Synthesis, Characterizations, and Mechanical Properties of Structurally Modified Poly(vinyl alcohol)

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ABSTRACT: Poly(vinyl alcohol) (PVA) was structurally modified with two different types of chemicals under nitrogen atmosphere in the presence of Sb_2O_3 as a catalyst at 80°C in an aqueous medium. An FTIR and NMR spectrum confirmed the structural modification of PVA. DSC and TGA counseled the thermal properties of structurally modified PVA. Urea modified PVA exhibited higher mechanical strength than the pristine PVA. The FTIR-relative intensities of olefin formation and ketone formation were increased with the increase of weight of water. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2059–2068, 2010

**Key words:** PVA; modification; FTIR; DSC; TGA; mechanical properties

INTRODUCTION

Day by day, the requirements of human beings are increased enormously particularly in the packaging and pharmaceutical sectors for their happy life. Poly(vinyl alcohol) (PVA), a water soluble polymer satisfied the requirements of human beings to some extend in the above mentioned fields. One more advantage of PVA is a biodegradable polymer with hydroxyl functionality. Unfortunately, its mechanical, thermal stability, and antimicrobial activities are very low. To boost up these properties, the structure of PVA should be modified. The research and development of novel soft materials that possess unique properties enable enormous opportunities in the areas of nanotechnology, biotechnology, and medicine fields. Structural modification of PVA can be done with monofunctional and bifunctional compounds. The bifunctional compounds led to the crosslinking of PVA whereas the mono functional compounds led to the simple chemical change with the hydroxyl group of PVA without any crosslinking.

Ossipov et al.[1] reported the structural modification of PVA with different functional groups. Kaur et al.[2] investigated the synthesis and characterization of PVA-g-PP. Surface selective modification of PVA with azobenzene was reported in the literature.[3] In 1996, Matsuda and research team[4] reported the UV irradiated surface grafting of PVA with pectic acid and alginic acid. PVA was modified with formaldehyde,[5] carbamates,[6] gallate,[7] Ibuproven,[8] glycosamines,[9] phosphenanthrene derivatives,[10] methyloil groups,[11] polypropylene,[12] fatty acids,[13] poly(methacrylic acid),[14] sodium benzoate,[15] and docosanoic acid chloride.[16] Rhim et al.[17] studied the poly(acrylic acid-co-maleic acid) crosslinked PVA with improved thermal properties. Sulfur succinic acid crosslinked PVA was synthesized and characterized with DSC and swelling properties.[18] Gimenez et al.[19] analyzed the carboxylic acid anhydride crosslinked PVA by NMR, TGA, and water absorption property and they reported the increased thermal stability. Bifunctionalized hardeners modified PVA report is also available in the literature.[20] Hexamethyl diisocyanate was used as a modifier for PVA in the year 1975.[21] Rhim et al.[18] reported the sulfo succinic acid modified PVA for per-vaporation separation of water alcohol mixture. Mukherjee et al.[22] successfully proved the improved mechanical strength and moisture resistance of PVA after structural modification. Modification of PVA with dimethyl dichlorosilane,[23] poly (organo phosphazene),[24] and vinyl sulfonamide[25] report is available in the literature. By thorough literature survey, we could not find any report based on the succinimide (SI) modification of PVA with FTIR based kinetic study. In this investigation, for the first time, we took this job as a challenge and

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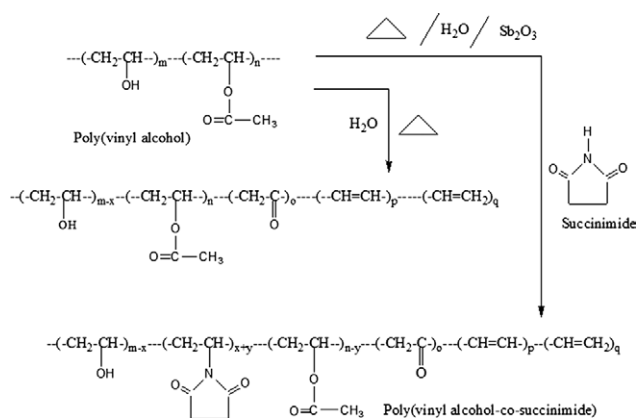
Scheme 1 Surface grafting of SI onto PVA.

successfully modified the structure of PVA with SI, and further characterized with various analytical tools.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA, Otto kemi, India, M_w-125,000, 85% hydrolyzed) was purchased and used as received. Succinimide (SI, Loba Chemie, India), urea (Merck, India), Thiourea (TU, Merck), Sb_2O_3 (SD Fine chemicals, India) were purchased and used as received. Double distilled (d.d) water was used for the solution preparation purpose.

Structural modification of PVA with SI

PVA (1 g) was dissolved in 100 mL of d.d water at 80°C for 1.5 h and 5% weight of SI was added with vigorous stirring. The contents were transferred into a 250 mL round bottom flask (RBF). Sb_2O_3 (0.03 g), condensation catalyst, was exactly weighed and added to the contents under vigorous stirring condition. The condensation reaction was effectively took place with the aid of Sb_2O_3 under nitrogen atmosphere. The condensation reaction was allowed for the next 3 h under nitrogen atmosphere with vigorous stirring. At the end of the reaction time, the contents were poured onto polyimide film for making the modified polymer in the form of film. Thus obtained poly(vinyl succinimide) (PVS) copolymer film was dried at 70°C for 2 h without pores. The reactions are shown in Scheme 1. Under different experimental conditions, the structure of PVA was modified with SI.

Structural modification of PVA with urea and TU

The aforementioned procedure was followed here for the structural modification of PVA with 1 g of urea or TU. The reactions are shown in Scheme 2.

Characterizations

FTIR spectrum confirmed the structural modification of PVA with SI. The instrument used here was Shimadzu 8400 S model FTIR spectrometer, Japan. The film sample was used to measure the FTIR spectra. For quantitative applications, the corrected peak area of the sample was determined after proper baseline corrections. DSC thermogram of the film samples before and after structural modification of PVA was measured by using Mettler Star SW8.10 model instrument (USA) under nitrogen atmosphere at the heating rate of 10°C/min. To erase the previous thermal history, the second time heating and cooling scan was considered here. Thermogravimetric analysis (TGA) was carried out for the modified and unmodified PVA film samples by SDT Q 600 V8.2 model instrument (USA) at the heating rate of 10°C/min under air atmosphere. NMR spectrum (both H^1-NMR and C^{13}-NMR) was recorded by using Varian Unity Inova 300 MHz spectrometer (Japan) in deutorated water as a solvent. Mechanical properties of the polymer film samples were measured by using Universal Tensile Tester (Lloyd D-882 according to ASTM standard) instrument (India). Opacity of the polymer film sample was done through FTIR spectroscopy. FTIR spectrum was recorded for the neat film sample and the absorbance value was noted. The relative intensity (RI) of the peak was determined as follows:

$$\text{RI of carbonyl peak} = \text{RI}_{[C=O/CH]} = A_{1733}/A_{847} \quad (1)$$

$$\text{RI of terminal double bond} = \text{RI}_{[C=C/CH]TD} = A_{1578}/A_{847} \quad (2)$$

$$\text{RI of middle double bond} = \text{RI}_{[C=C/CH]MD} = A_{1661}/A_{847} \quad (3)$$

Where A is the corrected area of the peak, 1730 cm^{-1} is due to the carbonyl stretching, 1578 cm^{-1} is
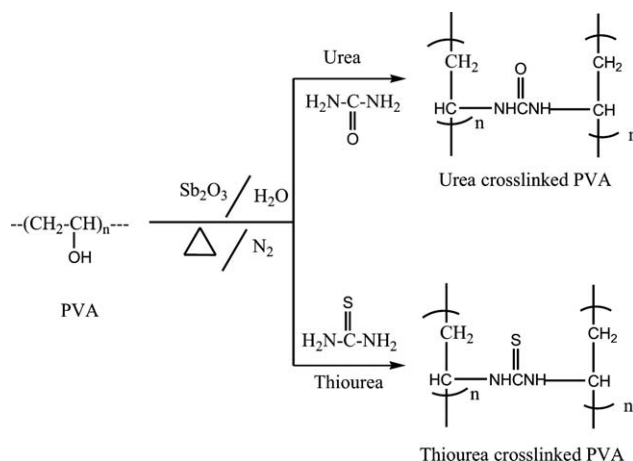
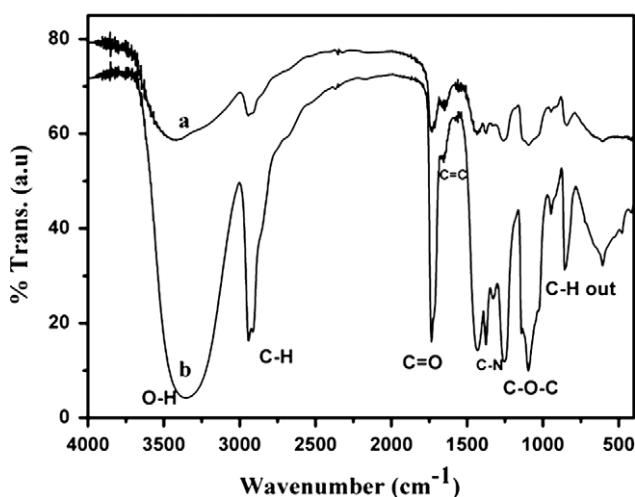**Scheme 2** Cross linking of PVA with urea and TU.

Figure 1 FTIR spectrum of (a) pristine PVA, (b) PVS copolymer.

corresponding to the terminal double bond stretching and 1661 cm^{-1} is due to the middle double bond. A C—H out of plane bending vibration is appeared at 847 cm^{-1}.

RESULTS AND DISCUSSION

Structure of PVA was modified under two different headings, namely, (1) structural modification of PVA without crosslinking (SI) and (2) structural modification of PVA with crosslinking (urea and TU).

Structural modification of PVA with SI

FTIR spectroscopy

FTIR spectrum of pristine PVA is represented in Figure 1(a). The important peaks are characterized below. A broad peak between 3500–3000 cm^{-1} is due to the OH stretching of PVA. The C—H symmetric and antisymmetric stretching vibrations are observed at 2923 and 2849 cm^{-1} respectively. A peak at 1723 cm^{-1} is corresponding to the carbonyl stretching of vinyl acetate in PVA. C—H out of plane bending vibration is observed at 847 cm^{-1}. Figure 1(b) showed the FTIR spectrum of poly(vinyl succinimide) (PVS) copolymer. Here also one can observe the same peaks as mentioned in PVA with some
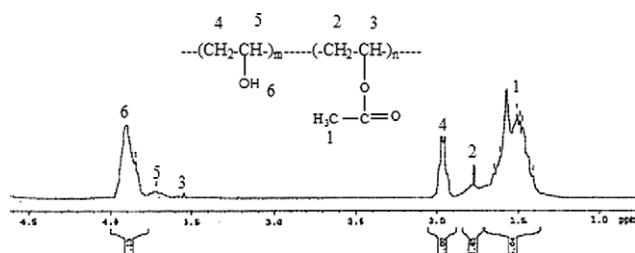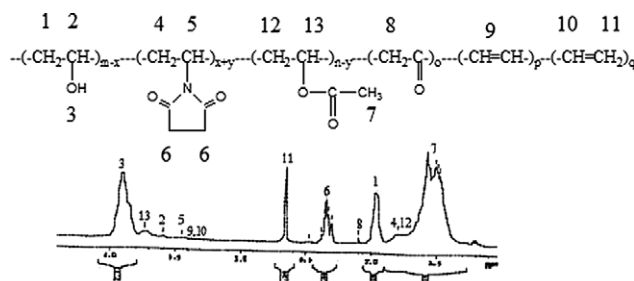

Figure 2 H^1-NMR spectroscopy of pristine PVA.

new peaks. The new peaks are characterized below:
1658 cm^{-1} —C=C stretching, 1363 cm^{-1} —C—N stretching of PVS copolymer. Hence, FTIR spectrum confirmed the chemical modification of PVA with SI.

H^1-NMR spectroscopy

The structure of PVA before and after chemical modification can be confirmed by H^1-NMR spectroscopy. Figure 2 showed the H^1-NMR spectrum of pristine PVA. The important peaks are characterized later: CH$_3$-1.5 ppm, CH$_2$-1.9–2.0 ppm, CH-3.5–3.7 ppm, OH-3.9 ppm. Figure 3 confirmed the structure of PVS copolymer. The new peaks are characterized below: From 2.1 to 2.7 ppm some new peaks are appeared due to the structural modification of PVA. The CH$_2$ proton of SI group is appeared at 2.3 ppm. A sharp peak at 2.7 ppm is depicted to the =CH$_2$, formed during the structural modification of PVA due to hydrolytic oxidation reaction. Structural modification of PVA with SI in an aqueous medium led to six different segments (i.e.) vinyl alcohol, vinyl SI, vinyl acetate, acyl group, middle alkenes and terminal alkenes. The NMR peaks are confirmed with the structure and mentioned in Figure 3.

C^{13}-NMR spectroscopy

The C^{13}-NMR spectrum of pristine PVA is shown in Figure 4. The important peaks are explained below:

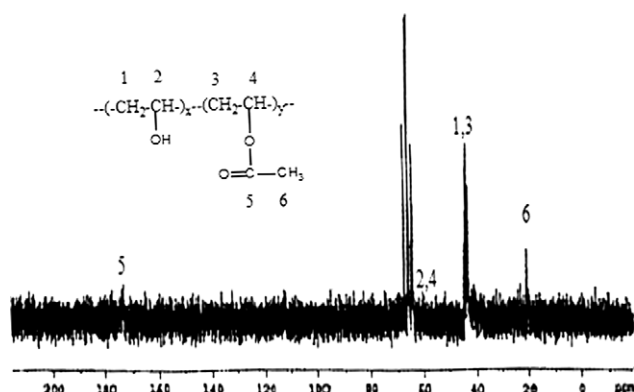**Figure 3** H^1-NMR spectroscopy of PVS copolymer.
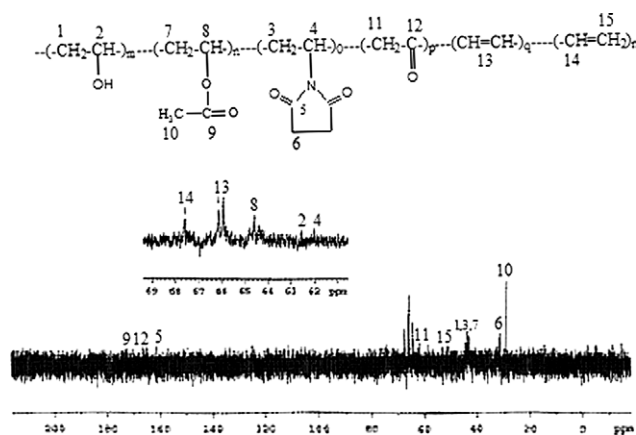

Figure 4 C^{13}-NMR spectrum of pristine PVA.

Figure 5   C^{13}-NMR spectrum of PVS copolymer.

CH$_3$-20 ppm, C=O-175 ppm, CH$_2$-44 ppm, CH-65 ppm. PVA after structural modification showed some new peaks. The peaks with structure are represented in Figure 5. Among them the important one is SI—CH$_2$ appeared at 31 ppm. Thus, the structural modification of PVA with SI was confirmed.

DSC study

DSC of PVA after structural modification with SI is shown in Figure 6. To erase the previous thermal history, the second heating scan was considered here. In the present system, the de-watering temperature ($T_{d.w}$), alpha transition temperature (T_α) and melting temperature (T_m) values are observed at 73.5, 171.1 and 291.6°C, respectively (Table I). PVS copolymer exhibited the increase in $T_{d.w}$ and T_m values but decrease in T_α value. The changes in the phase transition temperature are due to the structural modification of PVA with SI in an aqueous condition. The increase in $T_{d.w}$ and T_m values confirmed the structural modification of PVA backbone by SI.
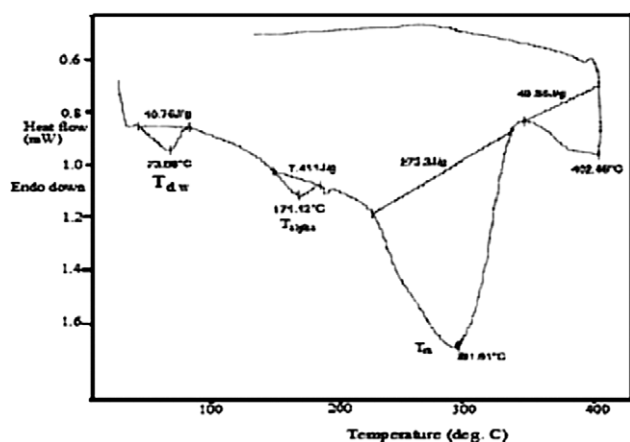
TABLE I
DSC Data of PVA Before and After Modification

System	$T_{D.W}$ (°C)	$T_{\alpha1}$ (°C)	$T_{\alpha2}$ (°C)	T_m (°C)
Pristine PVA	83.4	190.5	–	222.7
PVS copolymer	73.5	171.1	–	291.6
PVA-Urea	65.9	65.9	–	204.5
PVA-TU	87.3	171.5	140	210.3

TGA profile

Figure 7 shows the TGA of PVA before and after structural modification. Figure 7(a) showed the TGA of pristine PVA. It showed a three-step degradation process. The first minor weight loss step up to 225°C is due to the removal of moisture, physisorbed, and chemisorbed water molecules. This step coinside with the TGA thermogram below 200°C. The second major weight loss step is associated with the degradation of PVA backbone. The third minor weight loss step is depicted to the degradation of vinyl acetate group in PVA. Above 600°C, it showed approximately 7.1% weight residue remained due to the various carbonaceous matters. Figure 7(b) exhibited the TGA of SI modified PVA. The thermogram showed a four-step degradation process. The reason for first and second step degradation steps is similar to pristine PVA. The third weight loss step from 350 to 493°C is corresponding to the degradation of SI group in the copolymer structure. The fourth minor weight loss step revealed the degradation of vinyl acetate group of PVA copolymer. The important point is the degradation temperature of fourth step had increased due to the structural modification of PVA with SI. Above 600°C, it showed 5.8% weight residue remained due to the structural modification process. The carbonaceous mattes are responsible for the % weight residue remained above 600°C. This inferred that after structural modification with SI,
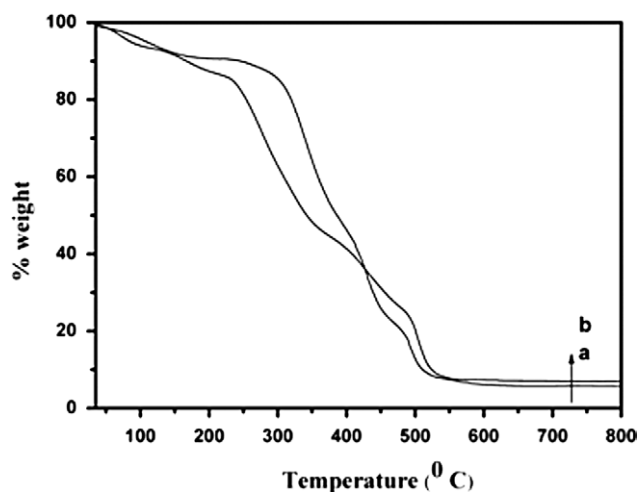

Figure 6   DSC of PVS copolymer.

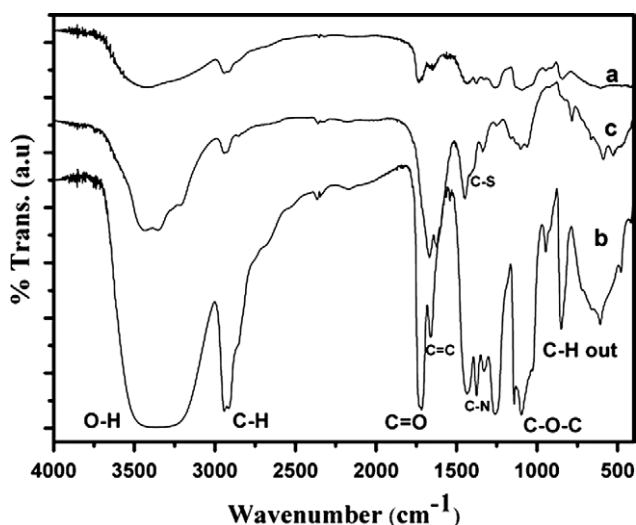**Figure 7**   TGA of (a) pristine PVA, (b) PVS copolymer.

Figure 8 FTIR spectra of (a) pristine PVA, (b) PVA-Urea, (c) PVA-TU.

the char forming behavior of PVA was decreased. In comparison, the PVS copolymer showed lower thermal stability due to the decrease in molecular weight of PVA during the structural modification reaction which was accelerated by the oxidative degradation and thermolytic oxidation reactions.

Structural modification of PVA with urea and TU

FTIR spectroscopy

Figure 8(a) exhibited the FTIR spectrum of pristine PVA. The important peaks are characterized later: A broad peak appeared around 3500 cm^{-1} explained the OH stretching of PVA. A twin peak around 2900 cm^{-1} accounted the C—H symmetric and antisymmetric stretching vibration of PVA. Peak at 1634 cm^{-1} informed about the C=O group present in PVA(vinyl acetate group). Figure 8(b) represented the FTIR spectrum of urea modified PVA. The aforementioned peaks are appeared here also. Apart from those peaks, we observed some new peaks. They are explained later: A sharp new peak at 1723 cm^{-1} declared the keto group. The C—N peak was appeared at 1446 cm^{-1}. A sharp peak at 847 cm^{-1}, indicated the C—H out of plane bending vibration. Appearance of these new peaks confirmed the structural modification of PVA with urea. Figure 8(c) mentioned the FTIR spectrum of TU modified PVA. Presence of C=S can be confirmed by seeing a hill at 1400 cm^{-1}. Thus, the structural modification of PVA with urea and TU are confirmed by FTIR spectroscopy.

DSC study

DSC can determine the phase transition of PVA before and after structural modification with urea.

Figure 9 explained the DSC of urea crosslinked PVA. DSC informed about the $T_{d.w}$, T_α, and T_m of urea crosslinked PVA. Figure 9(a) represented the DSC of pristine PVA. The $T_{d.w}$ value is appeared at 83.4°C. The T_α value is appeared at 190.5°C. In addition, the T_m is noted at 222.7°C. PVA after structural modification with urea is represented in Figure 9(b). The $T_{d.w}$ value (removal of physisorbed water molecules) was appeared at 65.9°C. The T_α was decreased to 127.4°C. This explained the change in crystallinity value of PVA. Because during the structural modification process, inter molecular and intra molecular hydrogen bonding forces were broken and the PVA chains were free to move. This leads to the change in the phase transition of PVA. Moreover, during the heating process again the freedom of rotation is increased. Hence the cooling curve is not presented here. The T_m value was still decreased to 204°C. The reduction in T_m is due the following reasons. (1) reduction in molecular weight of PVA through hydrolytic degradation reactions. (2) inner microstructure transition. (3) formation of keto group due to hydrolytic oxidation reaction. (4) formation of C=C due to thermal degradation reaction. (5) hydrolysis nature of urea crosslinked PVA. (6) lower % crosslinking of PVA chains with urea. (7) breaking of inter and intra molecular hydrogen bonding. This suggested that during the structural modification of PVA with urea, low % crosslinking reaction occurred between PVA and urea.

Figure 9(c) confirmed the DSC of TU modified PVA. The present system showed increase in $T_{d.w}$ value (87.3°C). During the structural modification of PVA with TU, due to hydrolytic oxidation and thermal degradation reactions, C=O and C=C were formed. This made the polymer amorphous. Here one can see two T_α values. The $T_{\alpha1}$ was appeared at 171.5°C, the $T_{\alpha2}$ was appeared at 140°C. Appearance
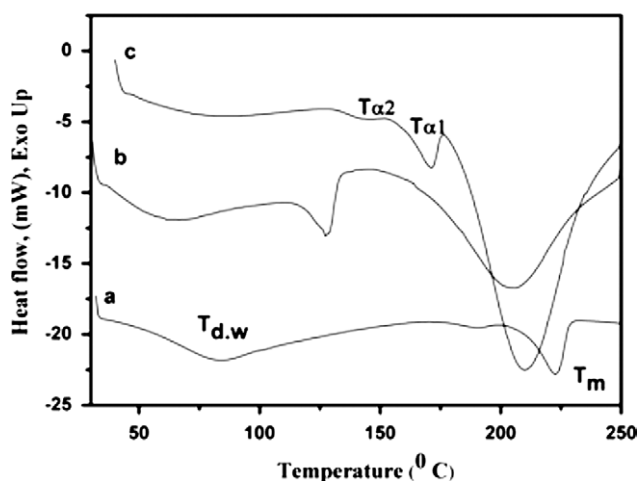

Figure 9 DSC of (a) pristine PVA, (b) PVA-Urea, (c) PVA-TU.

TABLE II
Mechanical Properties of PVA Before and After Modification

System	Tensile Strength (MPa)	% elongation
PVA-pristine	82.52	27
PVA-Urea	125.32	423
PVA-TU	38.75	3.5

of multi T_α informed about the semicrystalline nature of PVA. The T_m value was appeared at 210.3°C. This value is lower when compared with the pristine PVA. At the same time, this value is slightly higher than that of the urea modified PVA. In 2006, Bin et al.[26] explained the DSC of PVA and PVA nanocomposites, in which the author described that the T_m value of PVA – nano composite was lower than that of pristine PVA. Our T_m results coinside with their reports. Table I showed the DSC value of PVA before and after structural modification with urea and TU.

Mechanical properties

Mechanical properties of the polymer samples were measured by using Universal Tensile Tester (Lloyd D-882 according to ASTM standard) instrument through the procedure described elsewhere.[27] Table II explained the mechanical property value of PVA before and after modification. Pristine PVA showed the tensile strength value of 82.52 kN/mm^2 with the % elongation value of 27% (Fig. 10). PVA after structural modification with urea, the tensile strength value was raised to 125 kN/mm^2 with sudden hike in % elongation value (423 %) (Fig. 11), whereas the TU cross linked PVA showed the tensile strength value of 38.7 kN/mm^2 (Fig. 12). This reduction in tensile strength value is associated with the breaking of inter and intra molecular hydrogen bonding due
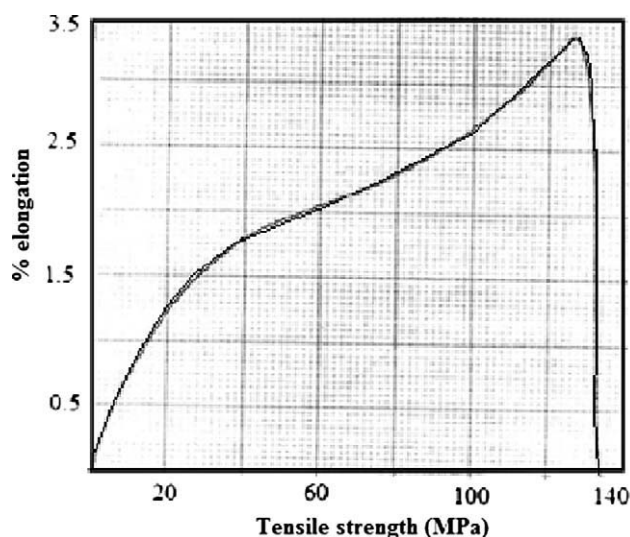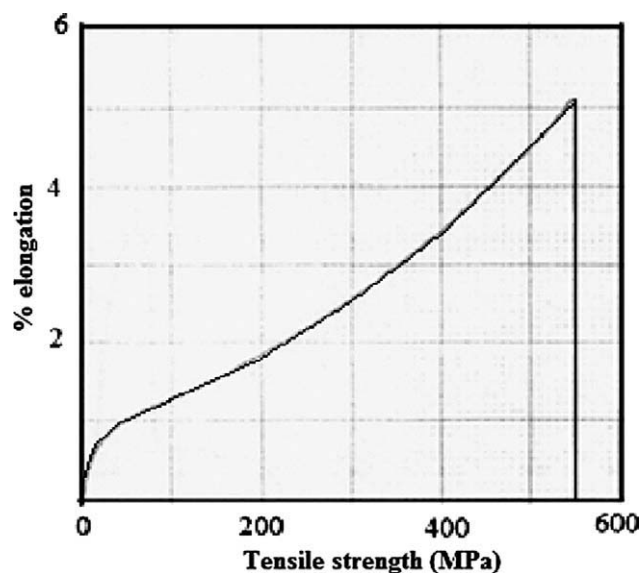

Figure 11 Mechanical behavior of PVA-Urea.

to the structural modification of PVA with TU in an aqueous condition at higher temperature. The extension at break and maximum load applied also expressed the same. Also the formation of C=O group and C=C accounted the destruction of mechanical property of TU modified PVA. Tian et al.[28] explained the reaction scheme for the structural modification of PVA. Our reaction scheme also explained the same concept. Here, Figures 10–12 are essential to prove the mechanical properties of PVA before and after structural modification with different agents. These figures are the solid evidences to prove our concept.
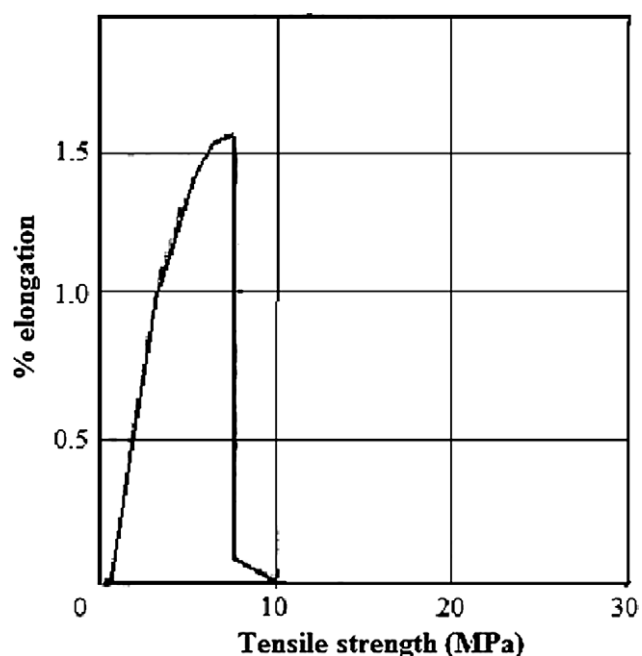

Figure 10 Mechanical behavior of pristine PVA.

Figure 12 Mechanical behavior of PVA-TU.

TABLE III
Optical Property

System	% opacity
PVA-pristine	0
PVA-Urea	22.04
PVA-TU	30.97

Opacity study

Table III represented the optical property of PVA and its modified structure. The TU modified PVA showed the highest opaque value. This indirectly informed that PVA after structural modification with TU, the crystallinity was slightly improved. This is due to the presence of hydrophilic S group in the TU units. The urea modified PVA showed the higher opaque value than the pristine PVA, again it confirmed the structural modification of PVA with urea in an aqueous condition. Recently Maria et al.[29] explained the opacity of PVA-gelatin blends. Our results coinside with that research article.

During the structural modification of PVA with SI, urea or TU, we found some new peaks in the FTIR spectrum, among them, $C=C$ is important one. The $C=C$ stretching is absent in the pristine PVA. Moreover, the SI units are not having $C=C$ bond in its structure. However, the modified PVA showed such a $C=C$ stretching. Hence, we concluded that the $C=C$ stretching must be formed during the structural modification of PVA due to thermolytic and hydrolytic oxidation reactions. In 2002, Alexy et al.[30] reported about the terminal double bond (TD) and middle double bond (MD) formations in PVA. By keeping their report in our mind, we have analyzed the FTIR spectrum of modified PVA films treated under different experimental conditions like variation in reaction time, temperature, amount of water and % weight of SI. During the FTIR spectral analysis, we found that the RI of carbonyl group was increased under different experimental conditions. For real calculation the RI of pristine PVA was subtracted from the modified one, due to ester carbonyl peak, from the structurally modified PVA. This informed us that the RI of $C=O$ was formed due to the oxidation of secondary alcoholic group in PVA. In this investigation, we have measured the order of $C=O$ and $C=C$ formation reactions from the FTIR – RI method under different experimental conditions.

Effect of time on the RI of $C=O$ and $C=C$ formation reactions

Figure 13(a–e) indicated the FTIR spectra of PVA heated in 100 mL of d.d water for different time interval at 80°C. The reaction time was varied between 1800 and 9000 sec, by keeping other experi-
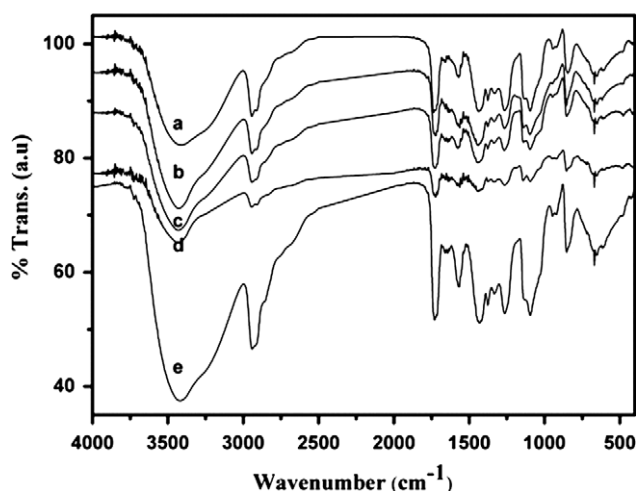

Figure 13 FTIR spectra of PVA heated in 100 mL of water at 80°C for (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min, (e) 150 min.

mental conditions as constant (without SI or urea or TU). While increasing the stirring time in an aqueous medium, the RI of $C=O$ as well as $C=C$ were increased due to hydrolytic oxidation reaction.

Figure 14 showed the plot of Time Vs RI. Figure 14(a) is a plot of Time Vs $RI_{[C=O/CH]}$, the plot showed a straight line. It indicated that while increasing the reaction time, the conversion of secondary alcoholic group into a ketone was increased. Moreover, the RI of MD as well as TD formation was also increased. Figure 14(b,c) are the plots of Time Vs $RI_{[C=C/CH]TD}$ and Time Vs $RI_{[C=C/CH]MD}$ respectively. In comparison, the RI of TD was higher than that of MD. This is due to the following reasons: (1) the OH groups in PVA were inter as well as intra molecularly associated with each other. (2) the thermolytic oxidation of free OH group was easier than that of the hydrogen bonded one. (3) the free OH groups exposed towards outside were subjected
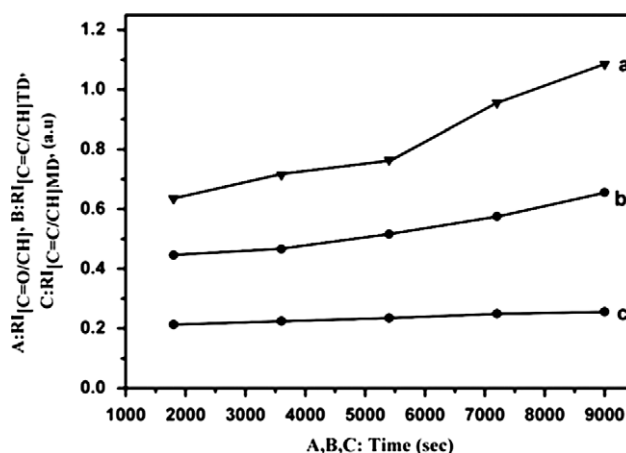

Figure 14 Effect of Time on the FTIR-RI of (a) [C=O/CH], (b) [C=C/CH]$_{TD}$, (c) [C=C/CH]$_{MD}$.
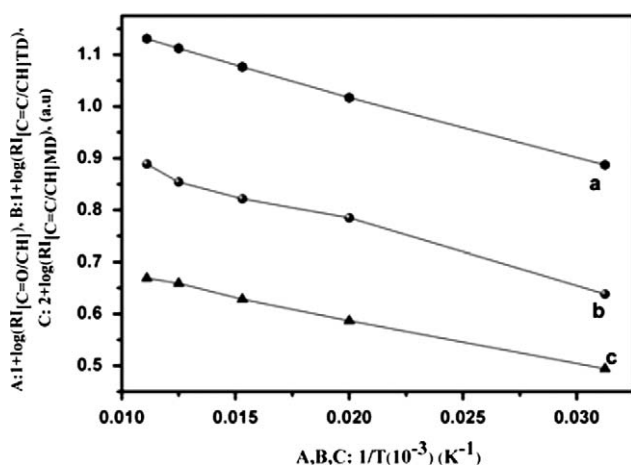
Figure 15 Effect of temperature on the FTIR-RI of (a) [C=O/CH], (b) [C=C/CH]$_{TD}$, (c) [C=C/CH]$_{MD}$.

to more vigorous hydrolytic oxidation reactions. As a result, water molecules were removed with the formation of C=C (TD) bond. After the complete dissolution of PVA in water, the secondary forces were broken, hydrolytic oxidation took place and C=C(MD) was resulted. The reduction in molecular weight of PVA is under investigation in our lab through GPC measurements. Due to the thermolytic oxidation reaction, hydrogen molecule was removed from PVA with the formation of C=O group. After the complete dissolution of PVA in water the formation of C=O and C=C(MD) were competitive one. In the present system, the RI of C=O is higher than C=C(TD) and C=C(MD). RI$_{[C=O/CH]}$ > RI$_{[C=C/CH]TD}$ > RI$_{[C=C/CH]MD}$. Recently, Parveen et al.[31,32] studied the effect of different metal hydroxides on the RI of carbonyl and alkene formation of PVA chains. The present investigation is in according with their results.

Effect of temperature on the RI of C=O and C=C formation reactions

PVA was heated in 100 mL of water at different temperature. The temperature was varied between 32 and 90°C while other experimental conditions were kept constant. While increasing the reaction temperature the RI of C=O and C=C were increased. This is due to the thermally activated reactions. For the sake of simplicity, the FTIR spectra of PVA treated at different temperature are not included. The energy of activation (E_a) can be determined from the famous Arrhenius equation. The plot of 1/T Vs log(RI$_{[C=O/CH]}$) [Fig. 15(a)] was drawn and the slope was noted, from which one can easily find out the E_a value. In the present system the C=O formation consumed 95.6 kJ/mol. This is very low when compared with the C=C(TD) formation. The plot of 1/T Vs log(RI$_{[C=C/CH]TD}$) [Fig. 15(b)]

yielded the E_a value of 128.1 kJ/mol. The plot of 1/T Vs log(RI$_{[C=C/CH]MD}$) [Fig. 15(c)] produced the E_a value of 143.8 kJ/mol. The higher E_a value for the MD is due to the inter and intra molecular hydrogen bonding associated with the PVA molecules. This is in accordance with the literature report.[31]

Effect of Volume/Weight of water on the RI of C=O and C=C formation reactions

Effect of volume or weight of water was also studied on the RI of C=O and C=C formations. Volume of water was varied from 25 to 150 mL. While increasing the volume of water, the RI of C=O was increased linearly. For the sake of convenience, the FTIR spectra are not included here. To find out the order of reaction, the plot of log(weight of water) Vs log(RI$_{[C=O/CH]}$) [Fig. 16(a)] was drawn and the slope was noted as 0.49. This inferred that C=O formation followed the 0.50 order of reaction with respect to weight of water. It means that 0.50 mole of water is required to form 1 mole of C=O group. Similar type of plot was made for alkene formation reactions. (i.e.) plots of log (weight of water) Vs log (RI$_{[C=C/CH]TD}$) [Fig. 16(b)] and log (weight of water) Vs log (RI$_{[C=C/CH]MD}$) [Fig. 16(c)]. The slope values for these systems were determined as 0.34 and 0.36, respectively. Both the TD and MD followed the 0.50 order of reaction with respect to weight of water, respectively. The MD formation was slightly influenced by the C=O formation.[31,32]

Effect of (% weight of SI) on the RI of C=O and C=C formation reactions

For the sake of comparison, 1 g of PVA was heated in 100 mL of d.d water for 1.5 h in the presence of different % weight of SI (in the presence of Sb$_2$O$_3$). The % weight of SI was varied from 1–9% weight,
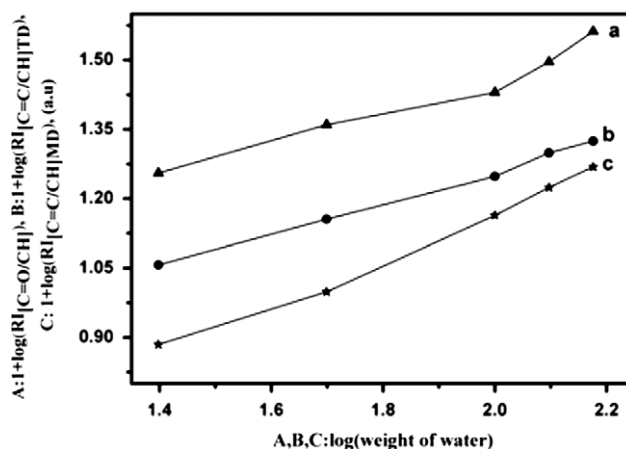

Figure 16 Effect of (weight of water) on the FTIR-RI of (a) [C=O/CH], (b) [C=C/CH]$_{TD}$, (c) [C=C/CH]$_{MD}$.
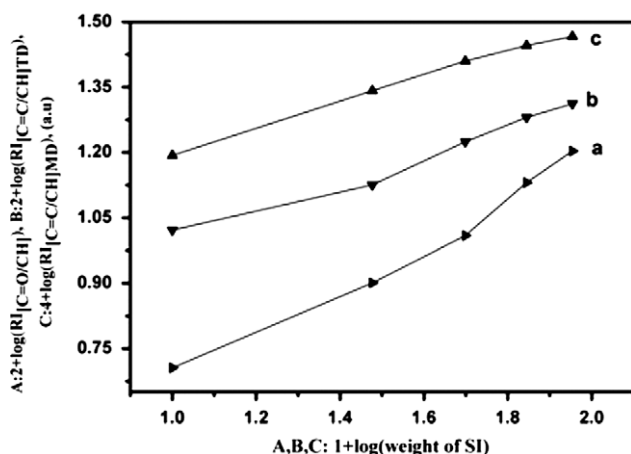
Figure 17 Effect of (% weight of SI) on the FTIR-RI of (a) [C=O/CH], (b) [C=C/CH]$_{TD}$, (c) [C=C/CH]$_{MD}$.

while the other experimental conditions were kept constant. While increasing the % weight of SI, the RI of C=O and C=C were increased linearly. The increase in RI of C=O is due to the grafting of SI onto the backbone of PVA (carbonyl group of SI) as well as the conversion of secondary alcoholic group of PVA into a keto group. In the case of C=C formation, the increase in RI is due to thermolytic and hydrolytic oxidation reactions. To find out the order of reaction, the following plots were made. Log (% weight of SI) Vs log (RI$_{[C=O/CH]}$) [Fig. 17(a)], log (% weight of SI) Vs log (RI$_{[C=C/CH]TD}$) [Fig. 17(b)], and log (% weight of SI) Vs log (RI$_{[C=C/CH]MD}$) [Fig. 17(c)]. These plots were found to be straight lines with the corresponding slope values of 0.50, 0.31, and 0.29, respectively. These values are compared with the results of PVA treated in different weight of water. After critical comparison, one can suggest that the increase in RI of C=O is dependent of amount of water used and independent of modifying agent like SI. (i.e.) the order of C=O formation reaction is not affected by the modifying agent like SI. However, the % of C=O formation will be varied. In the case of C=C formation reactions, the C=C[TD] is not affected by the modifying agent. The C=C[TD] was formed through the oxidation of free hydroxyl groups of PVA. Whereas the RI of C=C[MD] is slightly affected. This is due to the reduction in weight of water, because some amount of water molecules were consumed for the dissolution of SI and some of them were physically or chemically attached with the carbonyl (C=O) and imide (—NH—) groups of SI. Hence, the amount of water available for the hydrolytic oxidation reaction was reduced and resulted with slightly lower slope value in the plot. For the first time we observed this type of kinetic results.

CONCLUSIONS

To improve the thermal and mechanical properties of PVA, it was structurally modified with crosslinkable and noncrosslinkable type of chemicals. The important points are presented here as conclusions. A peak at 1363 cm^{-1} in FTIR spectroscopy confirmed the C—N stretching of SI, urea, or TU. The =CH$_2$ peak was appeared at 2.7 ppm in H^1-NMR spectroscopy. The T_m of PVS copolymer could be seen at 291.6°C. The char forming behavior of PVS copolymer was lower than that of pristine PVA. The % elongation value of urea modified PVA was 423% that was 15.6 times greater than that of pristine PVA. The TU modified PVA explored the highest opaque value, which argued the inner structural transitions. The RI of carbonyl and alkene formations were increased simultaneously while increased the weight of water and temperature due to hydrolytic and thermal oxidation reactions. In the weight of water variation, the carbonyl group formation followed the 0.50 order of reaction with respect to weight of water. The % weight of SI variation confirmed that the order of C=O formation was independent of (% weight of SI) modifying agent whereas the order of C=C formation (both TD and MD) were slightly dependent but within the limit.

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