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Plasticization and conglutination improve the tensile strength of electrospun starch fiber mats

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Abstract

Electrospun starch fiber mats have many potential applications, but an improvement in their mechanical properties is required to realize them. In the present study, wet-electrospun starch fiber mats were subjected to post-drying conditioning at controlled equilibrium relative humidity and equilibration time. The weight-normalized ultimate tensile strength of starch fiber mats increased significantly with equilibration at relative humidity >0.75 after 28 days. Morphological observation and X-ray diffraction analysis excluded significant changes in fiber size or crystallinity, and thus we concluded that conglutination brought about by the plasticizing effect of water and observed microscopically was primarily responsible for this mechanical improvement.

Keywords: starch fiber mat, water activity, relative humidity, tensile strength, conglutination

1. Introduction

Starch is among the most abundant and inexpensive biopolymers, making it a promising substitute for synthetic petroleum-based polymers. We recently developed a method to fabricate starch fiber mats by an electro-wet-spinning technique that produces fibers with diameters ranging from hundreds of nanometers to tens of microns (Kong & Ziegler, 2014). These starch fiber mats combine the inherent advantages of starch as a biopolymer, including its biodegradability, biocompatibility, and non-toxicity, and the geometrical and functional properties of micro- and nano-fibers, i.e., high surface area, high porosity, small pore size, and anisotropic mechanical properties. However, to practically utilize starch fiber mats, their mechanical properties need further improvement, a challenge that has been confronted by many researchers developing biopolymer-based products. The lack of a plasticizer is at least partially responsible for the brittleness and inferior tensile strength of dried starch fiber mats.

The mechanical properties of starch-based materials can be altered by plasticizers such as water. As a plasticizer, the presence of water molecules increases polymer mobility and depresses the glass transition temperature. The influence of plasticizing water on the properties of starch has been studied in various starch-based materials, e.g., its effect on the mechanical properties of starch gels and films (Mali, Grossmann, García, Martino, & Zaritzky, 2006; Saberi et al., 2015). However, the plasticizing and conglutinating effect of water on the tensile properties of starch fiber mats have not been reported. Conglutination is the term used to describe the attachment of intersected fiber segments (Reneker & Yarin, 2008). The conglutinated segments potentially contribute to the improvement in mechanical properties of electrospun fiber mats.

In this study, we hypothesized that conglutination caused by exposure to water vapor will increase the tensile strength of electrospun starch fiber mats. To test this hypothesis, dried starch fiber mats were equilibrated at preselected levels of relative humidity (RH) for up to 28 days, and their morphological, microstructural, and tensile properties were analyzed.

2. Material and methods

2.1. Material

Gelose 80 high amylose maize starch (HAMS) was supplied by Ingredion (Bridgewater, NJ). Drierite desiccant ($CaSO_4$), dimethyl sulfide (DMSO) and 200-proof ethanol were purchased from VWR International (Radnor, PA).

2.2. Sample preparation and electrospinning

HAMS (12%, w/v) dispersion in pure DMSO was prepared by heating with stirring in a boiling water bath for 1 h. The electrospinning apparatus comprised a high voltage power supply (ES40P, Gamma High Voltage Research, Inc., Ormond Beach, FL), a syringe pump (81620, Hamilton Company, Reno, NV), a 3 mL plastic syringe (Becton, Dickinson and Company, Franklin Lakes, NJ) with a 20-gauge blunt needle, and a grounded stainless steel mesh immersed in ethanol (Kong & Ziegler, 2014). Operational parameters used were as follows: positive voltage at 11 kV, needle to ground wire mesh in the coagulation bath distance of 7 cm, and flow rate at 10.5 mL/h. The fibrous mats recovered from the coagulation bath were washed with pure ethanol and dried in a desiccator containing Drierite under vacuum.

2.3. Equilibration under specific RH

Dried starch fiber mats were equilibrated in desiccators containing different supersaturated salt solutions. The desiccators were placed in a temperature-controlled incubator. Table 1 lists selected supersaturated salt solutions and corresponding RH in the desiccators at 25 °C. Starch

fiber mats were equilibrated for up to 28 days, and samples were removed from the desiccators without additional drying at day 3, 7, 14, 21, and 28, respectively, for further analyses. Dried as-spun starch fiber mats without any equilibration treatment served as the control.

Table 1. RH of supersaturated salt solutions at 25 ± 1 °C.

Supersaturated Salt Solution	RH
Drierite desiccant ($CaSO_4$)	10%
$CaCl_2$	34%
NaCl	75%
KCl	84%

2.4. Tensile test

Fiber mat samples (5.3 mm wide and approximately 25 mm long) were cut using a film cutter (PN 984485.901, TA Instrument, New Castle, DE). The weight of each fiber mat was recorded using a Mettler-Toledo XP2U ultra-microbalance (Mettler-Toledo International Inc., Columbus, OH). Uniaxial tension tests were carried out using a Q800 dynamic mechanical analyzer (DMA, TA Instrument, New Castle, DE), with a film tension clamp set at room temperature (20 °C). The control force mode was applied at a force rate of 0.05 N/min. Data were recorded until the sample yielded. The stress at yield was normalized using the following equation (Eq. 1) to account for variation in thickness and fiber density, and weight normalized ultimate tensile strength (WNUTS) was obtained after each measurement. At least 3 replicates of each sample were tested.

$$\text{Weight Normalized Ultimate Tensile Strength (WNUTS)} = \frac{Force\ at\ yield\ point}{Weight} \quad \text{(Eq. 1)}$$

2.5. Scanning electron microscopy (SEM)

Microscopic observation of the fibers was performed using a Phenom G2 Pro scanning electron microscope (SEM, Phenom-World, Eindhoven, The Netherlands) at an accelerating

voltage of 5 keV. Open software, ImageJ were used to analysis the SEM images (Hotaling, Bharti, Kriel, & Simon, 2015).

2.6. Wide angle X-ray diffraction (XRD)

XRD patterns of the starch fiber mats were obtained using a Rigaku MiniFlex II desktop X-ray diffractometer (Rigaku Americas Corporation, The Woodlands, TX). Samples were exposed to Cu Kα radiation (0.154 nm) and continuously scanned between 2θ = 4 and 35° at a scanning rate of 2°/min with a step size of 0.02°. A current of 15 mA and voltage of 30 kV were used.

2.7. Statistical analysis

A randomized 4 × 4 full factorial design was applied in analyzing the effect of equilibrium condition and time on tensile strength. WNUTS was the response variable. Two-way ANOVA was used to analyze the main effects and interactions (Minitab 18.1, Minitab, Inc., PA). The missing data were treated as likewise deletion by software default. One-way ANOVA and Tukey's test were used to compare the effect of re-drying after equilibration.

3. Results and discussion

The weight-normalized ultimate tensile strength (WNUTS) of dried starch fiber mats without the equilibration treatment, i.e., the control, was measured to be 30±3.4 N/g. Upon equilibration treatments, both the equilibrium RH ($P<0.0001$) and the equilibration time ($P=0.0165$) exerted significant influence on the WNUTS of starch fiber mats. However, we found that WNUTS values fluctuated without a clear trend with equilibration time within the first 14 days of treatment. It was probable that the contact and adsorption of water vapor on the fiber mats were not uniform at this initial stage. Therefore, only the main effect of RH on the WNUTS of starch fiber mats is displayed in Figure 1. Equilibration at low RH (10% and 30%) made the fiber mats more brittle, and the tensile strength of samples stored at RH=10% after 21 days could

not be obtained due to their fragility. So, the WNUTS of the fiber sample stored at RH=10% at day 28 was treated as missing data in further analysis. Large variations in WNUTS were observed for samples recovered from low RH environments. Similarly, due to the lack of true equilibrium, water absorption isotherm models failed to predict the water absorption accurately at low water activity (Li, Tang, & Chinachoti, 1996). After conditioning at higher RH, the WNUTS of starch fiber mats was either maintained (RH=75%) or steadily increased (RH=84%) over time.

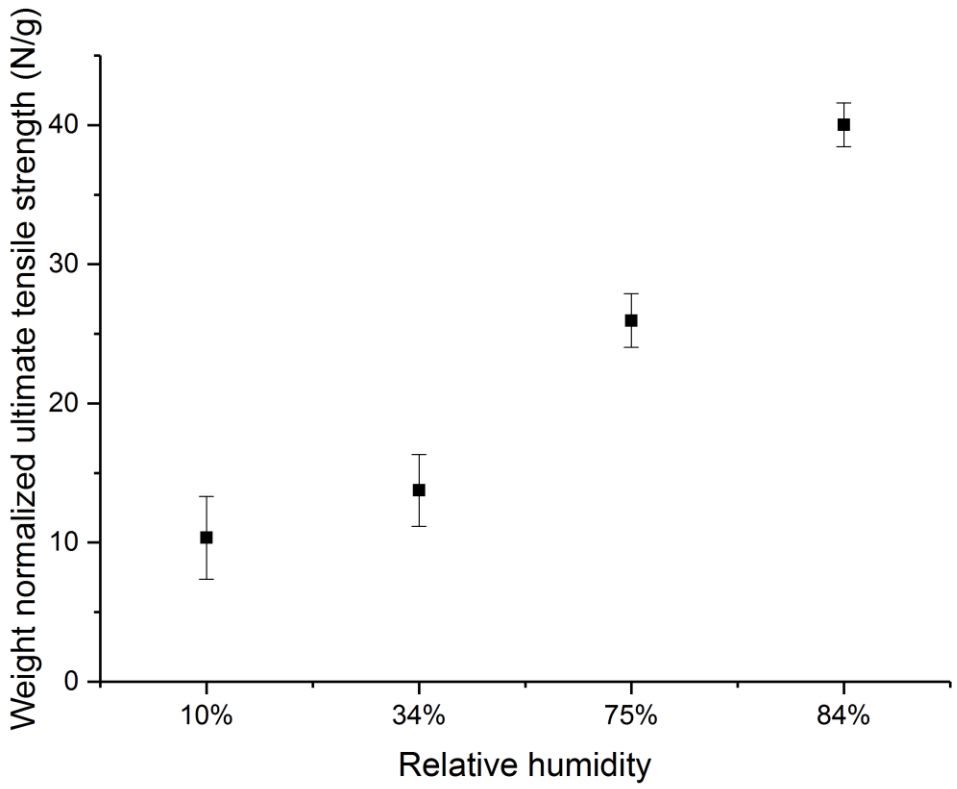

Figure 1. Main effect of RH on weight normalized ultimate tensile strength of starch fiber mats.

Figure 2 clearly shows the conglutination of starch fiber mats caused by the plasticizing water at high RH. The merging of superimposed or intersected fibers resulted in a web-like 3-D structure in starch fiber mats. Contact points among starch fibers would be an ideal spot for condensation to take place due to the effect of capillary condensation (Fisher, Gamble, &

Middlehurst, 1981), and the locally elevated water content at fiber intersections accelerated their conglutination. The conglutination effect at RH=84% was most noticeable. After conditioning for about 3 days, the WNUTS was significantly higher than control. Further conditioning time at RH=84% did not significantly contribute to conglutination of the fibers and thus no significant changes in WNUTS were observed thereafter. By conditioning at RH=75%, the WNUTS was comparable to that of the control. Compared with the equilibration time required for raw starch granules (2 to 3 weeks) to reach a constant weight under specified RH (Al-Muhtaseb, McMinn, & Magee, 2004), the relatively faster equilibration time for these starch fiber mats was likely due to their smaller size and higher surface area than native starch granules.

In order to confirm the contribution of both plasticization and conglutination on tensile property improvement, WNUTS of dried starch fiber mats without conditioning (the control), with conditioning at RH=84% for 3 days, and re-dried after conditioning at RH=84% for 3 days (Figure 2) were measured. One-way ANOVA shows significant difference in WNUTS among these samples (P=0.029). Though the WNUTS decreased on re-drying, the merged conglutination zones were still present. The WNUTS of the re-dried sample fell between that of the control sample and the sample prior to re-drying (Table 2), which suggested that both plasticization and conglutination strengthened the starch fiber mats.

Our results are in agreement with the mechanism of water sorption observed for starch-based materials. At water activity (a_w) below 0.2, starch gel is only surrounded with a monolayer of strongly “bound” water molecules. As a_w increases, multiple layers of “intermediate” water can be adsorbed via hydrogen bonds, until the a_w reaches 0.85, after which water molecules adsorbed are considered as “free” water (Li et al., 1996). As moisture content increases, water acts as a plasticizer in the matrix. Studies on starch granules also found that the amorphous

regions of starch started to plasticize when a_w fell between 0.3 and 0.85 (Al-Muhtaseb et al., 2004; Van den Berg, C., & Bruin, 1981). Therefore, starch fiber mats conditioned at higher RH likely attained the mobility necessary for conglutination to occur resulting in higher WNUTS.

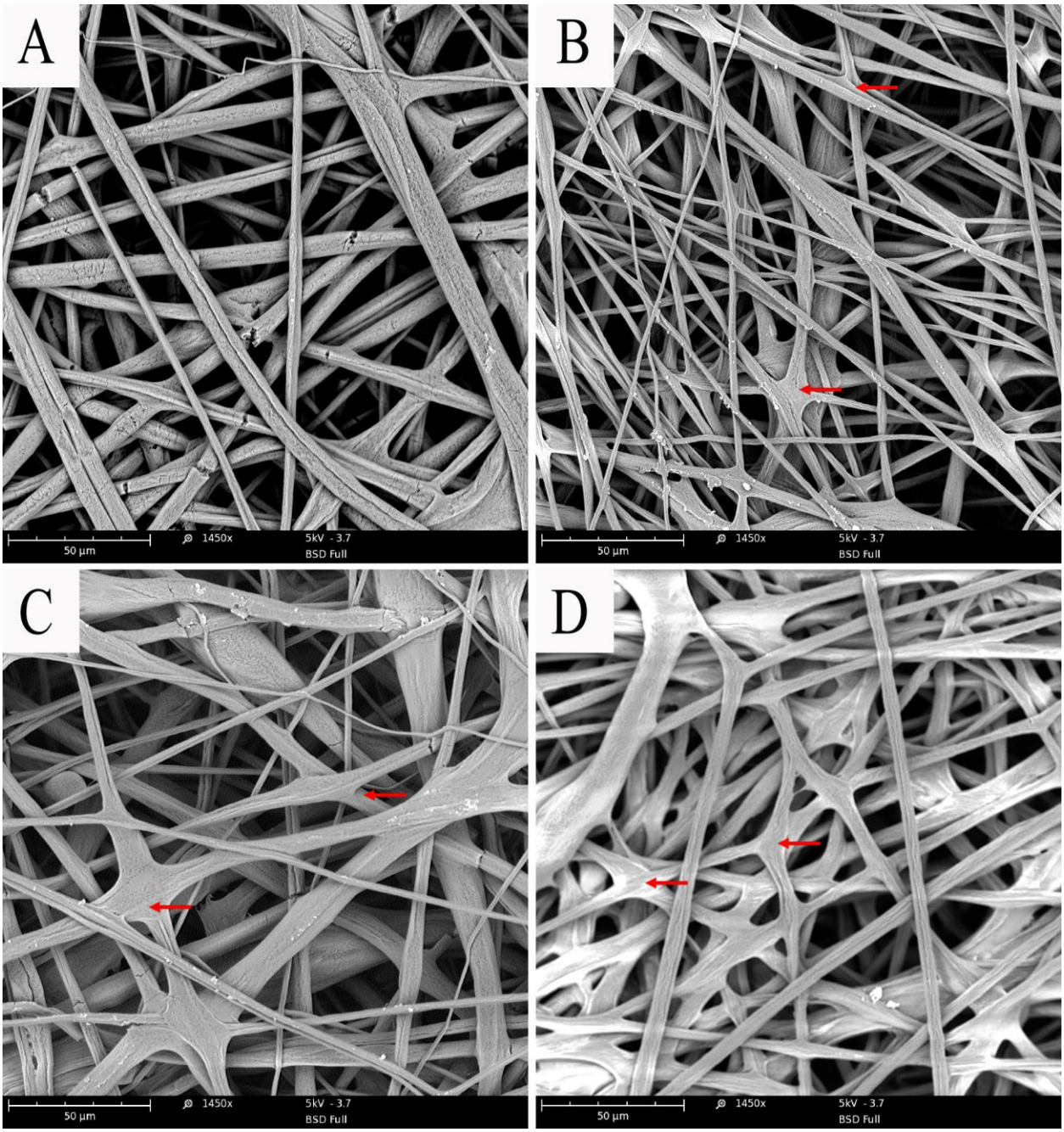

Figure 2. Scanning electron micrographs of starch fiber mats without conditioning (A), with conditioning at RH=84% for 3 days (B), re-dried after conditioning at RH=84% for 3 days (C),

and with conditioning at RH=84% for 28 days (D). Red arrows indicate observable conglutination zones.

Table 2. Fiber diameter distribution and analysis of WNUTS of starch fiber mats affected by different treatments based on the Tukey's test and 95% confidence.

Treatment of fiber mats	Mean*	Diameter mean and SD
Conditioning at RH=84% for 3 days	62.66 A	1.83 ± 0.91
Re-drying after conditioning at RH=84% for 3 days	39.18 AB	1.26 ± 0.81
Without conditioning (the control)	21.09 B	1.83 ± 0.91

*Means that do not share the same letter are significantly different.

Unlike the starch granules in sorption isotherm studies (Buléon, Bizot, Delage, & Multno, 1982), starch fiber mats remained amorphous on equilibration at high levels of RH (XRD data not shown). Therefore, the increase in tensile strength was not due to an increase in crystallinity. The intra- and inter-hydrogen bonding in starch fiber mats at high RH, resulting in conglutination, is more likely to have strengthened the starch fiber mats.

4. Conclusions

Dried electrospun starch fiber mats were subject to equilibration at various RH over 4 weeks. Both equilibration time and relative humidity significantly affected the WNUTS of the starch fiber mats. Conglutination at high levels of RH was evidenced on scanning electron micrographs and coincided with a significant increase in WNUTS of the starch fiber mats. Since the diameter and crystallinity of starch fiber mats were not altered significantly, we concluded that plasticization and conglutination were the likely cause for improvement in WNUTS. Our results also suggest the potential of using other plasticizers to enhance the mechanical properties of starch fiber mats.

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