

CROSSLINKING OF ELECTROSPUN POLY(VINYL ALCOHOL) NANOFIBERS WITH POLYCARBOXYLIC ACIDS

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ABSTRACT

Electrospun PVA nanofibers have been one of the most extensively studied topics due to its biocompatibility, nontoxicity, hydrophilicity and ease of processability. However solubility of the PVA matrix in the aqueous medium limits its applications. In this study, polycarboxylic acids; 1,2,3,4 butanetetracarboxylic acid (BTCA) and citric acid (CA) were selected as crosslinking agents. Their effects on the resultant nanofiber morphology, swelling behavior and weight loss of PVA mats were investigated. BTCA and CA concentrations were selected to be 5%, 10% and 20% (w/w_{polymer}), Fixation temperature and time were changed to be 110 °C, 130 °C and 150 °C, and 20, 40 and 60 minutes, respectively. Water stable PVA nanofiber mats were produced successfully. It was also observed that, incorporation of crosslinking agents have a significant effect on the fiber diameter.

Key Words: Electrospinning, PVA nanofibers, polycarboxylic acids, BTCA, crosslinking

1. INTRODUCTION

Electrospun poly(vinyl alcohol) (PVA) hydrogel nanofibers are believed to be a potential candidate for medical textile applications. Poly(vinyl alcohol) (PVA) is a hydrophilic, semi-crystalline polymer with good chemical and thermal stability [1-2]. Electrospun PVA nanofibers have been one of the most extensively studied topics due to its biocompatibility, nontoxicity, hydrophilicity and ease of processability [3-4]. However solubility of the PVA matrix in the aqueous medium limits its applications. To make PVA electrospun fibers water insoluble and to form PVA hydrogels, several crosslinking methods have been used such as freezing/thawing, methanol treatment, chemical crosslinking, and irradiation [5-7]. Methanol treatment and chemical crosslinking with glutaraldehyde are found to be most applied treatments in the literature [1-2-8] but they display toxicity problems and thus their potential applications as biomaterials are limited [9-10]. Therefore in this study, polycarboxylic acids; 1,2,3,4 butanetetracarboxylic acid (BTCA) and citric acid (CA) were selected as crosslinking agents. BTCA and citric acid are low cost, non-toxic alternatives that have been reported to crosslink electrospun PVA hydrogels [9-10]. Another advantage is the miscibility of them with PVA electrospinning solutions, thus they can directly be added into the spinning solutions [9]. In this study, the crosslinking of PVA nanofibers with different concentration of polycarboxylic acids and their effects on the resultant nanofiber morphology, swelling behavior and weight loss of PVA mats in terms of water stability were investigated.

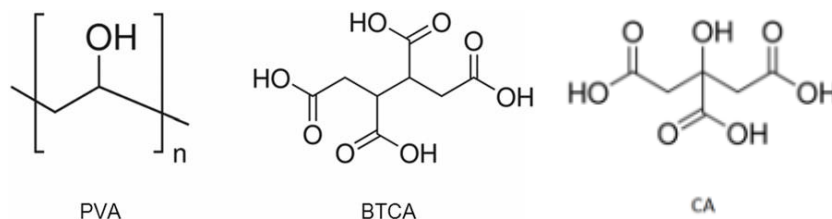


Figure 1. Poly(vinyl alcohol) (PVA), 1,2,3,4 butanetetracarboxylic acid (BTCA) and citric acid (CA)

2. EXPERIMENTAL

2.1 Materials

Poly(vinyl alcohol) (PVA) (Figure 1) with average molecular weight of ~125,000 g/mol, 1,2,3,4 butanetetracarboxylic acid (BTCA), citric acid (CA) and cyanamide were purchased from Sigma Aldrich Chemical Company. Chemical structures are given in Figure 1.

2.2 Electrospinning

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. It was stirred for 4 hours and cooled down to room temperature while it was stirring. After allowing the solution to cool down to room temperature, it was filtered through 43 mesh polyester fabric. BTCA or CA, as crosslinking agents, was directly added into the spinning solution with cyanamide as a catalyst in ratio of 2:1 (w/w) followed by stirring for 15 min. BTCA and CA concentrations were selected to be 5%, 10% and 20% (w/w_{polymer}).

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 mL) with a stainless steel needle (1.5-cm long, 22 gauges, and flat tip), a ground electrode and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). Polymer solutions were electrospun at a voltage of 18 kV, a tip-to-collector distance of 15 cm with a feeding rate of 0.5 ml/h. A grounded stationary rectangular metal collector covered by a piece of aluminum foil was used for the nanofiber deposition. Electrospinning of each sample were carried out for 5 h.

After electrospinning, PVA/BTCA and PVA/CA nanofibrous mats were heat set. Fixation temperature and time were changed to be 110 °C, 130 °C and 150 °C, and 20, 40 and 60 minutes, respectively in an oven to enhance the esterification reaction.

2.3 Characterization

The morphology of electrospun mats was observed by a scanning electron microscope (SEM; FEI Quanta250 FEG scanning electron microscope). The electrospun mats were sputtered by EMITECH K550X ion sputtering device with a thin layer of gold prior to SEM observation. The mean diameter of the resultant fibers was calculated from measurements on SEM images of 5000× magnification by using Image J program. Approximately 50 measurements were carried out from the different parts of each sample.

Viscosity of the polymer solutions was measured by using Brookfield DV-III Rheometer with the spindle type SC4-21 and 27 at 30 rpm. Surface tension measurements were carried out by Krüss Easy Dyne Analyser by Plate Method. Conductivity measurements were carried out using J.P. Selecta Conductivity meter, CD-2004.

Swelling and weight loss of the electrospun non-crosslinked and BTCA and CA crosslinked PVA fiber mats were characterized in distilled water at room temperature for 24 h according to the following equations:

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

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 submersion in distilled water for 24 h (samples were carefully blotted with tissue paper to remove excess water from the surface). M_d is the weight of the sample after drying at 37 °C, M_i is the initial weight of the samples.

3. RESULTS AND DISCUSSION

In this study the effects of crosslinker type and concentration were investigated in terms of mean fiber diameter; fixation temperature and time were investigated in terms of swelling and weight loss of resultant nanofibrous mats. Fiber formation and diameters were observed by SEM analysis. Fig. 2 illustrates the scanning electron micrographs of PVA and BTCA, CA crosslinked PVA nanofibers. In all cases smooth, uniform and bead free nanofibers were produced successfully. Since the solution parameters have a great importance on the resultant fiber morphology, surface tension, viscosity and conductivity measurements of each solution were tested and given in Table 1. The surface tension and viscosity of the polymer solutions was not affected significantly by the addition of BTCA or CA. But the conductivity of the solutions increased by the addition of the BTCA and CA, and their concentration increase. At all concentrations, CA added solutions have a higher conductivity value than BTCA added solutions.

Table 1. Properties of neat PVA, BTCA and CA added PVA solutions and mean fiber diameters

PVA (Mw:~125.000 g/mol) + Crosslinking agent	Crosslinking agent concentration	Surface Tension mN/m	Conductivity μ S/cm	Viscosity cP	Mean Diameter \pm S.D
10 %PVA	-	59.3	356	333.3	291.60 \pm 38.70 ^d
10%PVA + BTCA	%5	59.8	511	266.7	290.72 \pm 47.11 ^d
	%10	59.0	703	333.3	282.56 \pm 47.47 ^d
	%20	58.7	1128	333.3	235.92 \pm 64.41 ^{ab}
10%PVA +CA	%5	57.6	756	333.3	260.30 \pm 47.46 ^c
	%10	56.9	1179	333.3	253.37 \pm 58.15 ^{bc}
	%20	57.7	1776	333.3	223.72 \pm 62.08 ^a

^{a,b,c,d} $p < 0.05$. One Way ANOVA, Duncan post hoc test

It was observed that, incorporation of crosslinking agents have a significant effect on the fiber diameter (Table 1). The difference between mean fiber diameters of seven groups at $p < 0.05$ was considered statistically significant (one-way analysis of variance (ANOVA) followed by Duncan test for pairwise comparison). The resultant fiber diameters decreased by the addition of 5, 10 and 20% of CA and 20% of BTCA compared to neat PVA nanofibers. Mean fiber diameters of 20% of CA and BTCA added fibers were significantly thinner than their 5% and 10% added fibers. In addition there was not a significant difference between 5 and 10 % of BTCA and CA concentrations. Although there was a statistically significant difference between mean fiber diameters of some groups, 20-30 nm of difference is not a big difference in electrospinning process. But it can be clearly seen that the mean fiber diameters become thinner by the addition of higher concentration of polycarboxylic acids, probably because of the conductivity increase of the electrospinning solutions. It can be explained by higher stretching of the polymer jet due to the higher conductivity values which results thinner fiber formations. It was also shown that the mean fiber diameter of CA crosslinked PVA nanofibres is lower than those of BTCA crosslinked samples, possibly due to the higher conductivity of CA incorporated spinning solutions as aforementioned.

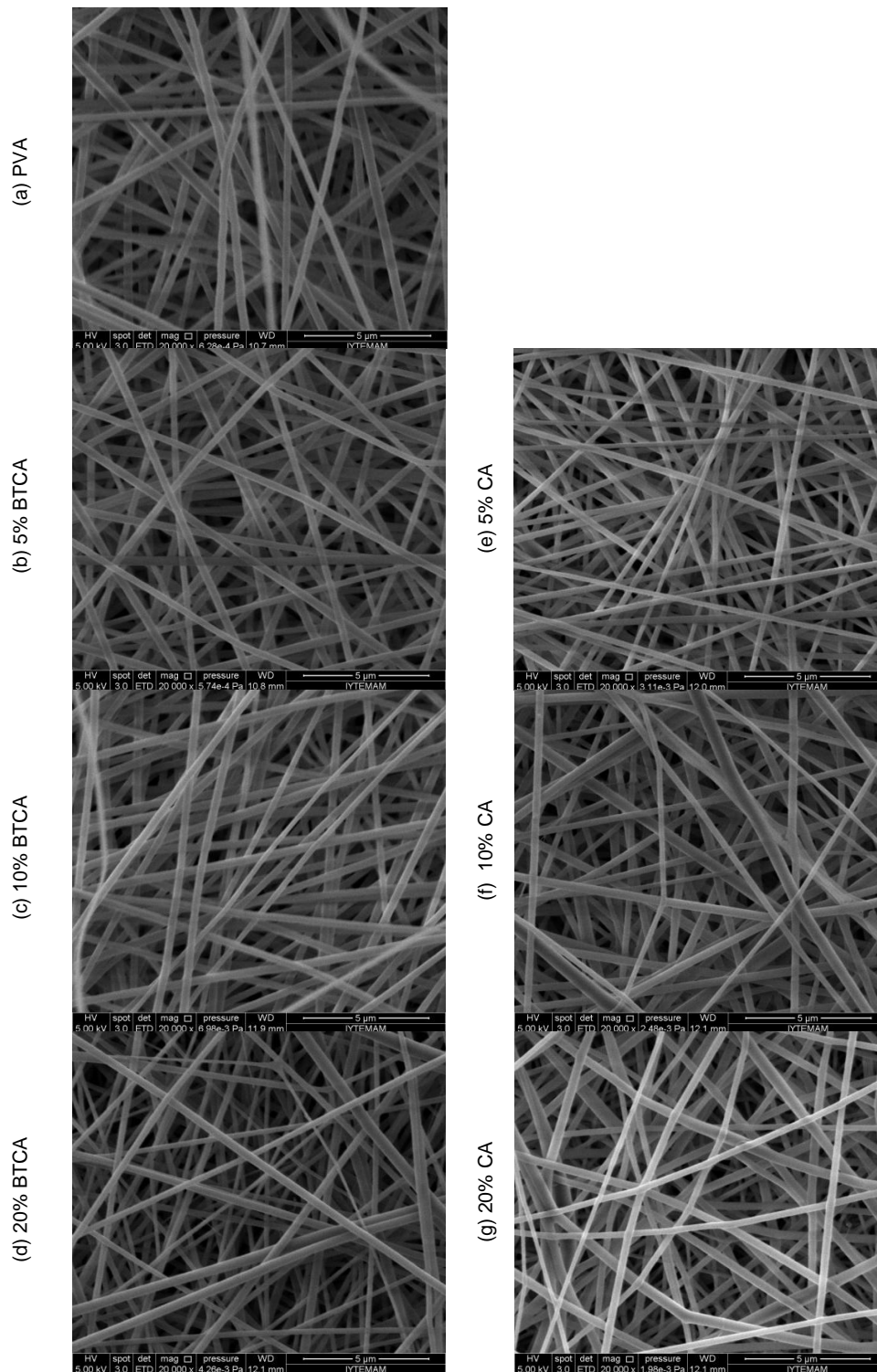


Figure 2. SEM images of PVA (a), %5(b), %10 (c) and %20 (d) BTCA, %5 (e), %10 (f), %20 (g) CA crosslinked PVA nanofibers

Swelling and weight loss degree of non-crosslinked, BTCA and CA crosslinked electrospun PVA nanofibres were given in Table 2 and 3, respectively. Without crosslinking, the degree of swelling of electrospun PVA nanofibers was ~1400-1200%, while the percentage of

weight loss was as much as ~60-70% and they were decreasing with the increasing fixation temperature and time. BTCA and CA crosslinking led to an increase in the degree of swelling compared to non-crosslinked samples except 20% of BTCA. Highest swelling ratios were achieved with CA especially at the fixation temperature of 110 °C. Swelling ratios are decreased with the increasing concentrations of the BTCA and CA because of the higher crosslinking density of the fiber matrix.

Table 2. Swelling % of electrospun non-crosslinked, BTCA and CA crosslinked PVA mats

	20'	40'	60'
BTCA			
110 °C			
%5 BTCA	1621.79	1319.79	1078.41
%10 BTCA	1536.57	1389.78	1314.71
%20 BTCA	896.67	789.92	817.35
130 °C			
%5 BTCA	1349.50	1519.64	1110.13
%10 BTCA	1483.93	1352.44	915.89
%20 BTCA	863.99	883.59	806.70
150 °C			
%5 BTCA	1229.29	864.44	735.80
%10 BTCA	890.94	881.53	646.51
%20 BTCA	640.94	573.98	580.00
CA			
110 °C			
%5 CA	2800.00	2747.76	1276.92
%10 CA	2276.19	1349.08	1304.61
%20 CA	2226.67	1180.0	1127.78
130 °C			
%5 CA	2311.78	2863.64	1430.00
%10 CA	1638.02	1580.28	1084.83
%20 CA	1301.01	1248.05	1008.33
150 °C			
%5 CA	1929.94	1635.85	1396.22
%10 CA	1067.02	1251.75	882.76
%20 CA	886.67	819.31	816.67
PVA			
110 °C	1460.32	1303.70	1205.88
130 °C	1201.90	1030.91	873.83
150 °C	770.18	739.02	690.42

On the other hand, the weight loss percent decreased to a great extent by BTCA crosslinking (~13% and ~80% for BTCA and CA, respectively at 110 °C and 20 min.). Increasing the fixation temperature and time, together with the PVA crystallization because of the high temperature, the weight loss of the PVA mats decreased which led to better water stability. Non-crosslinked mats barely preserved most of their weight above the fixation temperatures of 130 °C but 20% of BTCA crosslinked mats preserved almost 90% of their weight even at 110 °C fixation temperature. At higher fixation temperature, especially at 150 °C there is no need to extend the fixation time, 20 minutes is acceptable for satisfactory results.

Table 3. Weight Loss % of electrospun non-crosslinked, BTCA and CA crosslinked PVA mats

	20'	40'	60'
BTCA			
110 °C			
%5 BTCA	77,71	69,40	58,49
%10 BTCA	70,98	59,49	40,16
%20 BTCA	13,22	12,42	10,49
130 °C			
%5 BTCA	59,66	56,44	3,66
%10 BTCA	33,64	22,24	2,01
%20 BTCA	8,35	4,24	0,44
150 °C			
%5 BTCA	7,38	3,66	0
%10 BTCA	0,56	2,01	0
%20 BTCA	0,26	0,44	0
CA			
110 °C			
%5 CA	85,56	70,17	56,21
%10 CA	83,14	55,64	43,61
%20 CA	79,79	47,54	40,50
130 °C			
%5 CA	72,17	64,23	43,18
%10 CA	48,27	45,95	16,08
%20 CA	35,67	28,72	5,26
150 °C			
%5 CA	41,13	38,55	13,15
%10 CA	13,55	22,46	3,33
%20 CA	11,02	8,81	0
PVA			
110 °C	71,93	69,49	61,36
130 °C	62,25	63,33	52,89
150 °C	14,93	13,43	11,17

Figure 3 shows the scanning electron micrographs of the samples after immersion into distilled water for 24 h and a further drying. When non-crosslinked PVA nanofiber mats were immersed in distilled water, they shrunk immediately and became almost transparent. On the other hand, BTCA crosslinked mats became bulky and stay opaque whereas CA crosslinked samples became bulky but gel like transparent appearance. The nanofibrous structure of non-crosslinked PVA nanofibers was totally destroyed due to high solubility (Figure 3). The nanofibrous structure of the BTCA crosslinked membranes was observed to be preserved however CA crosslinked membranes almost lost their fibrous structure with a swollen and conjoint appearance. This is probably due to the highest swelling capacity of the CA crosslinked nanofibers. The results point out that the stabilization of the structure against water in terms of weight loss was successfully achieved by the use of BTCA as crosslinker, and it is categorically clear that the use of BTCA is more appropriate when the preservation of nanofibrous structure is an issue.

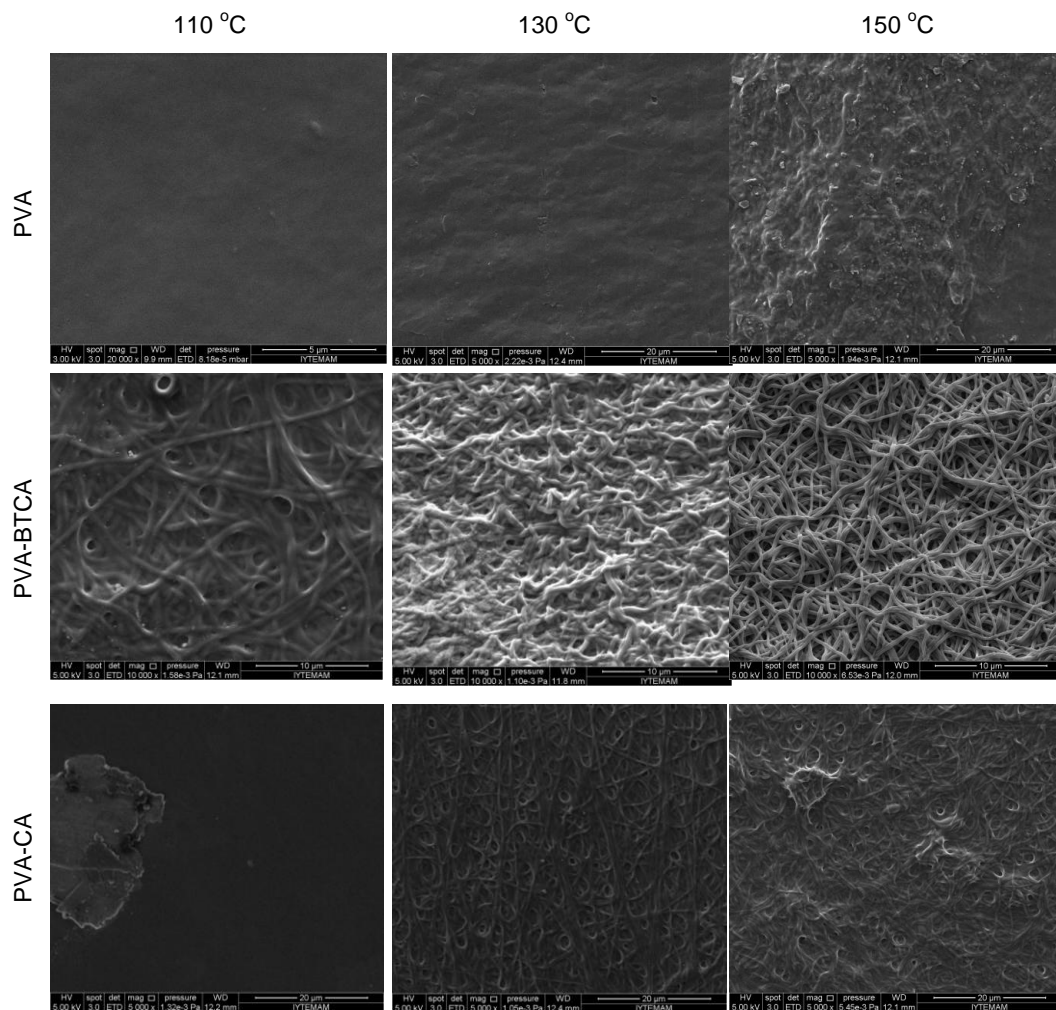


Figure 3. SEM images of 110, 130 and 150 °C, 20 minutes fixated non-crosslinked PVA, BTCA and CA crosslinked PVA mats after immersion of distilled water for 24 h

4. CONCLUSIONS

Electrospun non-crosslinked, BTCA and CA crosslinked smooth, uniform and bead free PVA nanofibers was produced. The effect of BTCA and CA crosslinking were investigated in terms of resultant fiber diameters, swelling and weight loss of the structure. It was seen that, stabilization of the PVA mats against dissolution in water could be significantly enhanced by crosslinking with polycarboxylic acids even at fixation of 110 °C. Swelling ratio of CA crosslinked PVA mats were found to be higher than BTCA crosslinked mats. Swelling ratio of the PVA mats decreased by the increase in the crosslinker concentration, fixation temperature and time for both BTCA and CA crosslinked mats. Weight loss of the BTCA crosslinked mats were lower than CA crosslinked samples and it was decreased by the increase of the concentration, fixation temperature and time. It was observed that the fully preservation of the nanofibrous structure after water treatment was obtained by BTCA crosslinking, while deterioration in nanofibrous structure was detected for CA crosslinked samples.

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