Chapter 9

Summary and Recommendations for Future Work

9.1 Summary

The essence of this research work is well encapsulated by the title of this work, namely, "*Crystallization, Morphology, Thermal Stability and Adhesive Properties of Novel High Performance Semicrystalline Polyimides*". Indeed the title is emblematic of the broad range of topics covered in this research. These topics were critically important in the way they were interrelated for the overall success of this work. In this regard, the present chapter concludes this thesis by summarizing the motivation and the achievements of this research and recommending future work in this area.

A number of advances have been made in the field of polyimides in the past two decades that have made possible their use in diverse applications ranging from 'interlayer dielectric' to 'structural adhesive' that helps to hold the wing panels and fuselage of aircraft together. Despite these advances, several research topics in this area have still not received adequate attention. One such major area has been the development of linear aromatic polyimides that are amenable to melt processing. It is thus no surprise, that to this day with very few exceptions like New-TPI[1,2] and possibly some versions of LARC-TPI, which can be processed from the melt to a small extent, almost all polyimides (including the thermoplastic ones) are exclusively being processed by the solvent route. While polyimides offer tremendous opportunities due to the diverse range of useful properties, this limitation has certainly impeded their advancement with respect to large scale applications. Melt processing is obviously beneficial as it is (1) environmentally friendly (does not require handling dangerous solvents often associated with polyimides) (2) involves significantly shorter cycle times (3) processing is easier (4) often economically more attractive and (5) makes some large scale applications viable.

Another attractive feature desirable in linear aromatic thermoplastic polyimides is the presence of crystallinity, which leads to substantial improvement in many properties including solvent resistance, radiation stability and partial retention and enhancement of certain mechanical properties much above the glass transition temperature. These attributes make semicrystalline polyimides especially attractive and efforts to develop these materials continue among various research groups around the world[3, 4] and here at Virginia Tech[5,6,7]. This work constitutes another step in this direction. In this regard, the present work has accomplished significant goals in this area both with regards to the fundamental viewpoint and with respect to future potential uses of these polymers as high temperature and high performance adhesives. The broad research objectives successively attained by the work presented within this dissertation can be briefly listed as:

(1) High temperature and high performance semicrystalline polyimides that display superior solvent resistance and higher thermal stability, have been developed.

(2) The polyimides are also melt processable. Melt viscosity was studied with respect to melt temperature, melt time (at different melt temperatures) and frequency (also at different melt temperatures).

(3) One of these polyimides has been used extensively as a hot-melt adhesive. Some of the promising results of this study were:
   - Simple and economical grit blasting was a sufficient surface treatment.
   - Bonding process was simple, solvent free and involved relatively less times.
   - Very high lap-shear strengths of ca. 6600-8400 psi were obtained.
   - The strengths remained unaffected on exposure to various common solvents.
   - Considerable durability of these strengths was observed with respect to high aging and testing temperatures.

(4) Wedge and DCB tests revealed the considerable solvent resistance and fracture toughness of this adhesive respectively.

(5) Also, another attractive and distinguishing feature of the research has been that all the polyimides synthesized are based on monomers that are commercially available. This makes these polyimides potentially attractive from the commercial standpoint in the future.

(6) One more important characteristic attained in these polyimides was the fast crystallization kinetics from the melt. This feature is particularly important as faster crystallization kinetics removes any need of a post annealing process to introduce crystallinity in the material. The semicrystalline morphology and bulk

crystallization kinetics was studied with respect to crystallization temperature, previous melt temperature and melt time.

(7) A new polyimide based on the same diamine but a different dianhydride, BTDA was developed. Some features of this study were:

- The polyimide displayed considerable bulk thermal stability and recrystallization stability from high melt temperatures.
- Intermediate dual melting behavior with an intermediate recrystallization exotherm.
- Additional melting shoulders due to secondary crystallization and absence of a continuous melting-recrystallization process.
- A crystal thickening phenomenon at high crystallization temperatures.

9.2 Recommendations for Future Work

While there were considerable doubts about the bulk melt processing of these materials at the start of this work, the research presented in this thesis has come a long way in removing many of these reservations. It has been proved that for at least one of the polyimides, TPER-BPDA, the melt processing can be effectively conducted. Although the lower molecular weight version of this polyimide (M_n=15,000 daltons) provided a sufficiently low viscosity for extensive testing as a hot melt adhesive, it also necessitated making large amounts of the polyimide film. For any such large applications of this material, the availability of large amounts of material in film form (which cannot be just made using the traditional film casting during synthesis) would be necessary. In this regard, there is an important need for film extrusion of this material. This could be a promising area of research as large scale film production, if possible, would make adhesive and other applications feasible. The melt extrusion itself could be attempted in two ways – (a) either the final polyimide could be extruded into a film form or (b) partially imidized polymer could be extruded (with the completion of imidization reaction during the extrusion process). For (a), the shear thinning behavior of the polyimide will make it easier to be extruded. For (b), the partially imidized polyimide would provide lower viscosity and possibly a lower melt temperature requirement for extrusion. The molecular weight of the polyimide, its degree of imidization and the extrusion temperature will be important factors in this regard. Also, there is some possibility of foam formation due to evolution of water during the imidization reaction.

Before the above mentioned experiment are attempted, it may be often more useful to first extrude the material into a fiber form as it requires less material and is usually easier to carry out. Once the conditions for such a process are optimized, film extrusion could be carried out subsequently. WAXD experiments on such fibers may produce a significantly better defined (in terms of increased and sharper reflections) pattern, thus making it possible to determine the unit cell crystal structure with considerable accuracy. Additionally, the effect of either a film and fiber extrusion process on the percentage crystallinity and melting behavior could be studied. The study of percentage orientation and the crystalline morphology could be an important area of research. It would also be interesting to see the effect of melt extrusion process on the partial melting and recrystallization behavior during the heating scan in a DSC, as the nature of the crystalline morphology (to the lamellar level) is expected to be different.

Another exercise attractive from a fundamental viewpoint is molecular modeling of the various polyimides. Such a study may throw considerable light on the nature of the *conformation* of the overall chain and the individual repeat units. Such information may then be correlated with the information from SAXS experiments to check if the lamellar thickness' could be correlated with such information. Also, the information on chain conformation together with the crystal unit cell data could be useful in getting to the constitution of an average unit cell and subsequently the crystalline density. Obtaining the absolute crystalline and amorphous densities could be a very useful information for subsequent studies with this material. The percentage crystallinity for a given sample could then be easily calculated using density measurement techniques. This information, in conjunction with other DSC experiments, would also be useful in calculating another useful parameter, the heat of fusion for the 100% crystalline material.

TPER-BPDA polyimide has yielded encouraging adhesion results with respect to lap-shear, wedge and DCB tests. However, 'peel test', which is another important and widely utilized adhesion test has not so far been conducted. This test, if conducted, could provide important information for this polyimide adhesive. The important parameters with respect to this study could include the bonding conditions, cooling rate from the melt and the peel rate. This study, however would require substantial amounts of the polyimide film and thin titanium alloy sheets (ca. 50 microns).

From an application viewpoint, another area of future research involves the potential use of this material as an interlayer dielectric. Obviously, the important parameter from this viewpoint is the 'dielectric constant' of the polyimide and will need to be determined first. The thermal expansion coefficient (CTE) is another important parameter from this viewpoint as a large CTE could cause significant mismatch between the bonded adherends. Some preliminary work by this author has yielded a very low CTE of 15 X 10^{-6}/°C (from room temperature till ca. 250°C), which is a very encouraging result. Further work, however, would need to be carried out in this regard.

While many polyimides and associated copolymers have been synthesized in this research work (see Table 8.1), only two of these polyimides have provided attractive properties. Especially, the results of the polyimide based on TPER diamine and BPDA dianhydride have been particularly encouraging from a thermal stability, crystallization and adhesion viewpoint. Thus, in this authors opinion, future work should focus more on the scaling up the synthesis of this polyimide rather than varying the chemical structure of the polyimide. Further work, that needs to be carried out in adhesion and other areas demands much larger quantities of this material than is presently available.

References:

[1] Hou, T.H. and Reddy, R.M. *SAMPE Journal*, **Jan** 1991, 38.

[2] Hsiao, B.S., Sauer, B.B. and Biswas, A. *J.Polym. Sci., Part B,* 1994, **32**, 737.

[3] Tamai, S., Ohta, M. and Yamaguchi, A. *Polymer* 1996, **37**, 3683.

[4] Hsiao, B.S., Kreuz, J.A. and Cheng, S.Z.D. *Macromolecules* 1996, **29**, 135.

[5] Muellerleile, J. *Ph.D. Thesis*, Virginia Polytechnic Institute and State University, Sep, 1991, Blacksburg, VA.

[6] Brandom, D.K. *Ph.D. Thesis*, Virginia Polytechnic Institute and State University, June 1996, Blacksburg, VA.

[7] Srinivas, S. *Ph.D. Thesis*, Virginia Polytechnic Institute and State University, June 1996, Blacksburg, VA.