Effect of crosslinking agent (glutaraldehyde) on the mechanical properties of (PVA/Starch) blend and (PVA/PEG) binary blend films

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Abstract: This paper displays the effect of glutaraldehyde (GA) as a crosslinking agent with different weight ratios (5, 8, and 10\%) on the mechanical properties (elongation at break and tensile strength) of polyvinyl alcohol/starch & polyvinyl alcohol/polyethylene glycol blend. Solution casting technique was used to prepare (75\%PVA/25\%corn starch), and (75\% PVA/25\% PEG) blend films. The results confirmed that when the increased concentration of GA, the tensile strength increased, while elongation at break decreased for both two blends. This study offers the groundwork for applications of this hydrogel membrane in a drug release system.

Keywords: Starch; PVA; PEG; glutaraldehyde; elongation at break; tensile strength

1. Introduction

Polyvinyl alcohol hydrogel is notable as a biodegradable \cite{1}, non-toxic, non-carcinogenic synthetic polymer \cite{2}, presents outstanding mechanical properties \cite{3}, attractive physical properties, e.g. rubbery or elastic nature \cite{2}, good film formation, strong conglutination \cite{3}, high thermal stability and good biocompatibility \cite{2} and their solubility in water \cite{3} makes it one of the best selections to combine with other polymers in multilayer structures, and it is set in the core layer \cite{3}. Polyvinyl alcohol (PVA) is a multipurpose polymer, and it might be the only synthesized polymer with a backbone that involves mainly of (–OH) bonds that is biodegradable \cite{1}. On the other hand, starch is amylose and amylpectin mixture. Starch is a completely biodegradable, renewable polymer, and also readily available at low cost and in high purity \cite{4}. Despite that, the starch has poor physicomechanical properties, poor processing properties \cite{4}, weak in the dimensional stability \cite{5}, also starch products are often brittle and water-soluble \cite{4}, natural starch cannot use directly \cite{5}. Poly (ethylene glycol) (PEG) is one of the best broadly used polymers that possess noble properties, e.g. hydrophilic, soluble in organic solvents and water, non-toxic \cite{6}, good thermal resistance, high polymer chain flexibility, high value for water absorption capacity and makes it perfect to use it in vivo applications \cite{2}, and removed from the body at a faster rate \cite{2}. It may be utilized within biomedical applications, for example, drug delivery, tissue scaffolding, and wound healing \cite{2}. Recently, high attention has been focused on investigation and polymeric properties development by polymers blending \cite{6}.
Cross-linking is a common method of chemically bonding two chains of polymer [7] by a covalent bond to produce permanent hydrogel [9]. It is used to improve [7] mechanical properties [8], the performance, and the water stability of PVA based products for several applications [8]. The cross-linking formation is achieved by adding small cross-linkers molecules [9], polymer-polymer conjugation [9], bonding chemical components with multi-active groups owing good reactivity with the polymer active groups that required being adjusted [10], enzyme-catalyzed reaction or by photosensitive agents [9]. Glutaraldehyde (GA) is the most commonly used crosslinker for PVA. It also well-known as a crosslinking agent for compounds having hydroxyl groups (like polysaccharides and cyclodextrins) [3] and it had two CHO functional groups used in diverse applications, for example, drug delivery, decreasing oxygen permeability, proton exchange film, evaporation systems, ultrafiltration films and coating [7]. Glutaraldehyde can be expected to cross-link with hydroxyl groups of PVA and starch, and improve the adhesion [8]. PVA /PEG hydrogels blends with diverse crosslinked microstructure make unique chances for adjusting pH-responsive drug carriers, biodegradability, and scaffolds of tissue engineering [6]. The present work describes the glutaraldehyde addition effect on the mechanical properties of PVA/starch and PVA/PEG binary blends as a crosslinking agent.

2. Experimental work

2.1 Materials
Poly (vinyl alcohol) (PVA), (Mw, 12000-18000) with assay (99.9%) and corn starch were purchased from Panreac (Barcelona, Espana). Polyethylene glycol (PEG), (Mw, 3600-4400) was supplied by Hi Media Laboratories Pvt. Li., LBS Marg, Mumbai, India. 25% aqueous solution of glutaraldehyde (GA) was obtained from Central Drug House (P) Ltd. New Delhi, India. The distilled water is widely used to dissolve these used polymers.

2.2. Samples Preparation

2.2.1 (75%PVA/25%St) blend Films Preparation
To prepare (75% PVA/25% St) blend, the solution casting technique was used. Dissolving (7.5) g of PVA in (75) ml of distilled water as previously stated and rise the solution heat gradually till getting clear solution and good homogeneity at 90 °C using a magnetic stirrer for two hours. 2.5 g of corn starch was added in (25) ml distilled water through continuous stirring and then mixed with PVA solution to achieve a homogenous solution. Lastly, the prepared blend solution was easily poured on a simple glass plate (30*30) cm to dry in air. Figure 1: Schematic diagram of (PVA/St) blend [11].

![Figure 1. Hydrogen bond formation between PVA and starch](image-url)
2.2.2 (75%PVA/25%PEG) Blend Films Preparation
The solution casting method is used to make (PVA/PEG) flexible films with (75/25) wt/wt % weight percentage in 100 ml distilled water.
They were prepared as follows: The PEG solution was prepared by dissolving (2.5) g in (25) ml distilled water using a magnetic stirrer at room temperature. After the PVA solution prepared as previously stated (2.2.1) and cooled to ambient temperature, the PEG solution was added to it. Then, both solutions were mixed till completely miscible and afterward cast onto a glass plate with a thickness of ~0.1 mm (less than 1mm). After that, the films were solidified in the air for (24–72) h to form the desired film. In the end, the prepared film was taken off from a glass plate. Figure 2: Schematic diagram of (PVA/PEG) blend [12].

\[ \text{Figure 2. Physical reaction between PVA and PEG} \]

2.2.3 Preparation of chemically crosslinked (75%PVA/25%St) blend with GA
The (75%PVA/25%St) blend was prepared as previously method as in point (2.2.1). Then glutaraldehyde (GA) as a crosslinker with different concentration (5, 8, and 10 wt %) was gradually dropped into the above solutions. The mixture was stirred for reaction time (30 min) with a mechanical stirrer until completely homogenous. Figure 3: Schematic illustration of crosslinking (PVA/St) with GA [8].

\[ \text{Figure 3. Schematic illustration of PVA/St crosslinked with glutaraldehyde} \]

2.2.4 Preparation of chemically crosslinked (75%PVA/25%PEG) blend with GA
The (75%PVA/25% PEG) blend was prepared as previously stated (2.2.2). After that, the GA crosslinked with different concentrations (5, 8, and 10 wt %) was gradually dropped into the above solutions. The mixture was stirred for reaction time (30 min) with a mechanical stirrer until completely homogenous. Figure 4: Schematic diagram of crosslinking (PVA/PEG) with GA [13].
2.3 Mechanical properties of the films

LARYEE, China testing machine was used for the tensile test at (5 mm/min) crosshead speed. Elongation at break (E%) and ultimate tensile strength (UTS) were calculated for films and the samples according to (D882-02) were cut into a strip of (50 mm) gauge length and it shall be at least longer than the grips distance, film thickness shall be lower than (1 mm) and the width shall be not lower than (5 mm) either larger than (25.4 mm). The ultimate tensile strength (UTS) was determined as follows [14]:

\[ \sigma_{ult} = \frac{F_{ult}}{A} \]  

Where \( \sigma_{ult} \): is the Ultimate Tensile Strength (MPa), \( F_{ult} \): is the Maximum tensile load (N), and \( A \): is sample cross-sectional area (mm\(^2\)).

The percentage elongation at break (E%) is determined by applying the relationships [15]:

\[ \text{Elongation (E\%) } = \frac{(L_f - L_i)}{L_i} \times 100 \]  

Where \( L_i \): is the initial sample length (mm), and \( L_f \): is the final sample length (mm).

2.4 Optical Microscope

MEIJI TECHNO CO., LTD. (MT9430) model, (Japan) light microscope at a magnification 100 times (10X) is used to test the surface morphology of PVA, (PVA/St) blend and (PVA/PEG) blend film.

4. The Results and Discussion

The effect of glutaraldehyde GA on the elongation and tensile strength of (PVA/starch) films and (PVA/PEG) films are illustrated in Figures (5, 6, 7, and 8).
Figure 5. Effect of various weight ratios of GA content on tensile strength of (75%PVA/25% St blends)

Figure 6. Effect of various weight ratios of GA content on elongation at break of (75%PVA/25% St blends)

Figure 7. Effect of various weight ratios of GA content on tensile strength of (75%PVA/25% PEG blends)

Figure 8. Effect of various weight ratios of GA content on elongation at break of (75%PVA/25% PEG blends)

The graphs (1,2) show that crosslinking modification improved the tensile strength values of (PVA/St) film except the elongation at break declined as GA concentration increased from 5% to 10 % wt which was also agreed upon by Ziqin Liu et.al. [16].

Crosslinking agent reinforces matrix film-forming covalent bonds with OH group of starch and PVA, which act as the bridges between both polymers and decrease the hydrating character [10]. The results exhibited that the tensile strength improvement of (PVA/St) and (PVA/PEG) with glutaraldehyde addition over the uncrosslinked films. Without cross-linking, starch acted as stress concentrations that crack reduced tensile strength and elongation but in the presence of glutaraldehyde, strong adhesion was induced between PVA and starch. A covalent bond is formed at the (PVA/starch) interface; thus caused in mechanical properties improvement [17]. PVA/Starch samples display a brittle behavior associated with the greatly crosslinking density inhibiting any plastic deformation. The strain at break decreases and the stress level
increases and as the crosslinking content is increased due to the decrease of the chemical entanglement mass containing an improvement of the rigidity and drop of the limit of ductility of chain segments between entanglements as shown in figure (3,4) [3]. The presence of glutaraldehyde as a crosslinking agent should decrease the mobility of polymer chains. This was attributed to the rise in stress-bearing ability of the polymer chains thereby raising the stress needed to break of (PVA/PEG) blend [18].

It was shown from figures (5, 6, 7, and 8) that (PVA/PEG) blends display a ductile behavior compare with (PVA/Starch) samples. It was seen from the optical microscope that a best homogenous and an undistorted starch particle arrangement in the (PVA/starch) film at 25 wt% of the starch as shown in Figure (9) [15].

![Figure 9](image-url)

**Figure 9.** Optical microscope image of a) (75%PVA/25%St) blend , b) (75%PVA/25%St + 5%GA) blend , c) (75%PVA/25%St +8% GA) blend and d) (75%PVA/25%St +10% GA) blend

It was also observed that a good transparent and acceptable film was only obtained for (PVA/PEG) blend films at 25 wt% of PEG as in figure (10).
Figure 10. Optical microscope image of a) (75%PVA/25% PEG) blend, c) (75%PVA/25% PEG+8%GA) blend and d) (75%PVA/25% PEG+10%GA) blend.

This result was in agreement with Abd Alla S. G. et al. 2004, who observed by visual observation that suitable and good transparent films were achieved for blend films containing up to 30 wt% PEG. This result is ascribed to PEG and PVA homopolymers miscibility [19]. In the case of adding glutaraldehyde, it was shown a regular increase with increasing GA crosslinking. It can be associated with the better polymer chains ordering in a network and the amorphous phase homogenization with the crystals disappearance. Maximum crosslinking densities lead to the relaxation intensity diminution and restrain the movements [20]. This behavior is described as a result of the competitive action of at least three factors during the crosslinking: (i) physical network reducing that was attributed to hydrogen bonding; (ii) chemical network formation; and (iii) flexible moieties introduction that were attributed to the crosslinker chemical structure of [20].

Table 1, and Table 2 show the mechanical properties of (PVA/St) blend films and (PVA/PEG) blend films.

Table 1. Tensile properties of PVA/starch blend films under tension test.

| 75%PVA/25%St blend | Tensile Strength (MPa) | Elongation at break (%) |
|---------------------|------------------------|------------------------|
| 0                   | 28.2                   | 4.21                   |
| 5                   | 33                     | 3.2                    |
| 8                   | 36.47                  | 2                      |
| 10                  | 41.19                  | 1.65                   |
Table 2. Tensile properties of PVA/PEG blend films under tension test.

| 75%PVA/25%PEG blend | Tensile Strength (MPa) | Elongation at break (%) |
|----------------------|------------------------|-------------------------|
| 0                    | 20.95                  | 41.41                   |
| 5                    | 26.66                  | 31                      |
| 8                    | 30.31                  | 15.1                    |
| 10                   | 35.15                  | 9.13                    |

Conclusion

The results showed that the mechanical properties (elongation at break and tensile strength) of (PVA/St) blend and (PVA/PEG) blend film were increased as a cross-linking agent (glutaraldehyde) increased. This cross-linking agent reduced the polymer chains mobility so it led to the rise in the stress-bearing ability of the polymer chains thereby raising the stress needed to break the blends.

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