

Preparation of Thiolated Polyvinyl Alcohol Hydrogels

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ABSTRACT: The esterification reaction of polyvinyl alcohol (PVA) with thioglycolic acid (TGA) in the presence of sulfuric acid as a catalyst offers an attractive route to develop thiolated functional material. During esterification maximum thiol content of 3.9 mmol/g was achieved. It was observed that the esterification is significantly influenced by the reaction conditions, such as TGA concentration, reaction time, reaction temperature and reactant concentration. Sulfuric acid had considerable influence on the thiolation. The thiol content was found to increase with the reaction temperature but showed significant increase beyond 60°C. The swelling decreases with the increasing reaction temperature indicating the role of crosslinking during the thiolation at higher temperature. Suitable conditions for the modification of PVA via thiolation have been investigated. The involvement of thiol group in the PVA matrix was confirmed by ATR-FTIR spectra. The micro analysis of sulfur in sample by EDX analysis showed the sulphur content of 3.7%. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: functionalization of polymers; hydrophilic polymers; swelling

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INTRODUCTION

Polymers obtained by introducing new functional groups in their structure may be used for the recovery of heavy metal ions from water.¹ Modification of polymers by chemical reaction is an interesting domain of functional material. The most studied polymers for the removal of metals include carboxylic, phosphoric, sulfonic, or ammonium groups in their structure. Interactions of metal ions with hydrophilic polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase.² Among these hydrophilic polymers, polyvinyl alcohol (PVA) is the most interesting polymer that has been studied extensively in diverse areas of technology development.^{3–5} PVA is soluble in water where the optimum conditions for dissolutions are primarily governed by the degree of hydrolysis, molecular weight, particle size distribution and crystallinity. From the previous literature, same studies are available for the removal of heavy metal ions from water with various PVA derivatives.^{6–11} To increase the potential use of PVA, modification could be performed by various routes and it is possible to improve properties such as water solubility, metal ion binding capability and selectivity.¹² Esterification of PVA by reaction with various acid chlorides or acid anhydrides to develop functional material.^{13–17}

Heavy metals have strong affinity toward mercaptan (thiol) groups existing in biomolecules, such as amino acids, peptides,

and proteins including some enzymes.^{18,19} Based on the above understanding, thioglycolic acid (TGA) may be used for the modification of PVA by the involvement of thiol as additional groups. Thiols are stronger acids than relevant alcohols and phenols. Sulfur group will easily react with bases, acid, ketones or halogens. Where as the carboxylic acid of TGA will preferentially react in the presence of alcohol or amines. TGA has been used mainly as polymer modifiers and polymer stabilizers.²⁰ Dicharry et al., reported the multifunctional macromolecular thiol-PVA (TPVA) obtained by esterification of PVA with 3-mercaptopropionic acid and used it as a wheat gluten reactive modifier.²¹ Moreno et al. reported the esterification reaction in between hydroxyl group of PVA and carboxylic group functionalized gold nanoparticles which were synthesized by the reaction of mercaptoundecanoic acid and hydrogen tetrachloroaurate.²²

The aim of the present work is the preparation of functional TPVA by imparting —SH group into a PVA frame work. The optimum processing conditions were investigated by single factor experiment with material ratios, the amount of catalyst, reaction temperature and reaction time to serve as targets. The structural changes of TPVA were observed from Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR) spectroscopy and were quantified by Volhard's silver nitrate method. The micro analysis of the samples have been studied by Energy Dispersive X-ray Microanalysis (EDX). The performance of derived TPVA as

chelating agents for the removal of arsenic ions from water has evaluate according to experimental design and response modeling approaches in the next section of the work. This methodology of experimental design is an adequate tool and of great importance for the optimization of thiol content in the base matrix.

EXPERIMENTAL

Chemicals

PVA (M_w 1,50,000 and degree of hydrolysis 85%) was purchased from Sigma. TGA, sulfuric acid (H_2SO_4), potassium thiocyanate (KSCN), silver nitrate, iron ammonium sulfate hexahydrate and methanol (HPLC grade) were purchased from Merck, India. All were used without further preparation. Ultra-pure water, resistivity less than $18 M\Omega cm^{-1}$, produced by a Millipore Milli-Q system was used throughout the experimental work.

Esterification Reaction

Homogenous solution of PVA was prepared by dissolving it in water under vigorous stirring overnight at room temperature. Mixture of TGA [5–25% (v/v)] and H_2SO_4 [0.5 and 1% (v/v)] was added slowly in PVA solution with varying reaction parameters. After completion of the reaction, the mixture was slowly poured into methanol (double ratio of the polymer solution). The white precipitate was the collected and washed repeatedly by methanol than dried under vacuum oven at room temperature.

Thiol Content Estimation

The amount of the thiol groups was determined according to a protocol of *Volhard's silver nitrate method*.¹⁴ The determination is based on the chemical affinity of silver by thiol groups. Following the protocol, 50 mg of dried thiolated PVA (TPVA) was immersed in 50 mL of 0.01M silver nitrate solution. The flask was 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 0.01M 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.

Steps:



(Modified Polymer)

Titration step



End point



(Red complex)

Swelling Studies

The swelling studies of the TPVA coagulate samples were carried out by immersing predried sample in milliQ water at pH 7 and at room temperature. The buffer solution of pH 7 was prepared as per the reference.²³ 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 put back in water immediately after weighing. The swelling of the sample was monitored as a function of time. The water absorption of the sample was calculated as the percent swelling by following equation²⁴:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (4)$$

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

ATR-IR

The ATR-IR spectra of film samples were recorded on Bruker Alpha P (Opus 65) spectrophotometer. The spectra of virgin PVA and optimized thiolated PVA film samples (having thiol content 3.9 mmol/g) were recorded over the range of 400–4500 cm^{-1} .

EDX

To identify the presence of sulfur in the thiolated-PVA 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 sulfur content of the pure PVA and optimized TPVA samples were obtained with EDX Model QuanTax 200 (RONTEC's, Germany).

RESULTS AND DISCUSSION

The esterification process of PVA has been carried out with TGA in the presence of H_2SO_4 as a catalyst at different reaction conditions. The schematic representation of the esterification process is presented in Figure 1. The hydroxyl groups of PVA react with the carboxyl groups of TGA and form thiolated PVA (TPVA) having $-SH$ terminal groups in the matrix. The effect of varying reaction conditions, such as, reaction time, reaction temperature, PVA concentration, TGA concentration and catalyst concentration on the thiol content have been investigated. The resultant TPVA coagulate had thiol content in the range of 0.5–3.9 mmol/g.

Influence of the PVA concentration

The effect of PVA concentration on the thiol content in feed mixture is presented in Figure 2. As the PVA content increased, thiol content showed increasing pattern from 0.5 to 2% (w/v) concentration and then decreases, subsequently. The reaction could not be monitored beyond 10% (w/v) PVA concentration due to the gel formation which leads to severe restriction on TGA diffusion within the viscous medium.²⁵ This leads to limited interaction between acid and base. As a result, the thiol content decreases significantly. From the above studies, 2% (w/v) PVA concentration was optimized for further reactions.

Influence of the Reaction Time

The effect of reaction time on the thiol content in esterification reaction is presented in Figure 3. It may be mentioned here that the time required to achieve equilibrium esterification depends on the nature of the alcohol used. It has been reported that if the chain length of the alcohol is larger, the rate of reaction slows down due to the lesser number of hydroxyl groups



Figure 1. Schematic representation of the esterification reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interacting with carboxyl groups of the respective acid.²⁶ Initially during the reaction, TGA has the characteristic smell (due to the presence of sulfur) and thereafter the smell gets distant indicating the completion of reaction.

The plot shows a sharp increase initially and tends to level off beyond 24 h. The thiol content reaches equilibrium within 24 h with the maximum thiol content of 2.6 mmol/g under our experimental conditions. The reaction began to slow down afterwards, which might be due to the aggregation of the water favouring the reverse reaction (hydrolysis). Shanmugam et al.²⁶ also reported that the longer time did not support the change in final product of the reaction and a noteworthy change was observed at 24 h reaction time.

Influence of the TGA Concentration

In esterification process, the consumption of alcohol was strongly dependent on the acid concentration. Therefore, higher concentration of acid favored the ester formation. The effect of varying ratio of TGA on the thiol content in esterification reaction is presented in Figure 4. The acid concentration variation was observed from 5 to 25% (v/v) with respect to PVA concentration. The continuous increase in acid in feed reaction

mixture leads to higher thiol content. The reaction could not be monitored beyond 25% (v/v) TGA concentration due to the high exothermic nature of the reaction and lower boiling point of TGA. From the above observation, 25% (v/v) TGA concentration was optimized.

Influence of the Catalyst Concentration

In esterification reaction, catalyst plays very important role in reaction acceleration. The effect of catalyst concentration on the thiol content in acid-alcohol mixture is investigated in Figure 5. As the catalyst, concentration increases from 0.5 and 1% (v/v), the thiol content showed an increasing trend. With the increase in catalyst concentration, the reaction medium become more acidic, which helps in the protonation of functional groups and leads the ester formation. Previous studies showed that a very little amount of catalyst is enough to initiate this process.²⁷ Therefore, 1% (v/v) H₂SO₄ concentration is optimized with respect to acid concentration keeping all other parameters constant from subsequent experiments.

Influence of the Reaction Temperature

The influence of the reaction temperature on the thiol content is presented in Figure 6. The reaction was carried out in the

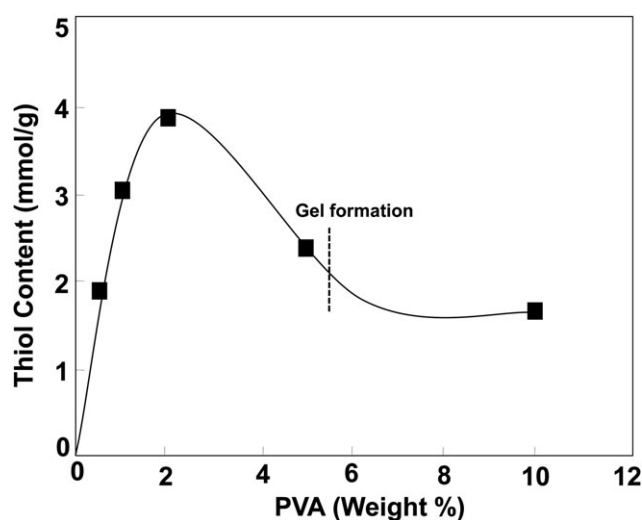


Figure 2. Variation of the thiol content with the PVA concentration. Reaction conditions: TGA concentration, 25% (v/v); H₂SO₄ concentration, 1% (v/v); reaction temperature, 60°C; reaction time, 24 h.

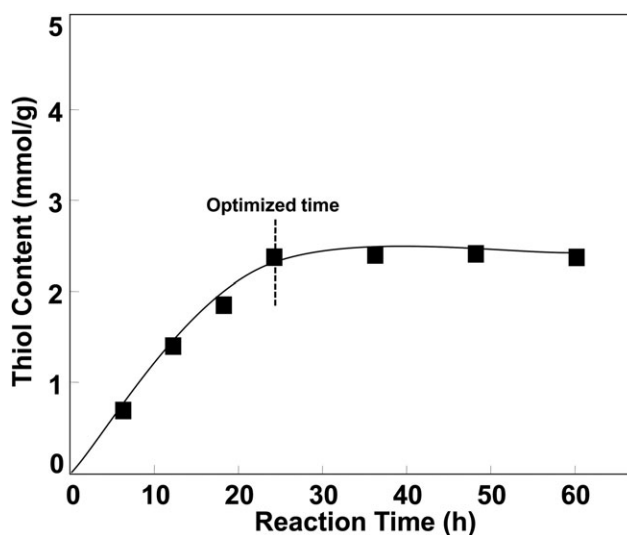


Figure 3. Variation of the thiol content with the reaction time. Reaction conditions: PVA concentration, 2% (w/v); TGA concentration, 5% (v/v); H₂SO₄ concentration, 1% (v/v); reaction temperature, 60°C.

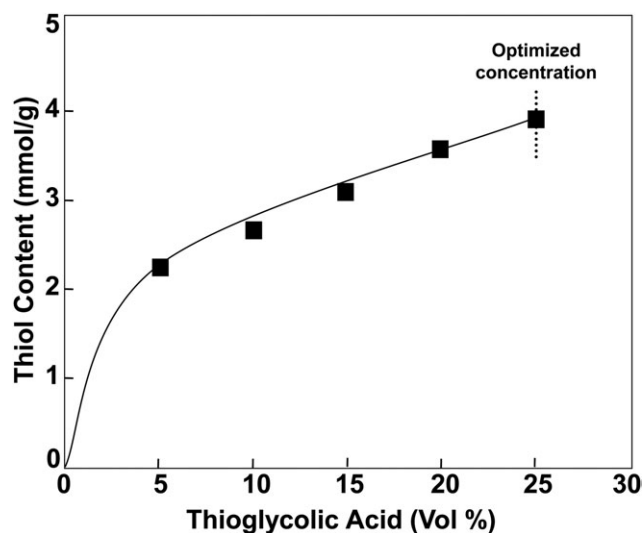


Figure 4. Variation of the thiol content with the TGA concentration. Reaction conditions: PVA concentration, 2% (w/v); H_2SO_4 concentration, 1% (v/v); reaction temperature, 60°C; reaction time, 24 h.

temperature range of 50–80°C at various thiol content to investigate the esterification process. The thiol content trend is strongly influenced by the reaction temperature. Thiol content increases very slowly, with increasing acid concentration upto 25% (v/v) TGA concentration, beyond that reaction is not possible due to the highly exothermic nature of reaction. Interestingly, the thiol content was very close to each other when reaction was carried out at temperature of 60–80°C. The sharp fall in the thiol content beyond 60°C may be the fall out of *in situ* crosslinking process between self hydroxyl groups of PVA. Therefore, at higher reaction temperature, the diffusion of TGA was minimum. It indicates that the optimized reaction temperature is 60°C for PVA esterification with TGA. Our

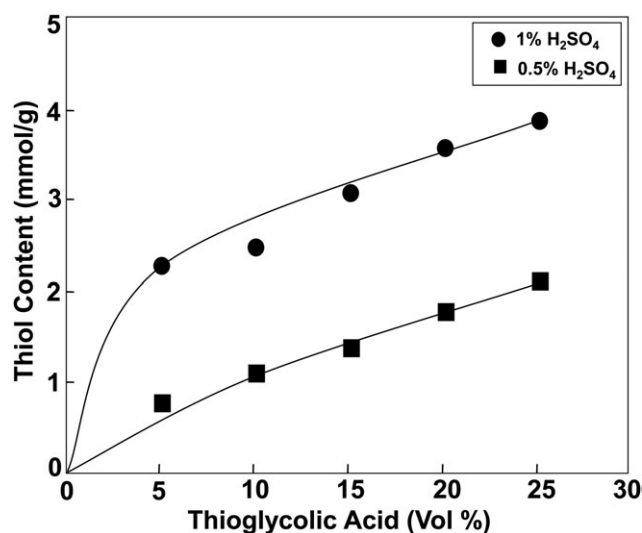


Figure 5. Variation of the thiol content with the TGA concentration at catalyst concentrations. Reaction conditions: PVA concentration, 2% (w/v); TGA concentration, 25% (v/v); reaction temperature, 60°C; reaction time, 24 h.

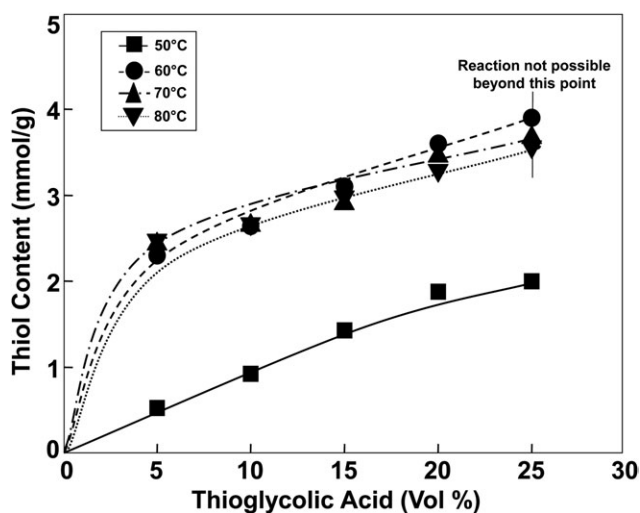


Figure 6. Variation of the thiol content with the TGA concentration and reaction temperature. Reaction conditions: PVA concentration, 2% (w/v); H_2SO_4 concentration, 1% (v/v); reaction time, 24 h.

observations are quite in line with other workers that PVA modification at higher temperature did not improve the esterification reaction.²⁸

Swelling Studies

Pure PVA films dissolve in water due to the high hydrophilic nature of the polymer and extensive formation of hydrogen bonding with water molecules. Therefore, after esterification the thiolated PVA films were hydrophobic in nature. The esterification was carried out in the reaction temperature of 50, 60, 70, and 80°C. The observation of swelling studies of different TPVA coagulate samples (prepared with different reaction temperature) is presented in Figure 7. A sharp decrease in the swelling of the TPVA was observed with the increase in the temperature, irrespective of the variation in the thiol content. It seems that structural changes in the samples take place due to the

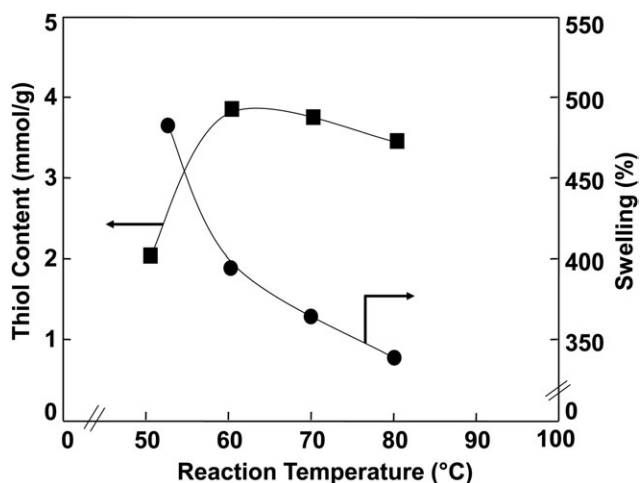


Figure 7. Variation of the thiol content and the swelling with the reaction temperature. Conditions: PVA, 2%(w/v); TGA, 25%(v/v); H_2SO_4 , 1% (v/v); reaction time, 24 h; swelling time, 24 h.

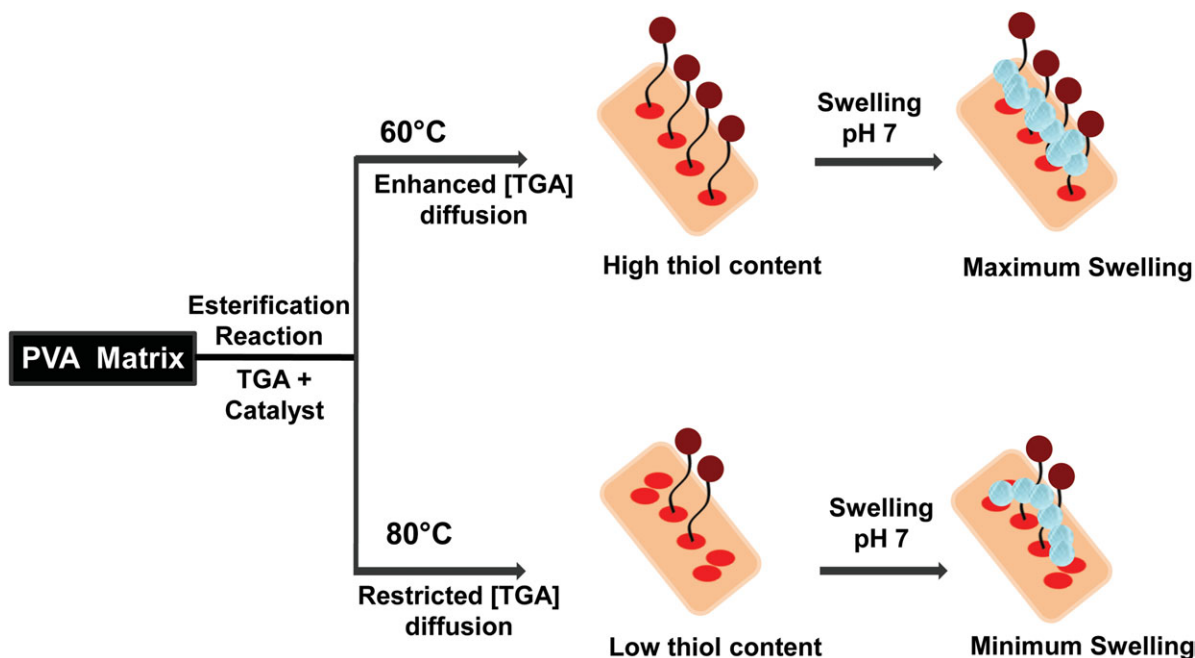


Figure 8. The schematic presentation of the esterification process at different reaction temperature. ● OH group, ● SH group, ● H₂O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of *in situ* crosslinking. The higher reaction temperature, more —OH groups undergo condensation with each other leading to the loss of the reactive sites and inhibit the TGA diffusion in the matrix. Moreover, this process leads to a cross-linked structure where chain mobility is diminished. The cumulative effect of the lower esterification and crosslinking leads to lower water uptake in the matrix prepared at 80°C. The schematic presentation of the esterification process at different temperature is shown in Figure 8. As the reaction temperature increases from 50 to 80°C, the resulting thiol content shows negligible decreasing trend. However, the swelling of the samples decreases, significantly.

The results are interesting and needed to ascertain whether the crosslinking reaction proceed during the esterification process. We carried out the reaction without TGA at different reaction temperatures and monitored the swelling behavior (Figure 9). The swelling of the samples kept at different temperature decreased significantly even without esterification. These observation suggest that etherification including two hydroxyl groups for the same as form adjacent chain leads to the loss of hydroxyl groups and crosslinking of chains. Therefore, at higher reaction temperature the lesser number of OH groups were available for the esterification and also inhibits the diffusion of TGA in the matrix.

ATR-IR Studies

The ATR-IR spectra in absorbance of virgin PVA and optimized thiolated PVA films are shown in Figure 10. The selected PVA has a degree of hydrolysis of 85–90%. The very strong band observed from 3200 to 3500 cm⁻¹ may be assigned to OH stretching due to the strong hydrogen bond of intramolecular and intermolecular type.²⁹ The CH stretching vibration was

observed at 2934 and 2904 cm⁻¹.³⁰ The peaks at 1712 and 1081 cm⁻¹ may be attributed to the stretching vibration of C=O and C—O of the remaining unhydrolyzed vinyl acetate group of the PVA.³¹ The peak at 1374 cm⁻¹ is due to —CH₂— wagging and that at 1323 cm⁻¹ is due to CH and OH bending.³²

In the ATR-IR spectrum of thiolated PVA film, the shape and intensity of peaks at 3457 cm⁻¹ is altered due the absence of free OH group in the matrix. In addition, the CO stretching absorption of an ester group at 1712 and 1711 cm⁻¹ is observed in both polymers. As a result of the unhydrolyzed acetate functionality in PVA and the newly formed ester group in TPVA,

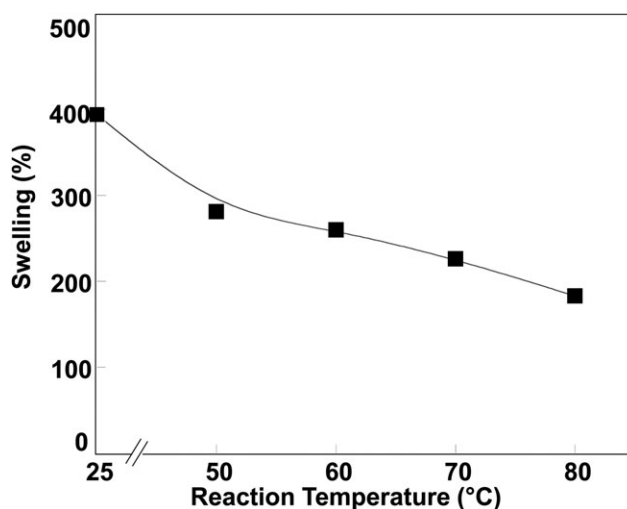


Figure 9. Variation of the swelling with the reaction temperature. Conditions: PVA, 2%(w/v); H₂SO₄, 1% (v/v); reaction time, 24 h; swelling time, 24 h.

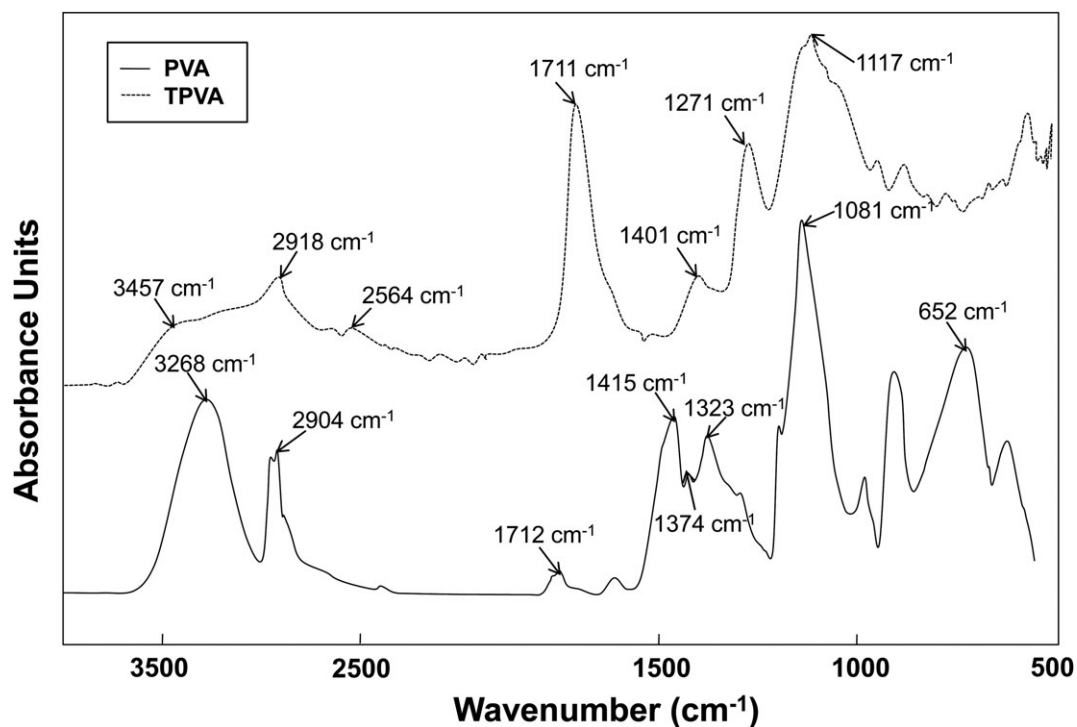


Figure 10. ATR-IR spectra of pure PVA and thiolated PVA films (thiol content 3.9 mmol/g).

respectively. A weak peak appears at 2564 cm^{-1} indicating the presence of thiol group in the matrix after esterification of PVA.³² The spectra of TPVA samples were similar to that of PVA except for the presence of the S—H vibration peak. There is no peak appearing for the S—S bond formation in the spectra. These results indicate that the thiolation process has indeed taken place and the thiol group was not taken part in the esterification reaction.

EDX Analysis

Additional elemental analysis and quantification of sulfur in the TPVA sample was done with EDX. The EDX analysis of both the pure PVA and TPVA samples shows a distinctive energy peak at around 2 keV, characteristic of carbon and oxygen. The new higher X-ray intensity was observed at around 3 keV in TPVA samples due to the presence of sulfur in the PVA matrix (Figure 11). This is more clearly demonstrated in the analysis of

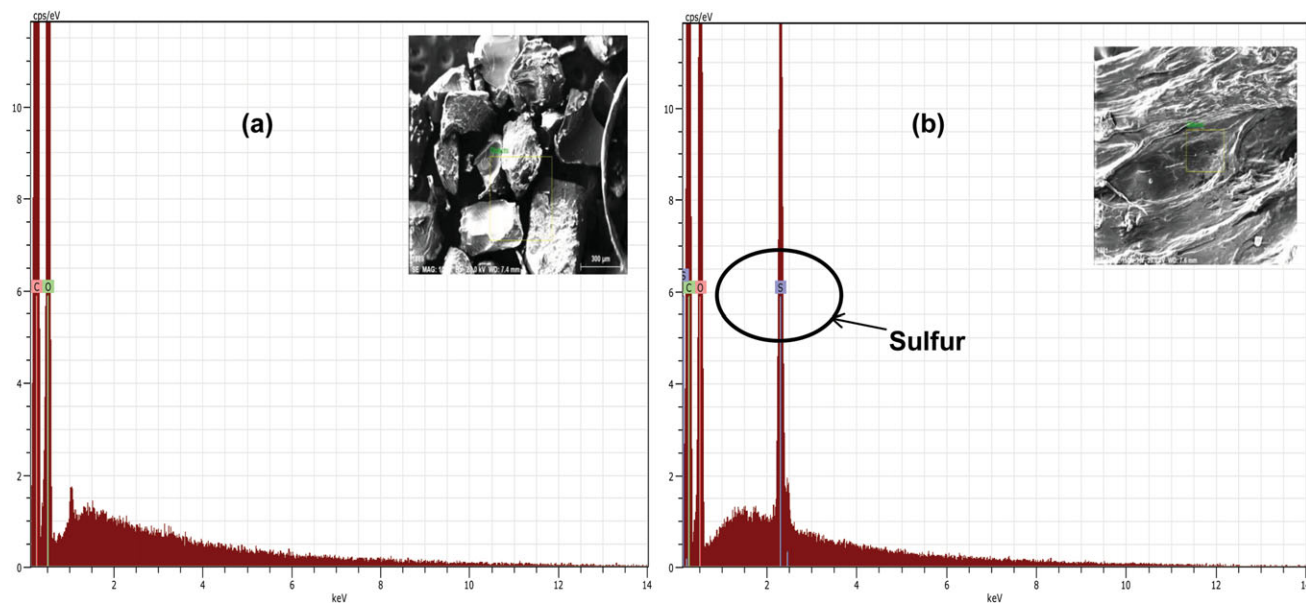


Figure 11. EDX-ray analysis of pure PVA and thiolated PVA films (thiol content 3.9 mmol/g). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the sulfur contents of the sample by EDX. The TPVA sample contained 3.7% (wt) of sulfur confirming the thiolation process.

CONCLUSION

Functionalization of PVA by esterification with TGA is a very promising process to develop a material for water treatment application. The thiol content in the modified materials was found to be in range of 0.5–3.9 mmol/g. It is observed that the reaction conditions such as reaction time, temperature, acid, and catalyst concentration have significant influence on the thiolation process. Consequently, it is important to note that temperature set up for this reaction shows exceptional behavior in aspect of thiol content. As the reaction temperature increases, thiol content decreases up to certain point. Even at higher temperature reaction get declined due to exothermic nature of reaction. The decrease in thiol content was observed due to the *in situ* interaction of hydroxyl groups of PVA. Swelling studies suggested that the decrease in thiol content is due to crosslinked structure of the polymer which inhibits the passage of water molecule in the polymer matrix. The ATR-IR spectra of the thiolated PVA has been support the involvement of thiol group in the PVA matrix due to the presence of the characteristic peak of thiols. The above study stated that the thiol group is stable as the end group in the matrix, it did not take part in the process. The experiment results showed that the presence of the SH deformation peak at 2593 cm^{-1} on TPVA in ATR-IR and the content of sulfur of TPVA was 3.7%. These TPVA materials have been extremely useful in arsenic separation and have been communicated as a separate work.³³

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