

National Textile Center FY 2003 (Year 12) Continuing Project Proposal

Project No.

M01-GT018

Competency: **Materials**

Fundamentals of High Modulus/High Tenacity Melt Spun Fibers

Project Team:

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Objective:

For many applications, a 50% increase in the modulus and tenacity of melt-spun fibers would greatly increase their value, *especially if they retain some of their high toughness* and can be produced at a price lower than the current high performance fibers. In melt-spun fibers, 40-60% of the polymer resides in noncrystalline regions and cannot be fully aligned with the fiber axis. This results in a substantial reduction in the modulus.

The objectives of the proposed work are to:

- Develop a knowledge base of the orientation distribution of polymer chains in the noncrystalline fraction of melt-spun fibers. This will allow us to ascertain the dependence of the modulus on the orientation distribution of the polymer chains in the noncrystalline region.
- Develop a fracture mechanics protocol for small fibers and apply it to determine the strength limitations of fibers.

The knowledge gained in the proposed research will provide insight for new processes to extend the range of moduli and tenacities available from melt-spinnable fibers.

Progress Statement:

Raman: During the past year, we have developed a Raman microspectroscopy technique to determine $\cos^2\theta$ and $\cos^4\theta$ for both the crystalline *and* the overall orientation of the chains in PET. We found that the orientation of the crystals (Figure 2) increase much more rapidly than the overall chains (Figure 1) and reach a plateau of near perfect orientation at very low levels of overall orientation. (Macromolecules, accepted, NTC Annual Review.) We also found that $\cos^4\theta \sim (\cos^2\theta)^2$. This *new* result is difficult to rationalize based on existing models of fiber spinning, and is being investigated further.

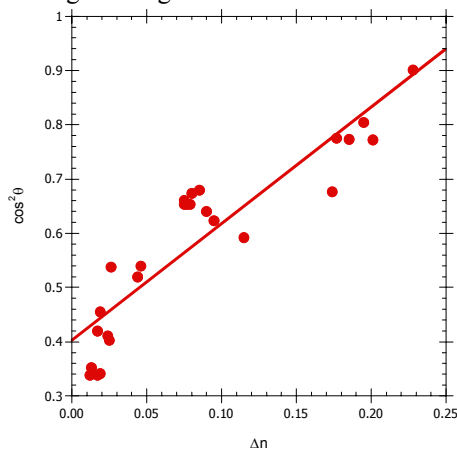


Figure 1. Average value of $\cos^2\theta$ for the 1616 cm^{-1} vibrational band of PET.

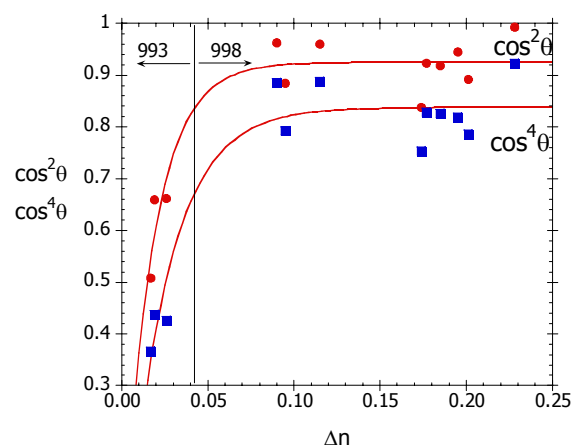


Figure 2. $\cos^2\theta$ and $\cos^4\theta$ vs. the birefringence of the 998 cm^{-1} and 993 vibrational bands.

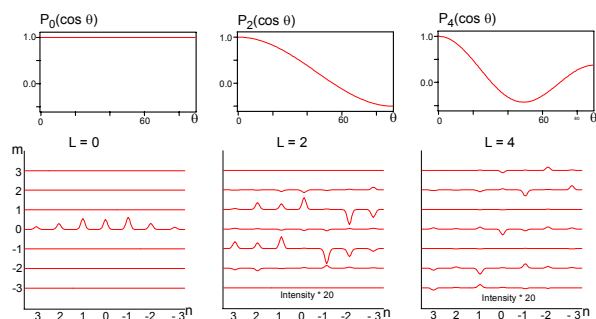


Figure 3. Theoretical calculations of 2D sync-MAS spectra for nylon-6,6 for an uniaxial distribution around an angle θ with a theoretical distribution function $P_L(\cos\theta)$. The experimental ODF may be readily obtained by fitting the experimental data of figure 2 to a weighted superposition of the individual distribution functions $P_L(\cos\theta)$.

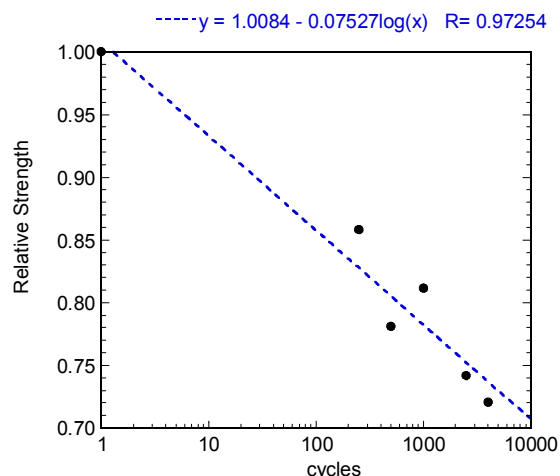


Figure 4. Relative strength after fatiguing fibers.

NMR: We have investigated several solid state NMR techniques claimed to be useful for measuring the orientation distribution function, ODF, of the chains in nylon-6,6 fibers. However, only two techniques were found to be useful for industrial fibers, 2D-DECODER and sync-MAS. They both rely on using the ^{13}C -nucleus as it occurs in natural abundance (ca. 2% of all carbon atoms) to detect ODFs. Of these two, we found that the sync-MAS-technique to be the most convenient. We have implemented the experimental procedures for the recording and processing of sync-MAS experiments on our NMR spectrometer. We have developed the software, which is needed for the complex calculations of theoretical spinning side band intensities. Using the developments, we have now determined the orientation distribution function of the solid state (below T_G) using the sync-MAS solid state NMR technique for one sample, Figure 3. Work is in progress to measure the crystalline and non-crystalline regions separately, and as a function of temperature for this and the remaining samples.

Fracture Mechanics: We have received and installed the EnduraTec cyclic tensile tester. We have resolved several instrumental issues and found that this instrument is far better for fatigue measurements than the other instruments we have used. It provides improved reproducibility while making it both easier and faster to operate. Sample preparation has also been simplified. We have now fatigued several samples to grow natural flaws to the critical size. A substantial strength reduction has been seen as shown in Figure 4.

We have also examined several fracture mechanics approaches for analyzing the data. It appears that the J-integral approach (NTC Annual Report) is able to properly deal with samples in which a large amount of plastic deformation occurs during fracture. This approach requires the measurement of the change in the energy under the stress-strain curve as the critical flaw grows. It also requires measurement of the crack growth. The EnduraTec stores *all* of the load-displacement data for all cycles including the final breaking cycle (which is usually different from the other cycles.) The crack growth will be measured on each sample using SEM and matched with the cyclic data. We are currently developing the SEM techniques to make these measurements.

Next Year's Goals:

During the next year, we will

- 1) Determine the crystalline orientation of the new set of nylon 6,6 fibers via x-ray analysis and solid-state NMR.
- 2) Determine the orientation distribution of nylon 6,6 polymer chain segments within the noncrystalline regions of these fibers using Raman spectroscopy.
- 3) Measure the J-R curve for these fibers.

Approach:

Only by understanding the evolution of molecular orientation within noncrystalline and crystalline phases will a full understanding of the structure property relationship for fibers be obtained. We therefore propose to fully investigate polymer fibers with respect to the orientation distribution function, ODF, in their noncrystalline and crystalline domains. The experimentally challenging part will be to characterize the noncrystalline domain in the presence of a

crystalline domain. We intend to use polarized Raman spectroscopy to measure both $\langle \cos^2\theta \rangle$ and $\langle \cos^4\theta \rangle$ of individual vibrations within the molecular chains in industrial nylon and PET fibers provided by DuPont and Kosa. From an analysis provided by Bowers, $\langle \cos^6\theta \rangle$, $\langle \cos^8\theta \rangle$, and $\langle \cos^{10}\theta \rangle$ will then be calculated. This provides a nearly complete description of the ODF of both the crystalline and the noncrystalline regions. In addition, solid-state NMR will be used to measure the full ODF of both the crystalline and the noncrystalline regions separately as described above. We will also use x-ray scattering to determine the ODF of the crystalline region. Combining the results of these three methods will provide a complete description of the morphology of the fiber. Simultaneously, mechanical testing will be used to measure the moduli and tenacities of these fibers. Fibers have been obtained from DuPont with systematic variations in the drawing conditions. Additional fibers with systematic variations in the spinning speed will be obtained. The Nanavati theory [H. Nanivati, Ph. D. thesis, 1999] will be extended to semicrystalline materials and verified. It is anticipated that by combining the mechanical testing, modeling and the new characterization techniques will enable the optimization of current processes beyond their current state to obtain higher moduli fibers.

Higher strength fibers will require a different approach. Tenacities may be predicted by understanding the effects of flaws on the strength through fracture mechanics. Flaws will be grown in a controlled manner by fatiguing the fibers and using the J-R curve approach to measure the energy required to grow these flaws to a critical size. The sizes of the flaws that limit the tenacity of current fibers will be determined. In addition, the effect of morphology on the energy required to grow flaws will be determined. SEM will be used to search for and identify inherent flaws leading to early failure. Finally, the ultimate strength of these fibers for various morphologies will be determined.

To ensure a proper analysis, the morphology of the fatigued fiber will be measured on the Raman microscope just prior to the tensile test. After measuring the morphology via Raman, the fiber will be mounted on a tensile stage within the SEM and the flaw distribution will be determined. Subsequently, the fiber will be tested to failure while still in the SEM. Finally, the critical flaw size will be measured by examining the fracture surface using SEM. Thus the same fiber will be fatigued to create a flaw; its morphology determined via Raman microscopy; its flaw size distribution determined via SEM; its tensile properties measured; and the critical flaw size determined. This will provide the most detailed analysis of the relationship between morphology and tensile properties currently possible.

By combining the orientation studies with the fracture studies, we propose that we will be able to provide a rational means for modifying the morphology of melt-spinnable industrial fibers to obtain substantial increases in both the modulus and the tenacity.

Outreach to Industry:

DuPont, Honeywell, and KoSa have expressed interest in a better understanding of the factors which limit the modulus and the tenacity of high strength, melt-spun fibers. We intend to consult with them as we proceed in this project to ensure that we address the needs of the industry and they will provide a range of fibers to be incorporated in this program. Fibers have been made by DuPont specifically for this project, and based on both our needs and theirs. The results have been presented at The Fiber Society meeting in October, 2002. We will continue to present results at professional meetings and publish them in well recognized journals.

New Resources Required:

Stroke extension system for fatigue testing instrument, \$ 12,000, is needed to accommodate samples whose extension after fatiguing are excessive.