National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No. M01-GT04

Competency: Materials

In-Situ Synchrotron Study during Fiber Processing

Project Team:

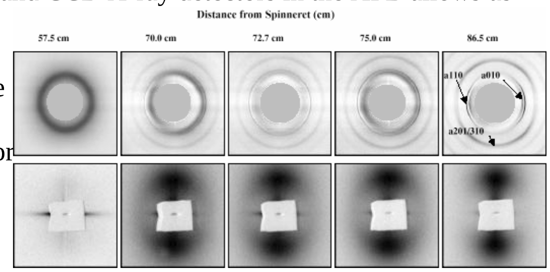
Leader Karl I. Jacob, Georgia Tech, Polymer Physics, Crystallization, Modeling
Email: jacob@moose.tfe.gatech.edu Phone: (404) 895-2541
Members: Ben Hsiao, SUNY Stony Brook , bhsiao@notes.cc.sunysb.edu, x-ray, polymer structures
Richard Stein UMass, Amherst, stein@ecs.umass.edu, Scattering Techniques
Steve Bechtel, Ohio State, bechtel@engg.osu.edu, Polymer jet flow in spinning
David McDowell, Georgia Tech, dlm@mail. Gatech.edu, modeling and characterization, ISV theory
Mike Ellison, Clemson, ellisom@clemson.edu, on-line Raman measurements

Objective:

The ultimate objective is to identify spinning conditions to produce strong and dyeable fibers in high speed spinning and to engineer specific fiber morphology and properties for lower spinning speeds. Specific objectives are: (1) identify the *development and history of evolution* of intermediate structures during fiber spinning and relate the intermediate structures with properties of the resulting fiber, (2) understand the development of crystallinity and orientation in the fiber during spinning with the objective of engineering fibers by modifying spinning conditions, (3) identify critical molecular weight and its distribution for improved orientation and optimum crystallinity for various spinning speeds and temperatures, (4) develop modeling techniques to predict the evolution of structure and morphology during fiber spinning based on in-situ data. These objectives are being addressed by using high brilliance synchrotron X-rays (10^5-10^8 times greater than typical in-laboratory source), integrated on-line experimental schemes with simultaneous small- and wide- angle X-ray scattering (SAXS/WAXD), birefringence, small-angle light scattering, and Raman polarization, by using advanced CCD X-ray detectors and unique image analysis software capable of separating crystal, amorphous and mesophase fractions in fibers and yielding corresponding shapes and dimensions. Further studies of strain-induced crystallization kinetics and orientation development will also be carried out with cross-linked polymer systems, which can be accurately characterized and modeled using a combination of simultaneous in-situ birefringence and light scattering techniques. In this study the effects of relaxation spectra (molecular weight, chain architecture, blend composition, etc.) on spinning dynamics will be included and process parameters will be changed to design optimum conditions for improved fiber structures for both low and high speed spinning conditions. This work will result in better understanding of spinning processes particularly for polymer blends, copolymers, and metallocene based polymers, which is currently lacking. On-line measurements is the *only way* to gain sufficient insight on morphology development with a far better chance of *utilizing the knowledge gained from studying one polymer system to another system* compared our current knowledge, since the *evolution* of structure is the focus of this study. In addition, morphology development results from local orientation which cannot be detected by conventional studies (eg., birefringence as it gives global averaged data) can only be studied using on-line synchrotron, and combined with light scattering and Raman polarization. The local morphological data thus obtained is required for the development of useful predictive mathematical models.

Progress Statement:

This project was funded only at the ***seed level*** from May 2001 to April 2002, and was converted to a full project starting May 2002. During this time significant progress has made in setting up highly complex experimental systems, refining the experiments to obtain accurate and valuable information from the experiments, techniques for the interpretation of the data, and in mathematical modeling. Literature reveals that very few on-line studies have been conducted to identify the history of structure development during fiber spinning processes. DuPont has conducted studies at HASYLAB in Hamburg, and obtained some new insight of crystallization along the spin line for selected polymers (nylon 66, and nylon 6 [1], PE). Since that study, unique capabilities for on-line experiments have improved substantially for SAXS and WAXD. We have integrated several advanced systems and sophisticated modeling techniques, which have not been available in the U.S. to date, for our in-situ synchrotron experiments, such as: (1)Synchrotron X-ray Technologies: Advanced Polymers Beamline (APB, X27C) as well as the SUNY Beamline (X3A2) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), as they are ideal for carrying out polymer studies of fundamental and practical importance. (2) Advanced Detection Technology: APB is now equipped with imaging plate detectors and gas-filled multi-wire proportional chamber (MWPC) area detectors. Advanced CCD detector has a large dynamic range (16-20 bits), good spatial resolution (about 80 m) and low noise characteristics. The availability of imaging plates, MWPC and CCD X-ray detectors in the APB allows us to tackle a variety of fiber characterization studies from weak scattering samples and minimal sample volumes (single filaments). (3) Unique Scattering Software Capability: We have developed some unique capability to extract extensive structure and morphology information from the measured scattering and diffraction images. For example, the volume fractions of crystal, amorphous and mesophase regions can be estimated, as well as their sizes, shapes and distributions. (4) a spinning unit at BNL.



As indicated in our annual report, shear and elongational studies with i-PP and PVDF were carried out using these techniques at the Brookheaven National Lab (BNL). Robust techniques for data collection and analysis are now in place and have been used in this project. The *evolution* of structure and morphology during actual fiber spinning process were identified for selected process conditions. We have found that critical orientation molecular weight M* reduces with shear rate, implying that at higher shear rate molecules with lower molecular weight in the distribution become oriented to produce extended chain crystals, thus diminishing folded chain (kebab) crystallization. Our spinning studies with PVDF supports the formation of shish-kebab mechanism in the fiber suggested by Keller (explained later) on morphology development (figure). We also characterized crystallization of iPP under a step shear using on-line techniques and combined with TEM to characterize the morphology development. An apparatus for measuring birefringence and light-scattering for studying crystallization of fully and lightly cross-linked PTHF polymers has been completed, as they can provide a wealth of "on-line" information on strain induced crystallization under tightly controlled conditions similar to spinning and is capable of separating chain entanglement slippage in crystallization. For mathematical models, crystalline growth kinetics has been incorporated in the polymer fluid flow model with an orientation dependent non-linear forcing function for the amorphous region characterizing the evolution of molecular orientation and crystallization. We have also developed a fundamental model to study crystallization and orientation development using an *Internal State Variable* theory. This powerful approach is capable of accounting for the entanglement slippage on crystallization. Initial modeling of nucleation accompanied by flow is complete, and the effect of multiple filaments in the spinning process has also been modeled. Multi-filaments models are important in capturing the realistic behavior of fiber spinning as opposed to idealized single filaments models. From our investigation, changes in process conditions are found to have a significant effect on the *evolution* of morphology. Hence, our study directed at a thorough understanding of the relation between the *development* of structure and resulting properties (rather than results from studying "dead" fibers) will ultimately lead to fibers with better properties, reduced cycle time for the process optimization, and rapid development of new products. Further study in this area will be vital to enhance the technical competitiveness of the U.S. fiber industry.

Next Year's Goals:

(1) Refinement and testing of our mathematical models to capture the development of morphology for more accuracy. **(2)** Carry out more simultaneous SAXS/WAXD measurements during fiber spinning with iPP, PVDF, and other polymers and understand the correct mechanism of structure development during the initial stages of crystallization along spin lines. **(3)** As Dupont is opening the APS facility for outside researchers, carry out preliminary experiments at Argonne National Laboratory using the Advanced Photon Source if we get permission. **(4)** Quantitative analysis of in-situ SAXS and WAXD data for a variety of spinning conditions, which can be used to develop a model for predicting structural development during shear and elongational flow. **(5)** Simultaneous light scattering and birefringence studies with cross-linked polymers of various degrees of cross-links to study the effect of fiber slippage on orientation development and crystallization.

Approach:

Presence of oriented mesophase has been proposed to play an important role in the final properties (such as mechanical, dyeability, etc.). It is extremely difficult to isolate or verify its existence by using final "dead" fibers.

In order to engineer a fiber with specific properties, it is important to understand the *development* of crystallinity and orientation in the fiber. Thus, by understanding the variation of structures in the fiber as it develops, one can vary the manufacturing parameters to study their effect on the evolution of structure, and can identify the optimum process parameters for specific fiber structures, and hence, fiber properties. We also plan to study the formation of the neck, since it is an important factor in determining the crystallization dynamics and development of orientation in high speed spinning. Not much is known about the events at the neck since only on-line measurements can provide such information. Using high brilliance synchrotron X-rays, we are studying the on-line development of structures using SAXS and WAXD measurements.

Representative selection from three types of polymers are used in this study: (1) polyesters: polyethyleneterephlate (PET), polytrimethyleneterephlate (PTT), polybutyleneterephthalate (PBT); (2) polyamides: nylon 66, nylon 6, and their blends; and (3) polyolefines: polyethylene (PE) homopolymer, PE copolymer with control short chain branches (metallocene based), polypropylenes (PP) with isotatic and syndiotatic tacticity. In some systems, polymorphism can be found as a function of temperature. With some polymers (nylon 6, nylon 66, PE, i-PP, and PVDF) we have already carried out in-situ synchrotron fiber spinning study to characterize crystallization along the spin line. We are carrying out further in-situ fiber spinning experiments in X27C or X3A2 beamline at the NSLS with additional process conditions, in order to develop a coherent theory of structure formation. The on-line SAXS measurements during fiber spinning are rare, because of the weak scattering signals. Recently, several laboratories observed that the SAXS signals occurred before WAXD crystalline patterns, indicating that density fluctuations are present prior to crystallization [2]. It was suggested that these density fluctuations might be due to a spinodal-like decomposition of the amorphous phase into material with a smoothly modulated, periodic density distribution. However, our recent fiber spinning study on PE and PVDF indicated that an equatorial streak occurred prior to the meridional lobes in the SAXS pattern, which favored the shish-kebab crystal formation during elongational flow as proposed by Keller, et al. Keller and coworkers argued that during flow (i.e., in strain-induced crystallization), only a fraction of the chains above a critical molecular weight M^* can be oriented at any given strain rate, implying that there is a critical strain rate for a given molecular weight or a critical molecular weight for a given strain rate. Only the chains longer than critical M^* will remain extended, where the rest of the chains will be unoriented due to rapid relaxation. The formation of shish-kebab morphology in crystalline polymers under flow is consistent with this model [3], which can be attributed to the crystallization of extended chains and the formation of the kebab can be attributed to the crystallization of unoriented chains. We are studying this mechanism and have developed mathematical expressions to describe and predict the polymer micro-structure during spinning. However, these mathematical models need further development for more accuracy. We also plan to determine the critical molecular weight and its distribution for desired fiber morphology.

We plan to extend our study in orientation development and crystallization of lightly-cross and fully cross-linked linked polymers using simultaneous in-situ birefringence and light scattering measurements. These are highly controlled repeatable experiments that will provide a wealth of information useful for the mathematical modeling. We also propose to carry out experiments at the at the third-generation insertion beamline using undulator in Sector 15 of the Advanced Photon Source (APS) in Argonne National Laboratory for higher speed spinning. The undulator synchrotron source will produce about 100 times more intensity than the bending magnet source (as in NSLS). We hope to do the high-speed spinning studies in collaboration with DuPont, using beamtime at Argonne under the independent investigator provision. There are no major technical barriers for this study other than logistical difficulties. The X-ray studies are being supplemented by simultaneous birefringence, small-angle light scattering, and Raman polarization studies to understand the evolution of orientation and morphology along the spinning line, which will provide us unique insight into the development of fiber morphology and properties during spinning.

References

(1) J. M. Samon, J. M. Schultz, J. Wu, B. S. Hsiao, F. Yeh and R. Kolb, J. Polym. Sci. Polym. Phys. 37, 1277-1287 (1999). (2) M. Imai, K. Kaji, and T. Kanaya, Macromol., 27, 7103 (1994). (3) A. Keller and H.W.H. Kolnaar, in Materials Science and Technology, A Comprehensive Treatment, VCH, 18, 1997, chap. 4, p. 190.

Outreach to Industry:

We have discussed this project with DuPont and we plan to work with them especially for APS work, probably in the next several months, if we get the approval.

New Resources Required:

Few detection devices will be requested on state line items or directly from NTC.