

# Physicochemical studies of crosslinked thiolated polyvinyl alcohol hydrogels

Bhuvanesh Gupta · Sadiya Anjum · Saiqa Ikram

Received: 15 January 2013 / Accepted: 22 April 2013 / Published online: 29 May 2013  
© Springer-Verlag Berlin Heidelberg 2013

**Abstract** This study is related to the post-crosslinking of thiolated polyvinyl alcohol (TPVA) hydrogels using three crosslinkers, sodium trimetaphosphate (STMP), boric acid (BA) and glyoxal (GLY) under alkaline conditions. The crosslinking reaction was carried out under different conditions: crosslinker nature, crosslinker content and crosslinking time. The influence of different crosslinkers on the physicochemical and structural characteristics of TPVA was evaluated. The three reagents used for crosslinking presented different action mode on hydrogels. The optimized crosslinking conditions were the crosslinker content is 0.1 % (w/v) at crosslinking time of 30 min. The results showed that the STMP-crosslinked TPVA had the maximum thiol content and swelling ability. All crosslinked TPVA samples were stable in different pH media. The involvement of thiol and other relevant groups after crosslinking in the different crosslinked TPVA samples was confirmed by attenuated total reflectance-infrared spectra. The microanalysis of elements present in the crosslinked samples were analyzed by energy-dispersive X-ray microanalysis.

**Keywords** Thiolated polyvinyl alcohol · Crosslinking · Thiol content · Swelling

## Introduction

Polyvinyl alcohol (PVA) is one of the most versatile polymers and has acquired special attention because of its excellent transparency, chemical resistance and

---

B. Gupta (✉)  
Bioengineering Laboratory, Department of Textile Technology, Indian Institute of Technology,  
New Delhi 110016, India  
e-mail: bgupta@textile.iitd.ernet.in

S. Anjum · S. Ikram  
Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi 110025, India

toughness. PVA is water-soluble polymer and is largely used as fiber (vinylon), film, in the paper industry, in textile sizing, as a modifier of thermosetting resins, in plywood manufacturing, as pressure-sensitive adhesives and emulsifier [1, 2]. Due to its readily soluble nature and low solubility in organic solvent, PVA shows very limited application in water treatment. Crosslinking is a vital tool for the modification of existing PVA through its hydroxyl groups and opens up a new domain of applications of this material [3]. The stability of crosslinked PVA in highly acidic or highly alkaline environments has been demonstrated [4]. While, the literature on applications as membranes or support material in water treatment is spasmodic, there has been a continuing effort in the water treatment applications to use PVA-based materials for metal separation [5–9].

One of the properties of PVA, however, is its tendency to become crosslinked by a number of chemical species, aldehydes, acids, borate, perborate, inorganic ligands and dyes [10–13]. A further point worth considering is the toxicity of the reagents or the by-products formed during the crosslinking process. However, traditional methods of crosslinking suffer from several disadvantages, such as lack of precise control over crosslinking, toxic effect of the crosslinker. Therefore, there is necessity to use ecofriendly crosslinker which inhibits the lethal effect. To avoid the disadvantages of toxic crosslinker, some nontoxic crosslinkers have been used [14]. The crosslinking agents for PVA were sodium trimetaphosphate (STMP), boric acid (BA) and glyoxal (GLY). STMP has been reported to be an effective crosslinking agent for various polymers [15–17]. BA is very well-known crosslinker for PVA by the formation of borate linkage with hydroxyl group of PVA [18, 19]. GLY has been the most promising aldehyde used as a crosslinker for PVA as well as other polymers [20–22].

In our previous study, we optimized esterification parameters including reaction time, reaction temperature and reactant concentrations for the esterification of PVA with thioglycolic acid (TGA) [23]. Thiol-functionalized mesoporous poly(vinyl alcohol)/SiO<sub>2</sub> composite nanofiber membranes were synthesized by electrospinning and used for the adsorption of heavy metal ions from aqueous solution [24]. Rebecca et al. [25] reported the multifunctional macromolecular thiol-polyvinyl alcohol (TPVA) obtained by esterification of PVA with 3-mercaptopropionic acid and used it as a wheat gluten (WG) reactive modifier. In the present study, we have investigated the crosslinking of TPVA with different crosslinkers at varying conditions, crosslinker nature, crosslinker content and crosslinking time in terms of thiol content and swelling studies. However, the crosslinked TPVA samples obtained by the afore-mentioned process are durable for long-term use, because of the presence of acetal, borate and phosphate bonding linkages. The structural changes of crosslinked TPVA were observed from attenuated total reflectance-infrared (ATR-IR) spectroscopy and thiol groups were quantified by Volhard's silver nitrate method. The microanalysis of the samples has been studied by energy-dispersive X-ray microanalysis (EDX). Our activity is focused on the formulation of new polymeric materials for arsenic separation from water. The requirements of an ideal material for this purpose are dictated not only by the selectivity and chelation of metal ions, but also by its capability to regenerate itself and nontoxic in nature.

## Experimental

### Chemicals

PVA (degree of hydrolysis 87–90 % and molecular weight 1,15,000) and sodium trimetaphosphate (STMP) were purchased from Sigma Aldrich. Thioglycolic acid (TGA), sodium hydroxide, sulfuric acid, glyoxal (GLY), potassium thiocyanate, silver nitrate, iron ammonium sulfate hexahydrate and methanol (HPLC grade) were purchased from Merck, India. Boric acid (BA) was purchased from SD Fine Chemicals. All the chemicals were used without further purification. Ultra-pure water, resistivity  $<18 \text{ M}\Omega \text{ cm}$ , produced by a Millipore Milli-Q system was used throughout the experimental work.

### Esterification of PVA

Homogenous solution of PVA was prepared by dissolving 2 g PVA powder in 100 ml water under vigorous stirring overnight at room temperature. Esterification reaction was carried out under optimized parameters of reaction time 24 h, reaction temperature  $60^\circ\text{C}$  and sulfuric acid (as catalyst) concentration of 1 % (v/v) as reported previously [25]. For the comparison, the influence of varying TGA concentration from 2 to 25 % (v/v) was monitored. After completion of the reaction, the esterified PVA solution was decanted to separate any residue remains in the solution and used for the further crosslinking.

### Crosslinking of thiolated polyvinyl alcohol (TPVA)

The TPVA solution was subjected further to the crosslinking reaction with three crosslinkers of different nature, viz. STMP, BA and GLY. Varying concentration of crosslinkers from 0.05 to 1 % (w/v) with respect to PVA concentration has been studied with increasing crosslinking time from 15 to 60 min at reaction temperature  $60^\circ\text{C}$ . After completion of reaction, the mixture was slowly poured into 12 M sodium hydroxide solution at pH 12. The white precipitate thus obtained was washed repeatedly with water and methanol, and dried in vacuum oven at  $25 \pm 2^\circ\text{C}$ .

### Thiol content estimation

The amount of the thiol groups was determined according to a protocol based on the *Volhard's silver nitrate method* [26]. The determination is based on the chemical affinity of silver by thiol groups. Following the protocol, 50 mg of dried TPVA was immersed in 50 ml of 0.01 M silver nitrate solution. The flasks were covered to avoid exposure to light and stirred in a shaker for 3 h prior to testing. The remaining silver nitrate was titrated with standardized 0.01 M potassium thiocyanate (KSCN) using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate anion formed a red colored complex with

the iron compound. The thiol content was expressed in mmol/g of polymer. In all cases, the tests were carried out in triplicate measurement.

### Swelling studies

The swelling studies of crosslinked TPVA coagulate samples were carried out by measuring the amount of water incorporated into the matrix. Pre-dried sample was immersed in water having different pH at room temperature. Different pH media was prepared by the cited Ref. [27]. The sample was taken out from water at certain time intervals and weighed after blotting out the excess of water from the surface of sample with tissue paper. They were placed back in water immediately after weighing. The swelling behavior of the sample was specified by a function of time and the weight was recorded as gram of water uptake per minute. After 24 h, the equilibrium state is also determined at water uptake during the time reach steady state. The water absorption of the sample was calculated as the percent swelling by following equation [28]:

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

where,  $W_s$  and  $W_d$  are the weight of the samples in the swollen and dry states, respectively.

### Attenuated total reflectance-infrared spectroscopy (ATR-IR)

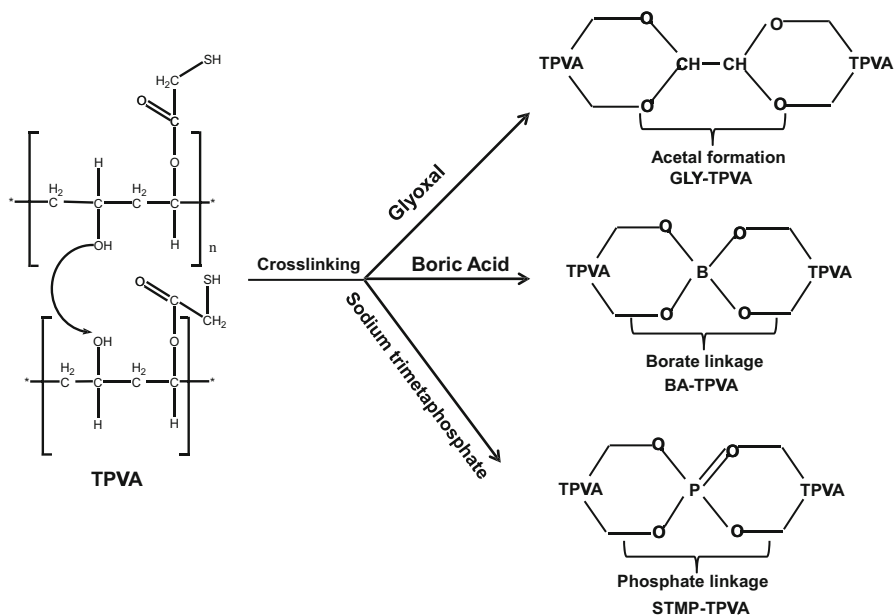
The ATR-IR spectra of samples were recorded on Bruker Alpha P(Opus 65) spectrophotometer. The spectra of crosslinked TPVA samples were recorded over the 400–4,500  $\text{cm}^{-1}$  range.

### Energy-dispersive X-ray microanalysis (EDX)

In order to identify the presence of sulfur and other elements in crosslinked TPVA samples, the SEM–EDX was used. The sample was placed on a sample stub and coated with carbon coating with Auto-Fine Coater K450X (EMITECH, Germany). The images and the elemental analysis in the crosslinked TPVA samples were obtained with EDX Model QuanTax 200 (RONTEC's, Germany).

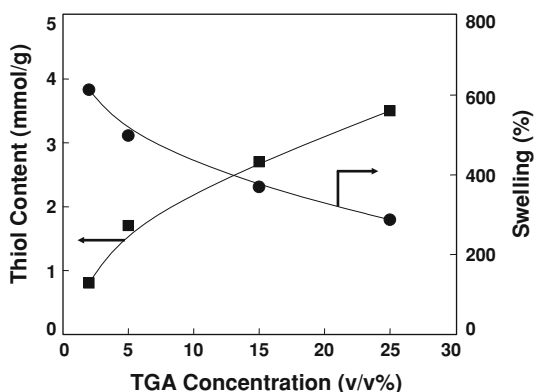
## Results and discussion

In this investigation, the crosslinking under different conditions leads to the formation of stable linkage in between different units of TPVA. The schematic representation of the crosslinking process of TPVA with different agents is presented in Fig. 1. The optimization of the crosslinking parameters was carried out with three crosslinkers, i.e., STMP, GLY and BA under specific conditions. All three crosslinkers showed different bonding strategy and distinct properties with each other. The crosslinking studies of TPVA coagulates were monitored by four



**Fig. 1** Schematic representation of the crosslinking process of TPVA hydrogels

**Fig. 2** Variation of the thiol content and the swelling with the TGA concentration. Reaction conditions: PVA, 2 % (w/v);  $\text{H}_2\text{SO}_4$ , 1 % (v/v); crosslinker, STMP; crosslinker content, 0.1 % (w/v); crosslinking time, 30 min; swelling temp,  $25 \pm 2^\circ\text{C}$ ; pH, 7



different parameters: (a) effect of nature of crosslinker, (b) effect of crosslinker content, (c) effect of crosslinking time, (d) effect of pH. They yielded different crosslinked TPVA coagulates with thiol content in the range of 0.2–3.5 mmol/g.

#### Influence of the TGA concentration

The esterification is strongly dependent on the acid concentration; therefore, higher TGA concentration favored the ester formation. The variation of thiol content and swelling with respect to TGA concentration are shown in Fig. 2. In our study, the acid concentration variation was investigated from 5 to 25 % (v/v) with respect to

PVA concentration and the STMP is used as crosslinker. The results suggested that the combination of crosslinking and esterification had more influence on the hydrophilicity of PVA than individual modifications. As the TGA concentration increases, more hydroxyl groups of PVA were esterified and the remaining hydroxyl groups were available for crosslinking. The reaction conditions were adjusted so that the resulting thiol content remains in the range of 0.5–4 mmol/g, so that we can monitor the influence of the esterification and crosslinking conditions on the physical structure of the PVA. As a result, the crosslinked TPVA matrix become more hydrophobic.

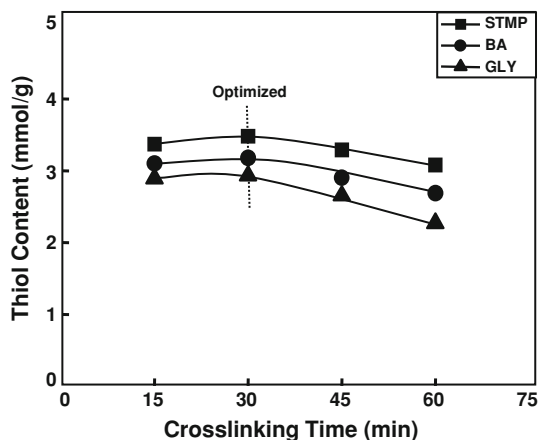
#### Influence of the crosslinking time

Crosslinking time plays a well-defined role in the crosslinking process. According to this study, more the crosslinking reaction time, the higher is the crosslinking degree which is possible due to the maximum interaction of crosslinker with the polymer. The variation of the thiol content and swelling with the crosslinking time is presented in Figs. 3 and 4. The result showed that, as the crosslinking time increases, the swelling and the thiol content showed slight decrease. It seems that 30-min crosslinking is sufficient for optimum thiol group formation. It is interesting to see that the thiol content reaches saturation within 30 min of the crosslinking reaction, beyond which there is slight decrease in the thiol content. On the other hand, the swelling shows much more decrease as the time of reaction increases. We do not anticipate any loss in thiol content with the increase in the reaction beyond 30 min. Perhaps, this is due to the diminishing accessibility of thiol groups within the crosslinked matrix. The swelling shows drastic decrease due to better interpenetrating network formation in the crosslinked matrix.

#### Influence of the crosslinker content

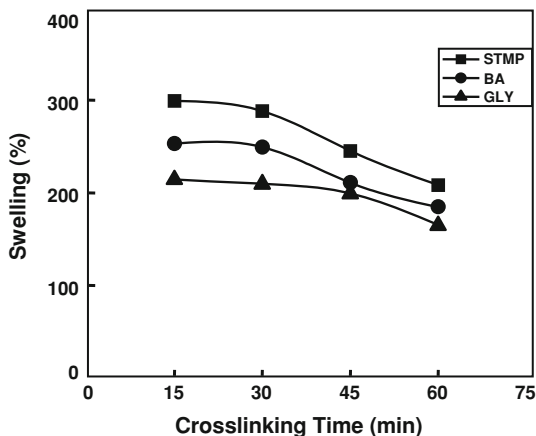
It is conceivable that the higher the crosslinker content, the lower the water absorbency will be. Higher crosslinker concentration produces more interlinking in

**Fig. 3** Variation of the thiol content with the crosslinking time. Reaction conditions: PVA, 2 % (w/v);  $\text{H}_2\text{SO}_4$ , 1 % (v/v); TGA, 25 % (v/v); crosslinker content, 0.1 % (w/v)

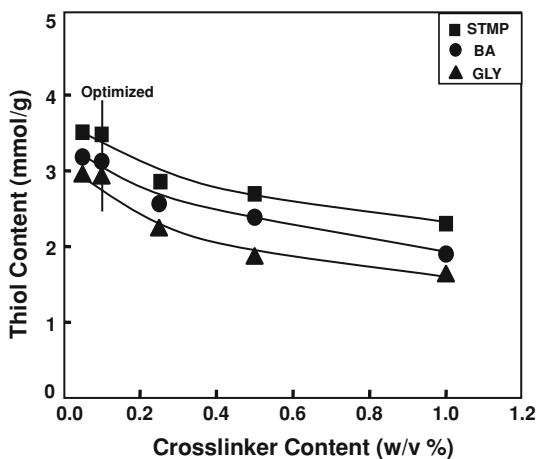


**Fig. 4** Variation of the swelling with the crosslinking time.

Reaction conditions: PVA, 2 % (w/v); H<sub>2</sub>SO<sub>4</sub>, 1 % (v/v); TGA, 25 % (v/v); crosslinker content, 0.1 % (w/v); swelling temp, 25 ± 2 °C; pH, 7

**Fig. 5** Variation of the thiol content with the crosslinker content.

Reaction conditions: PVA, 2 % (w/v); H<sub>2</sub>SO<sub>4</sub>, 1 % (v/v); TGA, 25 % (v/v); crosslinking time, 30 min



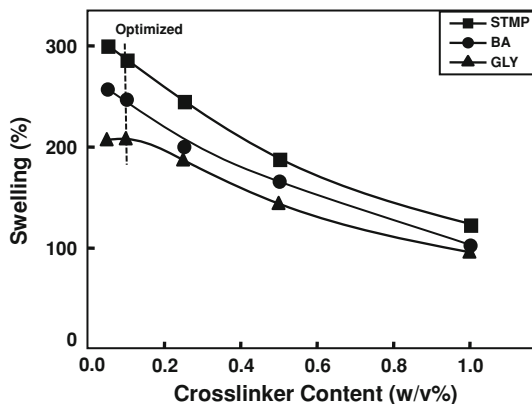
polymeric chains and higher extent of crosslinking of the polymer, which results in less swelling when it is brought into contact with the water. The variation of the thiol content and swelling with the crosslinker content are presented in Figs. 5 and 6. A lower crosslinker content of 0.05 % (w/v) was not able to promote a suitable network to prevent polymer solubility in water. The addition of more crosslinker to the polymeric solution favored the reaction in different edges of the crosslinker molecule and reduced the free volume of the material. Therefore, 0.1 % (w/v) crosslinker was the optimized crosslinker content for further studies.

#### Influence of the nature of crosslinkers

The thiol content of different TPVA samples crosslinked with three crosslinkers is presented in Fig. 7. The swelling property of TPVA hydrogels containing crosslinkers (Fig. 8) is changed by the nature of the crosslinker. However, when

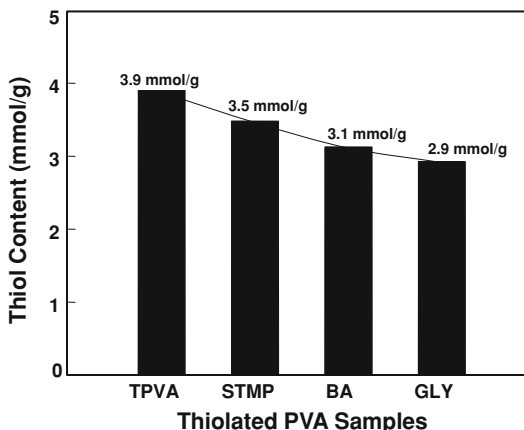
**Fig. 6** Variation of the swelling with the crosslinker content.

Reaction conditions: PVA, 2 % (w/v); H<sub>2</sub>SO<sub>4</sub>, 1 % (v/v); TGA, 25 % (v/v); crosslinking time, 30 min; swelling temp,  $25 \pm 2$  °C; pH, 7



**Fig. 7** Variation of the thiol content with the crosslinker nature.

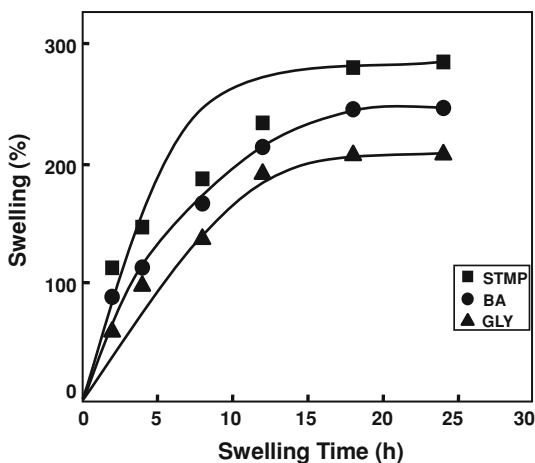
Reaction conditions: PVA, 2 % (w/v); H<sub>2</sub>SO<sub>4</sub>, 1 % (v/v); TGA, 25 % (v/v); crosslinker content, 0.1 % (w/v); crosslinking time, 30 min



crosslinkers are added to the TPVA hydrogels, it is known that there is a decrease in the swelling ability and thiol content, because the molecules of the crosslinkers are placed between the chains of TPVA. Certainly, the structural changes depend on the nature of the crosslinker and contribute to the variation in thiol content. In case of GLY, the aldehyde groups form covalent acetal bonds with the hydroxyl groups of PVA and the resonance established with adjacent double ethylenic bonds via a Schiff reaction [29, 30]. Ionic crosslinking is a simple and mild procedure in contrast to covalent crosslinking. Both BA and STMP are suitable examples of ionic crosslinkers. BA has active four hydroxyl groups in each unit which interact with hydroxyl groups of PVA. It forms stable borate linkage with active hydroxyl group of TPVA, while the STMP forms the phosphate linkage with hydroxyl group of thiolated PVA [29]. Swelling decreases in case of GLY due to efficient crosslinking; therefore, thiol content diminishes more in comparison to the other one. It is evident that crosslinking leads to the development of structure where a fraction of thiol is inaccessible for esterification and hence this is reflected in lower thiol content in crosslinked material.



**Fig. 8** Variation of the swelling with the time for the different crosslinkers. Swelling conditions: crosslinker content, 0.1 % (w/v); crosslinking time, 30 min; swelling temp,  $25 \pm 2$  °C; pH, 7

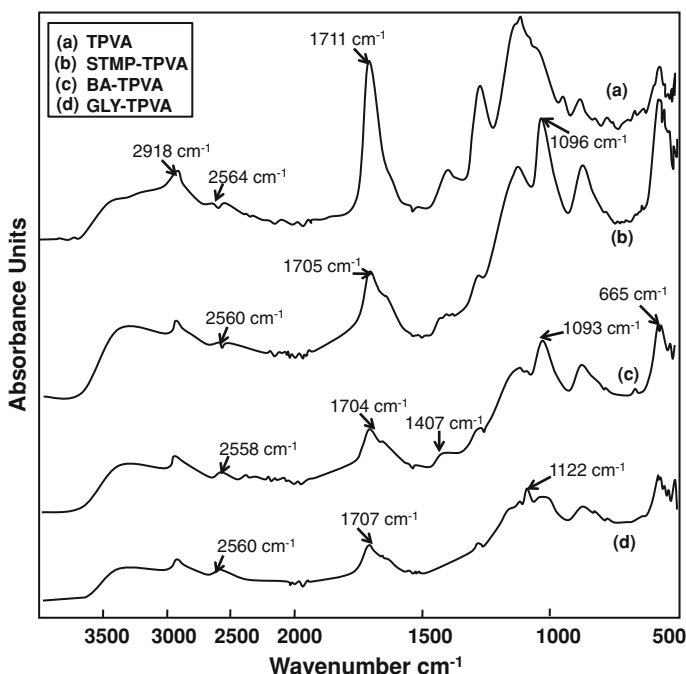


### ATR-IR studies

ATR-IR spectra of uncrosslinked TPVA and crosslinked TPVA with different crosslinkers are shown in Fig. 9. In the spectrum of uncrosslinked TPVA, a broad band appears at  $3,457\text{ cm}^{-1}$  due to the presence of hydroxyl groups in PVA. After crosslinking, this peak diminishes due to the loss of hydroxyl groups. Absorption of asymmetrical stretching of C–H in the PVA in all cases appears at  $2,918\text{ cm}^{-1}$ . The two peaks at  $1,401$  and  $1,271\text{ cm}^{-1}$  are from the secondary O–H in-plane bending and C–H wagging vibrations, respectively. The sharp band appears at  $1,711\text{ cm}^{-1}$  due to the presence of unhydrolyzed acetate groups from stock PVA and sharpness of peaks demonstrated the esterification of PVA [30]. After thiolation, although weak the new peak appears at the  $2,564\text{ cm}^{-1}$  due the presence of thiol group in the polymer chain. However, there is no peak appearing for the S–S bond formation in the spectra.

In STMP-crosslinked TPVA, the band centered at  $1,096\text{ cm}^{-1}$  can be related to the stretching vibrations of pyrophosphate system of P–O–H [31]. The appearance of two bands in the spectrum of STMP-TPVA confirms the ring opening of STMP and its subsequent binding to PVA chains, after crosslinking reaction. In GLY-TPVA, the C–C–C stretching band at  $1,122\text{ cm}^{-1}$  indicates the acetal formation after crosslinking of PVA with aldehyde group of glyoxal [4]. After crosslinking with GLY peak at  $2,567\text{ cm}^{-1}$  is shifted.

In BA-crosslinked TPVA, the intense peak at  $665\text{ cm}^{-1}$  is attributed to vibration of B–O bond. In addition, the absorption band near  $1,407\text{ cm}^{-1}$  is assigned to the antisymmetric stretching vibration of the B–O bond [31]. The band at  $1,093\text{ cm}^{-1}$  was due to the stretching of B–O–C, which confirms the condensation reaction of PVA with boric acid.



**Fig. 9** ATR-IR spectra of uncrosslinked and crosslinked TPVA samples

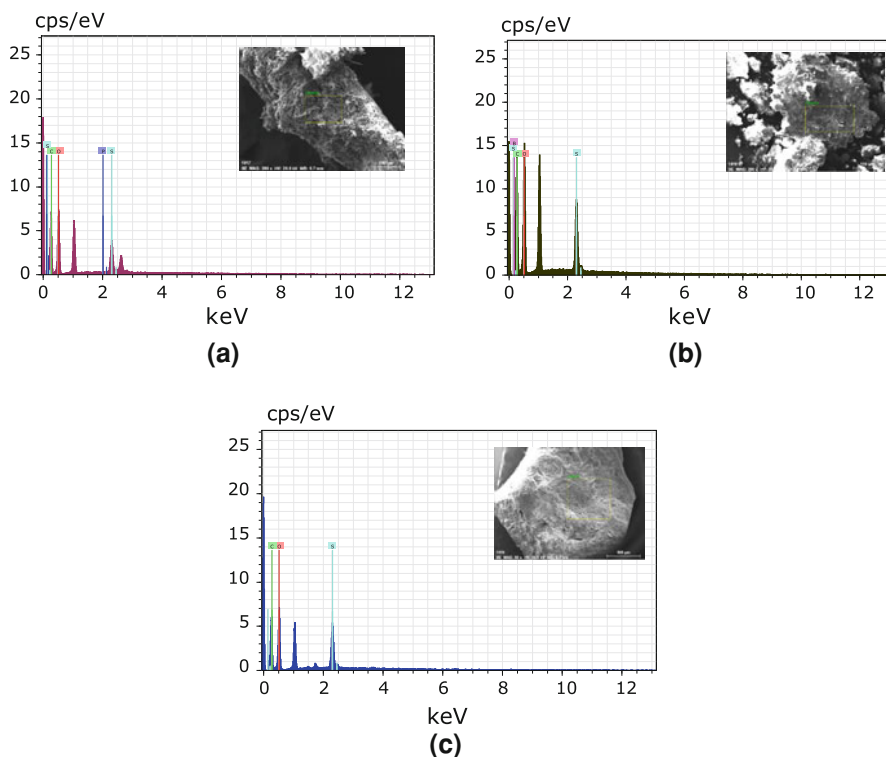
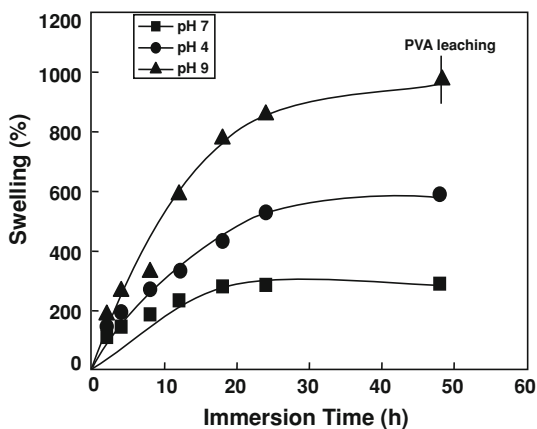
### Influence of the pH

The role of pH on the extent of swelling of the polymer is of great importance. Since a change in pH of swelling media often causes a fluctuation in free volume accessible to penetrating water molecules, it affects swelling properties of the base polymer. The variation of the swelling with immersion time and different pH media is presented in Fig. 10. In the present work, equilibrium swelling behavior of STMP-TPVA sample (thiol content 3.5 mmol/g) was investigated as a function of pH of 4, 7 and 9 at  $25 \pm 2$  °C. Swelling of crosslinked TPVA samples was found to be higher in both acidic and basic medium as compared to the neutral medium. The crosslinked sample is the outcome of the esterification reaction of PVA with TGA, and sensitive to pH of the medium. In acidic medium, the ester bond becomes weaker [32]. Even the phosphate bond is weaker in basic medium, due to this reason the swelling of TPVA in basic medium was not constant after 48 h. Therefore, the pH 7 was optimized for further experiments under above other constant parameters.

### EDX analysis

Additional elemental analysis and quantification of sulfur and other elements in the crosslinked TPVA samples were carried out with EDX. The EDX of both the uncrosslinked and crosslinked TPVA samples shows a distinctive energy peak at around 2 keV, characteristic of carbon and oxygen. The new higher X-ray intensity

**Fig. 10** Variation of the swelling with the different immersion time at varying pH. Crosslinking conditions: crosslinker, STMP; crosslinker content, 0.1 % (w/v); crosslinking time, 30 min; swelling temp,  $25 \pm 2^\circ\text{C}$



**Fig. 11** EDX-ray analysis of crosslinked TPVA. **a** STMP-TPVA, **b** BA-TPVA, **c** GLY-TPVA

was observed at around 3 keV in TPVA samples due to the presence of sulfur in the crosslinked TPVA matrix (Fig. 11). The elemental analysis for different elements present in the crosslinked TPVA samples has been presented in the Table 1 and is in line with our results discussed in previous sections.

**Table 1** The microanalysis of crosslinked TPVA hydrogels

Sample	Thiol content (mmol/g) <sup>b</sup>	Elemental analysis (%) <sup>c</sup>		
		Sulfur	Phosphorus	Boron
TPVA <sup>a</sup>	3.9	3.7	–	–
STMP–TPVA	3.5	3.4	1.8	–
BA–TPVA	3.1	2.8	–	1.3
GLY–TPVA	2.9	2.1	–	–

Conditions: crosslinking time, 30 min; crosslinker content, 0.1 % (w/v)

<sup>a</sup> [23]

<sup>b</sup> Calculated from titration method

<sup>c</sup> Calculated From EDX analysis

## Conclusion

PVA was functionalized by esterification with TGA, to introduce thiol group in the matrix. Subsequently, the TPVA was crosslinked with three crosslinkers: STMP, BA and GLY. The crosslinking reaction was studied through the proper design of the crosslinking reaction conditions and component formulation. Thiol content and swelling behavior of crosslinked TPVA were observed in terms of effect of nature of crosslinker, crosslinker concentration, crosslinking time and pH media. The swelling studies indicated that the crosslinking reduces the swelling capacity of the hydrogel due mainly to the growing crosslinking density and also due to the loss of hydroxyl groups in the PVA. This leads to diminishing molecular mobility and loss of hydrophilicity within the matrix. Due to this reason, the swelling and thiol content decreased. The ATR-IR spectra of the crosslinked TPVA support the involvement of the various groups in the PVA matrix due to the presence of respective components. The above observation suggested that the thiol group is stable as the end group in the matrix; it did not take part in the crosslinking process [23]. The crosslinking was observed due to the involvement of the free hydroxyl groups of PVA. The EDX analysis supports the presence of sulfur and other respective element in the TPVA hydrogels. From all optimizing conditions, we concluded that, STMP is a suitable crosslinker due to their nontoxic nature and moderate crosslinking ability as compared to others. In conclusion, the results provided here suggest that STMP–TPVA has the potential for use as an effective chelating agent for arsenic; the related work has been communicated as a separate work [33].

**Acknowledgments** The authors would like to express their appreciations to Ms. Deepti Gautam for helping their attempts in making the initial draft of this article. Sadiya Anjum sincerely thanks University Grant Commission for the award of a BSR fellowship.

## References

1. Katia CS, Figueiredo LM, Alves C, Borges P (2009) Poly(vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions. *J Appl Polym Sci* 111:3074–3080. doi:[10.1002/app.29263](https://doi.org/10.1002/app.29263)

2. Xiao S, Huang RYM, Feng X (2006) Preparation and properties of trimesoyl chloride crosslinked poly(vinyl alcohol) membranes for pervaporation dehydration of isopropanol. *J Membr Sci* 286:245–254. doi:[10.1016/j.memsci.2006.09.042](https://doi.org/10.1016/j.memsci.2006.09.042)
3. Gohil JM, Bhattacharya A, Ray P (2006) Studies on the crosslinking of polyvinyl alcohol. *J Polym Res* 13:161–169. doi:[10.1007/s10965-005-9023-9](https://doi.org/10.1007/s10965-005-9023-9)
4. Peter S, Hese N, Stefan R (1976) Phenol-selective, highly resistant RO membranes made from PVA for the purification of toxic industrial wastes. *Desalination* 19:161–167. doi:[10.1016/S0011-9164\(00\)88026-1](https://doi.org/10.1016/S0011-9164(00)88026-1)
5. Niğmet U, Agnieszka J, Agnieszka M, Grażyna ZT, Corneliu C (2011) Optimization of  $\text{Co}^{2+}$  ions removal from water solutions via polymer enhanced ultrafiltration with application of PVA and sulfonated PVA as complexing agents. *J Coll Interf Sci* 362:615–624. doi:[10.1016/j.jcis.2011.06.072](https://doi.org/10.1016/j.jcis.2011.06.072)
6. Li X, Li Y, Zhang S, Ye Z (2012) Preparation and characterization of new foam adsorbents of poly(vinyl alcohol)/chitosan composites and their removal for dye and heavy metal from aqueous solution. *Chem Eng J* 183:88–97. doi:[10.1016/j.cej.2011.12.025](https://doi.org/10.1016/j.cej.2011.12.025)
7. Çifci C, Kaya A (2010) Preparation of poly(vinyl alcohol)/cellulose composite membranes for metal removal from aqueous solutions. *Desalination* 253:175–179. doi:[10.1016/j.desal.2009.11.010](https://doi.org/10.1016/j.desal.2009.11.010)
8. Susan R, Sandeman VM, Guñko OM, Bakalinska CA, Howel Y, Zheng MT, Kartel GJ (2011) Adsorption of anionic and cationic dyes by activated carbons, PVA hydrogels, and PVA/AC composite. *J Coll Interf Sci* 358:582–592. doi:[10.1016/j.jcis.2011.02.031](https://doi.org/10.1016/j.jcis.2011.02.031)
9. Ying S, Yuelian P (2008) UF membrane of PVA modified with TDI. *Desalination* 221:324–330. doi:[10.1016/j.desal.2007.01.090](https://doi.org/10.1016/j.desal.2007.01.090)
10. Elena VB, Anis A, Sri B, Alvarez ZE, Sammy LI, Chana V, Basiuk A (2009) Poly(vinyl alcohol)/CNT composites: an effect of crosslinking with glutaraldehyde. *Superlatt Microstr* 46:379–383. doi:[10.1016/j.spmi.2008.10.007](https://doi.org/10.1016/j.spmi.2008.10.007)
11. Priscila MA, Rosemary AC, Izabel CFM, Carla GL, Ana-Mônica QB, Paulo JAS (2011) Development of films based on blends of gelatin and poly(vinyl alcohol), crosslinked with glutaraldehyde. *Food Hydrocoll* 25:1751–1757. doi:[10.1016/j.foodhyd.2011.03.018](https://doi.org/10.1016/j.foodhyd.2011.03.018)
12. Takei T, Ikeda K, Ijima H, Kawakami K (2011) Fabrication of poly(vinyl alcohol) hydrogel beads crosslinked using sodium sulfate for microorganism immobilization. *Proc Biochem* 46:566–571. doi:[10.1016/j.procbio.2010.10.011](https://doi.org/10.1016/j.procbio.2010.10.011)
13. Atta MA, Nermine EM, Arndt KF (2006) Swelling characteristics of pH and thermo-sensitive crosslinked polyvinyl alcohol grafts. *J Polym Res* 13:53–63. doi:[10.1007/s10965-005-9004-z](https://doi.org/10.1007/s10965-005-9004-z)
14. Rathna GVN (2008) Gelatin hydrogels: enhanced biocompatibility, drug release and cell viability. *J Mater Sci Mater Med* 19:2351–2358. doi:[10.1007/s10856-007-3334-9](https://doi.org/10.1007/s10856-007-3334-9)
15. Dulong V, Lack S, Cerf DL, Picton L, Vannier JP, Muller G (2004) Hyaluronan-based hydrogels particles prepared by crosslinking with trisodium trimetaphosphate. Synthesis and characterization. *Carbohydr Polym* 57:1–6. doi:[10.1016/j.carbpol.2003.12.006](https://doi.org/10.1016/j.carbpol.2003.12.006)
16. Chaouat M, Catherine LV, Wilms EB, Brigitte E, Frédéric C, Mircea AM, Didier LA (2008) Novel crosslinked polyvinyl alcohol (PVA) for vascular grafts. *Adv Funct Mater* 18:2855–2861. doi:[10.1002/adfm.200701261](https://doi.org/10.1002/adfm.200701261)
17. Liang S, Liu L, Huang Q, Yam KL (2009) Preparation of single or double-network chitosan/poly(vinyl alcohol) gel films through selectively crosslinking method. *Carbohydr Polym* 77:718–724. doi:[10.1016/j.carbpol.2009.02.007](https://doi.org/10.1016/j.carbpol.2009.02.007)
18. Miyazaki T, Yuuki T, Sachiko A, Takahiko I, Akie H, Keiko E (2010) Role of boric acid for a poly(vinyl alcohol) film as a crosslinking agent: melting behaviors of the films with boric acid. *Polymer* 51:5539–5549. doi:[10.1016/j.polymer.2010.09.048](https://doi.org/10.1016/j.polymer.2010.09.048)
19. Shin EJ, Won SL, Yang HL (2012) Effect of boric acid treatment method on the characteristics of poly(vinyl alcohol)/Iodine polarizing film. *J Appl Polym Sci* 123:672–681. doi:[10.1002/app.3449](https://doi.org/10.1002/app.3449)
20. Naozumi T, Masahiko S, Johta K, Mitsuhiro S, Ryutoku Y (2001) Morphology and mechanical properties of pullulan/poly(vinyl alcohol) blends crosslinked with glyoxal. *J Appl Polym Sci* 82:2273–2280. doi:[10.1002/app.2075](https://doi.org/10.1002/app.2075)
21. Zhang Y, Peter CZ, David E (2010) Crosslinking reaction of poly(vinyl alcohol) with glyoxal. *J Polym Res* 17:725–730. doi:[10.1007/s10965-009-9362-z](https://doi.org/10.1007/s10965-009-9362-z)
22. Blanes M, Gisbert MJ, Marco B, Bonet M, Gisbert J, Balart R (2010) Influence of glyoxal in the physical characterization of PVA nanofibers. *Text Res J* 80:1465–1472. doi:[10.1177/0040517509357654](https://doi.org/10.1177/0040517509357654)
23. Gupta B, Anjum S, Ikram S (2012) Preparation of thiolated polyvinyl alcohol hydrogels. *J Appl Polym Sci* 129:815–821. doi:[10.1002/APP.38856](https://doi.org/10.1002/APP.38856)

24. Shengju W, Fengting L, Hongtao W, Lin F, Bingru Z, Guangtao L (2010) Effects of poly(vinyl alcohol) content on preparation of novel thiol-functionalized mesoporous PVA/SiO<sub>2</sub> composite nanofiber membranes and their application for adsorption of heavy metal ions from aqueous solution. *Polymer* 51:6203–6211. doi:[10.1016/j.polymer.2010.10.015](https://doi.org/10.1016/j.polymer.2010.10.015)
25. Rebecca MD, Peng Y, Gobinda S, Eleanor W, Alexandru DA, Richard SP (2006) Wheat gluten-thiolated poly(vinyl alcohol) blends with improved mechanical properties. *Biomacromolecules* 7:2837–2844. doi:[10.1021/bm060432n](https://doi.org/10.1021/bm060432n)
26. Dominguez L, Yue Z, Economy J, Mangun CL (2002) Design of polyvinyl alcohol mercaptal fibers for arsenite chelation. *React Funct Polym* 53:205–215. doi:[10.1016/S1381-5148\(02\)00174-8](https://doi.org/10.1016/S1381-5148(02)00174-8)
27. Lloyd DD (2000) *Anal Chem Res*. <http://delloyd.50megs.com/moreinfo/buffers2.html>
28. Ahmad SI, Hasan N, Zainul Abid CKV, Mazumdar N (2008) Preparation and characterization of films based on crosslinked blends of gum acacia, polyvinylalcohol, and polyvinyl pyrrolidone-iodine complex. *J Appl Polym Sci* 109:775–781. doi:[10.1002/app.28140](https://doi.org/10.1002/app.28140)
29. Rodriguez E, Katime I (2003) Behavior of acrylic acid-itaconic acid hydrogels in swelling, shrinking and uptakes of some metal ions from aqueous solution. *J Appl Polym Sci* 90:530–536. doi:[10.1002/app.12725](https://doi.org/10.1002/app.12725)
30. Jose R, Cesteros LC, Katime I (1994) Hydrogen bonding and sequence distribution in poly(vinyl acetate-co-vinyl alcohol) copolymers. *Macromolecule* 27:2200–2205. doi:[10.1021/ma00086a033](https://doi.org/10.1021/ma00086a033)
31. Bellamy LJ (1980) *The infrared spectra of complex molecules*, 2nd edn. Chapman and Hall, London
32. Okumura H, Kitazawa N, Wada S, Hotta H (2011) Stability of sucrose fatty acid esters under acidic and basic conditions. *J Oleo Sci* 60:313–320. doi:[10.5650/jos.60.313](https://doi.org/10.5650/jos.60.313)
33. Gupta B, Anjum S, Ikram S (2013) Preparation of crosslinked thiolated poly(vinyl alcohol) hydrogels for arsenic removal from water. *Polym Bull* (communicated)