Chapter 8: Poly(urethane-urea) Fibers with Soft Segments of Ultra-low Monol Content Poly(propylene glycol)

The work presented in this chapter details the results of investigations of poly(urethane-urea) fibers with ultra-low monol content soft segments. Bayer Corporation, which sponsored and provided materials for this project, is a leading manufacturer of spandex fibers. They were able to supply a limited number of spandex fibers with compositions comparable to those used in the film studies. Chapters four through seven were accounts of the influence of various chemical variables on morphological, thermal, mechanical, and orientational properties of PUU elastomeric films. It is accepted that the trends seen in those chapters provide valid and valuable insights into the behavior of PUU elastomers. Several of these trends should, in general, be expected to also apply to dry spun PUU fibers. It was of interest to ascertain whether those results are directly applicable to PUU fibers since it is hypothesized that some differences between film and fibers will exist due to the differences in fabrication time scale and orientation effects induced during fiber drawing. The first group of investigations, presented in this chapter, ascertains differences between PUU film and fiber elastomers. A second group of investigations begins an assessment of the influence of process variables upon the morphology of the limited PUU fibers that were supplied by the sponsor.

Section 8-1: Overview

Fibers for these studies were synthesized and fabricated by Dr. Bruce Lawrey of Bayer Corporation via dry spinning from DMAc. Details of the dry spinning process are found in Section 8-3. They represent a culmination of a
development process that included the investigations of PUU fundamentals detailed in chapters 4-7. Those investigations resulted in an understanding of how various chemical variables, especially over the narrow compositional ranges relevant to spandex fibers, influenced the morphology, and ultimately the thermal, mechanical, and orientational properties of PUU films. That knowledge aided in the selection of compositions for preliminary fiber production. Fiber spinning was conducted at the facilities of Bayer AG in Germany and proved to be considerably more difficult than the fabrication of PUU elastomer films. Many of the compositions used in the elastomer film studies were unable to be spun into useful spandex fibers. This complication prevented obtaining fibers with compositions identical to those used in the film studies in Chapters 4-7, though in a few instances the compositions are very nearly the same. The first group of studies in this chapter relate the comparisons between this limited group of fibers and corresponding films. The second and limited group of studies begins to investigate the influence of process variables such as duct, air, and spin gas temperatures, line speed, and twister pressure on fiber structure and properties.

**Section 8-2: Introduction & Literature Review**

Section 2-5 discusses in greater depth the historical development of spandex fibers while only essential contributions to the art will be presented here. Spandex fibers were first invented in the 1950s as a result of a desire to improve upon "natural" rubber fibers.¹ Rubber fibers are produced slowly in comparison to synthetic fiber spinning processes and are subject to degradation in ambient atmospheric conditions due to the presence of the double bond in cis-
polyisoprene. As such, rubber fibers were deficient in terms of both process economics and material properties.

Otto Bayer, at I.G. Farben (later Bayer AG), developed the first poly(urethane)s and poly(urethane) fibers. It was due to the efforts of researchers at Bayer and DuPont that eventually led to what are now recognized as spandex fibers. “Fiber K”, a dry-spun spandex fiber, by DuPont was introduced in 1959 based upon a PTMEG soft segment. Fiber K became known as Lycra™ in 1962 when it went from pilot plant production to commercial plant production. The fibers were dry spun (Figure 8-1) from a solution of the polymer

---

**Figure 8-1. Dry Spinning Process Schematic.** a) metering pump, b) filter, c) spinning solution, d) heated gas, e) spinnerets, f) heated spinning chamber, g) onset of twisting, h) chamber length ca. 4 to 8 m, i) hot gas exhaust, k) fresh gas, l) false twisting device, m) finishing (Schematic is a modification of a figure provided by Dr. Bruce Lawrey of Bayer).
in dimethyl formamide (DMF). Bayer responded to developments in the United States in the late 1950s and introduced the first commercial version of “Dorlastan” in 1964. Dorlastan was a dry-spun spandex fiber, with a polyester soft segment, spun from solutions of polymer and dimethyl acetamide (DMAc).\(^1\)

Spandex as it is currently produced reflects the work done in the past with nearly all spandex fiber produced across the globe using poly(tetramethylene ether glycol) as the soft segment material. Most spandex formulations are still based upon MDI and either EDA and/or PDA and are produced by a dry-spinning process from solutions of polymer in either DMAc or DMF. In dry-spinning (Figure 8-1), a solution of the PUU in DMAc or DMF is exuded from a collection of spinnerets in a heated chamber where the solvent is flashed off. The resulting coagulated fibers are drawn and twisted together into bundles during this process. Spandex fibers produced using ultra-low monol content PPG have the potential for greatly impacting the process economics of spandex production. Such fibers can potentially be produced with soft segments that are more economical than PTMEG and may have higher solids throughput during processing due to lower solution viscosities as was discussed in Chapter 4.

The majority of literature relating to spandex is found within patents, with few systematic and/or detailed studies of chemical or process variables readily available. The compositions and spinning of spandex fibers is considered a proprietary art by the commercial producers and there is undoubtedly a wealth of information unavailable to the public regarding this area. The prohibitive expense of spinning equipment and the knowledge and experience base
necessary for successful fiber production has largely inhibited academic investigations of spandex fibers. Consequently, there are few studies to be found within journals and proceedings.

A recent study by Lee et al. on segmental and chain orientation of spandex fibers has particular relevance to the present work. Lee et al. investigated four PTMEG-based spandex fibers of varying composition and production history. Two of these fibers were PUs and two were PUUs, with much of the work being conducted on film analogs to the fibers. Lee’s film results are in agreement with the results presented for the first group of experiments described in Chapter 7. More importantly, when hard segment orientation was investigated for spandex fibers undergoing deformation, results

![Figure 8-2: Orientation of hard segments as of draw ratio in two spandex fibers](image)
supporting those seen for the second group of experiments in Chapter 7 were seen. It was seen that initially the hard segment orientation function had appreciable positive values (ca. 0.63 and 0.39 for DR=1) before decreasing and passing through a minimum (Figure 8-2).\textsuperscript{2} The decrease in hard segment orientation is minor (~0.1) in comparison to the magnitude of the overall orientation and Lee et al. describe it, perhaps mistakenly, as being relatively level.\textsuperscript{2} Their results provide additional support for the conclusion of residual hard segment orientation described in Chapter 7.

**Section 8-3: Experimental**

The fibers used in this study were dry-spun from DMAc by Dr. Bruce Lawrey of Bayer. Compositions varied, but were similar to those seen in Chapters 4-7. Isophorone diamine (IPDA) was used as a urea chain extender to disrupt HS symmetry. Duct temperatures varied from 220C to 240C, air temperature varied from 210C to 310C, and the spin gas temperature varied from 188C to 239C. The line speed varied from 420 to 1000 m/min, though most line speeds were 420 m/min. The twister pressure, which is a measure of the rate of fiber twisting, varied from 0.4 bar to 1.0 bar. Most twister pressures were either 0.6 or 1.0 bar. Fibers are twisted together to form bundles of 4 or more fibers (Figure 8-3), though the degree twisting is relatively low. Hence, unless otherwise specifically stated, the term fiber will refer to a bundle of four or more filaments.

There is a variety of difficulties encountered when evaluating fibers with the methods used in Chapters 4-7. Care must be taken during DSC experiments to ensure good sample to pan contact. This was done by cutting the fibers into
small whiskers (ca. 1-2 mm in length) and packing the whiskers into the DSC sample pan. Single fibers proved to be too small for analysis in the DMA available, necessitating that bundles of fibers be evaluated instead. Fiber circular cross-sectional areas are not constant, and thus the cross-sectional area provided for calculation of the storage and loss moduli is only an approximation. General information obtained from the tan delta curve will still be useful. Unlike films, the thickness of a fiber varies as a function of the radius leading to a nonconstant path length for birefringence preventing its use in this study. An infra-red microscope is necessary for linear dichroism studies of fibers, again due to inconstant path length through a fiber. Wide angle x-ray scattering and small

Figure 8-3: FESEM micrographs of spandex fibers.
angle x-ray scattering are still applicable, though analysis which requires the thickness of sample bundles will be more complicated. It was seen that for undeformed films, the alignment of the film sample (meridinal versus equatorial scans) within the Kratky camera did not affect the SAXS results (Figure 8-4). In contrast, meridinal and equatorial scans differed appreciably for fibers (Figure 8-4). The meridinal scans exhibited sharper, more well defined peaks and shoulders, whereas the equatorial scans showed lower intensity. The more defined meridinal scans, which show the interdomain distance along the fiber, were used in these studies. SAXS patterns along the meridinal were normalized only for exposure time, neglecting differences in fiber bundle thickness.

**Section 8-4: Experimental Results**

The SAXS profiles for three sets, film and fiber, of materials with comparable compositions are shown in Figure 8-5. In each case, the fiber material contains slightly less hard segment content than the film material. Each of the fibers also has a higher EDA/PDA chain extender ratio than the comparable film. Bearing in mind those two differences in composition, it is seen
that for each set of materials, the SAXS profiles differ in 3 ways. First, the fiber curves display lower intensity, which is likely due to the use of fiber samples that were thinner than the comparable film samples. It may also be due to differences in the electron density distributions for system with slightly different hard segment compositions (differences in chain extender ratios). Second, the film curves appear to have sharper peaks than the fiber curves. The film samples, which are thicker than the fibers, may have better resolved peaks. Third, in all instances in Figure 8-5 and in Figure 7-14A and 7-14B, the interdomain spacing is seen to decrease for oriented materials. The increase

**Figure 8-5: Small angle x-ray scattering profiles for fibers and films of comparable composition.**
seen in Figure 7-14C is very minor in contrast. Films and fibers differ in two key aspects of their production. The time-scale for evaporating the solvent during fiber spinning is on the order of seconds, while the time-scale for cast films is on the order of hours. The significantly longer times involved in film casting may allow for development of larger and more perfect hard domains, leading to larger interdomain spacings for films. Fibers, unlike films, undergo a drawing process during solvent evaporation. Due to these differences, it is likely that the initial structure of films and fibers will differ, with the film more likely to be in an equilibrium structure.

When the soft segment glass transition of a fiber and comparable film are compared (Figure 8-6), it is seen that there is only a very minor difference (~1.0°C). The film has the slightly higher soft segment glass transition, which may

![Figure 8-6: DSC determine soft segment glass transition of fiber and film PUUs of comparable composition.](image)
be due to stronger, more cohesive hard domains influencing soft segment mobility in the film slightly more than in the fiber. However, it should also be noted that there is slightly more hard segment content in the film case, may also provide a partial explanation of these results. Repeated DSC heatings of a PPG-based PUU fiber sample (Figure 8-7) showed no appreciable differences in the soft segment glass transition behavior. However, repeated DSC heatings of a PTMEG-based PUU fiber sample (Figure 8-8) clearly indicated that subsequent heatings resulted in minor increases of the soft segment melting point and amount of crystallization content (as determined from area under melting endotherm). In contrast, unoriented films did not show such behavior.

Comparing fibers and films with DMA is complicated by the uncertainty associated with determining the cross-sectional area of fiber bundles. This makes drawing conclusions regarding the absolute values of the storage and
loss moduli difficult and for this reason, only the tan delta curves will be considered. From the tan delta curves, it is seen that there is no appreciable difference in soft segment glass transition, though the film exhibits greater damping at this temperature. This is likely due to the fibers being in a non-equilibrium, slightly oriented form that is less able, than the film, to dissipate energy.

The lack of appreciable difference in soft segment glass transition can be taken as an indicator that there is not a significant variance in the degree of phase mixing between fibers and films. This while detracting somewhat from arguments regarding development of phase separation in fibers, does not counter the argument that there may be a greater number of smaller hard domains in a fiber than in a film.
From Figures 8-10 through 8-13, it appears that for the process variables investigated, none of them influence interdomain spacing significantly over the variable ranges considered.

**Figure 8-9:** Differences between fiber and film PUUs as denoted by DMA.

From Figures 8-10 through 8-13, it appears that for the process variables investigated, none of them influence interdomain spacing significantly over the variable ranges considered.

**Figure 8-10:** Influence of duct temperature on interdomain spacing.

**Section 8-5: Conclusions**

It was seen, that as hypothesized, there are differences between films and fibers as noted by these experiments. First, for comparable compositions, fibers have greater interdomain spacings than films, as determined from SAXS scans.
along the meridinal, possibly due to increased numbers of smaller hard domains. Second, fibers display lessened damping near the soft segment glass transition (for 1 Hz) than films. Third, though no appreciable differences exist for soft segment glass transitions for films and fibers, melting temperatures of PTMEG-based fiber soft segments display the influence of process history and increase with subsequent heatings.

Figure 8-11: Influence of air and spin gas temperature on interdomain spacing.

Figure 8-12: Influence of line speed on interdomain spacing.
Insights with respect to the dependence of morphology on process variables as determined with SAXS revealed that process variables have nearly no influence. Interdomain spacings for fibers over the ranges of process variable investigated were seen to be independent of those variables. From these results, it was seen that compositional variables have a pronouncedly greater effect upon the morphology of PUU fibers than process variables.

**Acknowledgments**

Fibers investigated were provided by Dr. Bruce Lawrey of Bayer Corporation. Financial support was provided by Bayer Corporation.

**Figure 8-13: Influence of twister gas pressure on interdomain spacing.**

Insights with respect to the dependence of morphology on process variables as determined with SAXS revealed that process variables have nearly no influence. Interdomain spacings for fibers over the ranges of process variable investigated were seen to be independent of those variables. From these results, it was seen that compositional variables have a pronouncedly greater effect upon the morphology of PUU fibers than process variables.

**Acknowledgments**

Fibers investigated were provided by Dr. Bruce Lawrey of Bayer Corporation. Financial support was provided by Bayer Corporation.
Section 8-7: Chapter 8 References