

## PREPARATION AND PROPERTIES OF ELECTROSPUN $\beta$ - AND HP- $\beta$ -CYCLODEXTRIN/PVA HYDROGEL NANOFIBERS

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### ABSTRACT (10 pt)

Poly(vinyl alcohol) (PVA) is a linear hydrophilic polymer that is nontoxic and biocompatible. Because of intra/intermolecular interactions via hydrogen bonding, PVA can form hydrogels. Cyclodextrins (CDs) are one of the most promising materials for the development of products with advanced properties due to inclusion complex formation ability. In this study, electrospinning method is used to produce PVA hydrogel nanofibers and CDs are added to PVA solutions to improve their swelling capacity. Heat setting is used to form crosslinking between the PVA matrix.  $\beta$ -CD and HP  $\beta$ -CD loaded PVA nanofibers were successfully electrospun. Heat setting enhances the stability of the PVA mats against dissolution in water.  $\beta$ -CD and HP-  $\beta$ -CD loading increased the swelling capacity of the PVA nanofibers compared to the neat PVA nanofibers at temperatures 110, 130 and 150°C, but weight loss percentages were not satisfactory. Compared to the neat PVA nanofibers; at 170 and 190°C, lower swelling percentages were seen. It was also seen that 170°C is high enough to achieve sufficient weight loss percentages and for preserving nanofibrous structure for both neat and  $\beta$ -CD and HP- $\beta$ -CD loaded PVA mats.

**Keywords:** Electrospinning, PVA, Cyclodextrin, Hydrogel nanofibers

### 1. INTRODUCTION

Hydrogels can be described as hydrophilic, crosslinked polymers (networks) which swell when placed in water or biological fluids [1]. They remain insoluble in their swollen state due to the presence of several crosslinks. They can absorb large quantities of water. These materials uniquely offer moderate-to-high physical, chemical, and mechanical stability in their swollen state [2]. Because of their extraordinary biocompatibility, hydrogels have been successfully used in a wide range of biomedical applications that include lubrication for surgical gloves, urinary catheters and surgical drainage systems, contact lenses, wound dressings, and drug delivery systems [3].

Poly(vinyl alcohol) (PVA) is a linear hydrophilic polymer that is nontoxic and biocompatible. Because of intra/intermolecular interactions via hydrogen bonding, PVA forms hydrogels (physical gels). Cyclodextrins (CDs) are one of the most promising materials for the development of products with advanced properties due to inclusion complex formation ability with a wide variety of substances [4]. Beta-cyclodextrin ( $\beta$ -CD) is the most commonly used CD due to the cavity size, availability and low cost [5]. Apart from parent CDs its alkylated derivatives, e.g. 2-hydroxy propyl- $\beta$ -CD (HP-  $\beta$ -CD) have also attracted growing interest due to their improved complexation efficiency, greater water solubility and less toxicity [6]. In this study, electrospinning method is used to produce PVA hydrogel nanofibers and CDs are added to PVA solutions to improve their swelling capacity and heat setting is used to form crosslinking between the PVA matrix.

## 2. EXPERIMENTAL

### 2.1 Materials

PVA with average molecular weight of ~125,000 g/mol was purchased from Sigma Aldrich Chemical Company.  $\beta$ -CD and HP- $\beta$ -CD were purchased from Wacker Chemie AG.

### 2.2 Method

#### 2.2.1 Preparation of the electrospinning solutions

A weighed amount of PVA was dissolved in distilled water at 100 °C to prepare an aqueous PVA stock solution at a fixed concentration of 10% w/w. The concentration of the  $\beta$ -CD and HP- $\beta$ -CD were used as 10, 20 and 30% (w/W<sub>polymer</sub>).

#### 2.2.2 Electrospinning

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 ml) and needle (2.5 cm long, 22 gauge, and flat tip), a ground electrode, and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). Neat PVA and CD loaded polymer solutions were electrospun at a voltage of 16 kV, a tip-to-collector distance of 15 cm with a feeding rate of 0.5 ml/h for 5 h. A grounded stationary rectangular metal collector covered by a piece of aluminium foil was used for the nanofiber deposition. The complete electrospinning apparatus was enclosed in a glass box, and the electrospinning of the nanofibers was carried out at room temperature.

After electrospinning, PVA and CD loaded PVA nanofibrous mats were heat set at five different temperatures (110, 130, 150, 170 and 190 °C) for 20 min in an oven to enhance the crosslinking reaction.

#### 2.2.3 Characterization of the electrospun PVA mats

The morphologies of the neat and CD-loaded electrospun PVA nanofibers were characterized using scanning electron microscopy (SEM, FEI Quanta 250 FEG). Each sample was coated with a thin film of gold using an EMITECH K550X ion sputtering device prior to SEM observation for two minutes. The mean diameter of the resultant fibers was calculated from measurements of SEM images by using Image J program. Fiber diameters were measured by drawing straight lines perpendicular to the fiber axis. Approximately fifty measurements were carried out from different parts of each sample.

The swelling and weight loss of the neat PVA and CD loaded electrospun PVA fiber mats were characterized in distilled water for 24 h according to the following Eq.(1) and (2):

$$\text{Degree of swelling (\%)} = \frac{M - M_d}{M_d} \times 100 \quad (1)$$

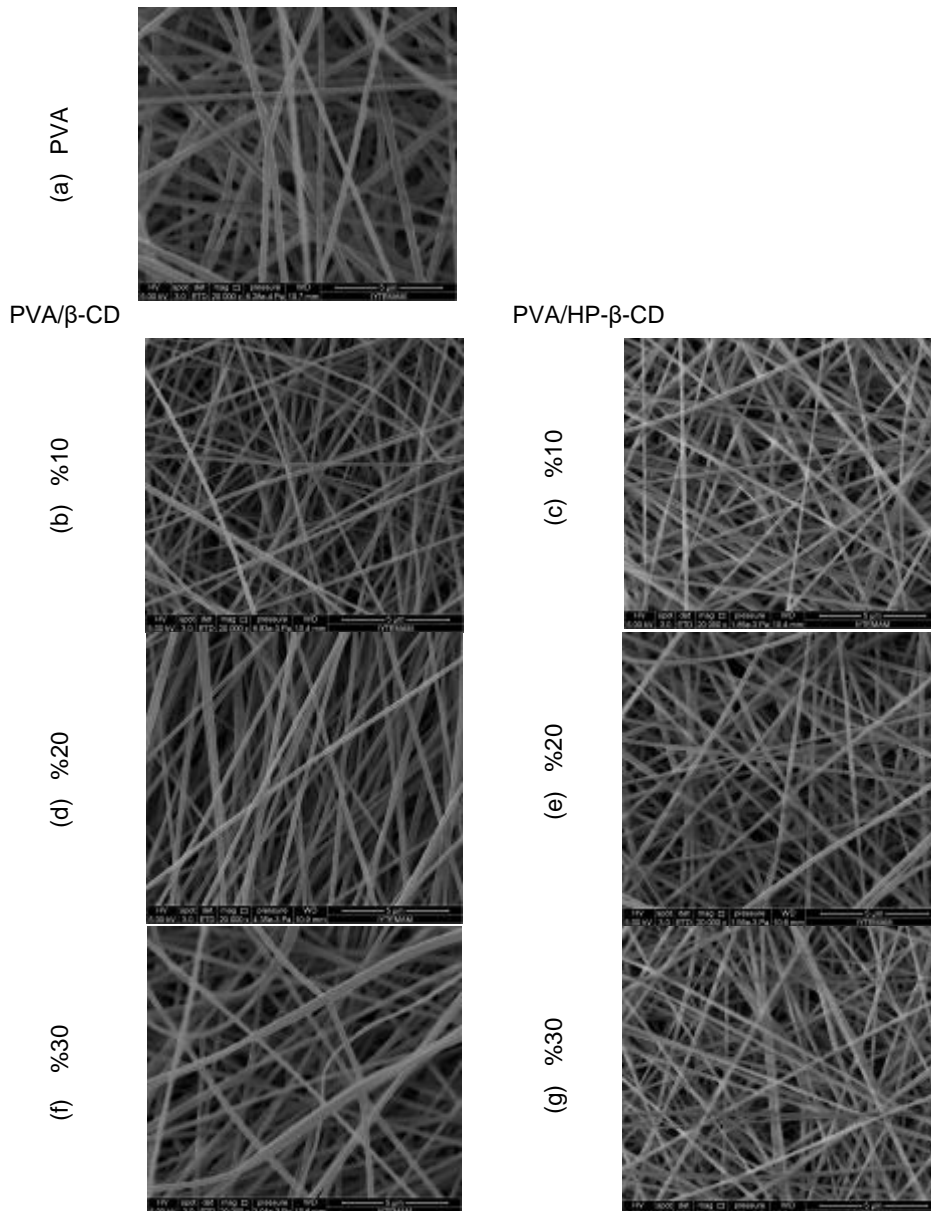
and

$$\text{Weight loss (\%)} = \frac{M_i - M_d}{M_i} \times 100 \quad (2)$$

where  $M$  is the weight of each fiber mat sample after immersion in distilled water for 24 h,  $M_d$  is the weight of the sample in its dry state,  $M_i$  is the initial weight of the sample in its dry state.

### 3. RESULTS AND DISCUSSION

The SEM images of the nanofibers are given in Figure 1. It was observed that  $\beta$ -CD and HP  $\beta$ -CD loaded PVA nanofibers were successfully electrospun. No CD crystals were detected by SEM either on the surface of the fibers or outside the fibers as shown in Figure 1. This indicated that, CDs were totally embedded within the fibers.



**Figure 1.** SEM Images of the neat and CD loaded PVA nanofibers

The mean diameters of CDs loaded PVA nanofibers were given in Table 1. Differences in the fiber diameters were analyzed by one-way analysis of variance (ANOVA) followed by a Tukey test for pairwise comparison and  $p < 0.05$  was considered statistically significant. It was observed that, there is a significant effect on the fiber diameter by the incorporation of CDs.

Considering  $\beta$ -CD, there is a significant difference between each  $\beta$ -CD concentration but 30%  $\beta$ -CD loading did not cause a significant difference compared to neat PVA nanofibers. This may be related to the high concentration of at  $\beta$ -CD. In case of HP- $\beta$ -CD, higher solubility of the HP- $\beta$ -CD than  $\beta$ -CD, HP- $\beta$ -CD loading significantly decreased the mean fiber diameters compared to the neat PVA nanofibers, but there is not a significant difference between 10% and 20% of HP- $\beta$ -CD loading.

**Table 1.** Mean diameter of electrospun PVA nanofibers

	<b>CD Concentration</b>	<b>Mean Fiber Diameter <math>\pm</math> S.D. (nm)</b>
%10 PVA	-	291.60 $\pm$ 38.70
	%10	187.76 $\pm$ 25.58
%10 PVA+ $\beta$ -CD	%20	226.69 $\pm$ 35.92
	%30	278.23 $\pm$ 51.33
%10 PVA+ HP- $\beta$ -CD	%10	213.86 $\pm$ 47.46
	%20	213.58 $\pm$ 35.51
	%30	193.41 $\pm$ 22.53

Hydrogels are hydrophilic, crosslinked polymers (networks) which swell when placed in water or biological fluids. Swelling and weight loss percentages of the neat PVA and CDs loaded non-crosslinked PVA nanofibers and heat fixation applied electrospun PVA nanofibers were given in Table 2 for each temperatures. After immersion of distilled water for 24h, these nanofibers were dried. Swelling and weight loss percentages were calculated according to Eq.(1) and (2). Their SEM images were given Fig. 2 and 3.

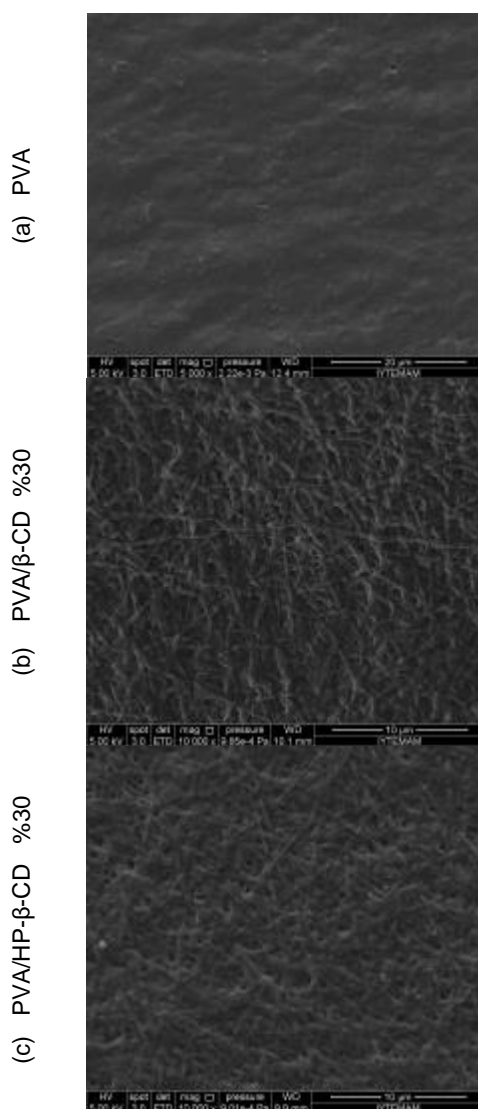
**Table 2.** Swelling and Weight Loss of neat and CDs loaded PVA nanofibers

	<b>% Swelling</b>	<b>% Weight Loss</b>	<b>% Swelling</b>	<b>% Weight Loss</b>	<b>% Swelling</b>	<b>% Weight Loss</b>
<b>PVA/ <math>\beta</math>-CD</b>	<b>%10 <math>\beta</math>-CD</b>		<b>%20 <math>\beta</math>-CD</b>		<b>%30 <math>\beta</math>-CD</b>	
<i>Without heat set</i>	2816.21	94.33	2385.08	90.44	3261.51	93.62
110 °C	2645.18	93.11	1810.57	88.76	1736.27	89.44
130 °C	2557.70	87.48	1978.39	86.33	1533.87	85.49
150 °C	1947.59	85.38	1813.57	75.22	1445.92	76.56
170 °C	651.62	0.0	580.69	1.28	533.96	3.77
190 °C	508.33	0.0	510.00	0.0	469.01	4.93
<b>PVA/HP-<math>\beta</math>-CD</b>	<b>%10 HP-<math>\beta</math>-CD</b>		<b>%20 HP-<math>\beta</math>-CD</b>		<b>%30 HP-<math>\beta</math>-CD</b>	
<i>Without heat set</i>	2276.10	91.49	2538.47	93.33	2914.11	92.89
110 °C	3011.83	93.25	3307.33	93.72	2905.11	92.37
130 °C	2195.41	79.58	2720.73	83.30	2333.86	83.15
150 °C	1478.04	68.33	1346.96	66.33	2113.70	77.78
170 °C	693.29	3.69	564.76	7.72	541.61	7.96
190 °C	554.25	0.0	488.33	4.40	430.23	3.74
<b>PVA</b>	<b>% Swelling</b>		<b>% Weight Loss</b>			
110 °C	1460.32		71.93			
130 °C	1201.90		62.25			
150 °C	770.18		14.93			
170 °C	728.42		0.58			
190 °C	725.24		0.68			

Obviously, crosslinking by heat set enhances the stability of the PVA mats against dissolution in water. It can be seen that 110, 130 and 150 °C were not enough to prevent dissolutions of  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats in water. They were both higher than neat PVA samples related to the dissolution of  $\beta$ -CD and HP-  $\beta$ -CD. But at 170 and 190°C, weight loss percentages of the CDs loaded PVA mats were close to the neat PVA mats. However with the increasing percentage of CDs, small amount of weight losses can be seen, related to the dissolutions of the CDs in water.

On the other hand,  $\beta$ -CD and HP-  $\beta$ -CD loading increased the swelling capacity of the PVA nanofibers compared to the neat PVA nanofibers at temperatures 110, 130 and 150°C. However because of the dissolutions of the  $\beta$ -CD and HP-  $\beta$ -CD in the water, results of swelling percentages of PVA mats do not show consistency. In general, with the increasing heat set temperature, swelling capacity decreased, due to the increasing several crosslinking between the PVA matrix. Main difference occurred at 170 and 190°C, lower swelling percentages can be seen compared to the neat PVA nanofibers. This can be explained, increased crosslinking of the PVA matrix did not allow  $\beta$ -CD and HP-  $\beta$ -CD to absorb more water and existence of  $\beta$ -CD and HP-  $\beta$ -CD inside the matrix increased the crosslinking, therefore the swelling capacities were decreased.

In case of weight loss is not an issue, CD loaded PVA hydrogel mats and lower heat-set temperatures like 150 °C can be used to achieve higher swelling capacity. Besides at higher temperatures like 170 and 190°C, better crosslinking of PVA matrix can be achieved and also cavity of the CDs can be still used for several host molecules.

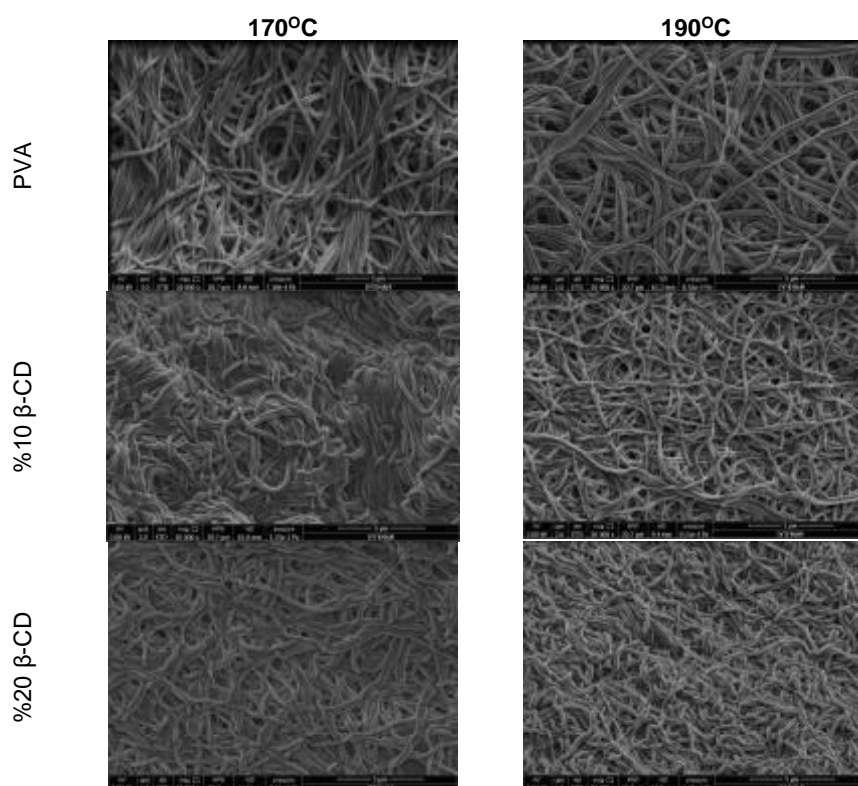


**Figure 2.** SEM Images of the neat (a) and 30%  $\beta$ -CD (b) and 30% HP-  $\beta$ -CD (c) loaded PVA nanofibers which were heat set at 150°C for 20 minutes, after immersion of distilled water for 24h.

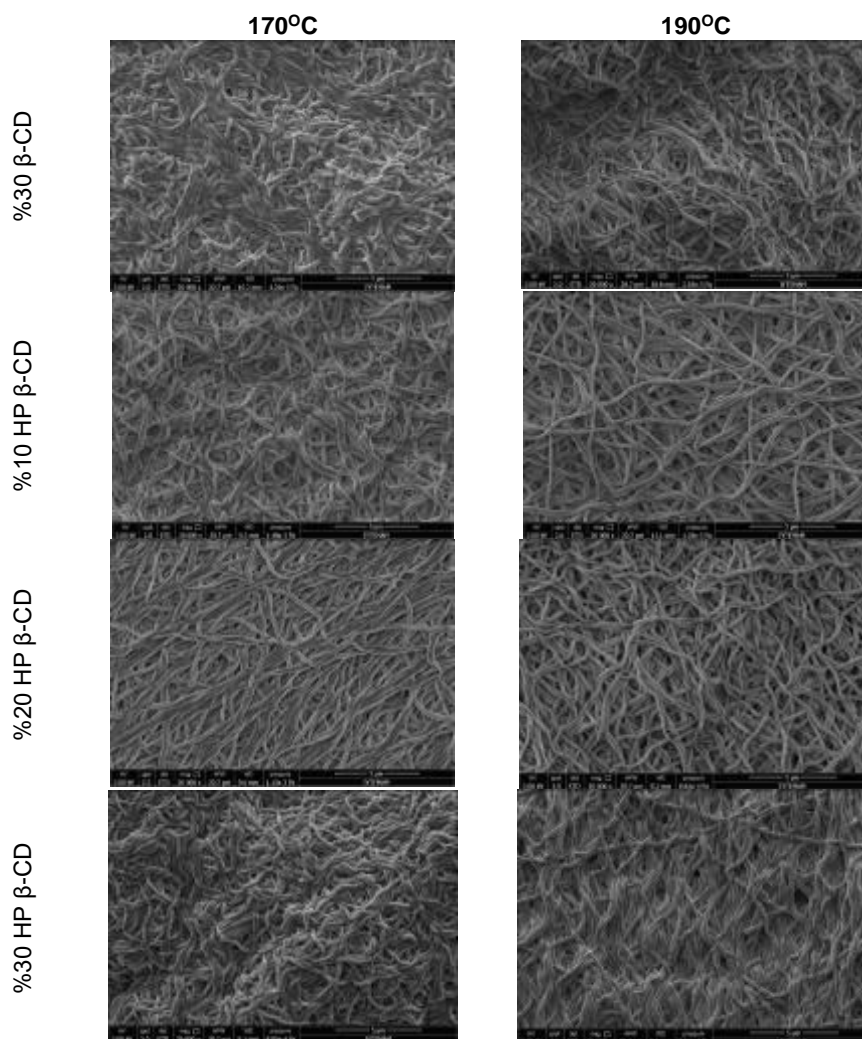
Fig.2 shows SEM images of neat electrospun PVA mats and 30%  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats after waiting 24 hours in distilled water and drying. Considering the weight loss percentages, 10 and 20%  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats, and 110 and 130 °C heat setting results were expected to be worse in case of preserving the nanofibrous structure. Therefore only 30%  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats which were heat set at 150 °C were selected for SEM images but for 170 and 190 °C, significantly better weight losses were achieved and SEM images were given for all three percentages of CDs in Fig. 3.

In Fig. 2a, PVA mats totally lost its nanofibrous structure at 150°C, however in Fig.2(b) and (c)  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats relatively preserved their nanofibrous structure. This can be explained CDs were embedded and incorporated into the nanofibers which promote self-crosslinking.

In Fig. 3 SEM images of the neat and 10, 20, 30%  $\beta$ -CD and 30% HP-  $\beta$ -CD loaded PVA nanofibers which were heat set at 170 and 190°C for 20 minutes were given. As expected, they all preserved their nanofibrous structure. Because of the wetting and drying they became tangled instead of their previous straight structure. When compared to the 150°C, at 170 and 190 °C, heat settings were successfully crosslinked the PVA mats for both neat and CDs loaded PVA mats. Considering the weight loss and swelling percentages, and also the SEM images which were given in Fig. 3, there is no need to be increase the crosslinking temperature to the 190°C; 170°C is high enough to achieve sufficient stability against to dissolution in water, preserving nanofibrous structure for both neat and  $\beta$ -CD and HP- $\beta$ -CD loaded PVA mats.



**Figure 3.** SEM Images of the neat, 10%, 20% and 30%  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA nanofibers which were heat set at 170 and 190°C for 20 minutes, after immersion of distilled water for 24h.



**Figure 3 (continued).** SEM Images of the neat, 10%, 20% and 30%  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA nanofibers which were heat set at 170 and 190°C for 20 minutes, after immersion of distilled water for 24h.

On the other hand at 170°C, increasing the CD concentration did affect much neither weight loss nor their nanofibrous structure after immersion in water. Anyway HP- $\beta$ -CD loaded PVA mats showed slightly higher weight loss due to the higher water solubility of the HP- $\beta$ -CD compared to the  $\beta$ -CD. Swelling percentages are higher at lower CD concentrations. At higher concentrations more CDs should be located at the inner parts of the PVA matrix, which may cause less swelling due to the crosslinking.

## 5. CONCLUSIONS

It was observed that  $\beta$ -CD and HP  $\beta$ -CD loaded PVA nanofibers were successfully electrospun. No CD crystals were detected by SEM either on the surface of the fibers or outside the fibers. Considering mean diameters of  $\beta$ -CD loaded PVA nanofibers, there is a significant difference between each  $\beta$ -CD concentration but 30%  $\beta$ -CD loading did not cause a significant difference compared to neat PVA nanofibers. In case of HP- $\beta$ -CD loaded samples, HP- $\beta$ -CD loading significantly decreased the mean fiber diameters compared to the neat PVA nanofibers, but there is not a significant difference between 10% and 20% of HP- $\beta$ -CD loading.

Heat setting enhances the stability of the PVA mats against dissolution in water. Heat-set temperatures of 110, 130 and 150 °C were not enough to prevent dissolutions of  $\beta$ -CD and HP-  $\beta$ -CD loaded PVA mats in water but at 170 and 190 °C, weight loss percentages of the CDs loaded PVA mats were close to the neat PVA mats. In general, with the increasing heat-set temperature, swelling capacity decreased, due to the increasing several crosslinking between the PVA matrix. Compared to the neat PVA nanofibers; at 170 and 190°C, lower swelling percentages were seen. In case of weight loss is not an issue, CD loaded PVA hydrogel mats and lower heat-set temperatures like 150 °C can be used to achieve higher swelling capacity. Besides at higher temperatures like 170 and 190 °C, better crosslinking of PVA matrix can be achieved and also cavity of the CDs can be still used for several host molecules. There is no need to be increase the crosslinking temperature to the 190°C; 170°C is high enough to achieve sufficient stability against to dissolution in water, preserving nanofibrous structure for both neat and  $\beta$ -CD and HP- $\beta$ -CD loaded PVA mats.

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