

Chapter 9: Conclusions and Recommendations

Section 9-1: Conclusions

In this study, ultra-low monol content PPG-based PUU elastomers with compositions comparable to those used in the manufacture of spandex fibers were evaluated in terms of their morphology, orientational, thermal, and mechanical properties. The PPG used in these investigations differed appreciably from the base-catalyzed PPG used in prior PUU investigations in that it had greatly enhanced difunctionality, and a narrower molecular weight distribution. In comparison to the PTMEG commonly used in PU and PUU elastomers and fiber, the ultra-low monol content PPG had an appreciably narrower molecular distribution, higher molecular weights (4000 g/mol and 8000 g/mol PPGs versus 2000 g/mol PTMEGs), and was atactic preventing soft segment crystallization. It had been proposed that compositional variables such as soft segment length, molecular weight distribution of the polyols used for soft segments, soft segment type, hard segment type, and hard segment content would influence the morphology, orientational, thermal and mechanical properties. It was acknowledged that the ranges of some of the variables, particularly hard segments content, being investigated were limited. Two variables of particular interest were soft segment length and molecular weight distribution. Prior to this endeavor, no investigations had been conducted on linear PUUs with PPG soft segments of molecular weight greater than ca. 3000 g/mol. Similarly, the influence of polyol (and soft segment) molecular weight distribution upon morphology and properties had been largely neglected.

Increasing the length of the soft segments resulted, unsurprisingly, in increased interdomain spacings (SAXS) and a less fine grain structure in the surface morphology (AFM). The thickness of the interphase between the hard and soft domains was independent of the soft segment length as determined by SAXS. Increased soft segment length resulted in decreased and narrower soft segment glass transitions. Coupled with constant interphase thickness, this implies that the fraction of the soft segment that is restricted by hard domains increases as soft segment length decreases. Birefringence was seen to increase for PUUs as soft segment length decreased and hard segment orientation was seen to dip less negatively for materials with shorter soft segments. Stretched PUUs with shorter soft segments also showed greater permanent set and residual system average and hard segment orientation. As soft segment molecular weight decreased the tensile strength of the elastomers increased and point of upturn in the stress-strain curves was seen as lower elongations.

Differing the type of hard segment by varying the diamine chain extender ratio (EDA:PDA) resulted in no appreciable changes. Increasing the amount of hard segment from 6.3wt% to 9.0wt% resulted in no significant change in SAXS results and only a slight increase in hard material (AFM). The interphase thickness was also seen to be unchanged over that small range of hard segment contents. The soft segment glass transition (DMA and DSC) was seen to slightly increase and broaden as the amount of hard segment material increased. Birefringence was seen to slightly increase with increasing hard segment content.

Investigation of the influence of soft segment molecular weight distribution was achieved by blending of 4000 g/mol and 8000 g/mol PPG diols with the low molecular homolog tri(propylene glycol). This blending resulted in diols with number average molecular weights ranging from 1500 g/mol to 2500 g/mol. The interdomain distances of these materials increased with decreasing soft segment molecular in stark contrast to what was seen when varying soft segment molecular weight of materials based upon unblended polyols. Additionally, as the MW of the polyol blend decreased, there was a striking increase in the amount of hard material seen by AFM. This prompted the conclusion that the polyols used to produce PUs and PUUs contribute to both soft and hard domain formation. These results and conclusion were verified through the use of tri(ethylene glycol) as a low molecular weight diol blending agent. The soft segment glass transition behavior (DMA and DSC) more greatly resembled that of PUUs based upon neat 4000 g/mol or 8000 g/mol PPG than that of those based upon a 2000 g/mol PPG. Birefringence behavior of TPG containing systems was comparable to that seen for materials with increased hard segment content and/or decreased soft segment molecular weight. Deformed TPG containing materials displayed less permanent set, presumably due to the decreased bidentate hydrogen bonding induced coherence of the hard domains and showed considerably less residual hard segment and system average orientation than those based upon 2000 g/mol PPG. PUUs based upon blends of 8000 g/mol PPG and TPG show increased tensile strength as compared to 8000 g/mol based materials without TPG. The TPG containing materials show

stress-strain behavior most comparable to neat 2000 g/mol based formulations. This indicates that the low molecular weight components of the soft segment molecular weight distribution distinctly influence the mechanical properties. Again, this is again believed to be a consequence of those low molecular diols being incorporated into the hard domains as urethane type chain extenders, resulting in more hard domain material.

Materials with mixed soft segments of PPG and PTMEG displayed both cold crystallization and strain-induced crystallization for the compositions studied. This was regardless of whether the prepolymers were synthesized using a mixture of polyols (PPG and PTMEG) or if each polyol is end-capped separately with 4,4'-MDI and then blended together prior to chain extension. When TPG is included in the blend of polyols, there is an apparent decrease in strain-induced crystallization as detected in WAXS patterns as contrasted with non-TPG containing PUUs with comparable composition. Similarly, the normalized extent of cold crystallization is decreased for TPG-containing formulations. It appears that inclusion of TPG leads to more hard domain material which restricts the ability of the soft segment PTMEG to crystallize.

It was seen that films and fibers of comparable composition, while being very similar, are not directly comparable. This was seen most pronouncedly in SAXS results which show fibers having a smaller interdomain spacing than comparable films. For the process variables and the ranges of those variable investigated, no significant influence of those factors upon morphology as assessed by interdomain spacing was seen.

To summarize, it was determined that compositional variables influence the morphology more greatly than process variables. Of the various compositional variable investigated and for the ranges of those variable investigated, that soft segment molecular weight and the molecular weight distribution of the polyols used for soft segments had the most impact upon the morphology, thermal, mechanical, and orientation properties. The influence of the different portions of the molecular weight distribution upon the properties of PUUs had until this time been largely neglected. With careful consideration of the molecular weight and molecular weight distribution of the polyol it is possible to fabricate PPG-based spandex fibers comparable in terms of percent elongation, permanent set, and tensile strength (though the onset point of strain-hardening may differ), to those produced with PTMEG soft segments.

Section 9-2: Recommendations

There are a number of suggestions for further studies that would further enhance the understanding of this topic. First, it would be interest to determine more definitively what portions of the polyol molecular weight distribution will act as soft segments and as hard segment chain extenders. The ultra-low monol content PPG produced by Bayer lends itself well to this endeavor, since it has a narrow molecular distribution (<1.1). Tri(propylene glycol) is the largest homolog of PPG that is readily available, which would require obtaining larger homologs of PPG (e.g. tetra-, penta-, hexa-) for use as a polyol blending agents.

Second, the studies presented in Chapter 8 would be much more definitive if the films and fibers could be fabricated from the same spinning solutions. The compositions of the materials would then be identical and the

effect of synthesis scale (bench versus pilot) would be eliminated. Any resulting differences in the films and fibers would then be solely attributable to fabrication technique.

Third, assessing the orientation of fibers and comparing those results to the studies on films in Chapter 7 may provide further insight into the behavior of spandex fibers. Lee et al. have seen the presence of residual orientation in spandex fibers though their work did not begin to investigate variables associated with the processing of fibers. Nor did their work consider systematic changes in compositional variables. While the process variables did not show an influence on the morphology as denoted by interdomain spacings, it is expected that drawing of the fibers will influence the molecular and/or segmental orientation.

Fourth, while the differences between films and fibers for thermal properties were not significant, a more systematic study of process variables on those properties may supply insights into the microstructure and behavior of the spandex fibers. Hopefully, more levels of each process variable could be provided and across a broader range when possible.

Fifth and finally, the present study was severely limited in terms of material compositions which would be appropriate for spandex fiber manufacture. Broadening the range of compositions, especially with regard to hard segment content and type, would lead to a much better understanding of PUU elastomers and fibers.

Section 9-3: Chapter 9 References

- 1) Lee HS, Ko JH, Song KS, Choi KH. J Appl Polym Sci 1997: 74, 1821.