, it was cast onto a polypropylene sheet and allowed to dry at 25 °C for 24 h. The dried films were cut into 5 cm × 5 cm size, and

different samples were cross-linked in hot air oven at 120 °C and 140 °C for 15, 30, 60, and 90 min. To examine the effect of curing temperature and time, percentage swelling of the film samples was calculated using Eq. 1.

For the evaluation of ion exchange capacities, cation exchange membrane (CXM) specimens were kept in solution of 1 M HCl for 1 h to convert into H<sup>+</sup> form, then washed with de-ionized water. Following this, the films were immersed in 1 M NaCl solution for 1 h for conversion to Na<sup>+</sup> form and subsequently were rinsed with de-ionized water. This regeneration/degeneration cycle was repeated for three times. Finally, CXMs in H<sup>+</sup> form were immersed in 0.1 M NaCl solution for 24 h, and the amount of liberated HCl was estimated by titrating against 0.1 M NaOH solution. The IEC was determined using Eq. 8:

$$\text{IEC (meq. g}^{-1}\text{)} = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}}}{W_{\text{DM}}} \times 100, \quad (8)$$

where  $V_{\text{NaOH}}$  denotes the volume of NaOH consumed during the titration (mL),  $N_{\text{NaOH}}$  represents the normality of NaOH solution, and  $W_{\text{DM}}$  indicates the dry weight of films (g).

### Preparation of PVA–PAA/PSF composite membranes and evaluation of desalination performance

PVA and PAA of known amounts were dissolved in de-ionized water for the preparation of 0.15 and 0.05% (w/v) PVA/PAA mixed solution, comprising of a PVA:PAA weight ratio of 1:1. For thin film composite (TFC) membrane preparation, the top surface of the polysulfone ultrafiltration membrane of 10 cm × 15 cm size was made to contact the PVA–PAA solution for 3 min, following which the excess solution was drained from the membrane surface. After superficial drying, cross-linking of PVA–PAA active layer was done by heat treatment in hot air oven at 140 °C and 90 °C to induce different cross-link densities.

TFC membranes were tested in a cross-flow cell; however, before testing, the membranes were immersed in water for 12 h and then assembled into the cross-flow cell. Desalination performance of the membranes was conducted by using 2000 ppm NaCl and Na<sub>2</sub>SO<sub>4</sub> aqueous solution as feed. After stabilizing the membrane at a set pressure for 1 h, the permeate was collected and the membrane flux and rejection were calculated using Eqs. 9 and 10, respectively:

$$\text{Flux (lm}^{-2}\text{h}^{-1}\text{)} = \frac{V_p}{A_{\text{TFCM}} t} \quad (9)$$

$$\text{Rejection (\%)} = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \times 100 \quad (10)$$

where  $V_p$  indicates the permeate volume collected (in L) after time  $t$  (in h), and  $A_{\text{TFCM}}$  denotes membrane area (in m<sup>2</sup>).  $C_{\text{feed}}$  and  $C_{\text{permeate}}$  represent the feed and permeate solution concentration, respectively, that was estimated by measuring feed and permeate solution conductivities by conductivity meter (ELICO®, CM 183EC-TDS Analyser).

## Results and discussion

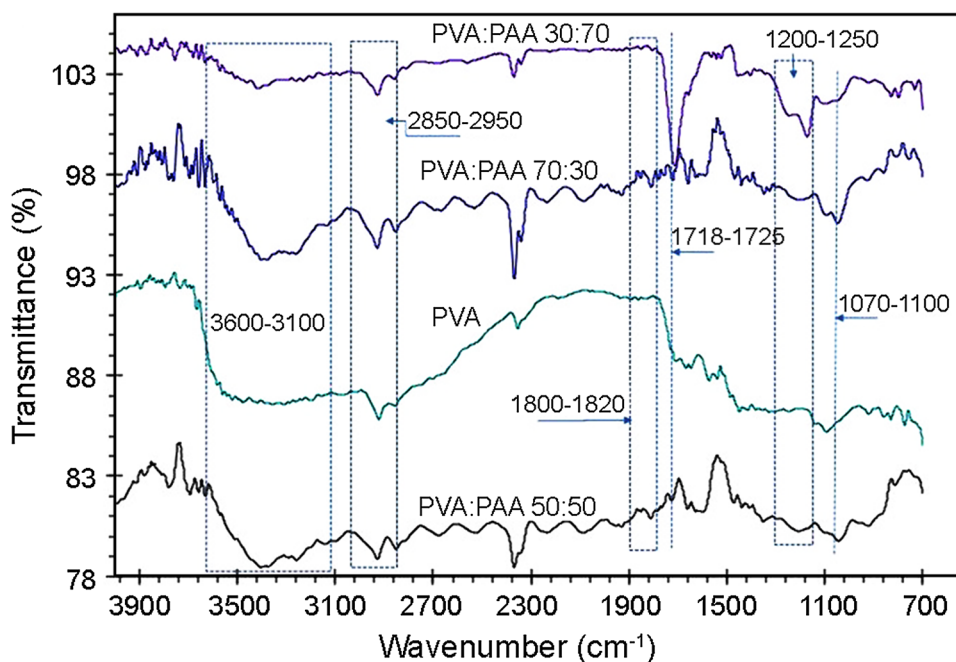
### Characterizations of the cross-linked thin films

The proposed cross-linking reaction between PVA and PAA is presented in Figure S2. FTIR was conducted on the cross-linked PVA–PAA film samples in order to confirm the formation of cross-links as well as the nature of the cross-links. In the spectra presented in Fig. 1, the band between 3350 and 3600 cm<sup>-1</sup> appeared due to the stretching frequency of O–H groups present in PVA. In PVA–PAA cross-linked film, the absorption band between 3350 and 3166 cm<sup>-1</sup> can be attributed to the stretching frequency of the O–H present in the carboxylic acid groups of PAA. While the C=O stretching frequency of PAA at 1718 cm<sup>-1</sup> appeared at a higher wavenumber, the C–O stretching vibration of pure PVA at 1241 cm<sup>-1</sup> was found to be gradually enhanced and broadened with increase in the PAA content. These observations indicate the increasing presence of carbonyl groups due to the formation of ester cross-links. Moreover, the C–O–C stretching vibrations appearing at 1032 cm<sup>-1</sup> and the C=O stretching vibrations appearing at 1803 and 1759 cm<sup>-1</sup> clearly indicate the formation of anhydrides [36]. Also, the band corresponding to the O–H stretching vibration of pure PVA film, appearing at 3350–3600 cm<sup>-1</sup>, is weakened and the C–O stretching vibration of PAA at 1090 cm<sup>-1</sup> is slightly strengthened in case of PVA–PAA cross-linked film. This is probably caused by the esterification reaction between carboxylic acid groups in PAA and hydroxyl groups in PVA.

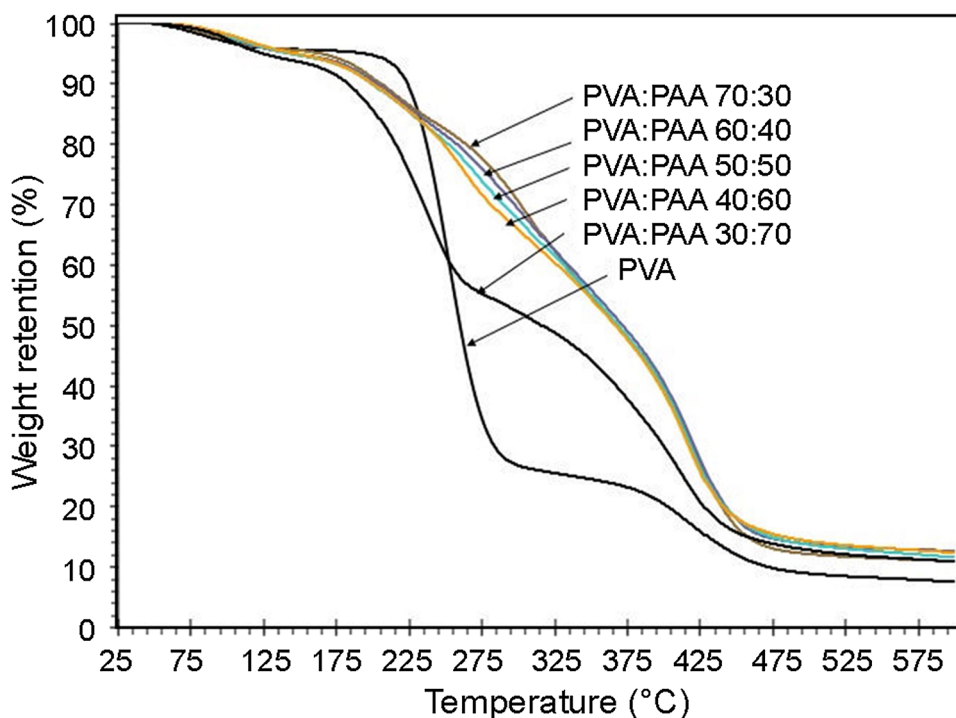
Figure 2 presents the temperature-dependent degradation of PVA–PAA cross-linked film, at varying PAA content obtained by TGA analysis. Weight loss appearing during the initial heating by ~130 °C is due to the removal of adsorbed water. Further heating from 130 to 370 °C resulted in steady decomposition by removal of side groups, i.e., –OH and –COOH groups, attached to the polymer matrix. In addition, decomposition of ester linkages, formed by cross-linking of PVA–PAA, also occurred during this heating stage. Finally, heating beyond 370 °C, maintaining the same heating rate, resulted in enhanced weight loss owing to the expected rupture of the polymer backbone [8, 37].

From the DSC curves, as shown in Fig. 3, the glass transition temperature ( $T_g$ ) has been determined by employing the midpoint technique, which indicates the temperature at the midpoint of the step height. It can be readily realized that

**Fig. 1** FTIR spectra of pure PVA and PVA–PAA-based thin films of varying constituent ratios, cross-linked at 140 °C for 90 min



**Fig. 2** TGA thermograms of thin PVA film and cross-linked PVA–PAA-based thin films prepared by solution casting using varying ratios, cross-linked at 140 °C for 90 min



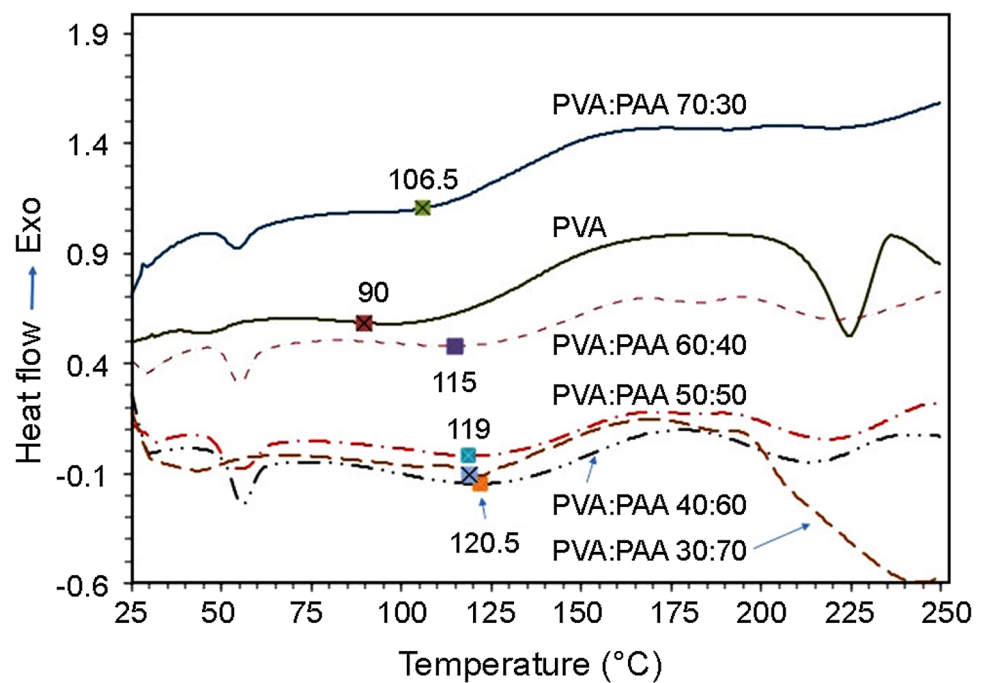
with increase in the PAA content of the cross-linked film, the  $T_g$  of the film increases. This increase in the  $T_g$  was found to be more prominent at PAA content below 50% (by wt). However, beyond 50% (by wt) of PAA, the increase in  $T_g$  with increase in the PAA content was negligible. Therefore, the film composition of 50:50 PVA–PAA was chosen to be the optimized one for the formation of free-standing films. The obtained  $T_g$  of 119 °C, for the 50:50 cross-linked thin film,

is much higher compared to those reported in the literature for similar PVA–PAA compositions [38].

Swelling analyses of the cross-linked thin films.

Extent of swelling is an extremely important parameter in several functional materials, such as ionic membranes, and hydrogels. Swelling is required for facilitating uptake, loading and transport; however, excessive swelling leads to deterioration of the mechanical integrity of the material.

**Fig. 3** Differential thermograms of thin PVA film and cross-linked PVA–PAA-based thin films prepared by solution casting using varying ratios, cross-linked at 140 °C for 90 min



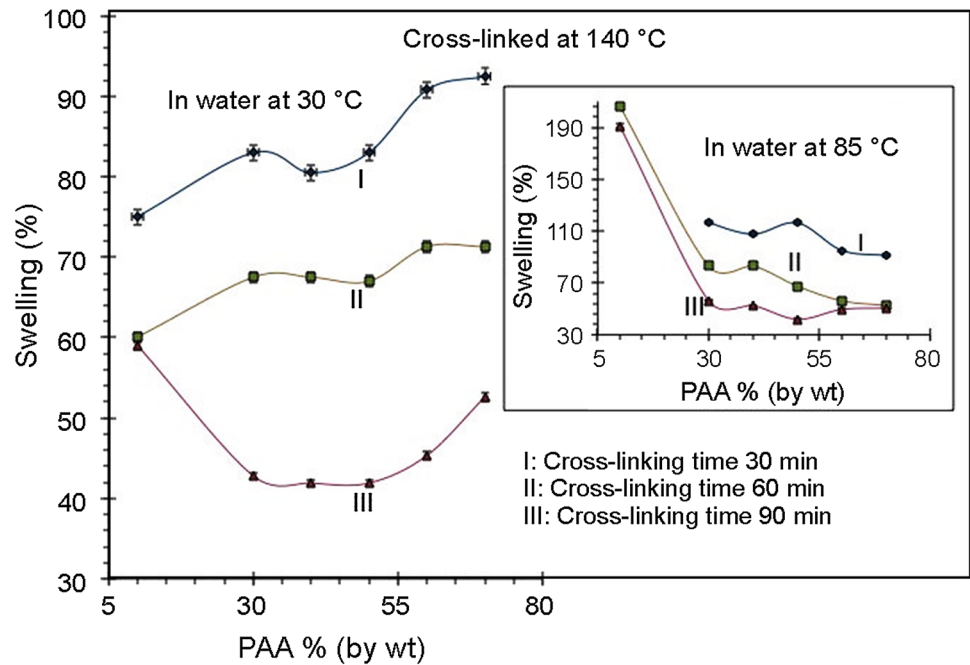
Therefore, this parameter has been investigated in great details in this work. Extent of swelling is dependent on the availability of free volume within the film structure [39]. In case of cross-linked films, the free volume depends on the extent and density of cross-links. For cross-linked films of water-soluble polymers, introduction of cross-links will first lead to a transition from solubility to swelling. Now, in general, as the number and density of cross-links increase, the swelling extent decreases. Swelling also depends on the type of polymers and the functional groups present. For example, in the present case, PAA possesses higher affinity toward water (by virtue of the presence of  $-\text{COOH}$  groups) compared to PVA (containing  $-\text{OH}$  groups); thus, increase in PAA content shall lead to increase in the swelling extent of the PVA–PAA cross-linked blend film. However, this extent of swelling can be controlled by introduction of more number of cross-links within the film structure. In essence, to understand the swellability of a cross-linked film, knowledge on the type of polymer, cross-link density and molecular weight between cross-links are essential.

Percentage swelling values of PVA–PAA cross-linked films, cured at 90, 120 and 140 °C, each for 30, 60 and 90 min, have been determined in water at 30 and 85 °C. It was found that the cross-linking time of 90 min produced the minimum percentage swelling, compared to the 30- and 60-min cross-linked variants (Fig. 4 and Figure S3a–S3b). It was further noted that 30-min cross-linking time was not sufficient to introduce significant number of cross-links for preventing solubility of the film in water at 85 °C (inset of Fig. 4 and Figure S3a). On the other hand, the cross-linking temperature of 140 °C produced the minimum percentage

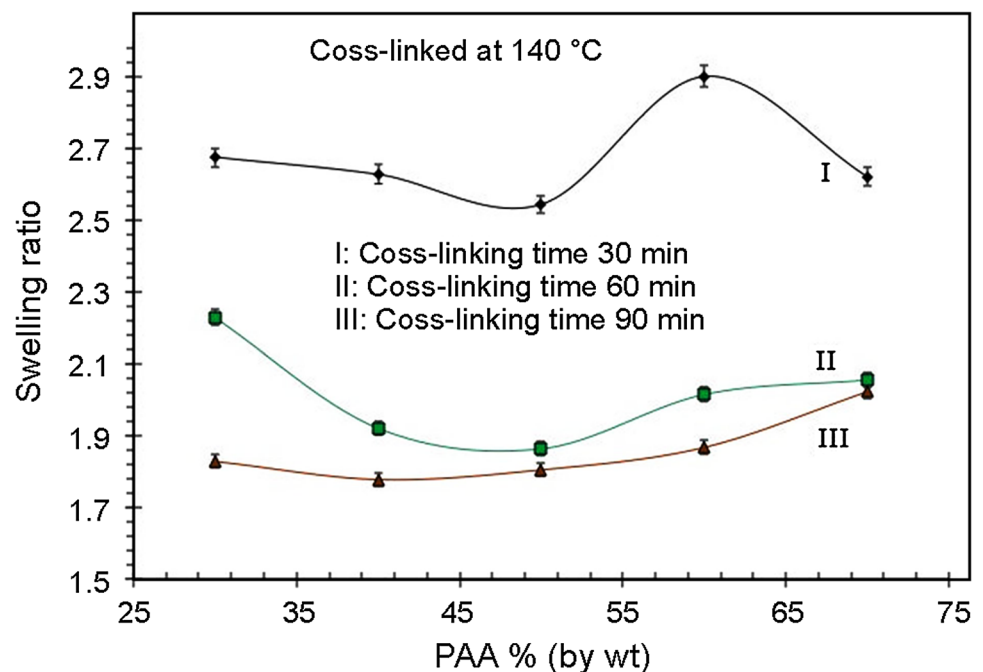
swelling, compared to 90 and 120 °C cross-linked variants (Fig. 4 and Figure S3a–S3b). These two observations clearly indicate that a cross-linking time of 90 min and a cross-linking temperature of 140 °C represent the optimized condition for PVA–PAA-based film cross-linking, in terms of swelling in water. Content of PAA within the PVA–PAA blend film is also an important factor in achieving the optimized swelling. Most importantly, very high PAA content in the PVA–PAA film is not suitable for fabrication of free-standing films. In our study, it was observed that 50% (by wt) of PAA and 50% (by wt) of PVA form the best composition in terms of film formation and swelling (Fig. 4, trace III).

Comparing the swelling result in water at 30 °C to that at 85 °C, it was observed that the percentage swelling was increased significantly at higher temperature (inset of Fig. 4 and Figure S3a–S3b). This result can be compared with that reported by Diken et al. [38]. The authors have shown that a 50:50 PVA–PAA hydrogel produced a swelling of  $466.22\% \pm 48$  at room temperature. It was further noted that the increase in percentage swelling at higher temperature was the least for the 50:50 PVA–PAA blend film, cured for 90 min at 140 °C. This further proves that this particular blend is the most optimized one in terms of percentage swelling. Again, the swelling ratio results plotted in Fig. 5 show a similar trend as that of the percentage swelling. Here likewise, it was realized that 140 °C curing temperature and 90-min curing time are the optimized cross-linking conditions for the 50:50 PVA–PAA films to achieve the desired swelling results. Similar trends also observed for swelling ratios of the films cross-linked at 120 °C and 90 °C, which are shown in Figure S4a–S4b.

**Fig. 4** Percentage swelling of PVA–PAA thin films as a function of PAA content (cross-linked at 140 °C for 30, 60 and 90 min); film immersed in water at 30 °C and 85 °C for swelling



**Fig. 5** Swelling ratio, PVA–PAA thin films as a function of PAA content (cross-linked at 140 °C for 30, 60 and 90 min); film immersed in water at 30 °C and 85 °C for swelling



The difference observed in the swelling of films in cold and hot water may be due to the presence of crystalline PVA at 30 °C. On the other hand, equilibrium swelling of films in hot water (i.e., 85 °C) causes breaking of the crystalline structure. Therefore, swelling at high temperatures depends upon the cross-link density, while, at the ambient temperature, it depends upon both the cross-link density and the crystalline structure [40]. This fact was validated in our observation that the PVA film, heat treated at 140 °C

for 90 min, demonstrated some swelling in water at room temperature; however, the same film, when immersed in water for equilibrium swelling, was dissolved after some time [21].

#### Molecular weight between cross-links of thin films

Number average molecular weight between cross-links  $\bar{M}_c$  can be used to acquire a reflection of the cross-link density



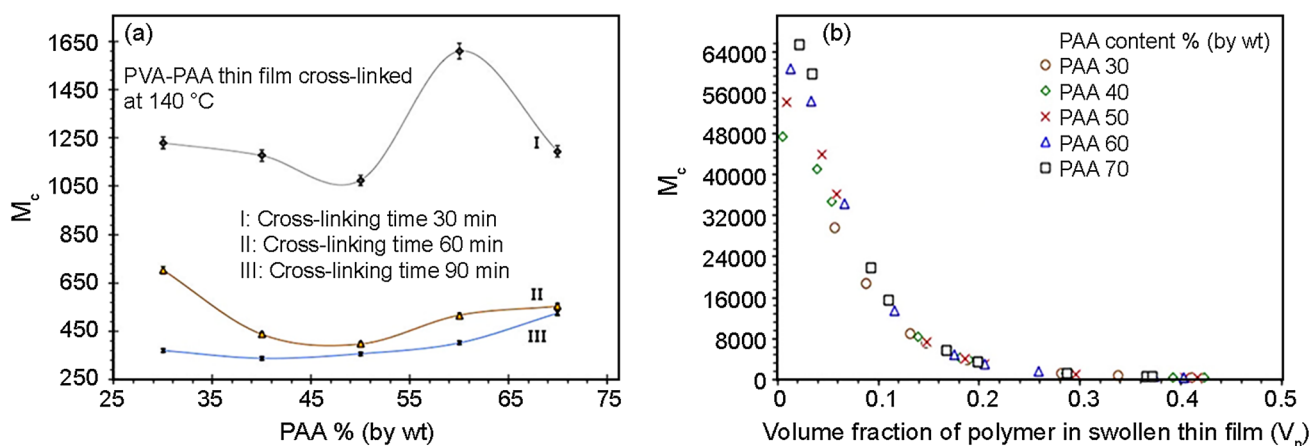
as well as the available free volume within the cross-linked structure. For aliphatic polymers that are devoid of highly bulky side groups, higher  $\overline{M}_c$  signifies higher flexibility of the polymeric chains. Higher flexibility shall, in turn, leads to availability of larger free volume, which shall enable accommodation of higher number of water molecules within the structure (i.e., higher extent of swelling). Therefore, our aim was to optimize an  $\overline{M}_c$ , so that an optimized value of swelling can be achieved. From Fig. 6a and Figure S5a–S5b, it can be realized that with increase in the curing temperature from 90 to 140 °C, the  $\overline{M}_c$  value was decreased. This is because increasing temperature led to the formation of higher number of cross-links, leading to reduction in the  $\overline{M}_c$  value. Also, increase in the curing time from 30 to 90 min led to decrease in  $\overline{M}_c$ , owing to the increase in the number of cross-links. These observations support the earlier realizations made during the swelling analysis, i.e., a curing time of 90 min and a curing temperature of 140 °C provide the optimized results for the PVA/PAA 50/50 wt/wt blend composition. This implies that decrease in the  $\overline{M}_c$  results in decrease of both the percentage swelling and swelling ratio of the PVA–PAA cross-linked film. Lastly, we have analyzed the relationship between  $\overline{M}_c$  and the  $V_p$  (Fig. 6b). As expected from Eqs. 3 and 4, it was observed that these two parameters possessed an inverse relationship, with higher values of  $\overline{M}_c$  corresponding to lower  $V_p$  and vice versa. Further, it was observed that for  $V_p$  values less than 0.1, the film having PVA/PAA 30/70 composition exhibited the highest  $\overline{M}_c$  value for a certain  $V_p$  value; and the  $\overline{M}_c$  value demonstrated a decrease with increase in the PVA content in the film.

### Mesh size and cross-link density in thin films

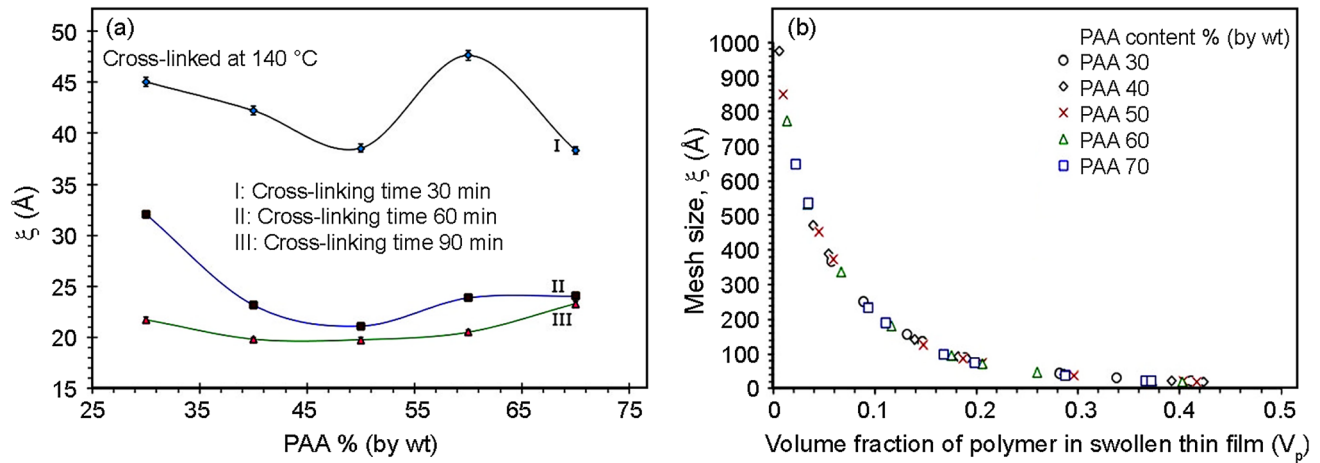
Mesh size ( $\xi$ ) of a polymeric thin film is dependent on the extent of swelling, cross-link density, and  $\overline{M}_c$ [41], along

with the chemical structure of the involved polymers. In the case of PVA–PAA cross-linked films, considering the swelling results discussed above, it can be expected that curing time of 90 min and curing temperature of 140 °C should produce the lowest mesh size for the cross-linked film having 50:50 PVA:PAA composition. It was gratifying to obtain this expected observation, as presented in Fig. 7a and Figure S6a–S6b. It is quite obvious that at higher curing time and temperature, the number of cross-links increases. This leads to reduction in the available free volume, resulting in decreased swelling. As a direct consequence of this reduced swelling, the mesh size also decreases. In addition, we have also analyzed the relationship between  $\xi$  and  $V_p$  (Fig. 7b). In compliance with Eq. 5, it was observed that an inverse relationship exists between these two parameters, such that higher values of  $\xi$  correspond to lower values of  $V_p$  and vice versa. In addition, it was noted that this inverse relationship curve was negligibly dependent on the weight ratio of PVA and PAA in polymer films.

In order to further confirm the above observations, we have carried out the cross-link density analysis of the PVA–PAA cross-linked films. It was expected from the results obtained so far that reduced swelling,  $\overline{M}_c$  and  $\xi$  must be associated with lower available free volume within the cross-linked blend film structure. Now, as already mentioned above, in PVA–PAA-type cross-linked films, free volume is mostly dependent on the number and density of cross-links. Therefore, it follows that with increase in curing temperature and time, the cross-link density must also increase. It was satisfying to note that in our analyses a curing temperature of 140 °C (Fig. 8) produced the highest cross-link density, compared to the films cross-linked at 90 °C and 120 °C (Figure S7a–S7b). Similarly, a curing time of 90 min produced the highest cross-link density, compared to the films

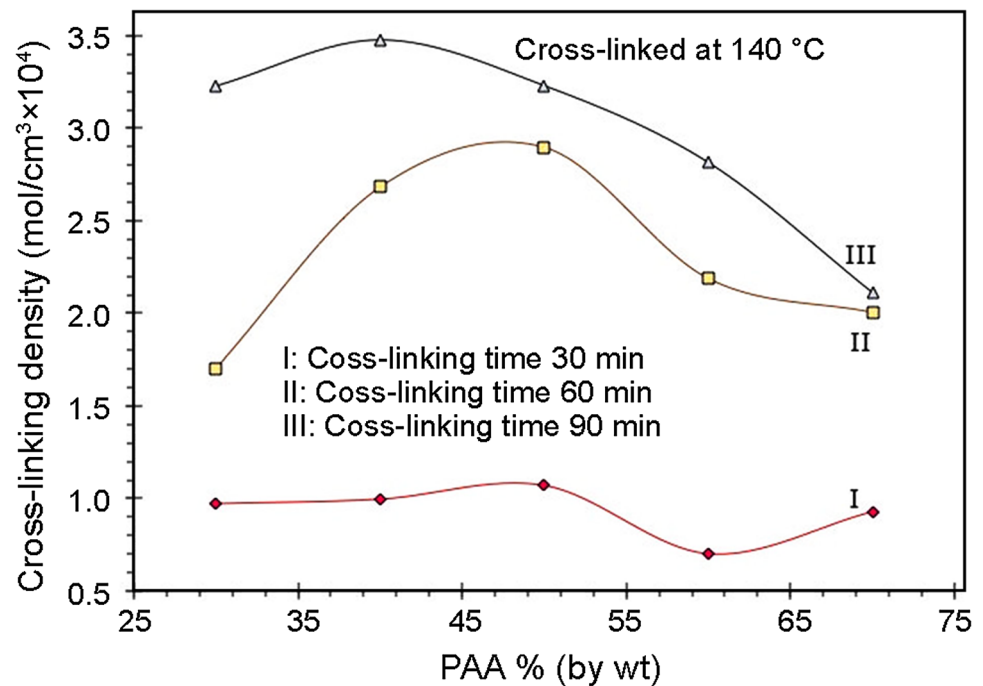


**Fig. 6** **a** Molecular weight between cross-links ( $\overline{M}_c$ ), as a function of PAA content, of PVA–PAA cross-linked films, cross-linked at 140 °C, for 30, 60, and 90 min; and **b**  $\overline{M}_c$  as a function of volume fraction of polymers for different PVA–PAA weight percent ratios



**Fig. 7** **a** Mesh size, as a function of PAA content, of PVA–PAA cross-linked films, cross-linked at 140 °C, for 30, 60, and 90 min, and **b** Mesh size as a function of volume fraction of polymers for different PVA–PAA weight ratios

**Fig. 8** Cross-link density, as a function of PAA content, of PVA–PAA cross-linked films, cross-linked at 40 °C, for 30, 60, and 90 min



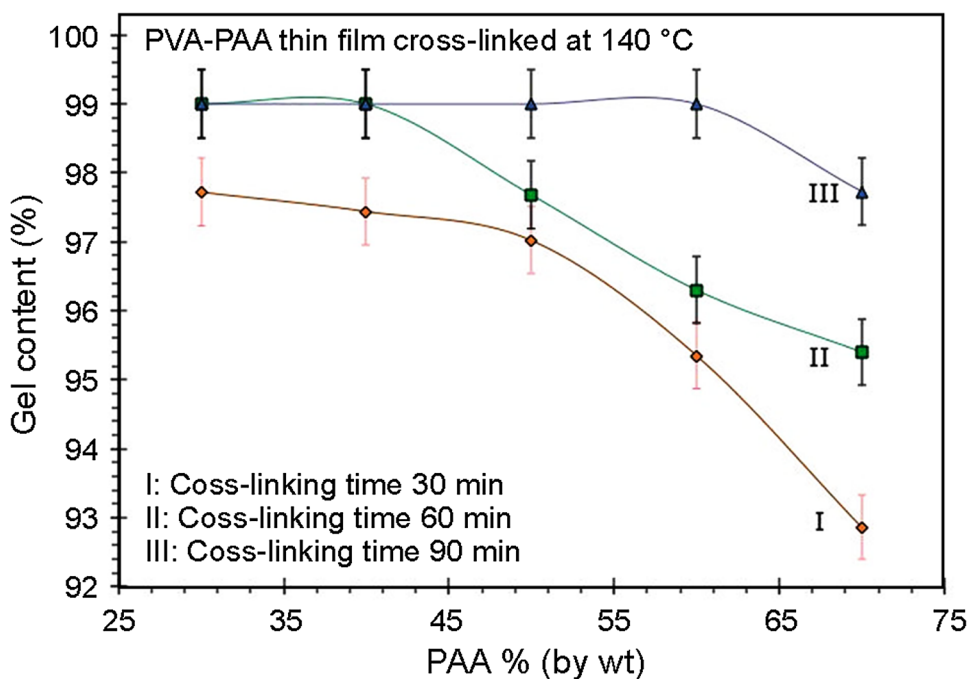
cross-linked for 30 and 60 min (Fig. 8 and Figure S7a–S7b). This result further confirms that cross-links have played a major role in the observed swelling behavior of PVA–PAA thin films.

### Gel content in cross-linked thin films

Gel content gives a measure of the extent of cross-linking and cross-link density between the constituent polymers, which in this case are PVA and PAA. Higher gel content of

the cross-linked blend film indicates higher water resistance and better mechanical strength of the film. From the results presented in Fig. 9 and Figure S8a–S8b, it can be easily realized that the gel content of the cross-linked film increases with cross-linking temperature and time. This result can be easily correlated with the above-mentioned observations made for the swelling and cross-linking analyses.

**Fig. 9** Percentage gel content, as a function of PAA content, of PVA–PAA cross-linked films, cross-linked at 140 °C, for 30, 60, and 90 min



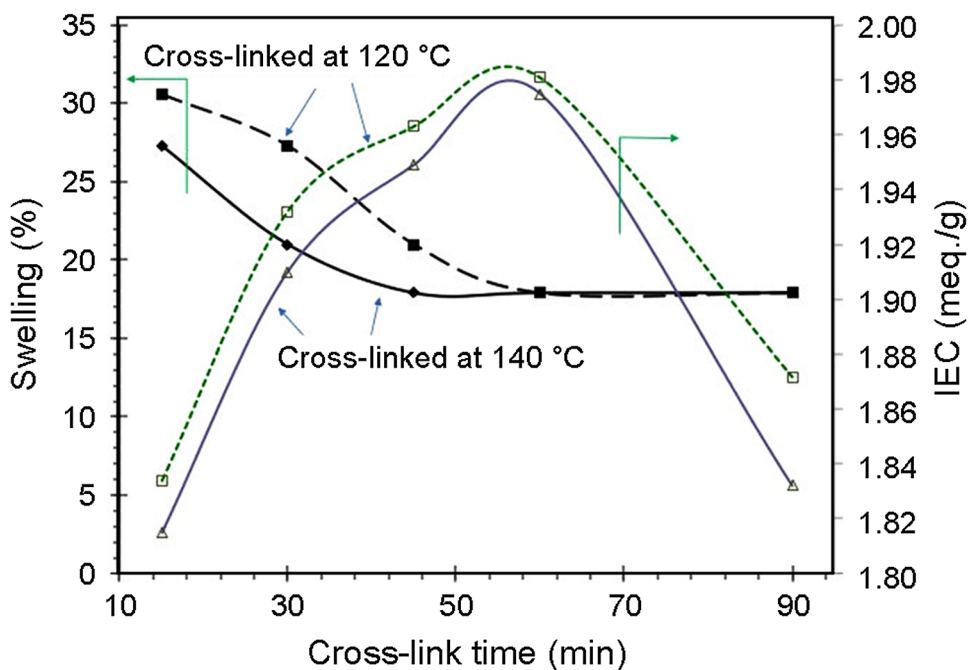
**Properties of cation exchange membranes**

Next, we were interested to see the possibility of using the PVA/PAA 50/50 wt/wt blend composition as a binder to form ionic membranes, in conjunction with a strong cation exchange resin (Indion 225). For this purpose, a binder/resin 40/60 wt/wt ratio was utilized. Following the fabrication of the membrane, we subjected it to two preliminary but essential tests, namely, percentage swelling versus curing time

and IEC versus curing time, at two different temperatures of 120 °C and 140 °C as shown in Fig. 10.

It was enticing to realize that the percentage swelling of the membrane decreased with increase in the curing time, for both temperatures. Below the curing time of 60 min, the membrane sample cured at 140 °C exhibited lower swelling. However, above 60 min, the effect of curing temperature on percentage swelling was found to be non-existent. The fact that a membrane cured at 140 °C demonstrated the lowest

**Fig. 10** Percentage swelling, and IEC as function of cross-linking time of ion exchange membrane prepared from 60:40 resin:binder weight ratio (PAA:PVA in 50:50 weight ratio used as binder)



swelling which can be correlated to the earlier observations that higher curing temperature produced higher cross-link density and lower molecular weight between the cross-links. This directly implies that the availability of free volume was reduced at higher curing temperature, leading to lower extent of swelling. In the case of IEC analysis, it was observed that the highest IEC value was exhibited by the sample that was cross-linked at 120 °C. This was achieved at a curing time of ~55 min. The fact that higher IEC was obtained for a membrane cured at lower temperature can be correlated to the presence of fewer cross-links in such a membrane. As a result, comparatively more number of sites within the constituent polymers remain accessible for taking part in ion exchange.

### Preliminary performance study of PVA–PAA-based TFC membranes for water treatment

PVA–PAA-based TFC membranes were fabricated to have some preliminary understanding of their water treatment ability. For this purpose, PVA/PAA of 50/50 weight ratio was used to prepare 0.15 and 0.05% (w/v) aqueous solution, and composite membranes were fabricated by applying a thin layer of coating of this solution onto the polysulfone ultrafiltration membrane (having molecular weight cut-off of 20 kD). This study was conducted to examine the effect of cross-linking temperature and solution concentration of the PVA–PAA on the flux and rejection characteristics of the resulting composite membranes. Table 1 lists the rejection and flux (average of three samples) of four composite membranes obtained by cross-flow filtration cell operated at 1.03 MPa and 1.55 MPa pressure using 2000 ppm NaCl and Na<sub>2</sub>SO<sub>4</sub> feed solutions, respectively.

The observed trend in the flux and rejection characteristics indicate that the membranes prepared using dilute solution, i.e., 0.05% (by wt) PVA–PAA, and cross-linked at lower temperature, i.e., 90 °C, produced higher water flux. This may be due to the formation of thinner selective layer, having low cross-link density and high mesh size. All the studied membranes exhibited flux and rejection characteristic in

the range of nanofiltration (NF) and Na<sub>2</sub>SO<sub>4</sub>/NaCl selectivity in the range of 2.14–2.6. This high rejection of Na<sub>2</sub>SO<sub>4</sub> indicates that the membrane surface possesses negative surface charge due to the presence of carboxylic groups; hence, it prominently repels the bigger sized negatively charged bivalent (SO<sub>4</sub><sup>2-</sup>) ions over the smaller sized negatively charged monovalent (Cl<sup>-</sup>) ions. The obtained membrane flux–rejection characteristics of PVA–PAA-based TFC NF membranes implies that the separation is expected to be governed by size exclusion and Donnan exclusion, and such membranes can be used for water softening applications, i.e., removal of bivalent ions from brackish water or seawater.

### Conclusion

PVA–PAA thin films have been prepared successfully by a simple solution casting technique. Cross-linking of the prepared films by heat treatment was carried out, using varying curing time and temperature. It was realized that the heat treatment-induced chemical cross-links takes place within the blend film through esterification reaction, which was confirmed by FTIR analysis. Overall, the cross-linking led to improvement in the thermal stability and the  $T_g$  of the films. Increasing the curing time and temperature of the films resulted in reduction of percentage swelling, swelling ratio, molecular weight between cross-links, and mesh size; and enhancement of cross-link density and gel content. All these swelling properties can be tuned by proper selection of PVA–PAA ratio, curing time and curing temperature for a given application. Insolubility of the cross-linked PVA–PAA films in hot water demonstrates its great potential as a membrane material for water treatment applications. Further, the cross-linked TFC membranes fabricated using PVA–PAA coating on polysulfone ultrafiltration matrix exhibited flux and rejection characteristic in the range of nanofiltration and Na<sub>2</sub>SO<sub>4</sub>/NaCl selectivity in the range of 2.14–2.6. In future, these types of membranes can be further modified by inclusions of functional nanomaterials for the purpose of

**Table 1** Flux and rejection characteristic of PVA–PAA-based TFC membranes prepared onto polysulfone support (all data are average of three samples)

TFC membrane	PVA/PAA solution (w/v) %	Cross-link temperature	TMP: 1.03 MPa			TMP: 1.55 MPa		
			R <sub>NaCl</sub> (%)	R <sub>Na<sub>2</sub>SO<sub>4</sub></sub> (%)	Flux (LMH)	R <sub>NaCl</sub> (%)	R <sub>Na<sub>2</sub>SO<sub>4</sub></sub> (%)	Flux (LMH)
PVA-A1	0.15	140 °C	44	94.3	16.4	44.3	95.1	20
PVA-A2	0.05	140 °C	39	85.66	16.1	39.8	86.2	22
PVA-A3	0.15	90 °C	41	90	65.7	42.1	91.7	74.3
PVA-A4	0.05	90 °C	32.35	84	42.9	33	84.9	64.3

TMP Operating pressure, i.e., transmembrane pressure, PVA/PAA solution contained 1:1 weight ratio of PVA and PAA, LMH liter per meter square per hour (Lm<sup>-2</sup> h<sup>-1</sup>), R<sub>NaCl</sub> and R<sub>Na<sub>2</sub>SO<sub>4</sub></sub>: rejection of NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively

improving their ionic characteristics for prospective applications, such as proton/cation exchange membrane in fuel cell/electrodialysis, as well as for improving the desalination and antifouling characteristics of composite NF membrane. The authors are currently exploring in details the prospect of application of this type of ionic thin film membranes in water treatment.

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## References

- Niamlang P, Tongrain T, Ekabutr P, Chuysinuan P, Supaphol P (2017) Preparation, characterization and biocompatibility of poly(vinyl alcohol) films containing tetracycline hydrochloride-loaded quaternized chitosan nanoparticles. *J Drug Deliv Sci Technol* 38:36–44
- López OBL, Sierra GL, Mejía GAI (1999) Biodegradability of poly(vinyl alcohol). *Polym Eng Sci* 39:1346–1352
- Ahmad AL, Yusuf NM, Ooi BS (2012) Preparation and modification of poly(vinyl alcohol) membrane: effect of crosslinking time towards its morphology. *Desalination* 287:35–40
- Bolto B, Tran T, Hoang M, Xie Z (2009) Crosslinked poly(vinyl alcohol) membranes. *Prog Polym Sci* 34:969–981
- Tretinnikov ON, Zagorskaya SA (2012) Determination of the degree of crystallinity of poly(vinyl alcohol) by FTIR spectroscopy. *J Appl Spectrosc* 79:521–526
- Park HK, Kong BS, Oh ES (2011) Effect of high adhesive poly(vinyl alcohol) binder on the anodes of lithium ion batteries. *Electrochim Commun* 13:1051–1053
- Jose J, Shehzad F, Al-Harhi MA (2014) Preparation method and physical, mechanical, thermal characterization of poly(vinyl alcohol)/poly(acrylic acid) blends. *Polym Bull* 71:2787–2802
- Lim M, Kim D, Seo J (2016) Enhanced oxygen-barrier and water-resistance properties of poly(vinyl alcohol) blended with poly(acrylic acid) for packaging applications. *Polym Int* 65:400
- Wong CY, Wong WY, Loh KS, Daud WRW, Lim KL, Khalid M, Walvekar R (2020) Development of poly(vinyl alcohol)-based polymers as proton exchange membranes and challenges in fuel cell application: a review. *Polym Rev* 60:171–202
- Ossipov DA, Hilborn J (2006) Poly(vinyl alcohol)-based hydrogels formed by “click chemistry.” *Macromolecules* 39:1709–1718
- Schuman T, Wikström M, Rigdahl M (2004) Coating of surface-modified papers with poly(vinyl alcohol). *Surf Coat Technol* 183:96–105
- Gutiérrez MC, García-Carvajal ZY, Jobbágy M, Rubio F, Yuste L, Rojo F, Ferrer ML, del Monte F (2017) Poly(vinyl alcohol) scaffolds with tailored morphologies for drug delivery and controlled release. *Adv Funct Mater* 17:3505–3513
- Hong KH (2007) Preparation and properties of electrospun poly(vinyl alcohol)/silver fiber web as wound dressings. *Polym Eng Sci* 47:43–49
- Kumeta K, Nagashima I, Matsui S, Mizoguchi K (2003) Crosslinking reaction of poly(vinyl alcohol) with poly(acrylic acid) (PAA) by heat treatment: effect of neutralization of PAA. *J Appl Polym Sci* 90:2420–2427
- Liu Y, Park M, Ding B, Kim J, El-Newehy M, Al-Deyab SS, Kim HY (2015) Facile electrospun polyacrylonitrile/poly(acrylic acid) nanofibrous membranes for high efficiency particulate air filtration. *Fiber Polym* 16:629–633
- Ismail AF, Khulbe KC, Matsuura T (2019). In: Ismail AF, Khulbe KC, Matsuura T (eds) *Reverse Osmosis*. Elsevier, Netherlands, pp 189–220
- Yang F, Fan X, Zhang M, Wang C, Zhao W, Zhao C (2019) A template-hatched method towards poly(acrylic acid) hydrogel spheres with ultrahigh ion exchange capacity and robust adsorption of environmental toxins. *J Ind Eng Chem* 69:422–431
- Czarnecka E, Nowaczyk J (2020) Semi-natural superabsorbents based on starch-g-poly(acrylic acid): modification, synthesis and application. *Polymer* 12:1794
- Hu X, Wei W, Qi X, Yu H, Feng L, Li J, Wang S, Zhang J, Dong W (2015) Preparation and characterization of a novel pH-sensitive Salecan-g-poly(acrylic acid) hydrogel for controlled release of doxorubicin. *J Mater Chem B* 3:2685–2697
- Chen N, Zhang JH (2010) The role of hydrogen-bonding interaction in poly(vinyl alcohol)/poly(acrylic acid) blending solutions and their films. *Chin J Polym Sci* 28:903–911
- Gohil JM, Bhattacharya A, Ray P (2006) Studies on the crosslinking of poly(vinyl alcohol). *J Polym Res* 13:161–169
- Al Munsur AZ, Goo BH, Kim Y, Kwon OJ, Paek SY, Lee SY, Kim HJ, Kim TH (2021) Nafion-based proton-exchange membranes built on cross-linked semi-interpenetrating polymer networks between poly(acrylic acid) and poly(vinyl alcohol). *ACS Appl Mater Interf* 13:28188–28200
- Li X, Wang Z, Li W, Sun J (2021) Superstrong water-based supramolecular adhesives derived from poly(vinyl alcohol)/poly(acrylic acid) complexes. *ACS Mater Lett* 3:875–882
- Kim J, Kwon O, Kim H, Kim DW, Jeon Y, Ji Y, Jeon OS, Lee C, Shul YG (2020) Cross-linked PVA/PAA fibrous web composite membrane for enhanced performance of PEM fuel cells under high-temperature and low-humidity conditions. *J Chem Eng Japan* 53:569–575
- Gohil JM, Ray P (2009) Studies on oxalic acid as a crosslinker of poly(vinyl alcohol). *Polym Compos* 17:403–410
- Choudhury RR, Gohil JM, Dutta K (2021) Poly(vinyl alcohol)-based membranes for fuel cell and water treatment applications: a review on recent advancements. *Polym Adv Technol* 32:4175–4203
- He J, Das C, Yang F, Maibach J (2022) Crosslinked poly(acrylic acid) enhances adhesion and electrochemical performance of Si anodes in Li-ion batteries. *Electrochim Acta* 411:140038
- Zhang X, Takegoshi K, Hikichi K (1992) Phase separation and thermal degradation of poly(vinyl alcohol)/poly(methacrylic acid) and poly(vinyl alcohol)/poly(acrylic acid) systems by  $^{13}\text{C}$  c.p./m.a.s. n.m.r. *Polymer* 33:718–724
- Kim HJ, Charoensri K, Ko JA, Park HJ (2022) Effects of layered double hydroxides on poly(vinyl alcohol)/poly(acrylic acid) films for green food packaging applications. *Prog Org Coat* 163:106634
- Min J, Zhou Z, Zheng J, Yan C, Sha H, Hong M, Fu H (2022) Self-healing, water-retaining, antifreeze, conductive PVA/PAA-PAM-IS/GC composite hydrogels for strain and temperature sensors. *Macromol Mater Eng* 2100948
- Kim J, Kang T, Kim H, Shin HJ, Oh SG (2019) Preparation of PVA/PAA nanofibers containing thiol-modified silica particles by electrospinning as an eco-friendly Cu (II) adsorbent. *J Ind Eng Chem* 77:273–279
- Arafat MT, Mahmud MM, Wong SY, Li X (2021) PVA/PAA based electrospun nanofibers with pH-responsive color change using bromothymol blue and on-demand ciprofloxacin release properties. *J Drug Deliv Sci Technol* 61:102297

33. Brandrup J, Immergut EH (1989) *Polymer Handbook*, 3rd edn. John Wiley, New York
34. Gudeman LF, Peppas NA (1995) pH-Sensitive membranes from poly(vinyl alcohol)/poly(acrylic acid) interpenetrating networks. *J Membr Sci* 107:239–248
35. Canal T, Peppas NA (1989) Correlation between mesh size and equilibrium degree of swelling of polymeric networks. *J Biomed Mater Res* 23:1183–1193
36. Dong J, Ozaki Y, Nakashima K (1997) FTIR studies of conformational energies of poly(acrylic acid) in cast films. *J Polym Sci B Polym Phys* 35:507–515
37. Park JY, Hwang KJ, Yoon SD, Lee JH, Lee IH (2015) Influence of glyoxal on preparation of poly(vinyl alcohol)/poly(acrylic acid) blend film. *J Nanosci Nanotechnol* 15:5955–5958
38. Diken ME, Berna KK, Begümhan YK, Enes ED, Mehmet D, Yasemin T, Serap D (2020) Synthesis, characterization, and their some chemical and biological properties of PVA/PAA/nPS hydrogel nanocomposites: hydrogel and wound dressing. *J Bioact Compat Polym* 35:203–215
39. Arif Z, Sethy NK, Mishra PK, Verma B, Upadhyay SN (2019) Swelling and sorption behaviour of PVA and PVA/silica nanocomposite membrane at different silica loadings. *Ind J Chem Technol* 26:44–51
40. Kumeta K, Nagashima I, Matsui S, Mizoguchi K (2004) Crosslinking of poly(vinyl alcohol) via bis( $\beta$ -hydroxyethyl) sulfone. *Polym J* 36:472–477
41. Sirousazar M, Kokabi M, Hassan ZM (2012) Swelling behavior and structural characteristics of polyvinyl alcohol/montmorillonite nanocomposite hydrogels. *J Appl Polym Sci* 123:50–58

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