ARMY RESEARCH LABORATORY

Parameter Study of Melt Spun Polypropylene Fibers by Centrifugal Spinning

by Daniel M Sweetser and Nicole E Zander

ARL-TN-0619 July 2014

NOTICES

Disclaimers

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ARL-TN-0619 **July 2014**

Parameter Study of Melt Spun Polypropylene Fibers by Centrifugal Spinning

Daniel M Sweetser and Nicole E Zander
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE						*Form Approved OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*
July 2014

2. REPORT TYPE
Final

3. DATES COVERED (From - To)
October 2013–June 2014

4. TITLE AND SUBTITLE
Parameter Study of Melt Spun Polypropylene Fibers by Centrifugal Spinning

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Daniel M Sweetser and Nicole E Zander

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WMM-G
Aberdeen Proving Ground, MD 21005-5066

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TN-0619

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Nanofibers and microfibers offer a myriad of applications ranging from filtration, composites, and energy harvesting to tissue engineering and drug delivery. Centrifugal spinning is a new technique that uses centrifugal forces to form nanofibers and microfibers both from solution and the melt. In this work, polypropylene fibers were prepared using centrifugal spinning from the melt. The effects of melt temperature, spinneret orifice diameter, collector distance, and rotation speed were evaluated with respect to fiber morphology and diameter. The optimal heating temperature was found to be between 200 and 230 ºC to produce bead-free fibers. Decreasing the spinneret orifice diameter and increasing the rotation speed of the spinneret yielded more uniform fibers with smaller diameters.

15. SUBJECT TERMS
centrifugal spinning, polypropylene, nanofibers, melt spinning, electron microscopy

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Nicole Zander
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (*Include area code*)
Unclassified	Unclassified	Unclassified	UU	16	410-306-1965

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures iv

List of Tables iv

1. Introduction 1

2. Materials and Methods 1

2.1 Materials ... 1

2.2 Methods ... 1

2.2.1 Fiber Formation ... 1

2.2.2 Fiber Characterization ... 2

3. Results and Discussion 2

3.1 Spinneret Gauge ... 2

3.2 Rotational Speed ... 2

3.3 Temperature ... 4

3.4 Working Distance ... 5

4. Conclusions 7

5. References 8

Distribution List 9

List of Figures

Fig. 1 SEM images paired with fiber diameter distributions of PP microfibers melt spun with a 30-G spinneret at 230 °C and a collector distance of 14 cm with varying rotational speeds. a/b) 6,000 rpm, c/d) 10,000 rpm, e/f) 14,000 rpm, and g/h) 18,000 rpm......................3

Fig. 2 Melt spun polypropylene fiber diameters prepared at 230 °C and at a working distance of 14 cm 4

Fig. 3 SEM micrographs of polypropylene fibers produced at 14,000 rpm, with a working distance of 14 cm at varying temperatures: a) 200 °C, b) 230 °C, and c) 250 °C 5

Fig. 4 SEM images of polypropylene fibers produced at 230 °C, 14,000 rpm, and varying spinneret-collector distances: a) 10 cm, b) 12 cm, and c) 14 cm...5

Fig. 4 SEM images of polypropylene fibers produced at 230 °C, 14,000 rpm, and varying spinneret-collector distance. a) 10 cm, b) 12 cm, and c) 14 cm 6

Fig. 5 Normalized distributions of fiber diameters produced at 230 °C, 14,000 rpm, and varying spinneret-collector distances...6

List of Tables

Table 1 Fiber diameter of melt-spun polypropylene fibers at varying rotational speeds 4

Table 2 Fiber diameter averages and standard deviations at different operating temperatures.....5

Table 3 Fiber diameter averages and standard deviations with distribution peak heights at different working distances...6

1. Introduction

The production of microfibers and nanofibers has drawn an increasing amount of attention during the last decade. The interest for nanofibers is rooted in the unique properties they contain such as their high surface area to volume ratios. These unique properties lead to many applications in areas such as energy, filtration, drug delivery, and tissue repair.[1–3] There are many methods of fabricating nanofibers including drawing, template synthesis, phase separation, self-assembly, and electrospinning. Most methods are only relevant on a laboratory scale and are not economically feasible enough to be scaled up to industry. Recently, nanofiber production via centrifugal spinning has received more attention as an alternative to electrospinning, the most common nanofiber formation method. Fibers of low dielectric constants and insoluble polymers that generally cannot be used in electrospinning can be produced through centrifugal spinning. The centrifugal spinning process has several key parameters that control fiber morphology (in addition to solution viscosity) including the rotational speed of the spinneret, working distance between spinneret and collector, and heating temperature.[4] In this work, we examined the effect of the aforementioned parameters on polypropylene fiber formation.

2. Materials and Methods

2.1 Materials

Polypropylene (PP) was provided by FibeRio (FibeRio Technology Corp.) and used as received.

2.2 Methods

2.2.1 Fiber Formation

Melt spun fibers were fabricated using the FiberLab L1000-D (Fiberio Technology Corp.). Polypropylene (PP) pellets (200 mg) were added to the 30-G and 20-G spinnerets purchased from Fiberio. The PP polymer was heated to temperatures ranging from 200 to 250 °C. Polymer temperature was measured with a thermocouple inserted into the spinneret. The spinneret was spun for 30 s at a rotational speed of 6,000–18,000 rpm. The 6-inch-high, 1/2-inch-wide collector bars were separated by 1 inch and arranged in a circle surrounding the spinneret. Collector bars were placed 10, 12, and 14 cm away from the spinneret orifices. Aluminum foil covered selected bars and was used to collect the melt spun PP fibers.

2.2.2 Fiber Characterization

Fiber morphology was observed using a field emission scanning electron microscope (SEM, Hitachi S-4700). The fiber webs were gold/palladium sputtered to reduce charging. Fibers from these images were selected at random to measure fiber diameter, performed with Image J software.

3. Results and Discussion

3.1 Spinneret Gauge

Two different spinneret gauges were used to fabricate the PP fibers under the same conditions of 230 °C, 14,000 rpm, and a working distance of 14 cm. The two gauges were 30-G and 20-G with 0.16- and 0.60-mm inner diameter orifices, respectively. The 30-G spinneret produced fibers with smaller diameters, 2.27 ± 0.99 µm versus 5.39 ± 2.08 µm. The fibers yielded when using the 30-G spinneret also were more uniform. Previous research observed these same trends when forming polyacrylonitrile fibers by centrifugal spinning.[5] The 30-G spinneret was used for the remainder of this study because it produced more desirable fibers than the 20-G spinneret.

3.2 Rotational Speed

The effect of the spinneret rotational speed on fiber formation and morphology was examined at rotational speeds between 6,000 and 18,000 rpm. Other conditions were fixed: heating temperature at 230 °C and a working distance of 14 cm. Figure 1 displays selected images of fibers formed at various rotation speeds and their resulting fiber diameter distributions. Faster rotational speeds yielded smaller fiber diameters (Table 1 and Fig. 2). At slower rotational speeds (6,000 rpm) not only were larger fiber diameters observed, but also large diameter distributions. Increasing the rotational speed to 10,000 rpm improved the fiber diameter and uniformity. Raising the rotational speed beyond 10,000 rpm yielded insignificant improvements.

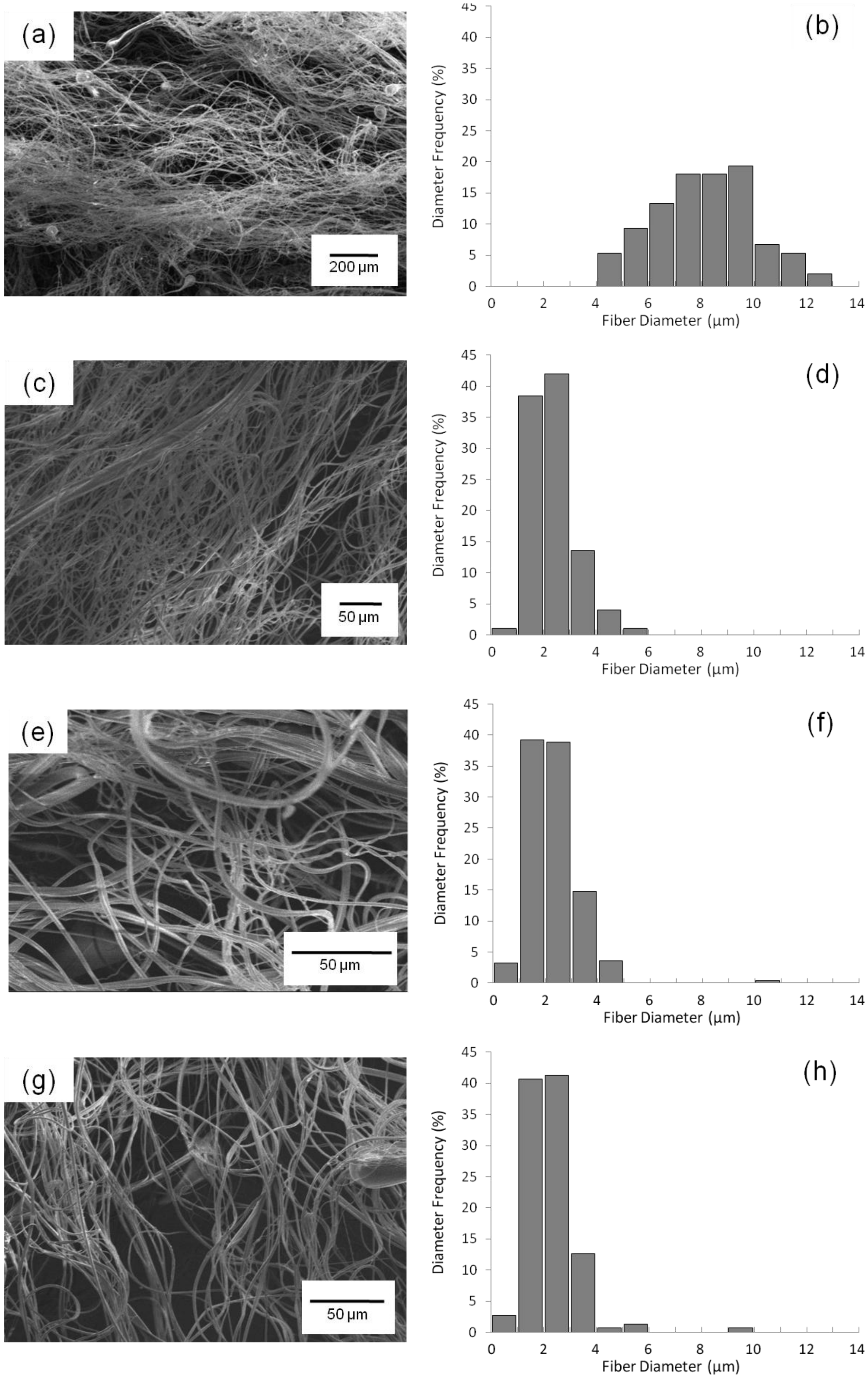

Fig. 1 SEM images paired with fiber diameter distributions of PP microfibers melt spun with a 30-G spinneret at 230 °C and a collector distance of 14 cm with varying rotational speeds. a/b) 6,000 rpm, c/d) 10,000 rpm, e/f) 14,000 rpm, and g/h) 18,000 rpm

Table 1 Fiber diameter of melt-spun polypropylene fibers at varying rotational speeds

Rotational Speed (rpm)	**Fiber Diameter (μm)**
6,000	8.28 ± 2.18
10,000	2.35 ± 0.81
14,000	2.27 ± 0.99
18,000	2.25 ± 1.01

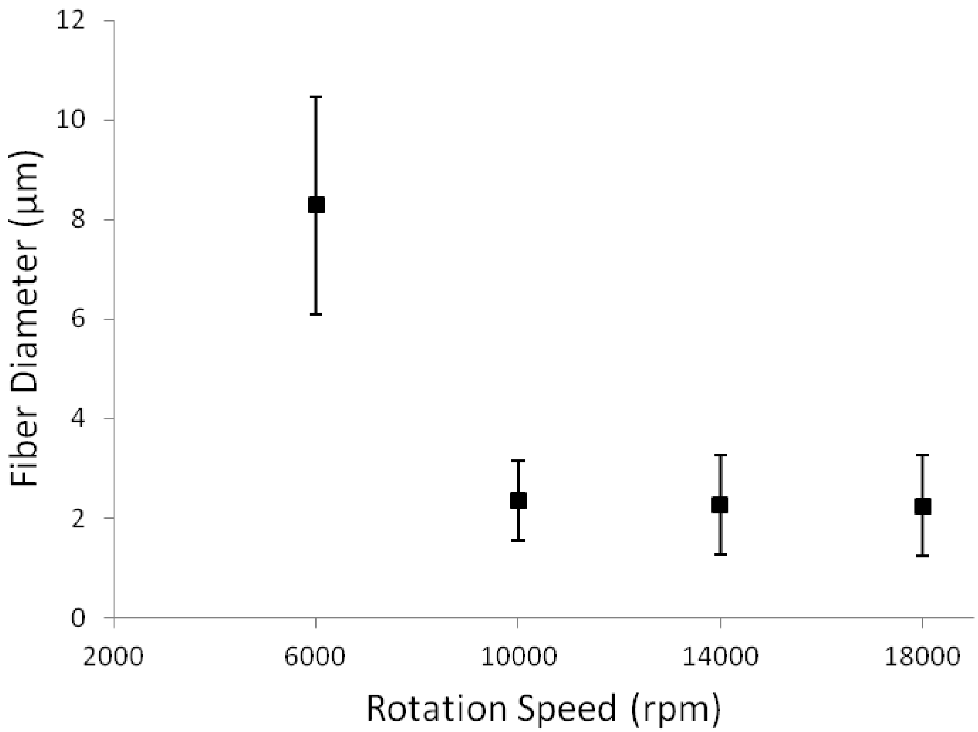

Fig. 2 Melt spun polypropylene fiber diameters prepared at 230 °C and at a working distance of 14 cm

3.3 Temperature

The temperature of the polymer during fiber formation between 200 and 250 °C did not significantly impact fiber diameter (see Table 2). Significant differences in morphology were observed in the SEM micrographs at these temperatures (see Fig. 3). Although the melting temperature of polypropylene is roughly 150 °C, the lowest temperature selected in this study was 200 °C to decrease the viscosity of the polymer to a degree that allowed the polymer to flow freely through the spinneret orifices. At operating temperatures close to the melting temperature, few fibers were produced. Between 200 and 250 °C, the fiber diameter distributions were fairly similar. But fibers produced at 250 °C had beads as well as evidence of polymer decomposition. This beading may be a result of the polymer having too low of a viscosity under these conditions.

Table 2 Fiber diameter averages and standard deviations at different operating temperatures

Temperature (°C)	**Fiber Diameter (μm)**
200	1.91 ± 0.86
230	2.27 ± 0.99
250	2.39 ± 0.85

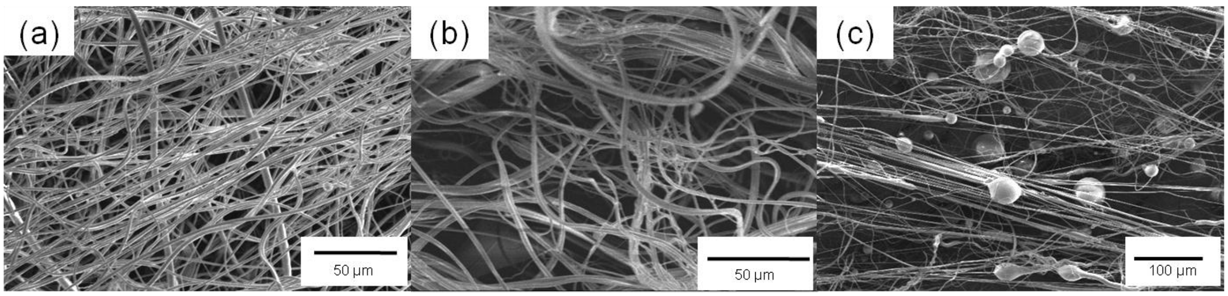

Fig. 3 SEM micrographs of polypropylene fibers produced at 14,000 rpm, with a working distance of 14 cm at varying temperatures: a) 200 °C, b) 230 °C, and c) 250 °C

3.4 Working Distance

The orifice to collector distance impacted the average fiber diameter by a small amount, with statistically smaller fibers formed for longer working distances. A more appreciable difference in the fibers formed at different working distances can be seen in the fiber uniformity and morphology. At a working distance of 10 and 12 cm, some fiber beading was present (Fig. 4). Fibers formed at these working distances also had higher standard deviations and therefore smaller normalized distribution peak heights (see Table 3 and Fig. 5). Fibers formed at a working distance of 14 cm were the most uniform and absent of beading.

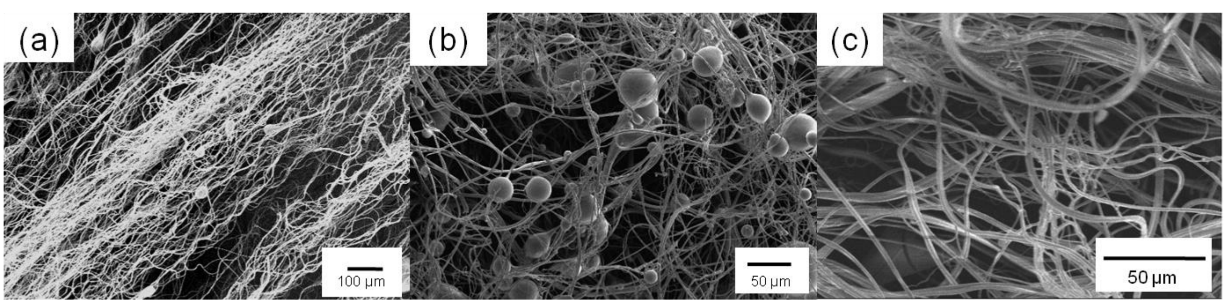

Fig. 4 SEM images of polypropylene fibers produced at 230 °C, 14,000 rpm, and varying spinneret-collector distances: a) 10 cm, b) 12 cm, and c) 14 cm

Table 3 Fiber diameter averages and standard deviations with distribution peak heights at different working distances.

Working Distance (cm)	Fiber Diameter (μm)	Normalized Distribution Peak Height
10	3.59 ± 1.41	0.283
12	3.00 ± 1.44	0.276
14	2.27 ± 0.99	0.401

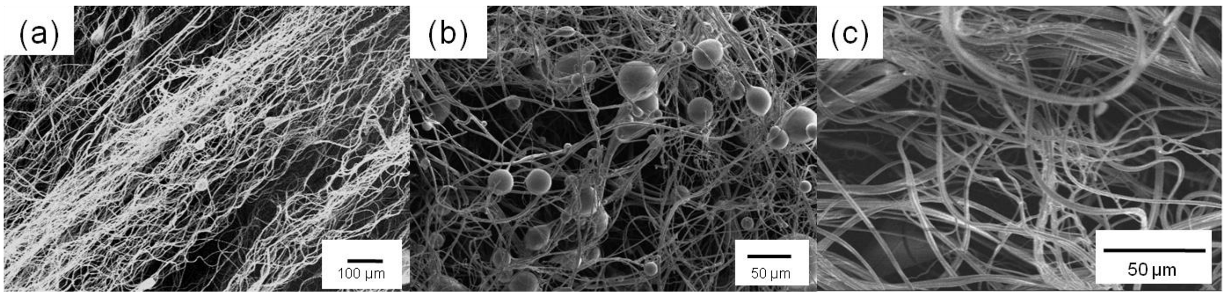

Fig. 5 SEM images of polypropylene fibers produced at 230 °C, 14,000 rpm, and varying spinneret-collector distance. a) 10 cm, b) 12 cm, and c) 14 cm

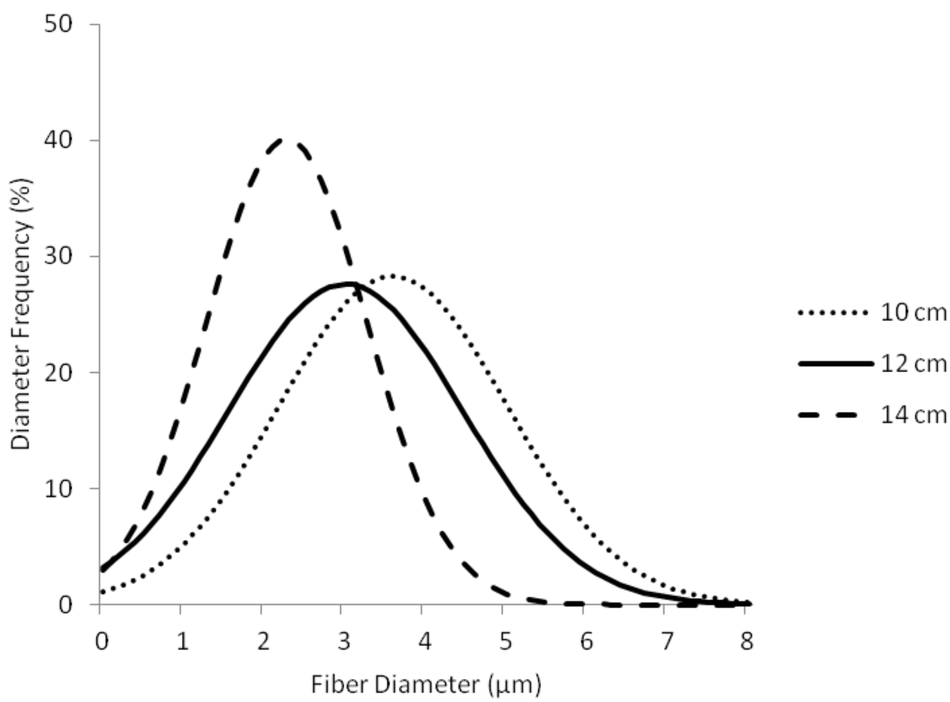

Fig. 6 Normalized distributions of fiber diameters produced at 230 °C, 14,000 rpm, and varying spinneret-collector distances

4. Conclusions

Many applications of nanofibers depend on the fiber diameters to be as small as possible because of the properties obtained from features such as high surface area to volume ratios. When fabricating polypropylene fibers via centrifugal spinning, certain operating parameters had significant effects on the average fiber diameters and morphology. The 30-G spinneret produced smaller and more uniform fibers. Increasing rotational speeds of the spinneret up to 10,000 rpm yielded uniform and relatively small fiber diameters. Increasing spinneret rotational speeds beyond 10,000 rpm was not justified by the small improvements in fiber diameter observed. Operating temperatures close to the melting point of polypropylene (<200 °C) reduced the total fiber yield significantly and high temperatures (>230 °C) resulted in fiber beading along with decomposition and burning of the fibers produced. A working distance of 14 cm was found to be optimal in reducing the polypropylene fiber diameters while increasing fiber uniformity.

5. References

1. Wang L, Yu Y, Chen PC, Zhang DW, Chen CH. Electrospinning synthesis of C/Fe3O4 composite nanofibers and their application for high performance lithium-ion batteries. J Power Sources. 2008;83:717–723.

2. Zhang Q, Welch J, Park H, Wu CY, Sigmund W, Marijnissen JCM. Improvement in nanofiber filtration by multiple thin layers of nanofiber mats. J Aerosol Sci. 2010;41: 230–236.

3. Sill TJ, von Recum HA. Electro spinning: applications in drug delivery and tissue engineering. Biomaterials. 2008;29:1989–2006.

4. Sarkar K, Gomez C, Zambrano S, Ramirez M, Hoyos, E, Vasquez H, Lozano, K. Electrospinning to Forcespinning. Mater Today. 2010;13:12–14.

5. Lu Y, Li Y, Zhang S, Xu G, Fu K, Lee H, Zhang X. Parameter study and characterization for polyacrylonitrile nanofibers fabricated via centrifugal spinning process. Eur Polym J. 2013;49:3834–3845.

1 DEFENSE TECHNICAL
(PDF) INFORMATION CTR
DTIC OCA

2 DIRECTOR
(PDF) US ARMY RESEARCH LAB
RDRL CIO LL
IMAL HRA MAIL & RECORDS MGMT

1 GOVT PRINTG OFC
(PDF) A MALHOTRA

1 DIR USARL
(PDF) RDRL WMM G
D SWEETSER
N ZANDER

INTENTIONALLY LEFT BLANK.