



Manipulating characteristic timescales and fiber morphology in simultaneous centrifugal spinning and photopolymerization



Yichen Fang^a, Austin D. Dulaney^a, Jesse Gadley^b, Joao M. Maia^b, Christopher J. Ellison^{a,*}

^a McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

^b Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, USA

ARTICLE INFO

Article history:

Received 5 May 2015

Received in revised form

16 June 2015

Accepted 11 July 2015

Available online 17 July 2015

Keywords:

Photopolymerization

Fibers

Polymer processing

ABSTRACT

In this study, the fabrication of crosslinked nonwoven fibers via simultaneous thiol-ene photopolymerization and spinning of monomer jets has been demonstrated in centrifugal Forcespinning for the first time. We observed that simultaneous Forcespinning and photopolymerization resulted in a wide variety of fiber morphologies including beads, beads-on-string, uniform fiber, fused fibers, and well-cured fibers. To elucidate the underlying mechanisms and parameter interactions that give rise to these morphologies, we systematically varied the light intensity, solution elasticity, and spin speed of the Forcespinning process. From these experimental results, an operating diagram was constructed based on the measured process parameters, their respective timescales, and observed effects on fiber morphology. While numerous parameters can individually affect fiber formation and morphology, the interplay between curing kinetics, solution viscoelasticity, and orifice-to-collector processing time window is also crucial in this process. Smooth and well-cured fibers were formed only when the photopolymerization occurred sufficiently quickly, before both the breakup of fibers into droplets due to a surface tension driven Rayleigh instability and the deposition of fibers on the collector. Our findings can serve as a predictive guideline for the fabrication of crosslinked fibers with desired morphology, the implementation of the in-situ polymerization and spinning concept into other commercial fiber manufacturing technologies, and the adaptation of other functional or high performance monomer systems.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nonwovens are composed of randomly oriented fibers held together by physical entanglements, or bonded by chemical, mechanical or thermal. They possess many unique properties such as high surface area to volume ratio and high surface functionality, usually processed into the form of a lightweight, porous mat. Recent advances in fiber production technologies have led to increasing opportunities to utilize nonwoven fibers for diverse applications such as filtration [1,2], superhydrophobic materials [3–5], catalysis [6], and tissue engineering [7–9], among others.

Currently, most nonwoven fibers with submicron or single micron average diameters are produced by melt blowing, electrospinning, or adaptations of the two, such as solution blow spinning [10] or melt state electrospinning [11,12]. In melt blowing, molten polymer is extruded through a die and drawn into thin continuous

fibers by high velocity hot air jets. The liquid fiber jet solidifies when the processing temperature drops below the glass transition or crystallization temperature of the polymer. Alternatively, for electrospinning, a polymeric solution is delivered through a nozzle by a syringe pump and elongated into a jet under the application of a strong electric field. The fiber jet elongates and solidifies into fine fibers as the solvent rapidly evaporates. In recent years, another fiber production technology, termed centrifugal spinning or Forcespinning, has attracted a significant amount of interest [13]. In this process, a polymer melt or solution is delivered through the orifices of a fast rotating spinneret. When the centrifugal force and the hydrostatic pressure overcome the surface tension of the drop formed at the orifice outlet, the droplet is stretched into a fluid jet and attenuated, often into submicron fibers. Forcespinning has been shown to be a versatile and high throughput method with the ability to process a variety of polymeric and inorganic materials in the melt or solution state [14–17].

All of the current fiber production technologies fundamentally involve transforming a pre-formed polymer into a liquid by either the application of heat or the addition of solvent, and

* Corresponding author.

E-mail address: ellison@che.utexas.edu (C.J. Ellison).

subsequently applying an extensional drawing force to draw the liquid into fibers, which later solidify by sufficient cooling or solvent evaporation. Processing with solvents or heat has both advantages and drawbacks. Melt state processing, although simple and convenient, requires significant thermal energy input [18] and has its upper processing limit constrained by the degradation temperature of the material. On the other hand, solution state processing is quite versatile and can be performed at room temperature but suffers from issues such as solvent recovery/recycling, safety of volatile/flammable solvents, and low process throughput, all of which present challenges for scale-up and commercial viability.

Recently, our group demonstrated a new method for fabricating nonwoven fibers directly from non-volatile liquid monomer mixtures instead of from polymer solutions or polymer melts [19], thereby foregoing the use of solvent and heat altogether. In this method, a mixture containing monomers and a photoinitiator was simultaneously electrospun and photopolymerized via UV initiated thiol-ene chemistry to produce solid fibers in ambient conditions. The method was also made even greener by replacing more than 50 wt% of petroleum based monomer with a bio-renewable soybean oil derived monomer without sacrificing the final fiber quality [20]. Despite the very limited curing time during the fiber spinning process, the fibers made by this method contained a highly cross-linked network, which imparted high thermal stability, chemical resistance, and mechanical strength to the resulting fibers [19]. Owing to the versatility of thiol-ene chemistry, fibers with drastically different mechanical, thermal, and network structural properties were fabricated by incorporating monomers with different chemical structures [21].

Other researchers have also reported related strategies for in-situ photocrosslinking during fiber formation. Notably, Boyd and coworkers successfully fabricated thiol-ene and thiol-yne fibers using hydrodynamic shaping in microfluidic channels [22]. In other studies, an extra step of thermal polymerization to convert some amount of the monomers into prepolymers prior to electrospinning or the incorporation of a high molecular weight (MW) polymer in significant amounts was necessary to produce crosslinked fibers due to the slow reaction kinetics [23–25]. However, most studies only report the chemical formulations and processing conditions that generated fibers, but do not address the many other factors that impact fiber formation and fiber morphology. In addition, the reported conditions usually do not reflect the entire operating space or the extent of tunability of the methods.

In contrast, controlling fiber formation and morphology has long been the subject of research for the more commonly studied fiber spinning techniques, since fiber diameter, quality and morphology ultimately determine the properties [1,3,4], and in turn, the end use of the fibers. For example, the effect of solvent properties, including solvent quality, conductivity, volatility, and surface tension, on generating fused, beaded, and uniform electrospun fibers has been investigated in great detail [26–28]. Other studies have examined the lower polymer concentration limit for fiber formation in electrospinning. They correlated the formation of beads, beaded fibers, bead-free and uniform fibers with the degree of chain entanglements in the polymer solution [29–33], solution elasticity [34], molecular weight distribution [34,35], and polymer architecture (branched polymer versus linear polymer) [31].

Although the simultaneous photopolymerization and fiber spinning process described herein may appear similar to electrospinning in that they are both solution-based processes, there are several key differences. First, the solutions for simultaneous photopolymerization and fiber spinning consist mainly of monomers

that are essentially non-volatile, unlike the polymeric solutions used in electrospinning, which often contain large amounts of volatile solvent. Naturally, these two different solutions are expected to have different viscoelastic properties, which will greatly influence the extensional behavior of the fiber jets during fiber spinning and in turn the morphological appearance of fibers. Second, the fiber jets herein solidify due to rapid photopolymerization triggered by UV light, instead of rapid solvent evaporation as for traditional electrospinning. The incorporation of in-situ photopolymerization is a unique feature to fiber spinning, and therefore the role and importance of reaction kinetics on fiber formation and morphology has become a new area for fundamental study. To date, a systematic and fundamental examination of the important parameters and underlying physics that govern fiber formation and fiber morphology in simultaneous photopolymerization and fiber spinning is still lacking and this motivates the present study.

Here, we demonstrate for the first time the integration of thiol-ene photopolymerization with a bench-top centrifugal Forcespinning apparatus equipped with a custom UV light source. The successful implementation demonstrates not only the universality (previous studies employed an electrospinning apparatus without using solvent) but also the scale-up potential of this concept, as Forcespinning's intrinsically larger fiber drawing force and higher throughput constitute significant advantages over electrospinning. In this process, the principle parameters that govern fiber formation and morphology include: reaction parameters – stoichiometric ratio of thiol to ene, monomer functionality and reactivity, light intensity, and photoinitiator content; viscoelastic parameters – viscosity and elasticity; and process parameters – spin speed, orifice diameter, and the location and width of the UV illuminated region. These three categories of parameters form a convoluted and in some cases interactive set of variables, making it challenging to study the effect of each variable in isolation. For example, a penta-functional acrylate monomer is different from a tetra-functional acrylate in terms of both monomer functionality and viscosity.

To overcome this complication, we characterized the timescales related to these categories: namely those of the reaction kinetics, viscoelastic response, and the orifice-to-collector processing time. By carefully selecting variables that are associated with only one of the aforementioned timescales, the morphology of the photopolymerized fibers could be finely tuned while keeping all other parameters constant. In this study, the light intensity, the concentration of an elasticity modifier, and the spin speed of the spinneret were varied systematically to change the reaction kinetics, the viscoelastic response, and the processing time, respectively. The morphological appearances of the resulting fibers, ranging from beads, beads-on-string, uniform fibers, fused fibers, to well cured fibers, were characterized using scanning electron microscopy (SEM), while the timescales were measured experimentally by a variety of characterization methods as described in detail in the following sections.

Finally, the morphological appearance and their timescales were superimposed to construct an operating diagram for the photopolymerization Forcespinning process. It was found that uniform and well-cured fibers were produced only when the three timescales were closely matched; fiber defects started to develop as one or more timescales deviated from the optimal values. These experiments and the resulting operating diagram elucidated the role of each timescale as well as the intricate interplay between the timescales and their effects on the formation and the morphological evolution of the fibers. With this fundamental knowledge, the process could be readily adapted to include many different monomer chemistries to produce a diverse profile of fibers, and implemented within other industrial fiber production technologies for widespread use in manufacturing.

Download English Version:

<https://daneshyari.com/en/article/5180075>

Download Persian Version:

<https://daneshyari.com/article/5180075>

[Daneshyari.com](https://daneshyari.com)