The effect of blend ratios on physico-mechanical properties and miscibility of cross-linked poly(vinyl alcohol)/urea blends

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Abstract: The present study investigates the effect of blend ratios on the miscibility and physico-mechanical properties of polyvinyl alcohol (PVA)/urea (U) blends. PVA/U blends were synthesized in aqueous solution with different blend ratios 65/35, 50/50 and 35/65 respectively, using glacial acetic acid as crosslinking. The properties of PVA/U blends examined included FT-IR, 1H NMR, 13C NMR, TGA, DSC and scanning electron microscopy (SEM). The obtained results showed that the miscibility and physico-mechanical properties of PVA/U blends are strongly dependent on PVA ratio in the blends. FT-IR spectroscopy was used to check the hydrogen bonding interaction between PVA and U in the blends. The formation of hydrogen bond was through the lone pair attraction from nitrogen atoms of U towards protonated hydroxyl of PVA. These blends have a single glass transition indicating that these blends are able to form a miscible phase due to the formation of hydrogen bonds. The addition of glacial acetic acid as cross-linking improved the thermal analysis of the blend. The scanning electron microscopy of PVA/U showed crystals of varying sizes with flake shapes compared to the pure PVA.

1. Introduction

Poly (vinyl alcohol) is a polymer of great interest because of its many desirable characteristics specifically for various pharmaceutical and biomedical applications [1, 2]. PVA is a water-soluble polymer and has a relatively simple chemical structure with a polar hydroxyl groups (-OH), these highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds, improving the integrity of blends accordingly [3, 4]. Properties, composition and structural features of PVA blends have been extensively studied [5-9]. PVA blends have been obtained with starch [1, 2, 10-12] chitosan [7-9], polysaccharides [13],
gelatin [14], polyvinylamine [5], polyvinyl pyrrolidone [6, 15] and hydroxy propyl methyl cellulose [16].

On the other hand, plasticizer and crosslink agent play a key role in the family of polymer blends. Cross-linking is a common approach to improve the performance of polymer blends for various applications. Different cross-linkers such as citric [17], maleic, and glutaraldehyde [8, 9] were used in blend procedure. The research involved in the study of the influence of cross-linkers and the relative content of plasticizer on blends. Their results indicated that due to the presence of carboxyl groups in cross-linking, they showed improve the mechanical properties and water resistibility of the film blend [18-20] have also studied the effect of citric acid (CA) percentages on the structure and physical properties of the PVA/starch blend films. It was found that the addition of CA to such blends led to the formation of crosslinks between PVA and starch via strong hydrogen bonds, which result in enhancement of the thermal stability of the PVA/starch blend films. Furthermore, authors [21, 22] studied the effect of glycerine (used as a plasticizer) on the mechanical properties, thermal behavior and biodegradation of PVA/starch blend films. The results showed that tensile strength decreases with increasing glycerine in the blends. An explanation of this behaviour can be due to the glycerine, which acts as a plasticizer, leading to a greater mobility of both the starch and PVA macromolecular chains and the presence of some strong intermolecular hydrogen bonds, as well as associations established between the macromolecules of the blend components.

This article describes the blend of PVA with urea in the presence of glacial acetic acid as a crosslinking agent. The influence of blend ratios on miscibility and physico-mechanical properties of PVA/U blend films was studied.

2. Experimental
2.1. Materials
Polyvinyl alcohol (PVA) of molecular weight 14 x 103 g/mol purchased from Merck (Germany). Urea (U), glacial acetic acid and methanol were purchased from Aldrich and used without purification.

2.2. Preparation of the blend films
PVA/U blends with different blend ratios (65/35, 50/50, 35/65) respectively were prepared. Briefly, PVA and urea (U) were dissolved in distilled water in a three-necked flask under continuous mechanical stirring and heating in a water bath at 90 °C for 20 min till complete dissolution of PVA and U, and then, the flask was sealed with a septum stopper. The prepared solution was flushed with Nitrogen gas, which was introduced through a hypodermic needle, and another needle was introduced inside the stopper for the outlet of Nitrogen gas. Glacial acetic acid was injected through a hypodermic needle during preparation in order to control the pH of the solution at 3±1. Nitrogen gas flushing was continued for a further 30 min and then stopped. The needles were removed from the stopper and then the flask was sealed with a Teflon tape. The temperature of the reaction was maintained at 90 °C for another 3 hours.

PVA/U blend films were prepared by casting their aqueous solutions onto flat glass surfaces and allowing them to dry at room temperature for 7 days, and then in an aerated oven at 60 °C, for 12 h to completely eliminate water [3, 12, 18, 23-25]. Then, the films were washed thoroughly with distilled water in order to eliminate the residual glacial acetic acid. Finally, the films were dried and stored in a desiccator at room temperature for further characterization and measurements.

2.3. Testing
FT-IR analyses for the prepared polymer blends were carried out using Perkin Elmer FTIR (300E, JASCO type, Japan). The 1H NMR spectra of the prepared polymers were carried out using (a JEOL type EX-270, MH, Japan). Thermogravimetric analysis (TGA) was recorded on TGA/SDTA851e, METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N2 flow at 20 mL min⁻¹. The measurements
were carried out between 0.0 °C and 270 °C at a heating rate of 10 °C Min⁻¹. The tensile properties of the blend films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. The microstructure of the hydrophilic copolymers was investigated by scanning electron microscopy (SEM) was recorded on Carl-Ziess SMT, Oberkochen

3. Results and discussion

3.1. FT-IR Spectra

Figure 1a–c shows FT-IR absorption spectra of pure PVA, PVA/U (50/50) blend and pure U respectively in the region 400–4000 cm⁻¹.

From Figure 1a, for pure PVA, the peaks appearing at 2946, 1264 and 1096 cm⁻¹ are attributed to the C–H stretching, C–H bending and C–O stretching bands of PVA, respectively. The band at 3408 cm⁻¹ is related to the O-H stretching frequencies of hydroxyl group [26-29]. Figure 1c for pure U, shows two peaks at 3439 and 3338 cm⁻¹ that are attributed to the –NH₂ groups and the one peak at 1622 cm⁻¹ is caused by carbonyl group and peak at1464 cm⁻¹ is related to C – N stretch. Figure 1b shows the FT-IR spectrum of PVA/U blend with ratio 50/50. After blending of PVA with U, the prepared film showed sharp single bands at 3448 cm⁻¹ is attributed to the hydrogen bond arising from the intermolecular hydrogen bonds between OH group of PVA and N groups of U. The bands at 1409 and 1164 cm⁻¹ are attributed to the stretching vibration of C–O in C–O–H groups. In addition, the characteristic absorption peak of the carbonyl group of acetic acid is observed at 1670 cm⁻¹, and the aliphatic C–H stretching vibration band appeared at 2946 cm⁻¹. Since the sample was thoroughly washed with water to remove the unbound acetic acid, the presence of the carbonyl peak confirms the chemical linkages between PVA and U in the presence of acetic acid, which promotes the interaction between PVA and U, as previously reported. 30 As shown in Figure 1b, the band around 1458 cm⁻¹ (C-H stretch) belongs to the spectrum of PVA. On the other hand, the absorption peaks appearing at 1409 and 788 cm⁻¹ are due to the U only and this is an ideal reference frequency to monitor U content in the samples.

Figure 1. FT-IR spectra for (a) pure PVA, (b) PVA/U blend and (c) pure U.

3.2. ¹H NMR spectra

The ¹H NMR spectrum gives more indication of the structure of the prepared PVA/U blends. The typical ¹H NMR spectrum for pure PVA, U and PVA/U blend with ratio 50/50 is shown in Figure 2a-c. The peak
observed at 5.5 ppm (NH₂) for proton in pure U (Figure 2a) and shifted to 3.8 ppm (NH₂) for proton in PVA/U blend (Figure 2c). Pure PVA shows proton at 4.5 ppm (OH) (Figure 2b) and shifted to 5.5 ppm (OH) in PVA/U blend (Figure 2c) due to the occurrence of the blend process and formation of hydrogen bond between hydroxyl group of PVA and nitrogen from U.

3.3. ¹³C NMR spectra
The structure of the blend was further confirmed by ¹³C NMR spectroscopy for the protonated carbons. The ¹³C NMR spectrum of the PVA, U and PVA/U blend is shown in Figure 3a-c. As shown in Figure 3a, pure U had one peak at δ = 160.65 ppm for carbonyl carbon atom. In Figure 3b, pure PVA had four distinct peaks. The absorption peak at δ = 68.62 ppm was for the carbon atom connected by OH group, the peak at δ = 68.43 ppm was for carbon atoms connected by hydrogen, and another two peaks at δ = 66.80 and 46.90 ppm which are attributed to the carbon atom at the end of the structure. In the case of PVA/U blend (Figure 3c), there were five peaks. The absorption peak at δ = 160.66 ppm for carbonyl carbon atom connected to two (NH₂) group, the peak at δ = 68.99 ppm for carbon atom attached to OH group and three peaks at 46.9, 64.6 and 66.7 ppm for three-carbon atom each of them attached to two hydrogen atoms. From Figure 3a-c, shown that the peaks shifted due to formation of intramolecular hydrogen bonding.

The prepared PVA/U blend is expected to have the following structure according to the above characteristics as shown in Figure 2 & 3 c.
3.4. Thermal properties

TGA is considered as the most important method for studying the thermal stability of blend polymer [6]. The thermal behaviour of pure PVA and PVA/U blends was evaluated with TGA, DTG in air at a heating rate of 10°C/min and DSC at the same heating rate under nitrogen atmosphere. The TGA thermogram for the pure PVA and PVA/U blends are given in Figure 4a-d. Five significant weight loss stages are observed in the TGA curve of pure PVA as shown in Fig. 4a. The first and second weight loss (about 5.85-68%) at 30-433.89 °C may be due to loss of moisture and thermo-chemical decomposition of the chemically active organic materials at this range. The third, fourth and fifth weight loss (about 4.9-12.10%) at 433.89-900.00 °C is attributed to the thermal degradation of CH, as previously reported by authors [32].

On the other hand, the thermal behavior of PVA/U blends proceeds in 6 stages for 35/65 (Figure 4b), in 5 stages for 50/50 (Figure 4c) and in 4 stages for 65/35 (Figure 4d) respectively. It is suggested that the intermolecular hydrogen bonds between the two components do not affect the process of anhydride formation, which corresponds to water loss and crosslinking, as the same result was obtained by authors [12]. The first and second weight loss (about 13.45-19.03%) occurs at 29.73 - 182.36 °C for (35/65), (about 32.11 - 47.75%) occurs at 29.74-385.85 °C for (50/50) and (about 8.11-25.94%) occurs at 29.76 - 266.96 °C for (65/35) respectively, which is related to the evaporation of residual moisture and solvents. The third and fourth weight loss occurs at 182.36 - 376.89 °C for (35/65), at 385.85- 688.27 °C for (50/50) and at 266.96-896.64 °C for (65/35). These weight losses could be attributed to the exothermic decomposition of the NH2 group, other part of PVA and residual acetic acid. The fifth and sixth weight loss occurs at 376.89-896.65 °C for (35/65) and at 688.27-896.72 °C for (50/50), which corresponds to the side chain decomposition of PVA and the main chain of the U molecule due to broken inter- and intra-molecular hydrogen bonds between
PVA and U. The weight loss of degradation depends upon many factors such as the surrounding atmosphere, temperature, kinds and composition of the polymer \cite{33,12}. For example, in the range between 387.38 and 896.64 °C, PVA/U blend with ratio 65/35 showed more thermal stability (lower weight loss) than 50/50, 35/65 and pure PVA respectively. The initial decomposition temperature (IDT) corresponds to the temperature at which the initial degradation may occur \cite{34,35}. It was observed that IDT of pure PVA is higher than 335 °C, which is above the highest rheological measurements employed in this study and decomposition temperature of PVA/U blends as shown in the Figure 4a. On the other hand, the maximum polymer degradation temperature (PDTmax) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared in the range 287-475 °C for PVA/U blends and 465 °C for pure PVA. However, the PDTmax of the blends increases as PVA content increases, which attributed to additional NH2 groups of urea and also to the increase in the cross-linking density due to the extension of the network.

![TGA curves for (a) pure PVA, and PVA/U blends: (b) 35/65, (c) 50/50 and (d) 65/35.](image)

**Figure 4.** TGA curves for (a) pure PVA, and PVA/U blends: (b) 35/65, (c) 50/50 and (d) 65/35.

### 3.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a conventional technique to judge the miscibility of a polymer blend. A miscible polymer blend that exhibits a single $T_g$ while partially miscible or incompatible blends display two or more glass transition temperatures of the individual components. Differential scanning calorimetry (DSC) was used to assess the extent of blending between PVA and U. Figure 5 shows DSC analysis of pure PVA and PVA/U blends at different composition ratios. The pure PVA exhibit one $T_g$ at 16.87 °C as shown in Figure 5a. After blending PVA with U (Figure 5b-d), the $T_g$ of polymer blends becomes higher, can be attributed to the hydrogen bonding specific interaction between the hydroxyl groups (PVA) and the nitrogen
groups (U). The nitrogen atom (U) has nonpair electrons that can act as proton acceptors to form hydrogen bond with hydroxyl group (PVA). Also, as the ratio of PVA increases, the $T_g$ of the PVA/U blends decreases. The decrease in $T_g$ is properly due to increased flexibility caused by increased ratios of PVA in polymer blend films. The DSC curve of each polymer blend showed a sharp endothermic peak, which appeared above 200 °C. This exothermic peak could be attributed to the melting temperature $T_m$. $T_m$ of pure PVA is not significant while $T_m$ for PVA/U blends were reasonably sharp and broadened. However, the $T_m$ of PVA/U blends contains 35% PVA is higher that contains 65% PVA, due to the level and nature of crystallinity [36], ion content and perhaps molecular orientation. The crystals generally have extremely high melting temperatures and can function as physical crosslinks in a system, leading to desirable thermal and mechanical properties. In addition, the higher PVA ratio means more hydroxyl sites for possible hydrogen bonding interactions with the nitrogen groups of U and thus a larger range of miscible compositions. Furthermore PVA/U blend with composition ratio (65/35) resulted in less crystalline than ratio (35/65) due to increased intramolecular hydrogen bond between PVA and U as in the study reported in Ref. [37, 38].

![DSC thermograms of pure PVA (a) and PVA/U blend: (b) 35/65, (c) 50/50 and (d) 65/35.](image)

3.6. Scanning electron microscopy (SEM)
Figure 6 illustrates the scanning electron micrographs (SEMs) for pure PVA and PVA/U blends with different composition ratios 35/65, 50/50 and 65/35 respectively. Figure 6a shows smooth area of pure PVA and homogenous; while the PVA/U blends exhibit plate type (flakes) crystals with high crystal density (Fig. 6b-d). However, the flakes are much smaller in PVA/U (35/65) and a loose rough surface. When PVA ratios increases up to 50%, rough surfaces and crystalline structures are the dominant features in Fig 6c, and indicating better compatibility between the PVA and U. This is attributed to a higher intermolecular interaction level between the components of blend. The SEM
confirm with DSC that PVA/U blend with ratio 63/35 is less crystalline in compared with another blend ratios and pure PVA.

Figure 6. Scanning electron micrographs of the pure PVA and PVA/U blend films.

4. Conclusion
PVA/U blend films were prepared at different blend ratios, by using casting method, in the presence of glacial acetic acid as a crosslinking agent. The physico-mechanical properties and miscibility behavior of PVA/U have been studied by several techniques such as FT-IR, $^1$H NMR, DSC, TGA, SEM. Analysis of FTIR spectra showed that the stretching vibration of hydroxyl and carbonyl groups shifted to higher and lower wave number respectively. These results suggested strong formation of hydrogen bonding between PVA and U. Differential scanning calorimetry was the main experimental technique used to study the thermal behaviour of the blends. All the blends exhibit one $T_g$ and decreased with increasing PVA ratio in the polymer blends. The decrease in $T_g$ is properly due to increased flexibility caused by increased ratio of PVA in polymer blend films. PVA/U blend samples show good thermal stability especially at ratio (65/35). The SEM’s of PVA/U showed flake crystals with high crystal density, when compared with the pure PVA. SEM image of blend film PVA/ U with ratio (50/50) illustrates a significantly more compatible due to a higher intermolecular interaction level between the components of blend. The results indicate that the blend ratios between the components of blend play a major role in the physico-mechanical properties and miscibility of PVA/U blends.

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References
1. Okaya T, Kohno H, Terada K, Sato T, Maruyama H, Yamauchi K 1992 J. App. Polym Sci 45 1127.
2. Lawton J W, Fanta G F 1994 Carbohydrate Polymers 23 275.
3. Sin L T, Rahman W A, Rahmat A R, Khan M I 2010 Carbohydrate Polymers 79 224.
4. Sin L T, Rahman W A, Rahmat A R, Mokhtar M 2011 Carbohydrate Polymers 83 303.
5. Liyuan D, Hagg M B 2014 International Journal of Greenhouse gas Control 26 127.
6. Abdelrazek E M, Elashmawi I S, Labeeb S 2010 Physica B 405 2021.
7. Naveen Kumar M P, Prabhakara M N, Venkata Prasada C, Madhusudhan Raoa K, Ashok Kumar Reddy T V, Chowdoji Raoa K, Subha M C S 2010 Carbohydrate Polymers, 82 251.
8. Tripathi S, Mehrotra G K, Dutta P K 2009 International Journal of Biological Macromolecules 45 372.
9. Costa-Júnior E S, Barbosa-Stancioli E F, Mansur A A P, Vasconcelos W L, Mansur H S 2009 Carbohydrate Polymers 76 472.
10. Fahmida P, Mubarak A K, Saadat A H M, Anwar M H K, Jahid M M I, Mostak A, Gafur M A 2011 J Polym Environ 19 1013.
11. Follain N, Joly C, Dole P, Bliard C 2005 Carbohydrate polymers 60 185.
12. Negim E S M, Urkimbaeva P I, Rakhmetullayeva R K, Primzharova S T, Yeligbayeva G Zh, Kaldybekov D B, Khatib J M, Mun G A, Craig W 2011 J Polym Environ 19 1013.
13. Carla S, Carla J S, Zsofia B, Rodrigo G, Sara B P, Paula T, Andrea Z 2014 Carbohydrate Polymers 99 584.
14. Gamal S E B, El-Sayed M E, Abdel A M, Noha M G 2012 Journal of Applied Sciences Research 8 3544.
15. Ragab H M 2011 Physica B 406 3759.
16. Chandralekha F, Illiger S R, Rao K P, Demappa T 2008 Carbohydrate Polymers 74, 779.
17. Narendra R, Yiqi Y 2009 Food Chemistry 118 702.
18. Shi R, Bi J, Zhang Z, Zhu A, Chen D, Zhou X, Zhang L, Tian W 2008 Carbohydrate Polymers 74 763.
19. Shi R, Zhang Z, Liu Q, Han Y, Zhang L, Chen D, Tian W 2007 Carbohydrate Polymers 69 748.
20. Rui S, Jingliang B, Zizheng Z, Aichen Z, Dafu C, Xinhua Z, Lijun Z, Wei T 2008 Carbohydrate Polymers 74 763.
21. Tudorachi N, Cascaval C N, Rusu M, Pruteanu M 2000 Polymer Testing 19 785.
22. Jiang Z, Yunhai M, Lili R, Jin T, Ziqin L, Liang X 2009 Carbohydrate Polymers 76, 632.
23. Luo X, Li J, Lin X 2012 Carbohydrate Polymers 90 1595.
24. Negim E S M, Bekbayeva L, Mun G A, Zhalyrkasyn A A, Idiris M S 2011 World Applied Science Journal 14 402.
25. Negim E S M, Bahrudin S, Mahyuddin R, Idiris M S 2011 J. Applied Polymer Science 121 8.
26. Li X, Goh S H, Lai Y H, Wee A T A 2000 Polymer 41 6563.
27. Finch C A 1992 Chemical reactions and stereochemistry of polyvinyl alcohol, in: Polyvinyl alcohol, Wiley and Sons, London 269.
28. Abdelaziz M, Abdelrazek E M 2007 Physica B 390 1.
29. Laot C M, Marand E, Oyama H T 1999 Polymer 40 1095.
30. Reddy N, Yang Y 2010 Food Chemistry 702.
31. Junrong Z, Kungwon K, Xin C, John B A, Fayer M D 2006 J. AM. CHEM. SOC 128 2977.
32. Lewandowska K 2009 Thermochimica Acta 493 42.
33. Hirenkumar K M, Steven J S 2011 Polymers 3 1377.
34. Holland B J, Hay J N 2001 Polymer 42, 6775.
35. Jianga X, Jiang T, Gana L, Zhanga X, Daia H, Zhang X 2012 Carbohydrate Polymers 901677.
36. Roovers J, Toporowski P M 1992 Macromolecules 25 1096.
37. Christie M H, Nikolaos A P 2000 Advances in Polymer Science 153 37.
38. Herman S M, Carolina M S, Adriana N S, Alexandra A P M 2008 Materials Science and Engineering: C 28 539.