

Study on the thermal properties of poly(vinyl alcohol) in the presence of collagen

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Abstract

Crystallization of poly(vinyl alcohol) (PVA) in the presence of 1%, 3% and 5% of collagen has been studied by Differential Scanning Calorimetry (DSC). PVA samples containing 1%, 3% and 5% of collagen after melting were crystallized with different cooling rate.

The melting temperature of poly(vinyl alcohol) PVA in the presence of 1%, 3% and 5% of collagen is little big bigger than that for pure PVA. Small amount of collagen in PVA increases melting temperature probably due to hydrogen bonding between PVA and collagen. Collagen contains several side groups capable to form hydrogen bonds with OH group of PVA.

The amount of crystallinity in PVA containing 1%, 3% and 5% of collagen is little big smaller than for pure PVA. Small amount of collagen in PVA causes disorder between polymer chains of polymer and leads to decrease of crystallinity. Crystallization process occurs slower in PVA containing small amount of collagen than for pure melt PVA.

1. Introduction

The thermal degradation of poly(vinyl alcohol) (PVA) has been studied by several researchers [1-4]. Thermal degradation of PVA in a solid state was considered to be due to the elimination of hydroxyl side groups. In the molten state thermal degradation leads to the production of volatile saturated and unsaturated aldehydes and ketones [1]. PVA is a widely used synthetic biomaterial and for this reason not only thermal degradation is very important but also the melting point of this polymer seems to be very important [5]. Sometimes it is very important to improve biocompatibility and/or surface properties of PVA. For this reason a small amount of natural polymer can be added to PVA.

Several natural polymers like starch [6], collagen [7,8], chitosan [9], silk [10] and lignin [11] have been already used to prepare PVA blends.

Polymeric materials based on PVA are often treated by high temperature during the sterilization of biomaterial.

Thermal stability of PVA can be modified by small addition of other polymers and/or biopolymers. In our study for modification of thermal stability of PVA we used small amount of collagen.

Collagen is a biopolymer, the most abundant protein in animals organisms where it provides the principal structural and mechanical support [12,13].

The aim of this work was to study the thermal properties of PVA in the presence of small amount of collagen (1%, 3% and 5%).

2. Materials and methods

PVA was obtained from Fluka (90.98% degree of hydrolysis). Collagen was obtained in our laboratory from tail tendons of young albino rats. Polymer blends were prepared by mixing suitable volumes of collagen and PVA aqueous solution and the final amount of collagen in PVA was 1%, 3% and 5% (by weight). Polymer films were obtained by casting solution onto glass plate. After solvent evaporation, the samples were dried in vacuum at room temperature.

Differential Scanning Calorimetry DSC measurements were performed using the

TA instrument Modulated 2930 at a rate of 10°C/min from 0 to 250°C. DSC curves for each film were obtained from the first heating run. In order to assess the crystallization temperature the specimens were heated with different rates (200°C/min, 100°C/min, 50°C/min, 20°C/min) to melt PVA films and later on they were cooled with the same rate to crystallize the polymer. The weight of each sample film was about 5 mg.

3. Results and discussion

PVA films used in this study were analysed by DSC. DSC curves for PVA film and PVA films containing collagen are presented in Figures 1.

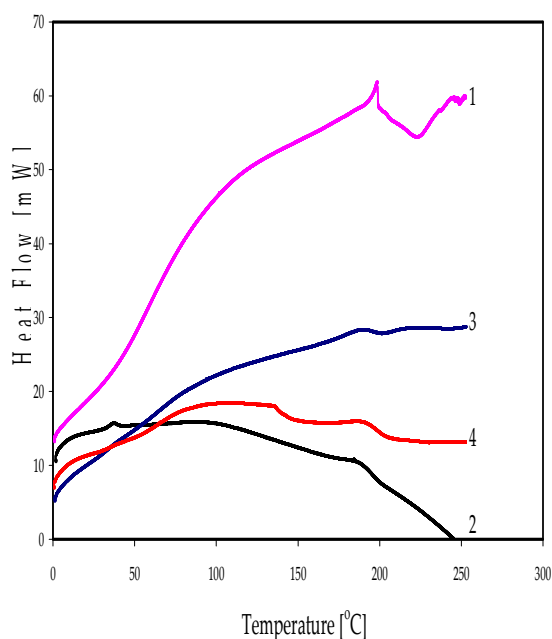


Fig. 1. DSC curves of PVA films, collagen films and PVA containing collagen (1- collagen, 2- PVA, 3- PVA+ 3% collagen, 4- PVA+5% collagen)

For pure PVA we observe a peak of melting temperature at 184°C. A glass transition temperature was not observe. The value of melting point depends on the degree of crystalline phase in PVA film and on water amount in PVA film. For highly crystalline PVA the melting point is about 230°C [1]. The melting point of PVA used in

our study was below 200°C and suggests that PVA in thin film is not highly crystalline. We observed that the thermal stability of PVA is different when PVA contains 1%, 3% and 5% of collagen (Figures 1, Table 1).

Table 1

Melting temperature of PVA and PVA containing 1%, 3% and 5% of collagen

Specimen	T_m [°C]
PVA	184
PVA +1% collagen	187
PVA+3% collagen	187
PVA+ 5% collagen	189
Collagen	198

In the presence of small amount of collagen the melting temperature of PVA slightly increases probably due to hydrogen bonding between PVA and collagen. Collagen contains several side groups capable to form hydrogen bonds with OH group of PVA.

In the Table 2 we compare the area of crystalline melting peak, (ΔH) for PVA films and PVA containing collagen. One can see that for PVA containing collagen the area of melting curve is smaller than for PVA.

Table 2

Enthalpy of the process of melting ΔH [J/g] of PVA and PVA containing 1%, 3% and 5% of collagen

Specimen	ΔH [J/g]
PVA	27.74
PVA +1% collagen	22.62
PVA+3% collagen	20.67
PVA+ 5% collagen	23.94
Collagen	15.45

The area of the crystalline melting point is usually used to deduce the amount of

crystallinity in the PVA sample. By a comparison of values for the heat fusion we can compare the crystallinity of the specimens. The amount of crystallinity in PVA containing 1%, 3% and 5% of collagen is little big smaller than the amount of crystallinity for pure PVA. One can say that small amount of collagen in PVA causes disorder between polymer chains of polymer and leads to decrease of crystallinity.

In order to assess the influence of collagen on crystallization temperature of PVA the specimens were heated with a rate 200°C/min, 100°C/min, 50°C/min and 20°C/min to melt polymer film, and later on they were cooled with the same rate. The DSC curves of PVA crystallization, obtained with cooling rate 200°C/min, have been presented in Figure 2.

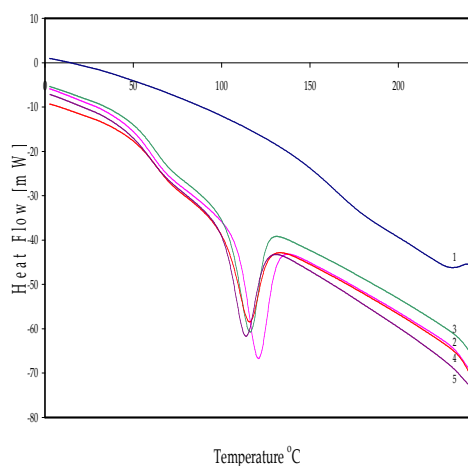


Fig. 2. DSC curves of PVA and PVA containing collagen after cooling from 250°C with cooling rate 200°C/min (1-collagen, 2- PVA, 3- PVA containing 1% of collagen, 4- PVA containing 3% of collagen, 5- PVA containing 5% of collagen)

As one can see the crystallization temperature is different for pure PVA and for PVA containing collagen. For pure collagen film we have not observed a crystallization peak. The crystallization temperatures of PVA and PVA containing 1%, 3% and 5% of collagen have been presented in Table 3. For pure PVA we observed a peak of crystallization at 121°C,

whereas for PVA containing 1% of collagen a wide peak was observed at 116°C. For PVA containing 3% and 5% of collagen a crystallization peak was observed at 116 and 113°C, respectively

Table 3

The crystallization temperature of PVA and PVA containing 1%, 3% and 5% of collagen

Specimen	Crystallization temperature After cooling rate [°C/min]			[°C]
	200	100	50	
Collagen	-	-	-	-
PVA	121	129	135	140
PVA + 1% collagen	116.	127	135	145
PVA+ 3% collagen	116	123	130	135
PVA+ 5% collagen	113.	123	130	133

The DSC curves of PVA crystallization, obtained with cooling rate 100°C/min, have been presented in Figure 3.

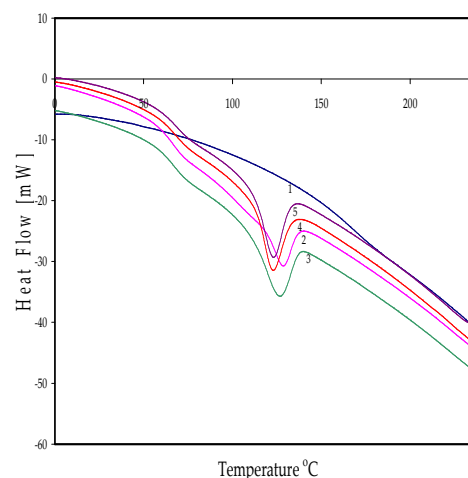


Fig. 3. DSC curves of PVA and PVA containing collagen after cooling from 250°C with cooling rate 100°C/min (1-collagen, 2- PVA, 3- PVA containing 1% of collagen, 4- PVA containing 3% of collagen, 5- PVA containing 5% of collagen)

Again one can see that the crystallization temperature is different for pure PVA and for PVA containing collagen. The crystallization temperatures of PVA and PVA containing 1%, 3% and 5% of collagen have been presented in Table 3. For pure PVA we observed a peak of

crystallization at 129°C, whereas for PVA containing 1% of collagen a wide peak was observed at 127°C. For PVA containing 3% and 5% of collagen a crystallization peak was observed at 123°C. Collagen does not crystallize after melting up to 250 °C and immediate cooling up to 20°C. One can say that during cooling of PVA in melting state in the presence of small amount of collagen the crystallization process occurs slower than for pure melt PVA. In melting state collagen molecules can easily penetrate PVA molecules and molecular interactions may occur. Crystallization temperature depends on cooling rate of the specimens (Figure 4 and Figure 5).

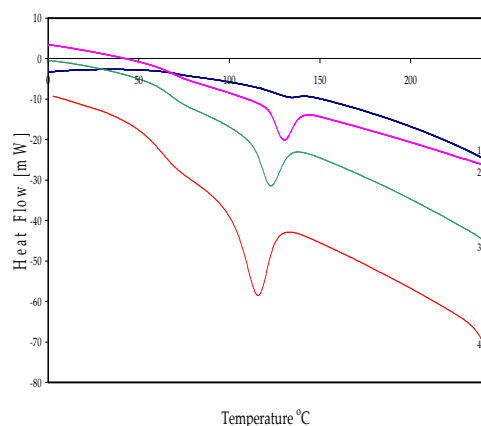


Fig. 4. DSC curves of PVA containing 3% of collagen after cooling from 250°C with different cooling rate. (1-20°C/min, 2- 50°C/min, 3- 100°C/min, 4- 200°C/min)

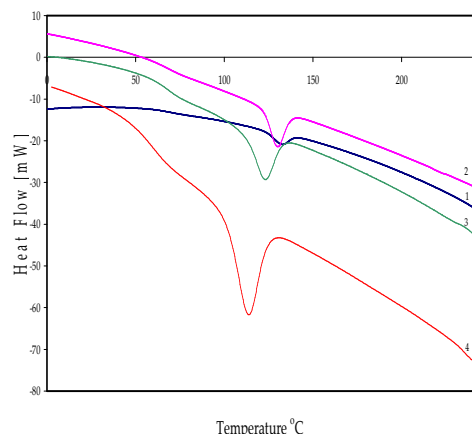


Fig. 5. DSC curves of PVA containing 5% of collagen after cooling from 250°C with different cooling rate. (1-20°C/min, 2- 50°C/min, 3- 100°C/min, 4- 200°C/min)

As can be clearly seen from Figs. 4-5 and the Table 3, for slow cooling rate (20°C/min) the crystallization temperature of PVA is bigger (140°C) than for fast cooling rate (for cooling rate 200°C/min the crystallization temperature was 121°C). However, for all cooling rates applied in our studies, for PVA in melting state in the presence of small amount of collagen the crystallization process occurs slower than for pure melt PVA.

4. Conclusions

The melting temperature of poly(vinyl alcohol) PVA in the presence of 1%, 3% and 5% of collagen is little big bigger than for pure PVA. Small amount of collagen in PVA increases melting temperature probably due to hydrogen bonding between PVA and collagen. Collagen contains several side groups capable to form hydrogen bonds with OH group of PVA.

The amount of crystallinity in PVA containing 1%, 3% and 5% of collagen is little big smaller than for pure PVA. Small amount of collagen in PVA causes disorder between polymer chains of polymer and leads to decrease of crystallinity.

During cooling of PVA in melting state in the presence of small amount of collagen the crystallization process occurs slower than for pure melt PVA.

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