Development and Characterization of Glandless Cottonseed Meal/Pullulan Fine Fiber Mats

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Abstract

Glandless cotton seed meal (GCSM) extracted from cotton is composed of nearly 50 percent protein. For about every 100kg of cotton fiber produced the cotton plant yields approximately 160kg of cottonseed. GCSM presents a unique opportunity to be used in the food industry. In this study, GCSM based polymer composite edible fine fibers were successfully produced using pullulan as the polymeric base. GCSM solutions were developed and spun as fine fibers using a centrifugal spinning technology. A synergistic approach among fiber output and fiber diameter was pursued by modifying angular velocity and concentration of pullulan and GCSM within an aqueous solution. The developed fibers show average fiber diameters of 720nm with a standard deviation of 200nm. Thermo-physical analysis was conducted. The opportunity to develop GCSM fine fiber mats opens up potential applications in food packaging and drug delivery systems to mention some.

Keywords: Nanofibers; Pullulan; Glandless Cotton Seed Meal; Forcespinning®

Introduction

In the past few years, fine fibers (nano and submicron) have attracted significant scientific interest mostly because of their high surface area to volume ratio and porous structure within and among the developed nanofibers. These properties have given rise to numerous promising applications such as filtration, smart textiles, sensors, solar cells, fuel cells, batteries, etc. In the biomedical area, nano fiber mats have received increasing attention due to potential to solve a variety of existing challenges in burn and wound care, tissue regeneration and treatment for a variety of diseases given its ability to enhance adhesion of drugs, proteins, and cells [1]. The focus of published nano fiber studies pertains to the development and production of nanofibers and investigation of their chemical, electrical, thermo-physical, rheological, and mechanical properties, correlated to the applications mentioned above. Few studies have related the use of nanofibers in food science and engineering fields. There are a variety of applications to explore ranging from food preservation and packaging to more complex ones such as nutrient delivery systems. Recently, the Forcespinning® technology has garnered significant attention for nano, submicron, and single digit microfiber development. The reason behind this tendency is due to its unprecedented yield when compared to other methods such as electro spinning and wet chemistry methods. Forcespinning® is a novel fine fiber production method where the electrical forces used in electro spinning are replaced by centrifugal forces. The Forcespinning® technique provides ample flexibility in materials selection since electric fields are not needed; therefore no need to select solvents with appropriate dielectric parameters. Water based systems can be effectively utilized as well as melt spinning, further lowering production costs by removing the need to budget solvent recovery steps. In Forcespinning®, centrifugal force is used to extrude the solution/melt through small orifices with a controlled length to diameter ratio [2]. As the extruded fibers exit the rotating spinneret, air drag forces elongation of the fibers and reduces their diameter to the nanometer scale. At the same time that fibers are being stretched the solvent evaporates (or melt cools down) leaving solidified fibers. The fibers can then be collected by different methods allowing the creation of non-woven mats, aligned fiber mats, or yarns. The system has spinnerets specifically
Materials and Methods

Materials

Pullulan (PULL) powder was purchased from Tokyo Chemical Industry Co., LTD. Glandless cottonseed meal (GCSM) was provided by Cotton Inc. (Texas, USA) containing 48.5 percent of crude protein and 11.8 percent of lipids. It was stored at 4°C until used. Protein was extracted utilizing a 0.1 M KOH solution at a 1:12 ratio (w/v; pH 12) via a thermal process at 65°C for 40 minutes. The liquid was centrifuged at 3500 rpm for 20min (RCF 4793g) at 4°C. Recovered supernatant was acidified to pH 4.5 with 0.5M HCl and distilled water was used to precipitate the protein. It was then centrifuged at 3500rpm for 20min at 4°C to recover protein solids. Protein solids were re-suspended in distilled water for storage and transportation in between laboratories [19]. Figure 1 shows the several steps used to prepare the fibers. The process started with developing pullulan solutions. Pullulan in its powder form was mixed with distilled water; 2.13g of PULL were used to prepare a 21 wt percentage PULL solution. The samples were prepared at room temperature and magnetically stirred for 2 hours. GCSM protein powder was obtained through vacuum filtration and added to the PULL solutions, two samples were prepared containing 5 and 8 wt. percentage of GCSM. The PULL solutions with the added GCSM were magnetically stirred in an oil bath for 2 hours at room temperature.

Experimental

PULL and PULL/GCSM nanofibers were produced by the Force spinning® technique, using a Cyclone L-1000M (manufactured by Fiberio Technology, Corp. USA). The spinneret equipped with 30G half-inch needles (Becton Dickinson and Company) at each end was filled with 1 mL of the developed solutions. The solutions were spun at different RPM (4500-8500) at room temperature under 52±3 R.H. The system was allowed to spin for three minutes. Nonwoven fiber mats were collected in between pillars (eight pillar collector system shown in Figure 1). Samples were placed in plastic bags for future characterization and desiccant was added to prevent moisture absorption. Morphological characterization of the PULL/GCSM nanofibers was conducted utilizing a Scanning Electron Microscope (SEM Carl Zeiss, model Sigma VP, Germany). The average fiber diameter was calculated using the Image J version 1.48 software, 100 fibers were measured per sample taken from at least 20 micrographs and conducting 3 measurements per fiber. 300 values were used. Thermal behavior of PULL and PULL/ GCSM fibers was studied using a Differential Scanning Calorimeter (DSC, model Q-100 TA Instruments, USA) under air and nitrogen flow conditions, the samples (5mg) were ramped from room temperature to 280°C, isothermal for 10 minutes, and then ramped down to 30°C. This cycle was repeated to account for thermal history effects. The scanning rate was 5°C/min. Thermogravimetric Analysis (TGA, model Q-500 TA Instruments, USA) was conducted using platinum crucibles. Samples of approximately 10 mg were tested under nitrogen purge, with a flow rate of 40ml/min. The samples were ramped from room temperature to 800°C at a heating rate of 10°C/min.

Results and Discussion

Fiber development was conducted at angular velocities starting from 4500 RPM up to 10000 RPM. It was observed that successful fiber production started at velocities higher than 5000 RPM, specifically at 5500 RPM and up to 8000 RPM. These range was considered the optimum for the pure pullulan, 5 and 8 weight percent GCSM solutions, respectively. Fibers were produced for all systems within the angular velocity range of 4500 to 8500 RPM though to determine optimum angular velocity, a synergy between fiber output and fiber diameter was considered. For example, fibers with diameters of less than 100 nm were observed though the fiber output was not significant. It was observed that the optimal RPM was around 5000-6000 RPM, the yield fiber output was the highest. Surpassing the previously stated speeds, the fiber output would significantly drop. At lower (< 5000) the fiber output was severely impacted; the fiber production was low, with beady morphology. Figure 2 shows scanning electron micrographs of the developed fiber mats with its corresponding fiber diameter statistical analysis. Figure 2a shows results for pure pullulan fibers, 2b for fibers prepared with 5 weight percent of GCSM, and 2c for fibers with 8 weight percent of GCSM. As observed, homogeneous, long, and continuous fine fibers were developed. Bead formation was not observed. The addition of the GCSM resulted in a small increase in fiber diameter being statistically insignificant for the different concentrations. The average fiber diameters were 720 nm respectively with a standard deviation of 200 nm. The developed nonwoven fiber mats are as shown in Figure 1, homogeneous, flexible and easy to handle.
DSC analysis was performed in order to assess the effect of
to enthalpy relaxation or enthalpy recovery. This endothermic peak
molecular elongation on the microstructure of the polymer. As can be
(in the fiber sample) allows to quantitatively analyze relaxation
seen in Figure 3, the DSC thermographs of the pullulan in bulk state
kinetics of amorphous systems, often conducted with moisture
and fiber state differ significantly. Pullulan powder is an amorphous
absorption tests [20]. In this case, the decrease in Tg and presence
polymer. As depicted in Figure 3, there was no melting transition,
of these broad transition peaks suggests certain degree of molecular
but subtle endothermic (Figure 3a) and exothermic (Figure
alignment and the tendency of the largely flexible chain to attain
3b) transitions were observed attributed to the glass transition
equilibrium. The fiber samples mimic a plasticized system. The
temperature (Tg). Upon spinning the polymer into fiber form, a
observed plasticizing effect implies an increase in free volume and
clear change in the location and magnitude of the glass transition
segmental movements, where consequently, water molecules can
temperature is observed. First of all, the location of the Tg is shifted
easily diffuse. These results could provide attractive opportunities
to lower temperature implying a plasticizing effect upon fiber
fibers to the use of pullulan fiber systems and GCSM/pullulan composites
formation, alignment of polymer molecules. Also, for the nonwoven
in edible systems and drug delivery applications. It is to be noted
fiber mats, the Tg depicted as a step in the bulk pullulan sample is
that the exothermic transitions presented in Figure 3b occur all at
now seen as an endothermic Tg peak. There is no evidence of cold
the same temperature, the thermal history of the polymer due to
crystallization (considering the great chain flexibility of pullulan)
fiber processing has been erased and now the bulk systems present
though, fiber formation certainly affected chain mobility and was
a transition similar to the one obtained for the raw pullulan.
manifested in the development of the observed Tg peak attributed

Figure 3: Dynamic scanning calorimetry thermo grams for the pullulan in bulk state (powder), and fiber form for pullulan and
its GCSM composites. Figures 3a and 3b, show first heating and first cooling, respectively, of the analyzed fibers.

Figure 4: Weight loss as a function of temperature for the GCSM, pullulan in powder and fiber form and the two (5 and 8 wt
percentage) composite fiber mats.
Thermo gravimetric analysis of the developed systems is shown in Figure 4. In this graph, it is clear that fiber samples absorb more humidity compared to the pullulan in powder form as can be seen in the weight loss occurring at around 100°C. The hydrophilicity of the polymer coupled with increased surface area due to fiber formation promotes a higher absorption of humidity, about 10 weight percent for all fiber samples. The fiber samples containing GCSM show a small reduction in thermal stability when compared to the pure pullulan fibers, this driven by the initial weight loss of the GCSM protein occurring at 211°C and attributed to rapid decomposition of small molecules (glycerol and protein domains) [20,21]. The main degradation occurs at 342°C and 347°C for the pullulan powder and pullulan fibers, respectively; and at 343°C for 5 weight percent and 340°C for 8 weight percent GCSM composite fibers.

Conclusion

Developing of nano and submicron fibers containing GCSM protein opens an opportunity to better utilize this abundant source of protein. Fine fibers containing pullulan as the polymer precursor reinforced with GCSM protein were developed. The developed pullulan and pullulan/GCSM solutions showed ease of fiber processing at angular velocities in between 5500 and 8000 RPM. The collected fibers were homogenous, long and continuous, with average diameters in the range of 650nm. Fine fiber diameters such as less than 100nm were also obtained though not is sufficiently high yield as to promote practical applications. The PLL/GCSM composite fibers showed a decrease in Tg when compared to the pullulan in its powder form. This decrease is attributed to induced alignment of the pullulan molecules. Further studies will focus on the viability of using these fibers as products with high nutritional protein content for human consumption and other potential applications such as in drug delivery and novel snacks to mention some.

References