

IV.F.1 High Strength Carbon Fibers

Felix L. Paulauskas, Bob Norris (Primary Contact),
Amit Naskar, Soydan Ozcan, and Ken Yarborough
Oak Ridge National Laboratory (ORNL)
MS 6053
Oak Ridge, TN 37831-6053
Phone: (865) 576-1179
Email: norrisrejr@ornl.gov

DOE Manager

HQ: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

Subcontractors:

- Ana Paula Vidigal, Paolo Correira, José Contreiras
Fibras Sinteticas de Portugal (FISIPE), SA, Lavradio,
Portugal
- Donald G. Baird, James E. McGrath, Jianhua Huang,
Myoungbae Lee, Yu Chen, and Ozma Lane
Virginia Polytechnic Institute and State University (VT),
Blacksburg, VA

Project Start Date: November 2006

Project End Date: Project continuation and direction
determined annually by DOE

Fiscal Year (FY) 2012 Objectives

- Demonstrate spinning of a 50 m continuous ~15 filament tow of ~10-12 micron fibers from high molecular weight (MW, >200,000) dope that can be easily spooled and de-spooled for conversion at ORNL's Precursor Development System and yielding 15 Msi modulus and 150 ksi strength.
- Demonstrate spinning of a 1,000 m continuous ~100 filament tow of ~10-12 micron fibers from high MW (>200,000) dope that can be easily spooled and de-spooled for conversion at ORNL's Precursor Development System and yielding 15 Msi modulus and 150 ksi.

Technical Barriers

High-strength carbon fibers account for approximately 65% of the cost of the high-pressure storage tanks. This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost

(D) Durability/Operatability

(G) Materials of Construction

High strength carbon fiber enables the manufacture of durable, lightweight, compressed hydrogen storage vessels for use in high-pressure storage. Unfortunately, current high-strength carbon fiber products are far too expensive to meet DOE goals for storage system costs.

Technical Targets

Working targets are approximate equivalence with Toray T-700 at substantially reduced production costs:

- 700 ksi ultimate tensile strength
- 33 Msi tensile modulus
- Production cost reduction of at least 25% versus baseline

FY 2012 Accomplishments

- Improved spinning equipment and techniques have been developed and demonstrated for producing initial sample quantities necessary for establishing feasibility of our approach for evaluating sample precursor chemistries and converting melt-spun polyacrylonitrile (PAN) precursor. A number of "engineering" obstacles associated with spinning samples into a pressure chamber and properly winding for feasibility demonstration purposes have been resolved and approaches for further scaling up to the next level of development have been identified.
- Melt-spun PAN-based precursor fiber has been produced in sufficient quality and quantity to begin carbon fiber conversion investigations. Mechanical data for the precursor fiber indicates strength and modulus is lower, but approaching levels typical for precursor utilized in production of commercial PAN-based carbon fiber, giving us confidence in our approach.



Introduction

The exceptional strength-to-weight ratio of carbon fiber composite tanks makes them prime candidates for use with materials-based, cryogenic, or high-pressure gas for both vehicular and stationary storage applications. Cost is the primary issue with composite tank technology. A critical challenge lies in the cost of the fiber and the manufacture of composite tanks. Current projections of the manufactured cost per unit for high production volumes are significantly higher than storage system targets, and it is estimated that

about 40-70% of the unit cost is due to the base cost of the carbon fiber (approximately 40% of the fiber cost is due to the precursor and the remainder due to thermal processing). Research and development (R&D) is needed as composite storage technology is most likely to be employed in the near term for transportation applications and will be needed for most materials-based approaches for hydrogen storage.

Currently, composite tanks require high-strength fiber made from carbon-fiber grade PAN precursor. Manufacturing R&D is needed to develop lower cost, high quality PAN or alternate precursors and reduced energy or faster conversion processes for carbon fiber, such as microwave and/or plasma processing. Developing and implementing advanced fiber processing methods has the potential to reduce cost by 50% as well as provide the technology basis to expand U. S. competitiveness in high-strength fiber manufacturing [1].

This project will leverage previous and ongoing work of the U.S. DRIVE's program to develop a low-cost, high-strength carbon fiber. This project will seek to develop carbon fibers with properties equivalent to Toray's T700/24k fiber (24k tow, 700 ksi ultimate tensile strength, 33 Msi tensile modulus), and reduce production costs by at least 25%.

Approach

This project is structured into tasks focused on precursor development and conversion process improvements. Development and demonstration of melt-spinnable PAN is the project's primary precursor option. This requires concurrent activities in both development of melt-stable PAN copolymer and blends as well as the processes necessary to successfully spin the formulations into filamentary tows. Backup options include textile PAN, polyolefins, and incorporation of nanomaterials. Demonstrating and down-selecting a precursor capable of meeting performance targets utilizing conventional conversion processing defines the pathway for the balance of project activities. In conversion, critical processability parameters include: (i) highly controlled stretching, especially during pre-treatment and stabilization; (ii) residence time in various conversion modules; (iii) optimal graphitization for maximum strength; (iv) uniform treatment of fibers throughout the tow; and (v) characterization of filaments at various stages of conversion operation. Related ORNL work in advanced processing technologies addresses these issues, with a focus on increasing line speed in a reduced footprint, with reduced energy consumption. Means to adapt these emerging processes will be developed and evaluated for applicability to meeting requirements of this project area. As the alternative approaches are demonstrated, the energy efficiency and overall economics of the complete system will be evaluated and forecast for production scale up.

Results

Melt processing of PAN is a difficult issue, although Virginia Tech and others have made modest progress over the last decade [2-6]. One of the principal problems is that PAN degrades even without main chain scission or weight loss, and this essentially precludes melt processing. Reactions of the side groups have been discussed in many reports [7-10]. These degradative reactions can take place both in an intramolecular manner, but also via inter-molecular branching and gelation, which quickly alters the capacity for these materials to be melt fabricated. At 200-220°C, the material can quickly increase in viscosity, thus rendering an intractable material in a very short time. Ideally, one would like to maintain constant viscosity for a required period, and practical considerations suggest that this should be at least 30 minutes or longer.

During this period, the project team with sponsor encouragement decided to put precursor chemistry development work on hold in order to focus limited resources on demonstrating feasibility of the melt spinning approach. For this demonstration effort, some baseline high molecular weight PAN-based formulations are being utilized that, while representative of the processing requirements ultimately required to meet program goals, probably cannot be converted themselves into carbon fiber meeting those performance goals. Significant "engineering" obstacles have been encountered in utilizing the very simple experimental equipment available in this project; a number of these hurdles have been overcome during this period and we have identified solutions for resolving others we expect to encounter on the pathway to our goals. Examples already implemented include improved spinneret design and construction, improved filtration, means for maximizing small sample utilization with integration of purging materials for maintaining open holes as the sample is expended, enhanced extrusion barrel heating, larger spinning pressure chamber, indexed take-up winding patterns, etc. As we continue to resolve these issues, we have gained confidence that the approaches we have proposed do have great potential for meeting program goals given appropriate levels of resources.

As example of our recent progress, Figure 1 shows the original and improved spinning systems developed and employed at Virginia Tech for this work. A demonstration PAN/VA formulation was melt-spun with the new spinning system. The resulting filament package generated on the new system is shown in Figure 2. The spinneret used had 18 holes and it is estimated that the filament tow collected with the same extrusion and take-up speeds (and thus the same/similar fiber size) was about 130 ft (40 meters) in length. The fiber sample was shipped to ORNL for carbon fiber conversion evaluation.

Figure 3 provides the scanning electron microscope images, cross-sectional view, of the melt-spun (VT) fibers produced in comparison with commercial wet-spun fibers.

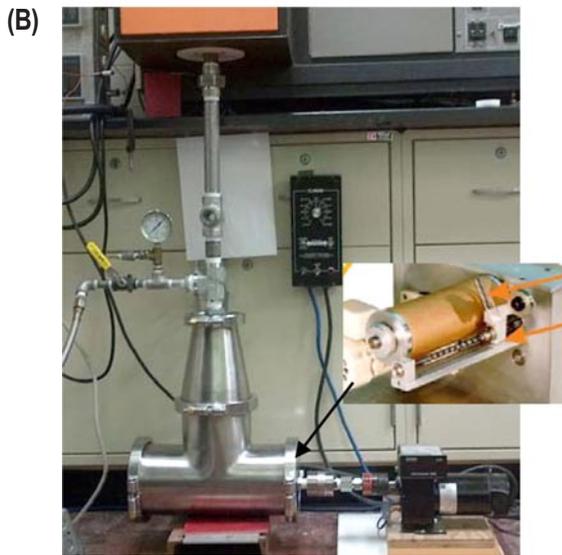
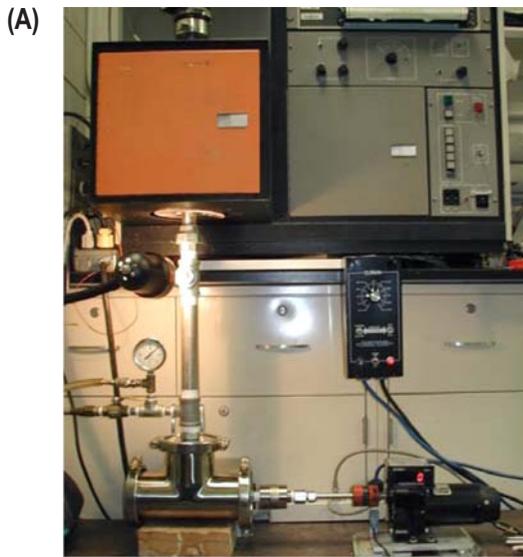


FIGURE 1. Picture of original pressurized fiber spinning system (A) and new system (B). A new take-up device with traverse fiber guide was installed inside the pressure chamber of the new system.

It can be seen that melt-spun fiber has a substantially more circular cross section, with no discrete outer sheath layer as observed by prior researchers who used water as plasticizers. The number and size of the voids also seemed to be acceptable. Figure 4 shows the surface of the melt-spun fibers and commercial PAN fibers. It seems that the surface of the VT fiber is comparable to that of the commercial wet-spun fibers.

The tensile mechanical properties of the PAN fibers are presented in Figures 5-7. Compared with our previous fiber samples (VT-1, 2), we got improvement in both tensile strength and modulus for the fibers generated in the most recent quarter of this reporting period (VT-3). Compared with wet-spun commercial products, the strength of VT-3 is still lower than that of the commercial product. The modulus of



FIGURE 2. Melt-spun PAN/VT fibers generated with new system/winder with traverse fiber guide

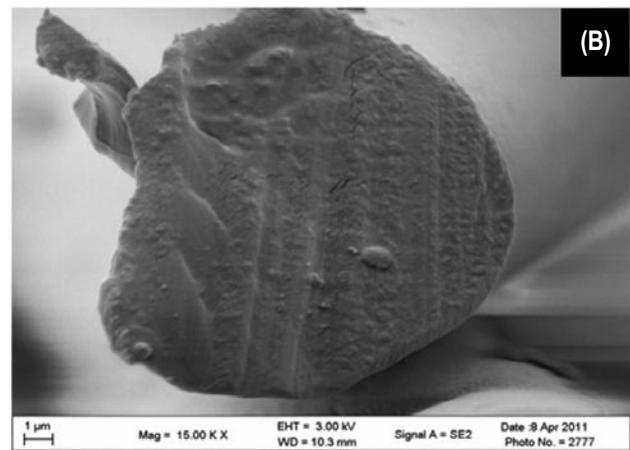
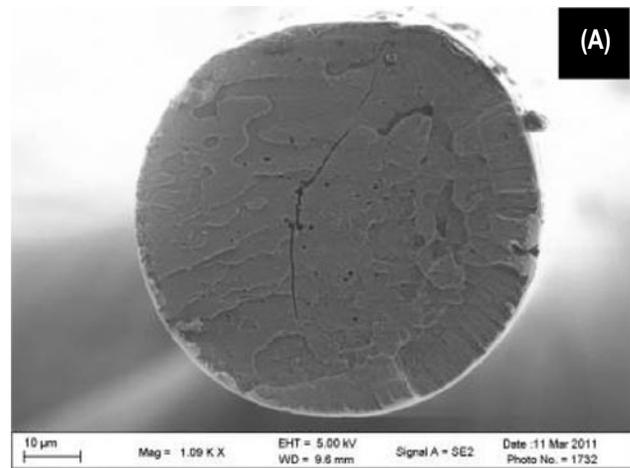


FIGURE 3. Cross-section of VT melt-spun PAN fibers (A) and commercial wet-spun PAN fibers (B)

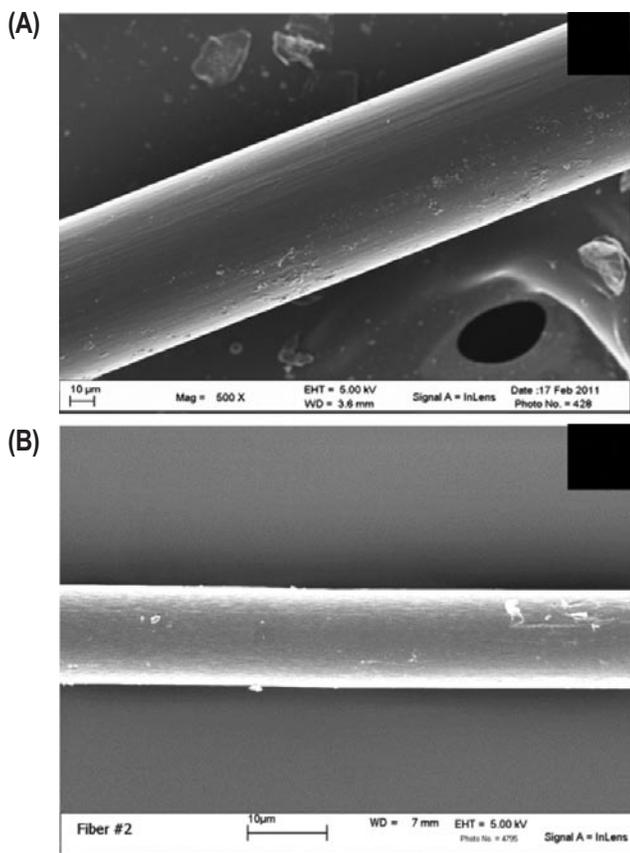


FIGURE 4. Surface of VT melt-spun PAN fibers (A) and commercial wet-spun PAN fibers (B)

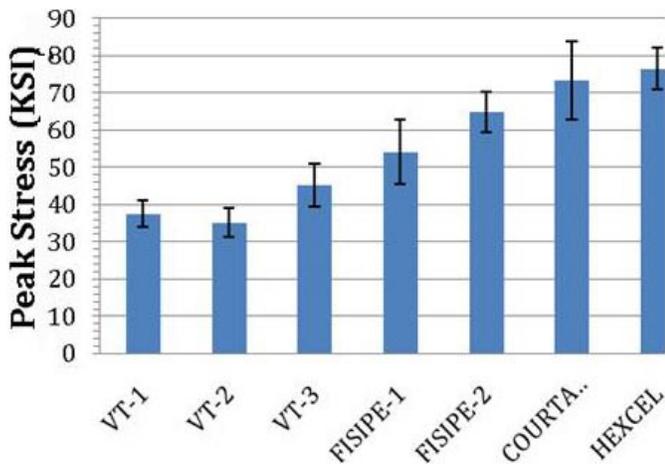


FIGURE 5. Tensile strength of PAN fibers

our fibers is, however, at the average level of the commercial PAN fibers. The elongation of our melt-spun fibers is also close to that of the commercial products.

It is not unusual for precursor fibers to be stretched progressively in steps as opposed to being fully stretched

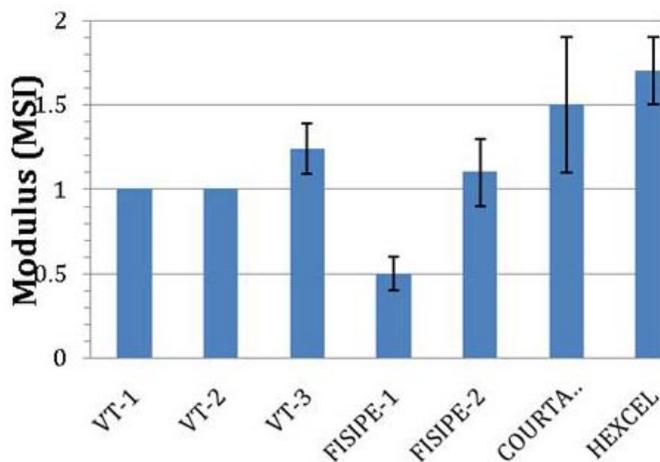


FIGURE 6. Tensile modulus of PAN fibers

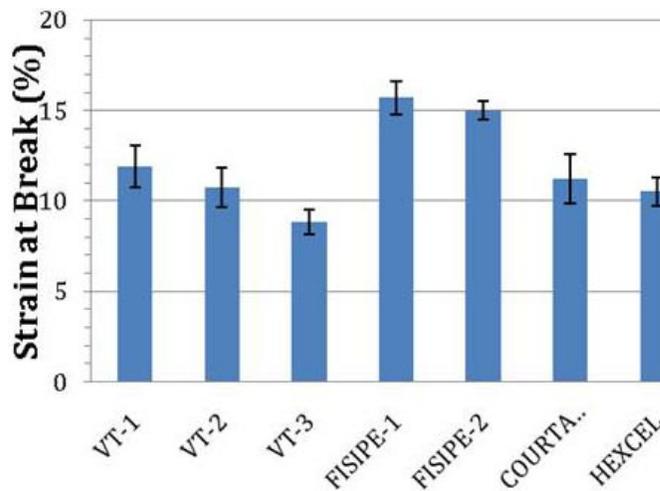


FIGURE 7. Elongation of PAN fibers

coming out of the spinneret. Although initially we were working towards getting the necessary drawing in the initial spinning process, we are now focused on a multi-stage approach more consistent with what BASF employed in its earlier melt-spinning development work. In order to perform the second stage (or post-spinning) stretch process, a steam chest including two rolls connected to two adjustable speed motors was designed and constructed (see Figure 8). The PAN/VA filaments with diameter of about 33 microns, corresponding to a stretch ratio of about 2.8, were generated for this purpose. Saturated steam with pressure of 30 psi (corresponding to temperature of 134°C) was used. We were able to stretch the as-spun fibers to a limited draw ratio (up to 2), but we have difficulty to stretch the fiber further (fibers broke when attempting to get higher stretch ratios). We are currently working on this issue and trying to increase the stretch ratio to the level that BASF reached (6.4 or higher).

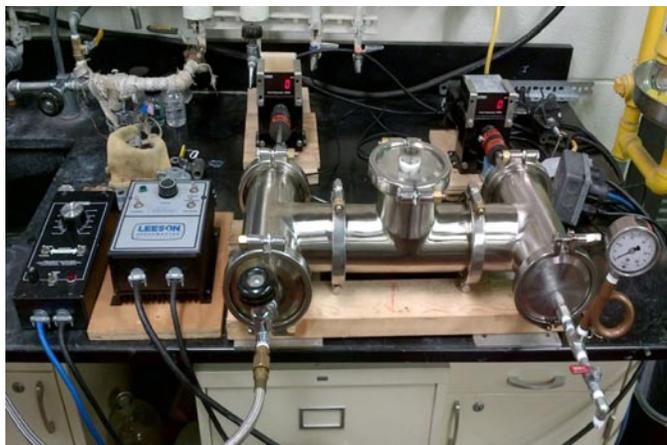


FIGURE 8. Picture of steam chest used to stretch PAN fibers (second stage stretch)

In the last quarter of this reporting period, melt-spun PAN-based precursor fiber has been produced in sufficient quality and quantity to begin carbon fiber conversion investigations. Utilizing ORNL's thermal analysis equipment and its unique suite of very small-scale, but very accurate tensioning systems married with oxidation ovens and carbonization furnaces frequently referred to as the Precursor Evaluation System, ORNL was able to develop conversion protocols and demonstrate both oxidation and carbonization processes. Although the mechanical data was again somewhat lower than for commercially available materials, the properties were consistent with first data from earlier developmental efforts where ORNL progressively increased properties for less costly alternative precursor formulations from below commercial baseline to property levels essentially comparable to those of commercial products. Current plans are to continue improving the precursor spinning, drawing, and conversion processes necessary to meet go-forward milestone levels agreed to as the stage-gate for resuming the larger development effort. Project participants and sponsors are optimistic on meeting these levels in the next year and then pushing forward with the integrated plan bringing all elements of the process – precursor chemistry, spinning, drawing, conversion, (potentially ORNL advanced conversion techniques), post treatment, etc. – necessary to meet cost and performance requirements for this application.

Conclusions and Future Directions

Significant progress has been made in demonstrating melt spinning processes and producing precursor fiber in sufficient quality and quantity to begin carbon fiber conversion investigations. Mechanical properties of the melt-spun precursor fiber are approaching those of commercially produced fibers. Initial conversion protocols have been developed and demonstrated, indicating that we are indeed

taking an effective approach and making progress towards the stage-gate milestone established for taking this initiative to the next level of development.

Near-term objectives are for Virginia Tech to produce longer and more uniform tows that are then drawn in a secondary step as previously described. ORNL will characterize fiber and conduct more extensive conversion trials on precursor filaments generated using its precursor evaluation system. We expect to achieve carbon fiber tensile properties of 15 Msi elastic modulus and 150 ksi tensile strength with 1st generation filaments. With this data, we will have accomplished the previously established stage-gate milestone for moving into the next stage of development and demonstration of this technology.

In this next stage of development, we will resume working the precursor chemistry we believe necessary to enhance baseline properties and move towards the ultimate goals of 33 Msi modulus and 700 ksi strength. We will need to scale the spinning processes up so that we can work with larger tow sizes and more continuous tows in further enhancing the conversion processes and providing feedback to the chemistry and fiber forming development. The filaments at various steps of the conversion process will be fully characterized and the data used to commence optimization of precursor chemistry and the filament generation process. In order to fully address application requirements, we will also need to evaluate and implement appropriate post treatment operations including surface treatment and sizing for the fiber. We will also evaluate whether advanced plasma-based conversion processes (oxidative stabilization and carbonization) under development at ORNL are appropriate for these fibers in reducing costs while meeting performance goals. As the technology is being successfully demonstrated at the Carbon Fiber Technology Facility in Oak Ridge, ORNL will concentrate on the commercialization strategy for technology transfer and implementation.

FY 2012 Publications/Presentations

1. Felix L. Paulauskas, "High Strength Carbon Fibers", presentation at 2012 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, May 14–17, 2012.
2. Felix L. Paulauskas, "High Strength Carbon Fibers and Status Report", presentation at Hydrogen Storage Tech Team Meeting, June 21, 2012.

References

1. Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan Planned program activities for 2005-2015, October 2007 update.
2. Wiles, K.B., V.A. Bhanu, A.J. Pasquale, T.E. Long, and J.E. McGrath, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 42, 2994-3001 (2004).

3. Bhanu, V.A. P. Rangarajan, K. Wiles, M. Bortner, S. Sankarapandian, D. Godshall, T.E. Glass, A.K. Banthia, J. Yang, G. Wilkes, D. Baird, and J.E. McGrath, *Polymer*, 43, 4841-4850, (2002).
4. Godshall, D., P. Rangarajan, D.G. Baird, G.L. Wilkes, V.A. Bhanu, and J.E. McGrath, *Polymer* 44 (2003), 4221-4228.
5. Rangarajan, P., V.A. Bhanu, D. Godshall, G.L. Wilkes, J.E. McGrath, and D.G. Baird, *Polymer* 43, 2699-2709 (2002).
6. Bortner, Michael J., Vinayak Bhanu, James E. McGrath, and Donald G. Baird, *Journal of Applied Polymer Science*, 93(6), 2856-2865 (2004).
7. Peng, Fred M., "Acrylonitrile Polymers," in Mark, Herman F.; Bikales, Norbert M.; Overberger, Charles G.; Menges, Georg; Editors. *Encyclopedia of Polymer Science and Engineering*, Vol. 1: A to Amorphous Polymers. (1986), 843 pp, pages 426-470, and references therein.
8. Back, Hartwig, C, and Knorr, Raymond S. "Acrylic Fibers," in Mark, Herman F.; Bikales, Norbert M.; Overberger, Charles G.; Menges, Georg; Editors. *Encyclopedia of Polymer Science and Engineering*, Vol. 1: A to Amorphous Polymers. (1986), 843 pp, pages 334-388, and references therein.
9. Capone, Gary J.; Masson, James C. *Fibers, acrylic*. *Kirk-Othmer Encyclopedia of Chemical Technology* (5th Edition) (2005), 11 188-224.
10. Frushour, Bruce G.; Knorr, Raymond S. *Acrylic fibers*. *International Fiber Science and Technology Series* (2007), 16(*Handbook of Fiber Chemistry* (3rd Edition)), 811-973.