

## Investigation on the Thermal Behaviour of Polyvinyl Alcohol/Alginate/ Polyethylene Glycol membranes

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### **Abstract**

Polyvinyl alcohol (PVA) membranes were modified by blending with sodium alginate (SA) and polyethylene glycol (PEG). The membranes exhibited good transparency and dimensional stability for different PEG content. The physical handling of membranes was good. The Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out to investigate the thermal stability of membranes. DSC showed reduction in the heat of fusion which may be due to the dilution of the inherent crystallinity of PVA by incorporation of the PEG fraction, The thermal stability of members with different PEG content as measured by TGA was also almost identical in trend. These flexible membranes are excellent materials for the biomedical application in human healthcare.

### **Introduction**

Poly(vinyl alcohol) (PVA) is a water-soluble and synthetic polymer consisting of hydroxyl groups arranged along the polymer chain. These groups not only provide the hydrophilicity but also offer site for bioimmobilization. PVA is a biocompatible polymer with adequate properties to serve as a film for drug delivery.(1) This is the reason that PVA has been innovated as hydrogel in the recent days for its application as advanced functional material, such as in drug delivery, antimicrobial materials, tissue engineering material(2-4), self-healing gels(5), shape-memory materials.(6) The advancement need to convert it into a crosslinked system by chemical crosslinking which involves the linking between PVA chains to form gels. Crosslinkers do influence the physical characteristics of the PVA structure which subsequently influences the biomedical applications as well.(7) A large number of crosslinking agents have been used for creating a water insoluble structure. These are glyoxal, boric acid, GLUTARALDEHYDE, and STMP which create the three dimensional structure by reacting with hydroxyl groups.(8-12) In an interesting work, dual crosslinking was carried out to have the matrix with high strength and the toughness.(13) The polymer was first crosslinked with glutaraldehyde and subsequently subjected to the controlled annealing process. A nice review on the PVA crosslinking in wound dressing is published, recently.(14)

We have carried out the blending of PVA and SA and PEG to develop a composite membrane that may be used for controlled delivery of a drug. Although, the PVA and SA combinations have been investigated in details by some workers, the influence of PEG on the physico-chemical structure of the composite membrane have not been investigated in details. The

present study is dedicated to the PEG induced structural changes in the membranes as a function of the PEG content.

## Experimental

### 3.1. Materials

Polyvinyl alcohol (PVA) (Mw 13000-23000) and glyoxal were obtained from central drug house (P) Ltd. India. Polyethylene glycol, (PEG-600) (Mw, 600) and hydrochloric acid (HCl) were purchased from Merck Life Science Private Limited, India. Sodium Alginate was supplied from titan biotech LTD, India. Glyoxal was received from Merck, India. Deionized water was used as the solvent in all experiments.

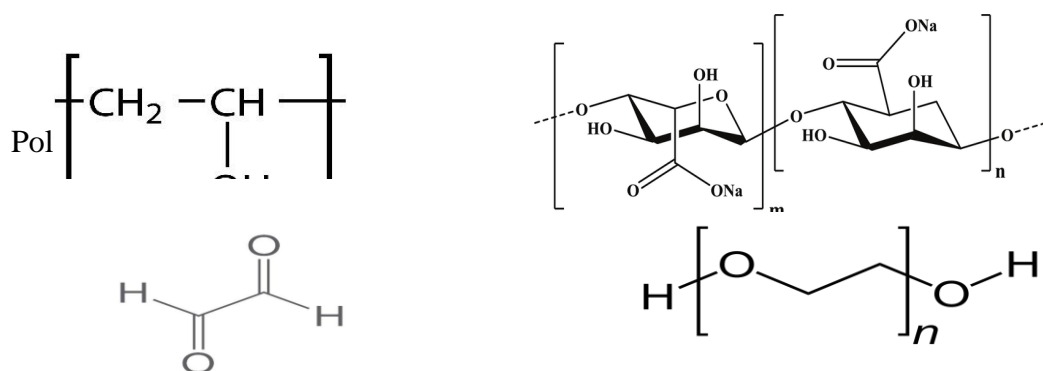


Figure 3.1. Structure four components of the antimicrobial membrane

### 3.2. Preparation of crosslinked PVA

PVA (5%) was dissolved in deionized water under constant stirring for 2 h at a temperature of 75°C. 20 $\mu$ l of HCl was added to the PVA solution to provide an acidic medium with continuous stirring for 1h. Glyoxal (GLY) in the range of 1% to 4% was added to acidic PVA solution at a temperature of 60°C with continuous stirring of 3h. SA was subsequently added to the PVA solution and PEG content was varied in the range of 10-40%.

### 3.3. Swelling stability

Dried samples were placed in in distilled water for 24 h at room temperature. Swollen samples were wiped out using tissue paper to remove excess water. Samples were subsequently used for the optical micrographs.

### 3.4. 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 thermograms were run in the range of 20-250°C, under nitrogen atmosphere at a heating rate of 10°C/min. The heat of fusion was calculated from the area under the endothermic peak of the thermogram. The following equation gives the crystallinity of samples.

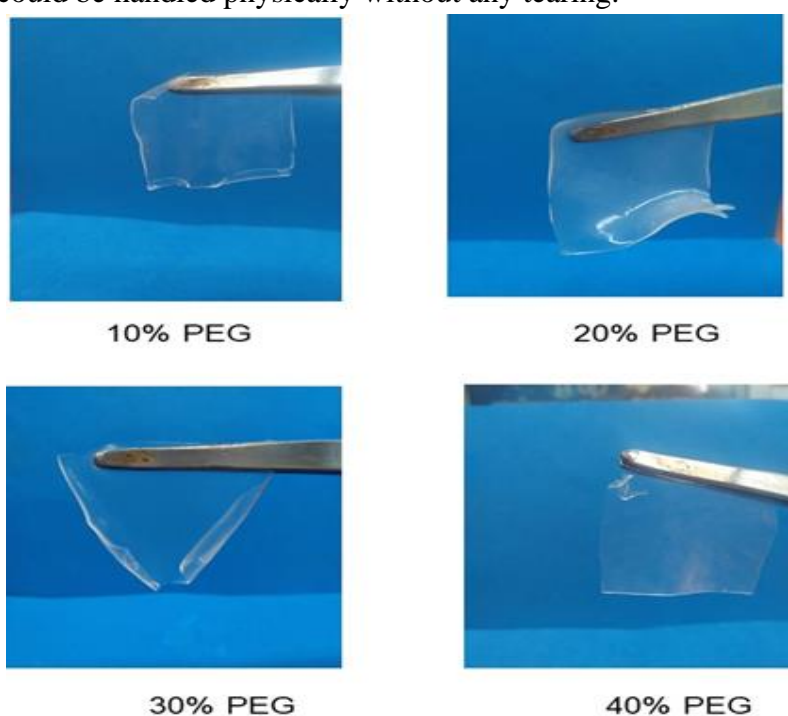
### 3.5. Thermogravimetric Analysis (TGA)

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 50-800°C at a heating rate of 10°C/min.

#### 4.0. Results & Discussion

The composite membrane comprising of PVA and SA matrix was prepared in our earlier studies. The study involved the influence of the SA fraction on the structure and properties of the blend membranes. We optimized SA content of 10% and the crosslinker content of 2% in PVA-SA composition for achieving the swelling and the dimensional stability of the membranes. PEG has been added to this composition to develop a flexible matrix for the drug immobilization and its release from the matrix. PEG was varied in the range of 10-40% in the blend composition and the structure-property correlation of membranes has been investigated as a function of the PEG content.

The films were investigated for their dimensional stability in aqueous system. It was observed that these films exhibited good stability in the swollen state. (Figure 1) The films were transparent and could be handled physically without any tearing.



*Figure 1. Photographs of the swollen PVA -SA-PEG membranes*

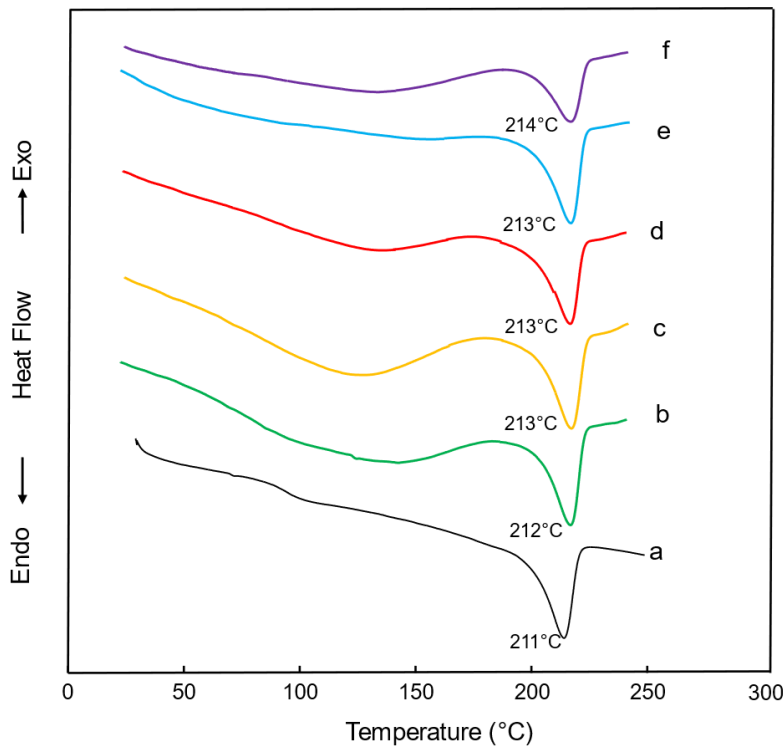


Figure 2. DSC thermograms of (a) PVA; (b) PVA-SA and PVA-SA-PEG membranes with PEG content of (c) 10%; (d) 20%; (e) 30%; (f) 40%.

The DSC thermograms for all membranes is presented in Figure 2. The melting thermogram of PVA shifted from 211°C to 212°C by the addition of 10% SA. Even, the melting temperature of membranes with PEG stayed almost identical with the increase in the PEG content except their relative area diminished. It seems that the SA or PEG addition does not interfere with the crystallization process of the PVA. However, the heat of fusion tends to decrease with the increase in the PEG content. (Figure 3) The observed decrease in the heat of fusion therefore may be regarded as the one due to dilution of the inherent crystallinity by the incorporation of the PEG component.

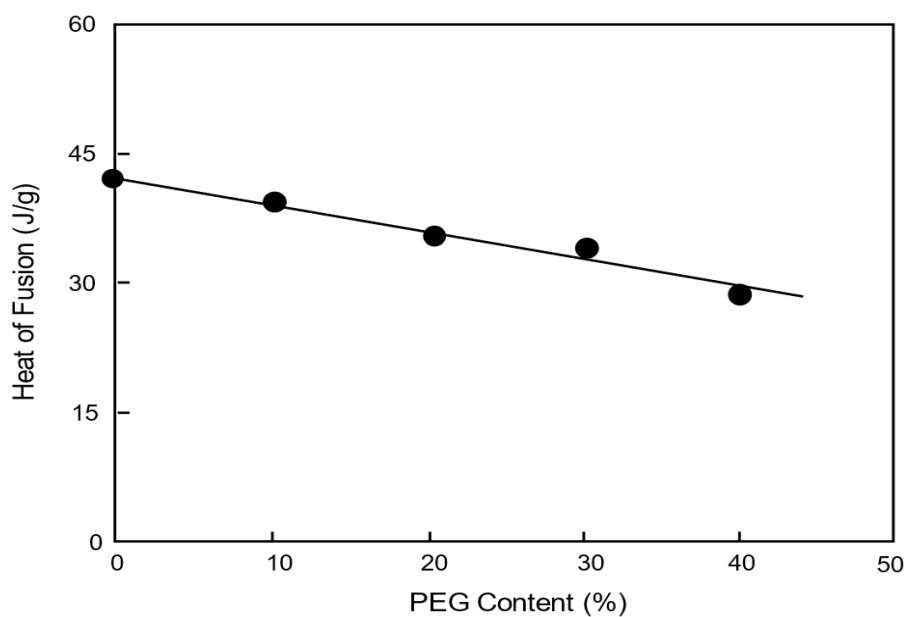


Figure 3. Variation of the heat of fusion as a function of the PEG content in membranes.

TGA thermograms of membranes are presented in Figure 4. PVA shows a very stable thermogram. Even the SA presence made some diminishing in the thermal stability. However, the addition of PEG to the membranes diminishes the stability of the material. It seems that the amount of PEG did not influence much the stability together. The only observation has been that the initial loss in weight up to 200°C may be the because of the dehydration of the hydrogel matrix and the decarboxylation process. In general, it may be stated that membranes are quite reasonably stable in spite of the addition of the PEG in its matrix.

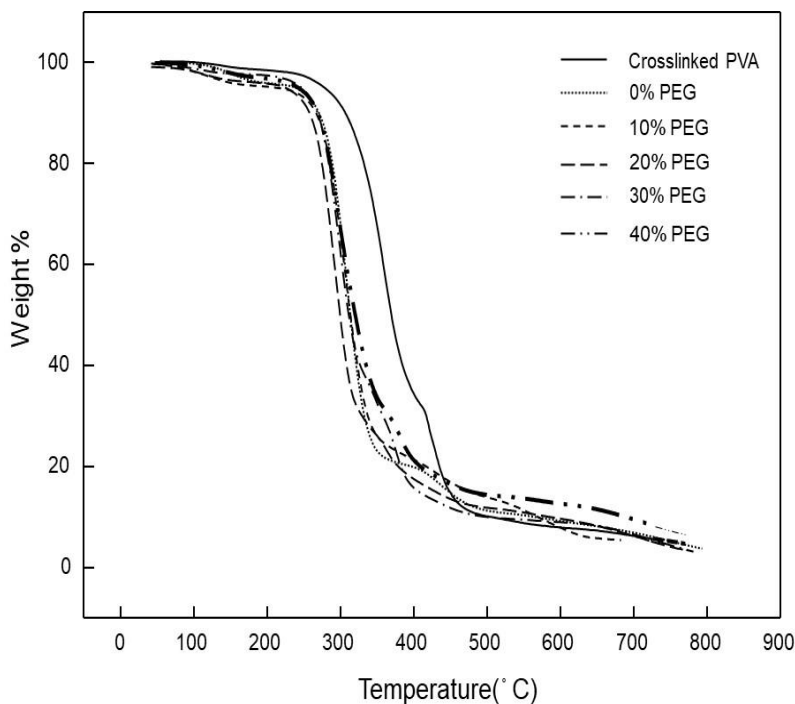


Figure 4. TGA diffractogram of PVA -SA-PEG membranes

## Conclusion

The blending of PVA with the SA and PEG leads to the development of flexible membranes with excellent dimensional stability. It was observed that the membranes undergo reduction in the thermogram size with the increase in the PEG content. It is due to the dilution of the inherent crystallinity in membranes by the addition of the PEG in their matrix. The membranes are thermally stable and do not show much change as the PEG content increased. This study shows that the membranes are excellent material where flexible matrix is obtained by PEG addition which may be used subsequently for biomedical applications.

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