Preparation and Characterization of Polyvinyl Alcohol/Alginate membranes for Biomedical Applications

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***Abstract*- Hydrogels have shown enough potential for developing wound dressings due to very high hydrophilicity and functionality. Several wound healing dressings have been prepared with natural and synthetic polymer combinations. Polyvinyl alcohol (PVA) has gained remarkable recognition in the biomedical field due to its excellent biocompatibility, hydrophilicity and biodegradability. PVA in combination with other biopolymers has come up as the most effective material in wound care management. Sodium alginate (SA), is a natural polymer derived from brown algae or bacteria. Keeping this in view, the present study aims at the preparation of the PVA/SA based hydrogel membrane. Prepared membranes were characterized by X-ray diffraction (XRD), to find out the functionality and crystallinity of membrane. Enhancement of thermal property and interaction between components of prepared hydrogel was evidenced by the increase in glass transition temperature by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The stability of the membrane under aqueous environment is also evaluated.**

***Keywords*: Hydrogel, Polyvinyl alcohol, Sodium Alginate, Glyoxal, Crosslinking, Wound dressing,**

INTRODUCTION

Hydrogels are three-dimensional networked structures consisting of hydrophilic polymer chains which do not dissolve in solvent but provide a moist or wetted environment to the wound area, it also absorbs the exudates which helps in reducing the time taken to heal the wound[1]. Hydrogels have the ability to hold a large amount of water within their structures and resemble the mechanical properties of soft tissue, emerging with high biocompatibility [2]. Hydrogels have become a promising material for particular applications such as drug carriers [3] [4] also as, tissue scaffolds [5] and wound dressing [6].

PVA (polyvinyl alcohol) is a petroleum-based thermoplastic and biocompatible polymer [7]. PVA is highly hydrophilic and soluble in water and has non-carcinogenicity, great biocompatibility, favorable physical characteristics, and a high degree of swelling in aqueous solutions. The novelty is to use different biopolymers and combine additional features in there. Because of its high healing properties, high hydrophilicity, biocompatibility, and low cost, alginate polymer has been widely employed in biomedical applications [8] such as wound dressings, scaffolds, and implants [9]. The blended polymeric materials have desirable qualities, enhanced physical properties and are biologically acceptable The importance of polymer blending with PVA has grown[10]. B. Gupta et al. prepared membranes of poly (vinyl alcohol) (PVA) and poly (ethylene oxide) (PEO) via solution casting method with the addition of carboxymethyl cellulose (CMC) as a stabilizer, this leads to the miscibility of these two components, with increased swelling % in membranes, increase in the concentration of CMC results in denser and mechanically strengthen membranes with decreased crystallinity due to irregular polymer arrangement[11]. Ghasemzadeh et al. synthesized the superabsorbent-silver nanocomposites based on sodium alginate and Polyvinyl alcohol via graft polymerization of acrylamide, methylene bisacrylamide has been used as a crosslinker, and this resulted in very good antibacterial activity on gram-positive and gram-negative microorganisms[12].

We have developed the blend membranes of PVA with sodium alginate as the biopolymer combination which will be evaluated for its controlled drug delivery system. The structural characterization of membranes using several techniques is reported in this work.

2. EXPERIMENTAL

2.1. Materials

PVA Powder (Mw 13000-23000) and Glyoxal were obtained from central drug house (P) Ltd. India. HCl was purchased from Merck Life Science Private Limited, India. Sodium Alginate was supplied from titan biotech LTD, India. Deionized water was used as the solvent in all experiments.

2.2. Preparation of crosslinked PVA using Glyoxal as crosslinker.

PVA (5%) was dissolved in deionized water under constant stirring for 2h at a temperature of 75°C. 20µl of HCl was added to the PVA solution to provide an acidic medium with continuous stirring for 1h. Glyoxal of different compositions in the range of 1% to 4% was added to acidic PVA solution at a temperature of 60°C with continuous stirring of 3h. After completion of the reaction, crosslinked PVA was poured into the petri dish and left to completely dry for further studies[11].

2.3. Preparation of crosslinked PVA/SA membranes.
PVA/SA membranes of different SA concentration (10%, 20%, 30%, 40%, w/v) was prepared via solution casting method. Shortly, PVA Solution and Sodium alginate solution was prepared separately by dissolving in deionized water with constant stirring for 2h at 75°C and at room temperature respectively to achieve homogeneous solutions. In continuation, SA solution was mixed with PVA solution and kept for stirring for 3h at 60°C. Lastly, 2% glyoxal was added to the solution as a crosslinker in presence of an acidic medium (20µl of HCl). At the end of the reaction, the prepared solutions were poured into the petri dish and kept for drying for further studies.

2.4. Differential Scanning Calorimetry (DSC)
DSC studies on the samples were performed by using the Perkin Elmer DSC-7 system. Samples were loaded onto the DSC pan and the thermogram was run in the range of 20°C -250°C, under a nitrogen atmosphere at a heating rate of 10°C/min. The endothermic peak of the thermogram gives melting temperature (T_m). Thermogram was also assessed for glass transition temperature (T_g) and heat of fusion (ΔH_m) [6]. The heat of fusion was calculated from the area under the endothermic peak of the thermogram. The following equation gives the crystallinity of samples.

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f\,(\mathbf{crys})}} \times 100$$

Where, ΔH_f is heat of fusion of sample and $\Delta H_{f\,(crys)}$ is heat of fusion of pristine PVA i.e. 156J/g.

2.5. X- ray Diffraction (XRD)
XRD patterns of the samples were recorded in the 2θ range of 20° - 80° on a Phillips X-ray diffractometer equipped with a scintillation counter. CuKa radiation (wavelength, 1.54 A˚ filament current, 30 mA; voltage, 40 kV) is used for the generation of X-rays. The degree of crystallinity of samples was examined from the X-ray diffraction pattern by separating the amorphous and crystalline parts under the diffraction pattern.

$$\text{Crystallinity (\%)} = \frac{A_{cr}}{A_{cr} + A_m} \text{ X } 100$$

Where, A_{cr} is area under crystalline peak and A_m is area under amorphous region.

2.6. Thermogravimetric Analysis (TGA)
The thermal stability of the samples was determined by TGA performed on a Perkin-Elmer TGA-7, using a nitrogen stream as a purge gas, while the temperature was gradually increased from 50°C – 800°C at a heating rate of 10°C/min.

2.7. Swelling studies
Samples were dried completely, before conducting the swelling test. Specimens were weighed to obtain their initial dry weight and then dip in distilled water for 24 h at room temperature. Swollen samples were wiped out using tissue paper to remove excess water. It was weighed again to obtain the swollen weight. Then the swelling % was calculated by using the following equation.

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

Where, W_S is swelled weight and W_d is dry weight of sample.

3. RESULTS AND DISCUSSION
The present study aims the development of crosslinked PVA/SA hydrogel membrane. The main purpose of this analysis is to determine the effect of SA composition on the structure of the hydrogel. The glyoxal interacts with the hydroxyl group of PVA in an acidic medium with the elimination of water molecules to produce the crosslinked PVA structure. The developed crosslinked hydrogel membranes were transparent, white, and mechanically stable. While the addition of SA in the PVA solution gives a homogeneous mixture, therefore it can be stated that both polymers interacted with each other via hydrogen bonding, and the interaction among components of the blend results in the formation of crosslinked PVA/SA hydrogel membrane can be seen in figure 1. All developed hydrogel membranes were smooth, uniform, and flexible and no change in morphology was observed upon storage.

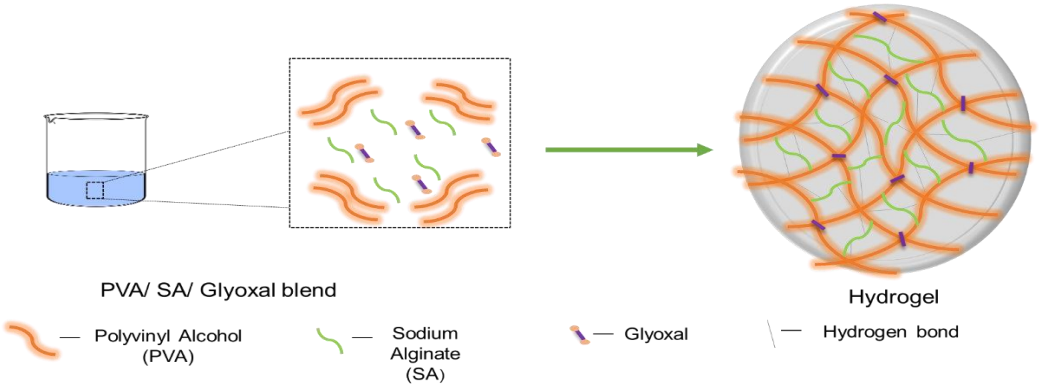

Figure 1- Schematic representation of the preparation of Crosslinked PVA-SA hydrogel.

The membranes were placed in water to look at the dimensional stability. It was found that the membranes with low SA content up to 20% were stable enough to handle them mechanically. However, the increasing amount of the SA led to the dissolution of the membrane. It may be mentioned here that even the crosslinking of the membrane does not help in dimensional stability at higher SA content. (Figure 2)

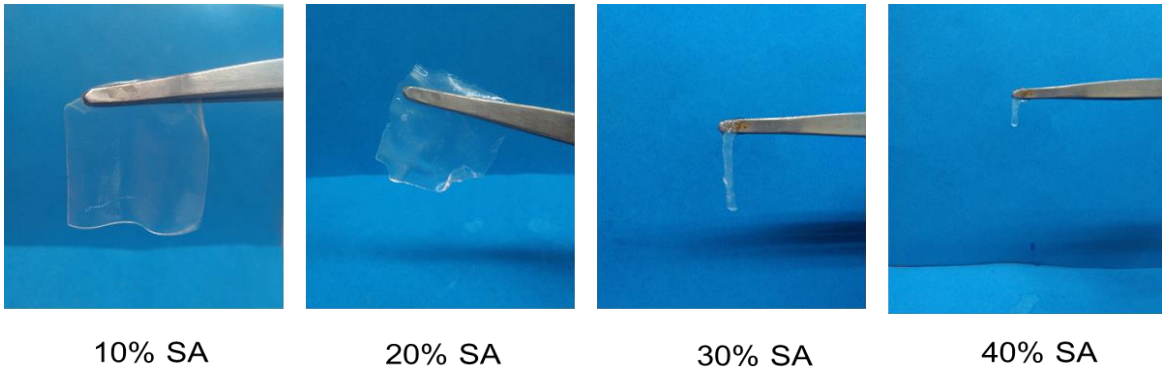

Figure 2. Dimensional stability of the membranes with different amount of SA

3.4. Differential scanning calorimetry (DSC)

DSC is a technique used to determine the quantity of heat either absorbed or released when substances undergo physical or chemical changes. DSC thermograms of pristine PVA, and blends with various concentrations of PVA/Glyoxal showing with varying concentration of SA are shown in figure 2 (a) and & (b). The pure PVA sample gives a relatively large melting endotherm with a peak maximum (T_m) at 225.4°C. The glyoxal acts as the crosslinker, this leads to increase in the hydrogen bonding of the hydroxyl group and dialdehyde of glyoxal. This leads to the chain lengthening of the polymer which also reduces the voids between the blends and thus results in decrease in chain mobility, this causes the increase in glass transition temperature of crosslinked membranes as shown in table. The increased glass transition of crosslinked membranes signifies the crosslinking effect of glyoxal, similar results were studied by the Vineeth S.K et al. in case of PVA/MCC membranes crosslinked by glyoxal. [7] The melting of PVA also showed an increase in the melting temperature. It seems that the crystalline structure moves to a better perfection when SA is added to the PVA.

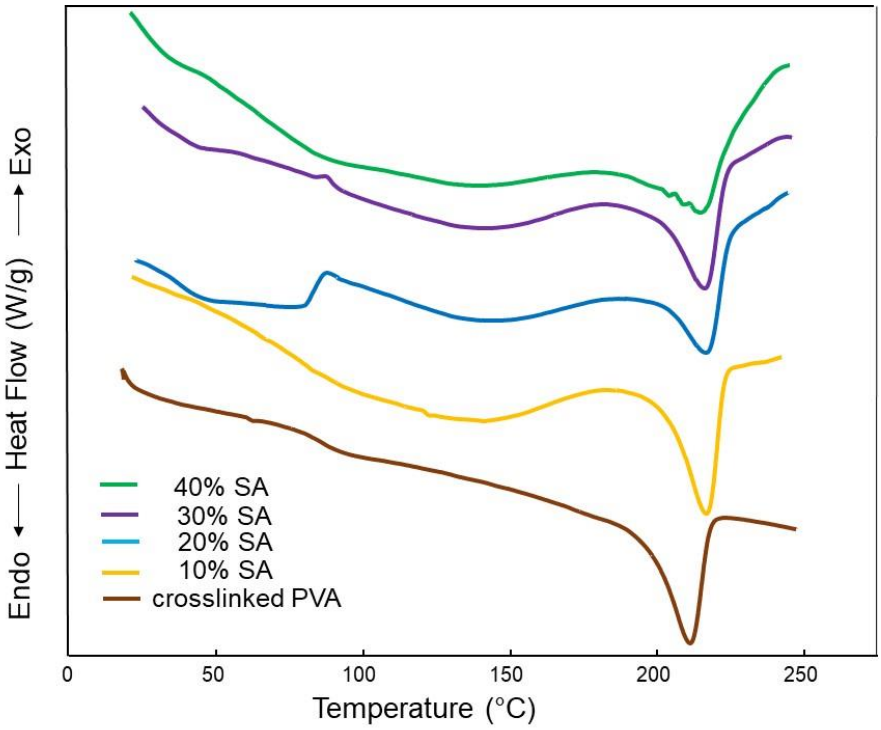

Figure 3. DSC thermograms of pristine PVA and PVA/SA blends

3.2. Thermogravimetric (TGA) analysis

TGA was performed to evaluate the thermal stability of the polymers and the developed hydrogel membranes. The TGA thermograms of Crosslinked PVA membranes and PVA/SA membranes are shown in figure 4. Two stages of thermal degradation were observed for pure PVA. The weight loss in the first stage from 100°C - 250°C was due to the elimination of water molecules present in the membranes. The second stage was due to the main chain degradation between 300 and 500°C and can be related to main chain degradation. Interestingly, higher the SA content, weight loss begins much earlier. This loss may be due to the decarboxylation from the SA.

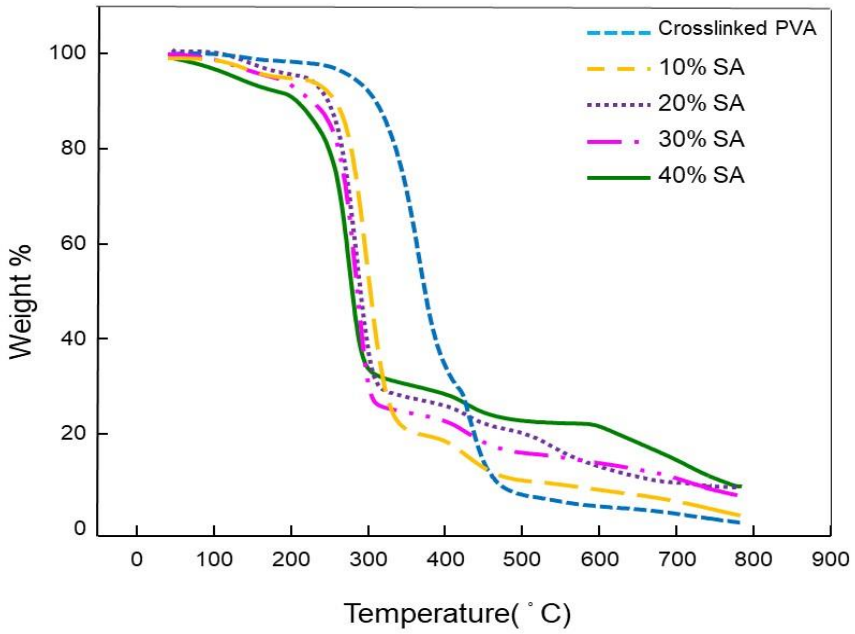

Figure 4 - TGA thermogram depicting PVA/SA membrane with different SA content

3.3. X-Ray diffraction (XRD) study

X-ray diffraction is used to study crystal lattice arrangements and get very useful information on the degree of sample crystallinity. X-ray patterns of pristine PVA membrane, glyoxal crosslinked PVA hydrogel membranes, and PVA/SA membrane were obtained as shown in Fig 5. PVA shows one diffraction peak at 19.6 degrees. On increasing the crosslinker percentage, the intensity of diffraction peaks decreases. It inferred that the cross-linkage decreases the crystallinity of polymer and hence can be of great advantage while drug release. There is a decrease in the intensity in the peaks of PVA/SA membranes in comparison to the crosslinked PVA membranes. This is the indication of the interference of SA in PVA crystallization.

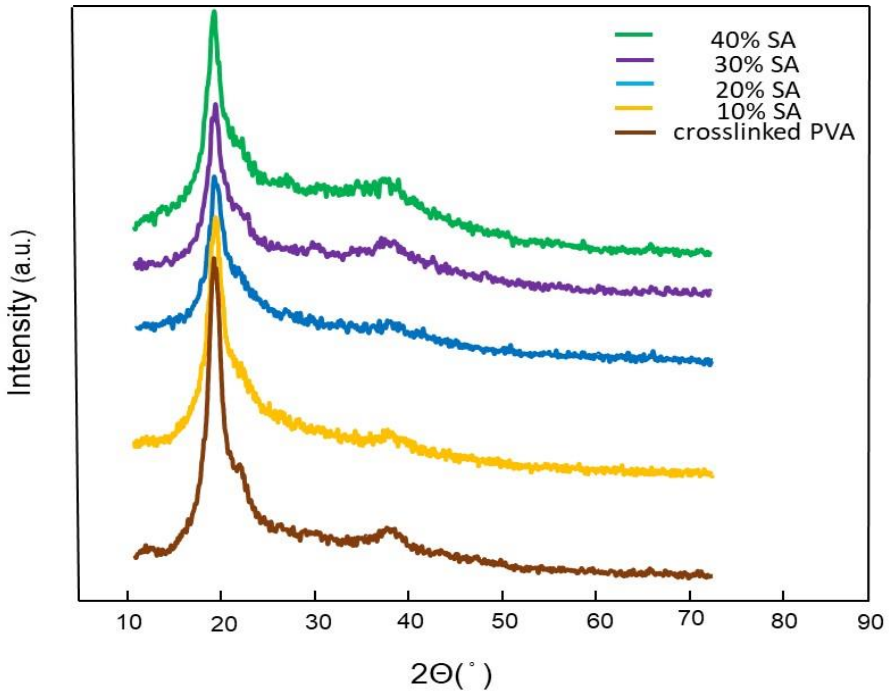

Figure 5- XRD diffractogram of PVA /SA membranes

4. CONCLUSION

Crosslinked PVA/SA hydrogel membranes were prepared by a simple solution casting method. These hydrogel films showed excellent mechanical properties both in the dry and swollen state, as well as greatly improved with a high swelling ratio, which could prevent the wound bed from accumulation. At higher SA content the stability in aqueous medium is significantly lowered. XRD shows that the crystallinity decreases as the SA content increases. These membranes have god potential in several biomedical applications are needed.

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