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IMPREGNATION AND COATING OF HIGH-MODULUS POLYMER FIBERS: EFFECTS ON THE COMPRESSIVE STRENGTH AND OTHER MECHANICAL PROPERTIES

A Dissertation Presented
by
CHRISTIAN LIETZAU

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1993

Department of Polymer Science and Engineering
IMPREGNATION AND COATING OF HIGH-MODULUS POLYMER FIBERS:
EFFECTS ON THE COMPRESSION STRENGTH
AND OTHER MECHANICAL PROPERTIES

A Dissertation Presented
by
CHRISTIAN LIETZAU

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ABSTRACT

IMPREGNATION AND COATING OF HIGH-MODULUS POLYMER FIBERS:
EFFECTS ON THE COMRESSIVE STRENGTH
AND OTHER MECHANICAL PROPERTIES
SEPTEMBER 1993
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The compressive failure of high-modulus polymer fibers, such as poly(p-phenylene terephthalamide) (PPTA) and poly(p-phenylene benzobisthiazole) (PBZT), occurs at stresses an order of magnitude smaller than their tensile failure. A literature review is presented which covers the numerous theories and models for the compressive strength and failure of these fibers as well as of uniaxial composites, which are structurally similar and fail in an analogous fashion. It is pointed out that the smallest shear modulus of any material is a fundamental upper bound to its compressive strength.

Physical combination of high-modulus polymers with rigid inorganic materials by impregnation or by deposition of coatings are presently the most promising routes to improved compressive strength and are the research topics presented in this dissertation.
PPTA fibers, obtained by spinning from nematic solution, have been impregnated with up to 20 wt-% of a waterborne, highly crosslinkable melamine-formaldehyde resin and with approximately 5 wt-% of sodium silicate from a colloidal aqueous solution. PBZT fibers have also been impregnated with approximately 5 wt-% of sodium silicate. PPTA fibers, obtained by spinning from isotropic solution, have been impregnated with up to 40 wt-% of sodium silicate. None of the impregnations has led to improved compressive strength or other mechanical properties.

Kevlar® 49 PPTA fibers and heat-treated PBZT fibers have been surface modified with siloxane and silicate functionalities in order to make fibers wettable by aqueous solutions of sodium silicate and to provide good adhesion to silicate coatings. The surfaces of as-received and modified fibers have been characterized by X-ray photoelectron spectroscopy. PBZT and PPTA fibers showed little or no decrease of their tensile properties as a consequence of the surface modification. Glass coatings have been applied to single filaments by dip-coating in aqueous sodium silicate solution followed by drying. Coated PPTA and PBZT fibers with shear moduli as high as 5 GPa have been prepared. The compressive strain at failure of PPTA filaments coated with a 0.5 μm thick silicate coating was raised to 0.6%, compared to 0.4% for uncoated filaments. These compressive failure strains correspond to compressive strengths of approximately 500 and 400 MPa, respectively.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGEMENTS</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
</tbody>
</table>

## Chapter

**1. INTRODUCTION** ................................................................. 1

1.1 Description of Problem and Motivation .................................. 1
1.2 Scope of Dissertation ....................................................... 5

**REFERENCES** ........................................................................ 7

**2. BACKGROUND** .................................................................... 9

2.1 Introduction to High-Modulus Polymer Fibers ............................ 9
2.2 Compressive Failure of Uniaxial Composites and High-Modulus Polymer Fibers ................................................................. 13

2.2.1 Compressive Failure of Uniaxial Composites .......................... 13

2.2.1.1 Theories and Models of Compressive Failure in Composites .... 13
2.2.1.2 Correlation of Composite Compressive Strength with Other Material Properties .......................................................... 20

2.2.2 Compressive Failure of High-Modulus Polymer Fibers .............. 23

2.2.2.1 Theories of Compressive Failure of High-Modulus-Polymer Fibers ........................................................................... 23
2.2.2.2 Experimental Observations of Compressive Failure in Highly Oriented Polymers .............................................................. 28
2.2.2.3 Correlations between Fiber Compressive Strength and Other Fiber Properties ............................................................. 34

2.3 Attempted Routes to Improving the Compressive Strength of Polymer Fibers and Uniaxial Composites ............................... 39

2.3.1 Improving the Compressive Strength of Uniaxial Composites ...... 39
2.3.2 Improving the Compressive Strength of High-Modulus Polymer Fibers

REFERENCES

3. EXPERIMENTALS

3.1 Materials

3.2 Microscopy

3.2.1 Optical Microscopy
3.2.2 Scanning Electron Microscopy

3.3 Mechanical Tests

3.3.1 Tensile Tests
3.3.2 Torsion Test
3.3.3 Compression Tests

REFERENCES

4. IMPREGNATED HIGH-MODULUS POLYMER FIBERS

4.1 Introduction

4.1.1 As-Coagulated Structure of Polymers Precipitated from Lyotropic Solutions
4.1.2 Impregnated High-Modulus Polymer Films and Fibers

4.2 Experimental

4.3 Results

4.3.1 Diffusion through Isotropic and Anisotropic PPTA Films
4.3.2 Impregnation of PPTA Films and Fibers
4.3.3 Mechanical Properties of Impregnated Fibers

4.4 Summary of Impregnation Results

REFERENCES

5. GLASS COATED HIGH-MODULUS POLYMER FIBERS

5.1 Introduction

5.2 Experimental

5.2.1 Surface Modification
5.2.2 Analysis

REFERENCES
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Comparison of typical properties of some uniaxial (0°) composites</td>
<td>2</td>
</tr>
<tr>
<td>2.1. Mechanical properties of various reinforcing fibers</td>
<td>12</td>
</tr>
<tr>
<td>2.2. Summary of results of LRS studies of the compressive deformation of HM-polymer fibers</td>
<td>32</td>
</tr>
<tr>
<td>2.3. Properties of PBZT and brominated PBZT (Br-PBZT) fibers after heat-treatment</td>
<td>43</td>
</tr>
<tr>
<td>3.1. Mechanical properties of polymer filaments used in this work</td>
<td>58</td>
</tr>
<tr>
<td>4.1. Spinning parameters for wet-spinning of isotropic and dry-jet wet-spinning of nematic solutions of PPTA in sulfuric acid</td>
<td>75</td>
</tr>
<tr>
<td>4.2. Results of U-tube diffusion experiment</td>
<td>80</td>
</tr>
<tr>
<td>4.3. Dimensional changes observed upon drying of polymer filaments</td>
<td>81</td>
</tr>
<tr>
<td>4.4. Composition of various sodium silicate impregnated fibers as determined by elemental analysis</td>
<td>83</td>
</tr>
<tr>
<td>4.5. Compositions of as-coagulated PPTA fiber, spun from nematic solution and impregnated with melamine-formaldehyde resin in aqueous solution by soaking for 10 days</td>
<td>85</td>
</tr>
<tr>
<td>4.6. Resin and silicate contents in impregnated PPTA fiber determined by elemental analysis, ash content, or thermogravimetric analysis</td>
<td>86</td>
</tr>
<tr>
<td>4.7. Average mechanical properties of as-spun (AS) and with sodium silicate impregnated (Imp) polymer fibers</td>
<td>90</td>
</tr>
<tr>
<td>4.8. Mechanical properties of melamine-formaldehyde impregnated PPTA fibers</td>
<td>92</td>
</tr>
<tr>
<td>4.9. Mechanical properties of glycerol impregnated PPTA fibers</td>
<td>96</td>
</tr>
<tr>
<td>5.1. Parameters for XPS multiplex scans of PPTA and PBZT fibers and films</td>
<td>109</td>
</tr>
<tr>
<td>5.2. Elemental surface composition of modified Kevlar 49 fibers in mole-% as determined by XPS (take-off angle = 85°)</td>
<td>117</td>
</tr>
</tbody>
</table>
5.3. Elemental surface composition of Kevlar 49 fibers in mole-% as determined by XPS (take-off angle = 85°) dried by two different drying methods................................................................. 118

5.4. Elemental surface composition of modified PPTA films in mole-% as determined by XPS (take-off angle = 60°) ............................................................ 119

5.5. Elemental surface composition of modified Aftech 1 fibers in mole-% as determined by XPS (take-off angle = 75°) ............................................................ 120

5.6. Elemental surface composition of as-prepared PBZT film and fiber in mole-% as determined by XPS ................................................................. 121

5.7. Elemental surface composition of some modified and vacuum-dried Kevlar 49 by XPS as a function of take-off angle................................................................. 122

5.8. Tensile strength of modified Kevlar 49 and Aftech 1 filaments............................ 126

5.9. Diameter and shear modulus of as-received (*) and glass-coated Aftech 1 and Kevlar 49 fibers................................................................. 127

5.10. Compressive failure strains of uncoated and sodium silicate-coated (t = 0.5μm) Kevlar 49 fibers................................................................. 129

A.1. Elemental compositions and melting points of 2,4-hexadiyne-1,6-diol (HDD) and 1,6-bis(phenylurethane)-2,4-hexadiyne (PUHD)................................. 148
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Repeat units of poly(p-phenylene terephthalamide) (PPTA) and poly(p-phenylene benzobisthiazole) (PBZT)</td>
<td>3</td>
</tr>
<tr>
<td>1.2. Optical micrograph of kink bands in Kevlar 49 filament</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Schematic drawing of a kinked structure</td>
<td>4</td>
</tr>
<tr>
<td>2.1. Failure phenomena in uniaxial composites under compression</td>
<td>15</td>
</tr>
<tr>
<td>2.2. Chemical modifications of PBZT aimed at improving fiber compressive strength</td>
<td>46</td>
</tr>
<tr>
<td>2.3. Chemical modifications of PPTA aimed at improving fiber compressive strength</td>
<td>47</td>
</tr>
<tr>
<td>3.1. Stress-strain curves of the filaments used in this research</td>
<td>58</td>
</tr>
<tr>
<td>3.2. Electric spark cutter set-up for use in the tensile recoil test</td>
<td>62</td>
</tr>
<tr>
<td>3.3. Typical force-time record of a tensile recoil experiment</td>
<td>63</td>
</tr>
<tr>
<td>3.4. Cantilever beam bending test</td>
<td>65</td>
</tr>
<tr>
<td>4.1. Schematic drawing showing swollen network structure of as-coagulated filament [Pottick, 1986]</td>
<td>68</td>
</tr>
<tr>
<td>4.2. Schematic of fiber spinning apparatus</td>
<td>76</td>
</tr>
<tr>
<td>4.3. Schematic of U-tube diffusion experiments</td>
<td>76</td>
</tr>
<tr>
<td>4.4. Generic structure of melamine-formaldehyde resin used for impregnation</td>
<td>77</td>
</tr>
<tr>
<td>4.5. Schematic of set-up used for continuous solution exchange in impregnation experiments</td>
<td>78</td>
</tr>
<tr>
<td>4.6. Melamine-formaldehyde content in impregnated PPTA fibers as a function of resin content in the solution</td>
<td>84</td>
</tr>
<tr>
<td>4.7. Overlays of thermogravimetric analysis plots of as-spun (1) and sodium silicate impregnated (2) isotropic PPTA fibers heated in air</td>
<td>87</td>
</tr>
</tbody>
</table>
4.8. Overlays of thermogravimetric analysis plots of as-spun and melamine-formaldehyde resin impregnated, anisotropic PPTA tape heated in nitrogen ................................................................. 87

4.9. Overlay of XPS high resolution scans of films cast from solutions of PPTA nitrated in the swollen (1) or collapsed state (2) ......................................................... 89

4.10. SEM micrographs of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber ........................................................................ 93

4.11. SEM micrographs (low magnification) of the fracture faces of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber ......................................................... 93

4.12. SEM micrographs (higher magnification) of the fracture faces of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber ........................................................................ 95

5.1. Reactions used to modify PPTA and PBZT fibers, examplified here showing PPTA .................................................................................. 106

5.2. Schematic of pneumatic/hydraulic fiber coating setup .................................................................................................................. 111

5.3. XPS survey spectra of modified PPTA fibers .......................................................................................................................... 114

5.4. XPS survey spectra of modified PBZT fibers .......................................................................................................................... 115

5.5. Overlay of XPS high-resolution scans of as-received and nitrated Kevlar 49 fiber showing a new peak for the nitrated sample due to the nitro-group .......................................................... 116

5.6. Overlay of XPS high-resolution scans of Aftech 1 fiber nitrated for 1) 0, 2) 50, 3) 100, and 4) 150 minutes ..................................................... 116

5.7. Optical micrograph of interference fringes on thinly glass-coated Kevlar 49 filament ........................................................................... 123

5.8. Optical micrograph showing silicate glass beads formed during rapid dip-coating .................................................................................. 124

5.9. Optical micrograph showing kink bands formed in a thickly coated Kevlar 49 filament due to coating drying stresses .......................................................... 124

5.10. Optical micrograph showing helical crack in heat-treated coating on Kevlar 49 ............................................................................... 125
5.11. Electron micrograph showing helical crack in heat-treated coating on Kevlar 49 ................................................................. 125

5.12. Regression plot of data for Kevlar 49 fibers from Table 5.9 for determination of the coating's shear modulus ............................................ 128

5.13. Electron micrograph of silver deposited on a Kevlar 49 filament ....................... 131

A.1. Reaction scheme for the syntheses of 2,4-hexadiyne-1,6-diol (HDD), 1,6-bis(phenylurethane)-2,4-hexadiyne (PUHD) and polyPUHD ................. 146
CHAPTER 1
INTRODUCTION

1.1 Description of Problem and Motivation

Over the last four decades, polymeric composite materials have increasingly been used as substitutes for wood and various metals in structural applications, such as in aircraft, boat hulls, cars, and for man-made space-objects. Of particular interest are the continuous fiber reinforced laminates. The reasons for the wide-spread use of this class of composites are their high performance/weight ratio, the possibility of making fiber reinforced laminates with an in-plane thermal expansion coefficient close to zero, the ease of fabrication via pre-pregs, and the low price/performance ratio. Common matrix materials are thermosetting polyester and epoxy resins as well as a wide variety of thermoplastics for applications where high thermal stability is not of concern. Steel, glass, ceramic, carbon and high-modulus polymer fibers have all distinct properties which may qualify them as the optimal reinforcement for a given application, but in most cases it is the overall balance of properties, including the material costs, which will determine the components of a composite material. Table 1.1 compares some properties of a few uniaxially reinforced composites and also includes some "traditional" structural materials [Franck and Biederbick, 1984].

Advances in polymeric composite materials are often brought about by novel or improved reinforcing fibers, because these dominate the primary composite properties. One of those advances was the introduction of poly(p-phenylene terephthalamide) (PPTA) fibers under the tradename Kevlar® in 1971 by Du Pont. Composites of these fibers had the highest specific tensile strength and stiffness and still rank today at the top with these properties [Moore and Sturgeon, 1973].
Table 1.1: Comparison of typical properties of some uniaxial (0°) composites. $\rho$: volumetric density, E: tensile modulus, $\sigma_t$: tensile strength, $\sigma_f$: flexural strength, J: impact toughness, EP: epoxy resin, GF: glass fiber, HM/S-CF: high-modulus/strength carbon fiber, PPTA: poly(p-phenylene terephthalamide)

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>E [GPa]</th>
<th>$\sigma_t$ [MPa]</th>
<th>$\sigma_f$ [MPa]</th>
<th>J [kJ/m$^2$]</th>
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</thead>
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<tr>
<td>EP</td>
<td>1.22</td>
<td>3</td>
<td>80</td>
<td>120</td>
<td>22</td>
</tr>
<tr>
<td>GF-EP</td>
<td>1.98</td>
<td>33</td>
<td>1100</td>
<td>1100</td>
<td>390</td>
</tr>
<tr>
<td>HM-CF-EP</td>
<td>1.55</td>
<td>150</td>
<td>900</td>
<td>800</td>
<td>12</td>
</tr>
<tr>
<td>HS-CF-EP</td>
<td>1.50</td>
<td>110</td>
<td>1250</td>
<td>1100</td>
<td>-</td>
</tr>
<tr>
<td>PPTA-EP</td>
<td>1.38</td>
<td>60</td>
<td>1380</td>
<td>850</td>
<td>500</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.70</td>
<td>70</td>
<td>250</td>
<td>180</td>
<td>40</td>
</tr>
<tr>
<td>Steel</td>
<td>7.80</td>
<td>210</td>
<td>840</td>
<td>460</td>
<td>100</td>
</tr>
</tbody>
</table>

In the Air Force Ordered Polymer program, other lyotropic, fully aromatic polymers with even greater obtainable strength and stiffness were developed [Wolfe et al., 1981], two of which, poly(p-phenylene benzobisoxazole) (PBO) and poly(p-phenylene benzobisthiazole) (PBZT), are now owned and developed by Dow. The repeat units of PPTA and PBZT are pictured in Figure 1.1. Fibers of these two polymers are the main subjects of this dissertation.

In strong contrast to the very high tensile properties of these polymer fibers, their compressive properties are similar to those of "ordinary", oriented, semi-crystalline polymers such as nylons, polyethylene and polypropylene. They all show the formation of so-called kink bands at low compressive strains like the example shown in Figure 1.2 [Robertson, 1969; DeTeresa, 1985].
Formation of kink bands, or kinking, is a quite frequently observed feature of localized deformation. It is observed not only in uniaxial composites and high-modulus polymer fibers, but also in wood, rocks, metals, stacks of cards, phone books [Parry and Wronski, 1981]. A kink, such as illustrated schematically in Figure 1.3, is defined as a volume of material in which a rotation of material elements and shear parallel to their orientation direction has led to localized, permanent deformation.

Kinking is not observed in inorganic reinforcing fibers and organic high-modulus polymer fibers have therefore been labeled as "weak in compression" despite the fact that the compressive strength of PPTA fibers is actually greater than that of any other organic polymer with the possible exception of a high molecular weight polyimide resin, which has been evaluated in bulk form [Ward, 1987]. Yet, the translation of this "compressive weakness" into the composite properties limits the use of high-modulus polymer fiber composites in numerous structural applications.
Figure 1.2: Optical micrograph of kink bands in Kevlar 49 filament

Figure 1.3: Schematic drawing of a kinked structure. The arrow indicates the kink.
There are many failure criteria for a structure in compression; exceeding the compressive strength of the structural material is only one of many possibilities. Other failure criteria invoke the material's shear strength, fracture toughness, yield strength, interfacial shear strength, bending rigidity, or shear rigidity. In the two latter cases, it is important to note that the compressive failure leading to kink bands is due to an elastic instability of the structure and not due to low compressive strength of the material.

One of the distinguishing features of a stability failure is that the material at the onset of failure is undamaged, because no cracks are formed and all deformation up to this point is reversible. Cracking and/or irreversible deformations may occur, though, due to post-buckling behavior of the structure.

Thermoelastic properties, elastic constants, tensile and shear strength of composites can be predicted quite accurately when ply-sequence, fiber and matrix properties are known using composite theory [Tsai et al., 1968; Ashton et al., 1969; Vinson and Chou, 1975; Christensen, 1979]. Similarly, the tensile properties of high-modulus polymer fibers are understood quite well and the predictive power of computer simulations as well as of mathematical models is improving [Termonia and Smith, 1986, 1987 & 1988; Rutledge and Suter, 1991; Yang and Hsu, 1991]. By contrast, there is no single theory suited to predict a priori the compressive strengths of all uniaxial composites and the reasons for the poor compressive properties of highly oriented polymers are still insufficiently understood.

1.2 Scope of Dissertation

The goal of the research described in this thesis is to enhance the understanding of the compressive failure of anisotropic polymer fibers, with the ultimate objective to use that knowledge to improve the compressive strength of the fibers. The experiments
carried out have been aimed at verifying and exploiting the relationship between longitudinal shear modulus and axial compressive strength of oriented polymer fibers. By increasing the torsional modulus a concurrent improvement of the compressive strength should be observed [DeTeresa et al., 1985]. Presented in this thesis are two approaches that have the potential to achieve this improvement in mechanical properties: impregnation and coating of polymer fibers with rigid, inorganic glasses.

A brief introduction to high-modulus polymer fibers and a review of the present understanding of their compressive strength and failure will be presented in the following Chapter. Theories and models of the compressive strength and failure of unidirectional, fiber-reinforced composites will be included as well, because it is the poor compressive strength of high-modulus polymer fiber reinforced composites that lies at the origin of this research, but also because they can be regarded as macroscopic analogs of anisotropic fibers. In addition, Chapter 2 contains a review of other attempts aimed at improving the compressive strength of high-modulus polymer fibers.

Chapter 3 describes the materials and experimental methods used throughout this research as well as a brief discussion of different compressive strength tests. Specific experiments, relevant only to fiber impregnation or fiber coating are described in the corresponding Chapters 4 and 5.

Chapters 4 and 5 also describe the results obtained during the polymer fiber impregnation and coating work, respectively, as well as their discussion.

Chapter 6 summarizes the findings and concludes with suggestions for related, further research in high-modulus polymer fibers.
REFERENCES


DeTeresa, S.J., Porter, R.S., Farris, R.J., "Model for the Compressive Buckling of Extended Chain Polymers", *J. Mater. Sci.* 1985, 20, 1645-1659


CHAPTER 2

BACKGROUND

2.1 Introduction to High-Modulus Polymer Fibers

Many books, monographs and review articles on this topic are available [Jaffe, 1987; Dobb and McIntyre, 1979; Dobb, 1985; Dobb and Johnson, 1987]. Frequently, the term "high-performance polymer fibers" is used, but since "performance" is evaluated differently in different applications, i.e., as a reinforcing fiber, as an optical waveguide, in a filter membrane, in fire-protection fabrics, etc., the term high-modulus polymer fibers, abbreviated as HM-polymer fibers, is used instead throughout this dissertation. It is also preferred over the more descriptive, but longer term "high-modulus/high-strength polymer fibers". The ASTM standard on tensile testing of high-modulus fibers [1989] considers all fibers with an elastic modulus greater than 21 GPa as high-modulus fibers, but in this dissertation only those fibers having moduli in excess of 60 GPa and finding application as reinforcing fibers in structural composites, will be referred to using that designation. Very high tensile strength and good to excellent thermal stability are further characteristics of those high-modulus polymer fibers consisting of all-aromatic polymer chains. While the thermal stability of polyethylene fiber is limited by its low melting transition (=140°C), gel-spinning and other ultra-drawing processes give low density fibers with the highest specific tensile properties presently achievable [Kanamoto et al., 1983& 1988]. Besides the already mentioned PPTA, PBZT, PBO, and PE fibers, further HM-polymer fibers are based on other all-aromatic polyamides, lyotropic polybenzimidazoles, and thermotropic, all-aromatic copolyesters.

All HM-polymer fibers derive their tremendous tensile properties from the high degree of molecular extension and orientation parallel to the fiber axis. Chain
extension and orientation are obtained by subjecting the polymer chains to an extensional flow field, while they are in a state of sufficient mobility, followed by a deliberate reduction of that mobility to maintain the orientation achieved under flow. The practical realization of this generalized description depends in turn on other physico-chemical properties of the polymers. Mobility can be achieved by dissolving, melting, heating or a combination thereof; the extensional flow field is provided by flow through a spinneret and/or drawing of the orientable polymer; the "freezing-in" of the chain extension and orientation is achieved by solvent removal and/or cooling. Post-treatments such as drying and heating to elevated temperatures under tension further improve the molecular extension and orientation leading to increased tensile properties.

All HM-polymer fibers share certain morphological and structural features [Jaffe, 1987; Sawyer and Jaffe, 1986]. Only those features believed to be related to the compressive strength of the fibers will be pointed out in the following paragraphs. These features are: anisotropy, fibrillar structure and, particular to PPTA fibers, a pleated-sheet morphology.

An obvious structural difference between polymer fibers and glass or ceramic fibers is the former's one-dimensionality of constituting molecules. The orientation of all the polymer backbone bonds in the fiber direction leads to a tremendous anisotropy of physical properties. Numerous attempts to improve the compressive strength of polymer fibers, which are reviewed later in this Chapter (section 2.3), have been aimed at reducing that anisotropy by crosslinking the polymer chains or by making them interact stronger with adjacent chains by other structural modifications.

It has been established for all HM-polymer fibers that the fibrillar structure observed after tensile fracture or peeling off of thin layers is not an artifact of the mechanical processes involved, but is a priori present in the fibers [Jaffe, 1987]. The fibrillar
morphology is a result of the solidification mechanism for fibers spun from lyotropic solutions [Tohyama and Miller, 1981; Xu et al., 1984; Miller et al., 1978] or from thermotropic melts [Sawyer and Jaffe, 1986]. For micromechanical considerations, the fibrils and microfibrils constituting the polymer fiber can be considered as interacting but separate mechanical elements [Jaffe, 1987]. This is important in the tensile failure, which occurs through shear failure between these elements rather than the elements' tensile failure [Knoff, 1987; Allen et al., 1992], and should be expected to be significant for the compressive failure behavior as well. Only very few attempts have been made to improve the compressive strength by physically modifying the microfibrillar morphology.

The pleated-sheet morphology of PPTA fibers has been described by Dobb et al. [1977]. The "pleats" are periodic, small changes in the orientation of the polymer chains along the fiber axis. It is intuitive that such a "zigzag"-feature can affect the axial mechanical properties.

Table 2.1 lists the mechanical properties and densities of high-modulus polymer fibers, carbon, ceramic and metallic fibers. These data, which have been compiled from Franck and Biederbick [1984], Allen [1987], DeTeresa et al. [1988], and Kumar and Helminiak [1989], show the differences and similarities between various kinds or grades of fibers, as well as their strengths and weaknesses.
Table 2.1: Mechanical properties of various reinforcing fibers. E: (specific) elastic modulus, \( \sigma_b \): (specific) tensile strength, \( \varepsilon_b \): elongation at break, G: longitudinal shear modulus, \( \sigma_c \): (specific) compressive strength, \( \rho \): volumetric density. Kevlar is the tradename for PPTA fibers made by Du Pont. Vectra is the tradename for all-aromatic polyester fibers made by Hoechst-Celanese. Spectra is the tradename for polyethylene fibers made by Allied-Signal. Thornel is the tradename for carbon fibers made by Union Carbide; P-100 is pitch-based, T-1000 is PAN-based.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>E [GPa] (E [g/den])</th>
<th>( \sigma_b ) [GPa] (( \sigma_b ) [g/den])</th>
<th>( \varepsilon_b ) [%]</th>
<th>G [GPa]</th>
<th>( \sigma_c ) [GPa] (( \sigma_c ) [g/den])</th>
<th>( \rho ) [g/cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 29</td>
<td>85 (669)</td>
<td>3.6 (28)</td>
<td>3.5</td>
<td>1.6</td>
<td>0.36 (2.8)</td>
<td>1.44</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>125 (977)</td>
<td>3.6 (28)</td>
<td>2.8</td>
<td>1.5</td>
<td>0.36 (2.8)</td>
<td>1.45</td>
</tr>
<tr>
<td>Kevlar 149</td>
<td>185 (1416)</td>
<td>3.4 (26)</td>
<td>1.5</td>
<td>1.0</td>
<td>0.32 (2.4)</td>
<td>1.48</td>
</tr>
<tr>
<td>Vectra A900</td>
<td>77 (602)</td>
<td>3.2 (25)</td>
<td>4.0</td>
<td>0.5</td>
<td>0.12 (0.9)</td>
<td>1.45</td>
</tr>
<tr>
<td>Spectra 1000</td>
<td>170 (1986)</td>
<td>3.0 (35)</td>
<td>3.5</td>
<td>0.7</td>
<td>0.07 (0.8)</td>
<td>0.97</td>
</tr>
<tr>
<td>PBZT</td>
<td>320 (2295)</td>
<td>4.1 (29)</td>
<td>1.2</td>
<td>1.2</td>
<td>0.26 (1.9)</td>
<td>1.58</td>
</tr>
<tr>
<td>PBO</td>
<td>360 (2582)</td>
<td>5.7 (41)</td>
<td>1.2</td>
<td>1.2</td>
<td>0.20 (1.4)</td>
<td>1.58</td>
</tr>
<tr>
<td>Thornel P-100</td>
<td>720 (3794)</td>
<td>2.2 (12)</td>
<td>0.5</td>
<td>-</td>
<td>0.48 (2.5)</td>
<td>2.15</td>
</tr>
<tr>
<td>Thornel T-1000</td>
<td>230 (1432)</td>
<td>3.2 (20)</td>
<td>1.5</td>
<td>-</td>
<td>2.88 (18)</td>
<td>1.82</td>
</tr>
<tr>
<td>S-Glass</td>
<td>90 (415)</td>
<td>4.6 (21)</td>
<td>5.0</td>
<td>38</td>
<td>*1.10 (5.0)</td>
<td>2.46</td>
</tr>
<tr>
<td>E-Glass</td>
<td>75 (329)</td>
<td>3.4 (15)</td>
<td>5.0</td>
<td>32</td>
<td>*0.8 (3.5)</td>
<td>2.58</td>
</tr>
<tr>
<td>Boron</td>
<td>410 (1822)</td>
<td>3.4 (15)</td>
<td>0.8</td>
<td>170</td>
<td>5.90 (26)</td>
<td>2.55</td>
</tr>
<tr>
<td>Alumina</td>
<td>360 (1275)</td>
<td>1.7 (6)</td>
<td>0.4</td>
<td>150</td>
<td>6.90 (24)</td>
<td>3.2</td>
</tr>
<tr>
<td>Steel</td>
<td>210 (305)</td>
<td>3.8 (6)</td>
<td>30</td>
<td>80</td>
<td>1.80 (2.6)</td>
<td>7.8</td>
</tr>
</tbody>
</table>

* data from composites: Strength limited by EP-matrix; glass fibers are stronger in compression than in tension.
2.2 Compressive Failure of Uniaxial Composites and High-Modulus Polymer Fibers

The first part of this section reviews theories for the compressive failure of uniaxial composites, micromechanical models of kink band formation and supporting or contradicting experimental evidence, while the second part treats the compressive failure of high-performance fibers in an analogous fashion.

For this section and all the following, compressive failure is defined as the onset of inelastic load-bearing behavior. This is a very broad definition of failure encompassing all the failure modes listed below and is somewhat akin to broadening the definition of tensile failure to include yielding as well as material fracture.

2.2.1 Compressive Failure of Uniaxial Composites

Of particular interest in this section are the compressive failure mechanisms leading to the formation of kink bands in the composite, because HM-polymer fibers show the same failure feature and it is therefore reasonable to assume a similar failure mechanism. In addition, the correlation between the compressive strength of uniaxial composites and the properties of their constituents is experimentally easier to study than the correlation between the compressive strength of a polymer fiber and the properties of its microscopic and submicroscopic constituents. While of great practical interest in their own right, the results of studies on the compressive failure of uniaxial composites are included here as an illustrative framework from which to draw and examine analogies for the compressive failure of HM-polymer fibers.

2.2.1.1 Theories and Models of Compressive Failure in Composites

Many different failure types can be observed in uniaxial composites under compression. The most important ones are illustrated in Figure 2.1. The large number
of observed failure phenomena and their possible interrelations complicate the investigation and understanding of the determining factors of composite compressive strength.

Euler-buckling is possibly the simplest kind of compressive failure, but even though it can occur in anisotropic materials at much smaller aspect ratios than in isotropic ones [Weaver and Williams, 1975], it is well understood and easily avoidable by proper structural design and, therefore, not of great practical concern.

Longitudinal splitting or delamination has been named as a compressive failure mode for low fiber volume fraction composites [Weaver and Williams, 1975] and weak or poorly adhering matrices [Martinez et al., 1981]. Though, this failure mode should be considered as a post-buckling behavior of unidirectional composites, because in a state of uniaxial compression there are no transverse or shear stresses that could lead to the observed effects [Farris, 1993].

Kinking, though, is the most frequently observed feature of compressive failure in uniaxial composites. Despite the frequency of its occurrence, no theory or proposed sequence of micromechanical processes leading to kink formation has found universal acceptance, yet. It is qualitatively described in the following paragraphs before presenting some of the theories of compressive strength.

HM-polymer fiber reinforced composites fail also by kink formation, but compressive failure of the fibers, i.e. kink formation in the fibers, occurs prior to any permanent global failure features in the composite [Piggott and Harris, 1980].
Figure 2.1: Failure phenomena in uniaxial composites under compression. a) compressed composite prior to failure, b) "true" compressive failure (yielding or cracking), c) shear failure of composite, d) Euler-buckling of composite, e) kinking of composite, f) externally intact composite, but g) reinforcement fibers are shear-buckled, h) failed in shear, or i) kinked by j) shear-buckling of the microfibrils.
It is a characteristic of HM-polymer fiber composites, that no fiber fracture is caused by the sharp bending involved in the kink formation, which is in marked contrast to glass or carbon fiber reinforced composites [Piggott and Harris, 1980]. Due to these attributes, the compressive failure of HM-polymer fibers and their composites is often described using the terms "ductile" and "yielding". One of the characteristics of kinking is that it is often initiated by elastic or plastic buckling [Weaver and Williams, 1975]. Thus, the failure structure itself gives the first indication of the underlying mechanism. It should be noted, though, that processes during kink propagation may not be identical to the processes initiating the kink in the first place; in fact, the latter might not be observable at all.

Because kinking always occurs at an oblique angle between 40 and 70° with respect to the direction of the applied load [i.e. the fiber direction] and leads to completely fractured samples in some cases, Ewins and Potter [1980] interpreted this as failure along a plane of maximum shear stress by shear strength failure instead of failure by an instability mechanism. More careful microscopical examination of failed carbon fiber composites revealed this hypothesis to be incorrect [Parry and Wronski, 1982].

The buckling of reinforcing fibers or fiber bundles inside of a compressed but unbuckled composite structure is called microbuckling. At practically significant fiber volume fractions, the in-phase or shear-mode of the microbuckling failure is observed [Rosen, 1964]. In the shear-mode, all the material elements in the microbuckled region are deformed only in shear and, thus, experience no volume change. Rosen's analysis of the critical stress, necessary for shear-microbuckling of a collection of fibers in an elastic matrix to occur, showed that the compressive strength, \( \sigma_c \), equals the matrix shear modulus, \( G_m \), divided by the volume fraction of matrix, \( V_m = 1 - V_f \), as shown in equation 2.1:

\[
\sigma_c = \frac{G_m}{1-V_f}
\]  

(2.1)
Rosen's model has several shortcomings: It predicts compressive strengths much larger than experimentally observed, it disregards fiber properties and it clearly looses validity at very large fiber volume fractions [Piggott and Harris, 1980]. Rosen suggested that matrix plasticity was responsible for the lower compressive strengths measured in composites, but most matrices are still in the elastic regime at the small compressive strains at which microbuckling occurs. In order to overcome these drawbacks, several variations of Rosen's model have been developed.

Lager and June [1969] introduced an empirical "influence coefficient" which was attributed to non-planar buckling in real systems versus Rosen's two-dimensional model. The resulting equation correlated well with the experimentally observed dependence of composite compressive strength on the fiber volume fraction and the matrix shear modulus. Similar results were obtained by DeFerran and Harris [1970] as well as by Davis [1970].

\[
\sigma_c = \frac{0.63G_m}{1-V_f}
\]  

(2.2)

Lagoudas et al. [1991] found that their microbuckling analysis accounting for initial fiber misalignment could predict the "influence coefficient" found by Lager and June and correlate also well with other experimental data. In the limiting case of perfectly aligned fibers their result reduced to equation 2.1, but in the more realistic case of imperfect alignment a reduced compressive strength was predicted. A simplified equation based on an expansion of their analytical result takes on the form shown in equation 2.3.

\[
\sigma_c = \left(0.14 + 0.78V_f\right)\frac{G_m}{1-V_f}
\]  

(2.3)

The importance of alignment is confirmed by the results obtained by Martinez et al. [1981], who found that initial misalignment significantly reduced the compressive
strength of glass and carbon fiber composites. On the other hand, they did not observe any effect of misalignment on the compressive strength of Kevlar 49 fiber composites. Contrary to this last result, Wu and Yeh [1992] obtained good correlation between measured compressive strength of Kevlar 49 composites and that predicted by a failure analysis that accounted for initial misalignment of fibers and non-linear shear deformation of the matrix [Yeh and Teply, 1988].

Rosen's theory is also based on the assumption that the fiber shear modulus is much greater than the matrix shear modulus. While this is a reasonable assumption for glass, ceramic, and some types of carbon fibers, it does not hold true for polymer fibers. Shear moduli of the latter are of approximately the same magnitude as those of epoxy resins, for example [Kulkarni et al., 1975]. Taking this into account yields equation 2.4. This expression for the composite compressive strength is identical to that for the longitudinal shear modulus of a unidirectional composite.

\[
\sigma_c = G_m \left[ 1 - V_f \left( 1 - \frac{G_m}{G_f} \right) \right]^{-1}
\] (2.4)

Other approaches, like Biot's analyses of internal buckling [1963a] or surface instabilities [1963b], predict also a compressive failure limited by the materials effective shear modulus.

When the fiber strength sets the upper bound for the composite compressive strength, as is the case for HM-polymer fiber reinforced composites [Greenwood and Rose, 1974], the composite compressive strength was observed to follow a "rule-of-mixture" type relationship [Piggott, 1981; Greszczuk, 1982]:

\[
\sigma_{c,\text{composite}} = V_f \sigma_{c,\text{fiber}} + V_m \sigma_{c,\text{matrix}}
\] (2.5)

where, \( V \) are the fiber and matrix volume fractions and \( \sigma_c \) are the stresses carried by the fibers or the matrix at the onset of composite failure.
Piggott [1981] predicted for composites with imperfectly aligned and curved reinforcing fibers a proportionality between composite compressive strength, $\sigma_c$, and matrix yield or ultimate compressive strength, $\sigma_{my/u}$. The proportionality factor, $k$, is a function of fiber volume fraction, fiber misalignment and curvature.

$$\sigma_c = k\sigma_{my/u}$$

(2.6)

The following, micromechanical models for compressive failure and kink formation process have been proposed:

Chaplin [1977] proposed the following sequence of events for the kink band formation in glass fiber-epoxy composites: increasing shear deformation in a non-rotating band of material after shear-instability failure followed by bending (tensile) failure along kink band boundaries and debonding within the kink band leading to the observed debris formation. Looking at compressive failure from a fracture mechanics point of view, Chaplin cites material defects as the reason of finding experimentally a compressive strength only one fourth of the theoretically expected strength.

Williams and Weaver [1975] and Parry and Wronski [1982] proposed compressive failure in carbon fiber reinforced composites to occur by bending of fiber bundles in the compressed composite, followed by delamination, buckling and bending fracture near the composite surface and propagation of the crack through the thickness of the sample.

Steif [1990] analyzed the critical strain for kink band formation in uniaxial composite materials based on the following model: Fibers or fiber bundles are bent via microbuckling until they fracture. Then, a finite deformation brings the fractured segments into the kinked configuration.

The fracture of fibers or fiber bundles is no necessity in either of these micromechanical models, so they can be projected directly onto the kink formation in
HM-polymer reinforced composites by substituting fiber bending and kinking for fiber fracture.

This section reviewed a few representative theories for the compressive failure of uniaxially reinforced fibrous composites. A large fraction of these theories predicts a compressive strength proportional to the longitudinal composite shear modulus, consistent with the starting hypothesis of an elastic instability failure, which in turn is based on the experimental observations of microbuckling and kinking. The inclusion of matrix properties, especially its yield strength has led to more variations of the basic shear-instability, microbuckling failure model.

2.2.1.2 Correlation of Composite Compressive Strength with Other Material Properties

The following paragraphs review some of the correlations between composite compressive strength and fiber, matrix or other composite properties.

Fiber properties possibly affecting composite compressive strength are the fiber's own compressive strength, its diameter, and its shear modulus. The first of these three properties is subject of a more extensive review in section 2.2.2. Norita et al. [1988] investigated the effect of fiber properties on the composite compressive strength and concluded that, if fiber compressive strength is sufficiently large, the composite compressive strength is accurately predicted by Rosen's microbuckling model. Though, for organic reinforcing fibers, the composite compressive strength is predicted by a rule-of-mixtures type relationship (cf. equation 2.5). Increasing fiber diameters are thought to improve the composite compressive strength primarily by facilitating the alignment of the fibers [Norita et al., 1988].

The fiber shear modulus is not only important to the composite compressive strength by limiting the fiber's compressive strength as discussed later, but also by
affecting the composite shear modulus shown to be an upper limit to the composite
compressive strength (cf. equation 2.4) [Kulkarni et al., 1975; Greszczuk, 1982].

While the fiber compressive strength of HM-polymer fibers, some carbon and metal
fibers sets the upper bound to the compressive strength of their composites, in a
majority of carbon and glass fiber composites it is the matrix which limits the composite
compressive strength. The results of a few studies on the effect of various matrix
properties on the composite compressive strength are reviewed in the following
paragraphs.

Matrix yield strength is the key parameter in the kink formation models of several
other authors (cf. equation 2.6) [Piggott and Harris, 1980; Piggott, 1981; Wronski and
Parry, 1982]. These models are based on the idea that the permanent deformation
observed in kinked composites necessarily involves the plastic deformation of the
matrix and that no compressive stress smaller than the matrix yield strength would
cause such a deformation. Evaluations of the compressive strength of uniaxial
composites in which the matrix yield strength was varied by partial curing, superposed
hydrostatic pressure, different resins, plasticizing and reinforcing the matrix provided
some support for this hypothesis [Weaver and Williams, 1975; Piggott and Harris,
1980; Wronski and Parry, 1982; Sigley et al., 1991]. But all these modifications also
resulted in changes of the matrix rigidity so that an unambiguous correlation between
matrix yield strength and composite compressive strength was not possible. Also, in
most HM-fiber composites (except glass fiber composites), compressive failure occurs
at low compressive strains, large enough only for the onset of elastic instabilities but
too small for matrix yielding.

A close correlation between composite compressive strength and matrix shear
modulus is predicted by microbuckling theories (cf. equations 2.1 to 2.4) and has also
been observed experimentally [Rosen, 1964; Lager and June, 1969; Kulkarni et al.,
1975; Ewins and Potter, 1980; Greszczuk, 1982]. Changes in matrix rigidity have been produced by filling the matrix with metal oxides, choosing different matrices, changes in testing temperature and the degree of crosslinking.

The importance of fiber-matrix adhesion for the composite compressive strength is ambiguous. Kulkarni et al. [1975] found no decrease in the compressive strength of Kevlar 49-epoxy composites in which adhesion was deliberately destroyed by moisture-coating the fibers. In other composite systems, though, the compressive strength improved with adhesion [Martinez et al., 1981; Greszczuk, 1982].

Fiber alignment was found to be important for glass and carbon fiber reinforced composites [Martinez et al., 1981], as well as for Kevlar 49 composites [Allen, 1992; Wu and Yeh, 1992]. Yet, there are also a few studies which did not observe an effect of fiber alignment on compressive strength for Kevlar 49 composites [Kulkarni et al., 1975; Martinez et al., 1981].

Residual compressive thermal stresses due to matrix curing are sometimes mentioned as potentially detrimental to the composite compressive strength, but DeTeresa and Nicolais [1988] showed that this effect is negligible in uniaxial composites with practically important volume fractions of reinforcing fibers. Pretensioning of the reinforcing fibers decreased the compressive strength, because this placed the matrix under compression [Kulkarni et al., 1975]. Ewins and Potter [1980] observed a considerable decrease of compressive strength in composites under a small applied shear stress. Consistent with a shear-instability failure, they attributed this to an earlier onset of the instability.

In summary, the compressive strength of uniaxial composites can be limited by the fiber strength, matrix or composite shear modulus, or the matrix yield strength. Good adhesion and fiber alignment also affect the compressive strength in many composites. Yet, the importance of one or the other property for the compressive strength of a
particular composite is not rigorously predictable and may even change as a function of experimental variables such as the ambient pressure. The experimental difficulty to vary material properties independent of each other is also a fundamental obstacle to the study of property-performance correlations.

2.2.2 Compressive Failure of High-Modulus Polymer Fibers

Soon after the commercial introduction of Kevlar 49 in 1971, publications by Däppen [1973] as well as Greenwood and Rose [1974] attributed the relatively poor compressive strength of its uniaxial composites to the compressive properties of the fiber rather than those of the composite or matrix. Despite considerable interest in the origin of this perceived "compressive weakness" of HM-polymer fibers, progress towards an understanding of the failure mechanism has been fairly slow. In this section, various theories attempting to predict the compressive strength of highly anisotropic polymers as well as micromechanical models of the compressive failure processes are reviewed. Experimentally observed correlations between compressive strength and other fiber properties are also presented. Studies of such correlations can test some of the theories quantitatively and can show the importance of other structural aspects that have not yet been included in current theories.

2.2.2.1 Theories of Compressive Failure of High-Modulus-Polymer Fibers

This section will review some of the theories developed to interpret experimental observations and predict the compressive strength of HM-polymer fibers. Analogous to the compressive failure of uniaxial composites, there are also different failure modes for HM-fibers in compression.
High compressive strength fibers fail by Euler-buckling [Kumar and Helminiak, 1989] or by shear strength failure [Dobb et al., 1990]. In the former case, the buckling stress for a slender column is given by equation 2.7:

$$\sigma_c = k \frac{\pi^2 EI}{AL^2}$$

(2.7)

where $\sigma_c$ is the critical buckling stress, $k$ is a coefficient characterizing the boundary conditions at the ends of the column, $E$ is the elastic modulus, $I$ is the moment of inertia, $A$ is the cross-sectional area, and $L$ is the length of the column. In the case of shear strength failure, the compressive strength of a fiber equals its shear strength along the plane where the shear stress exceeds the shear strength:

$$\sigma_c = \frac{\tau(\theta)}{\cos \theta}$$

(2.8)

where $\tau(\theta)$ is the shear strength of the anisotropic fiber along a plane with a normal oriented at an angle $\theta$ with respect to the fiber axis. Shear strength failure occurs only when the shear strength is smaller than the torsional or bending rigidity of the fiber. This is the case for some types of carbon, alumina, boron, and glass fibers, but not for HM-polymer fibers.

HM-polymer fibers form kinks in compression like uniaxial composites. This is an indication that the same mechanism, namely shear microbuckling, is involved in the compressive failure of both kinds of materials. Based on this observation, DeTeresa et al. [1985] performed a buckling analysis for HM-polymer fibers including molecular concepts. Molecules and/or microfibrils were modeled as a collection of rods. Assuming no interactions between the rods resulted in the prediction of Euler-type buckling for PPTA molecules under a compressive stress of 60 kPa, orders of magnitude smaller than observed experimentally. Including intermolecular interactions
in the analysis led to the prediction of a shear-instability and microbuckling failure under a compressive stress equal to the fiber's longitudinal shear modulus.

\[ \sigma_c = G \]  

(2.9)

One important point of this result is that it is not the molecular properties, e.g. the molecular bending rigidity, which determines the materials compressive strength, but the interactions between the structural elements. Equation 2.9 is analogous to that obtained by Rosen [1964] for uniaxial composites (equation 2.1). The microbuckling analysis neglects the bending contribution of the microfibrils to the critical buckling stress, because of its small magnitude. Other simplifications in this theory are the disregard of morphology, structural defects and inhomogeneities, as well as the assumption of linear elastic behavior until the onset of compressive failure.

An independent validation of the prediction of the microbuckling theories was obtained by Allen [1988]. Analyzing the stress coupling in anisotropic materials in a state of combined axial and torsional stress, he obtained:

\[ G_{meas} = G_{true} + A \sigma_{zz} \]  

(2.10)

where \( G_{meas} \) is the measured or apparent shear modulus, \( G_{true} \) is the "true" shear modulus of the stress-free material, \( \sigma_{zz} \) the applied axial stress, and \( A \) is a factor characterizing the degree of anisotropy. Measuring the apparent shear modulus as a function of applied axial stress showed indeed a linear increase of the former and gave an intercept \( G_{true} = 2 \text{ GPa} \) and a slope \( A = 0.95 \) for Kevlar 49 filaments. In addition, the equation predicts for highly anisotropic materials (\( A = 1 \)) a vanishing of the apparent shear modulus at a compressive load equal in magnitude to the "true" shear modulus. An identical relationship between measured shear modulus and applied axial stress was derived by Biot [1965] for the general case of an isotropic materials in an initial state of stress using a different approach. This approach also predicted a
dependence of the anisotropy factor, $A$, on the symmetry of the cross-section with a circular one giving the smallest anisotropy factor. This dependence is not predicted by the results of Allen's analysis.

The first direct experimental verification of the shear microbuckling theory for HM-polymer fibers was reported by DeTeresa et al. [1988]. They measured the longitudinal shear moduli and axial compressive strengths of several kinds of high-modulus fibers. The results of these measurements confirmed the proportionality between the two properties, but a linear fit of the data gave the relationship:

$$\sigma_c = 0.3 \ G$$

(2.11)

The prefactor is somewhat dependent on the technique which is used for the determination of the compressive strength and ranges from approximately 0.2 to 0.4. The origin of this discrepancy between experiment and theory is still unclear at present. DeTeresa [1985] proposed the following origins:

The shear modulus measured macroscopically is larger than the actual interfibrillar shear modulus, i.e., tests measure a "composite" shear modulus of fibrillar and interfibrillar material with the latter being determinant for the compressive strength as shown in equation 2.9. The presence of structural inhomogeneities, voids, or an unsupported fiber surface could also lead to the initiation of local instabilities at lower than predicted stresses.

Schaffer [1991], including shear deformation of the buckling elements in a microbuckling analysis, obtained the relation shown in equation 2.12:

$$\sigma_c = \frac{G}{5n}$$

(2.12)

where $n$ is a geometric factor and equal to 1.1 for circular fiber cross-sections. This results in a prefactor of about 0.2 in fairly good agreement with experimental results.
A simple static analysis of a body under compressive load and subjected to an infinitely small shear perturbation demonstrates that a prefactor is introduced, if the body is divided into elements buckling rather independently of each other [Farris, 1989]. One concrete example of such behavior could be the buckling of microfibrils at the fiber surface before propagation of the buckling mode through the bulk of the fiber. This buckling geometry would give a prefactor equal to 0.5 [DeTeresa, 1985]. In general, the value of the prefactor cannot be predicted unless the geometry of the buckling elements is known exactly. For some simple geometries it is found to lie in the range of experimentally observed values. It is certain, however, that the prefactor cannot exceed unity, because the shear modulus is an upper limit for the compressive strength of any material.

Lee et al. [1989] included the bending contribution in their microbuckling analysis of a fiber with fibrillar morphology and arrived at the following result:

\[ \sigma_e = G + \frac{\pi^3 Ed^2}{64L^2} \]  

(2.13)

where \( G \) is the shear modulus, \( E \), the tensile modulus, \( d \), the diameter of the buckling elements (microfibrils), and \( L \), the length of the fiber.

General mathematical theories about the occurrence of surface instabilities apply of course to HM-polymer fibers as well as to uniaxial composites. They also predict a compressive strength limited by and proportional to the shear modulus [Biot, 1963a,b, 1965] and show that strain localization, i.e., kink band formation, is always preceded by a global instability, i.e., surface buckling [Reddy, 1983].

The following conceptual model for kink band formation in HM-polymer fibers was proposed by DeTeresa [1985]: At a critical compressive stress, an elastic shear instability is initiated resulting in large elastic buckling deformations. The instability propagates by shear failure between microfibrils and stress transfer to the now
unsupported neighboring microfibrils. Post-buckling bending at the kink band boundaries collapses the material to the angular kink band.

Martin and Thomas [1991] proposed the following micromechanical model based on their observations with high-resolution electron microscopy of kinked PBZT and PBO fibers. The kink formation in rigid-rod polymer fibers is initiated by the formation of a bundle of partial dislocation near the fiber surface due to a shear instability. Subsequently, the kink propagates through cooperative rotation of polymer chain segments adjacent to the dislocation bundle, causing further instabilities and the formation of new dislocations.

This section presented some of the theories for compressive failure of highly anisotropic polymer fibers and experimental evidence supporting them or demonstrating their shortcomings. Different approaches all point to compressive failure of HM-polymer fibers by an elastic shear instability mechanism, predicting a proportionality, if not equality of the compressive strength and the smallest longitudinal shear modulus. While the experimental correlation between longitudinal fiber shear modulus and compressive strength shows a quantitative difference from the predictions of the microbuckling theory, presently, the shear modulus is the only material property correlating with the microbuckling failure stress, and it is also a definite upper bound to the compressive strength of any material.

2.2.2.2 Experimental Observations of Compressive Failure in Highly Oriented Polymers

The formation of kink bands in oriented polymers was already observed before the availability of HM-polymer fibers. Robertson [1969] and Shigematsu et al. [1975] examined the kink band morphology in compressed, uniaxially oriented polyethylene extrudates. Wide-angle X-ray scattering (WAXS) showed rotation of the orientation
axis inside the kink band. Small-angle X-ray scattering showed that lamellar crystals were broken into smaller blocks, and transmission electron microscopy (TEM) showed lamellar crystals to be inclined with respect to the orientation axis and stacked parallel to the kink band boundary. Based on these observations, they proposed a mechanism involving shear along the kink band boundary and intermicrofibrillar or intercrystalline slip [Robertson, 1969; Shigematsu et al., 1975].

Takahashi et al. [1983] used the same tools to study the morphology of Kevlar 29 fibers after compression in composites. WAXS showed that a large degree of crystallinity was maintained inside the kink band pointing to intercrystalline slip along planes of hydrogen-bonded sheets as the deformation mechanism. TEM and electron diffraction experiments revealed the occurrence of intermicrofibrillar slip and fibrillation within the kink band. Kink bands formed initially at approximately 55° with respect to the fiber axis. The pleat angle (cf. sections 2.1 and 2.2.2.3) in compressed PPTA fibers was observed to increase.

Dobb et al. [1981] observed the deformation of Kevlar filaments directly during the elastica-loop test using scanning electron microscopy and described the structural changes. In the initial stage of the test, the formation of narrow kink bands was observed as the development of surface steps in wedge-shaped regions at angles of 40 to 50° with respect to the fiber axis. Subsequently, the wedge widens as the kink band domain propagates through the fiber and additional kink bands form. At a later stage, the kink bands cross to form another larger material wedge which is displaced towards the loop center. The observation were interpreted as shear and/or delamination of polymer chains induced by compressive stresses. Transmission electron microscopy revealed longitudinal microcracks within the kink bands.

The elastica loop test showed deviations from linear elastic behavior at a compressive strain of approximately 0.5% for Kevlar 29 and Kevlar 49 filaments. The
decrease of tensile strength after 10 compression cycles at 2.5% strain was attributed to
the introduction of structural inhomogeneities and voids acting as defects. This was
confirmed by the confinement of the axial extent of tensile fracture faces to the kink
band region, which is in contrast to the normally observed tensile failure features.

Similar results were obtained by DeTeresa et al. [1984]. Three-point-bending of
Kevlar 49 filaments mounted on the compression side of a polycarbonate beam and
observation under an optical microscope showed the onset of kink formation at a
compressive strain of 0.5%, and a drop of 10% in tensile strength resulted after 100
loading cycles to 1.2% compressive strain. Tensile loading was found to straighten out
the kink bands, but permanent structural damage remained as was seen by scanning
electron microscopy.

Martin and Thomas [1989, 1991] used high-resolution TEM (HR-TEM) to study
the molecular motions involved in kinking after its initiation. For the PBZT and PBO
fibers studied, the material within kink bands remained highly crystalline, i.e., lateral
packing was maintained, but some micro-voids were observed as well. Evidence from
TEM observations suggests that the kink initiation takes place at the free surface of the
fiber. Use of HR-TEM permitted the measurement of the axial extent of kink band,
which was only 20-30 nm, and that the change in direction at the kink band boundary
of 38° occurs over only 3-5 Å. Tanner et al. [1986] suggested that a molecular
rotation of the amide bond in PPTA from a trans- into a cis-conformation would cause
a 45°-bend in the chain, which would then propagate across the entire fiber and result
in a kink band. The limited axial extent of kink bands in HM-polymer fibers and the
sharp kink band boundaries observed by Martin and Thomas [1991] show that
conformational changes ("kinking") of polymer chains must take place. These changes,
are a consequence of fiber compressive failure and not its cause, so that "molecular
bending rigidities" or "molecular buckling stresses" are inappropriate to estimate fiber compressive strengths.

Vlattas and Galiotis [1991] used laser Raman spectroscopy (LRS) to follow the molecular deformation during compression of single fibers of different grades of PPTA and PBZT in the cantilever beam-bending test [DeTeresa et al., 1988]. The dependence of the Raman frequency shift of the macroscopically applied deformation, also called Raman frequency gauge factor (RFGF), was used to estimate a compressive modulus from the experimental tensile moduli and the ratio of the RFGF's of the various fibers in compression and tension, respectively. The compressive strains at failure were taken where the RFGF deviated from linear behavior in compression. Table 2.2 summarizes their findings. The compressive modulus determined in this fashion was practically linear up to the compressive failure strain yet it was also found to be up to 50% smaller than the tensile modulus depending on the particular kind of fiber. The smaller compressive modulus is explained as arising from the rotation of crystals within the fibers under an applied load rather than the deformation of bonds, which is monitored by LRS and observed in fibers under tension. The compressive failure stresses for the fibers studied, calculated as the product of compressive modulus and compressive strain at failure, agree well with those obtained from compression tests of uniaxial composites.

But while Vlattas and Galiotis [1991] observed identical compressive failure strains by optical microscopy and LRS for PPTA and PBZT fibers, Young and Ang [1992] found the LRS to give smaller strains at failure. The results of Vlattas and Galiotis [1991] are misleading in suggesting that there is a discontinuity in the modulus-strain curve when passing from tensile to compressive strains. Such behavior is impossible, as was also noted by Young and Ang [1992].
Table 2.2: Summary of results of LRS studies of the compressive deformation of HM-polymer fibers. \( E_t \): tensile modulus, \( E_c \): compressive modulus, \( \varepsilon_c \): compressive strain at failure

<table>
<thead>
<tr>
<th>Fiber</th>
<th>( E_t ) [GPa]</th>
<th>( E_c ) [GPa]</th>
<th>( \varepsilon_c ) [%]</th>
<th>( E_c \varepsilon_c ) [MPa]</th>
<th>( E_c / E_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 29</td>
<td>80</td>
<td>76</td>
<td>0.55</td>
<td>418</td>
<td>0.95</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>130</td>
<td>85</td>
<td>0.45</td>
<td>382</td>
<td>0.55</td>
</tr>
<tr>
<td>Kevlar 149</td>
<td>160</td>
<td>115</td>
<td>0.25</td>
<td>287</td>
<td>0.72</td>
</tr>
<tr>
<td>PBZT</td>
<td>280</td>
<td>222</td>
<td>0.15</td>
<td>333</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Because of the frequent occurrence of this subject in discussions of the compressive strength of HM-polymers, the physical origin of possible differences between the magnitudes of tensile and compressive moduli are briefly examined in the following paragraphs.

Roche et al. [1987] showed that the elastic response of Kevlar samples under tension is nonlinear and demonstrated with light scattering experiments that this nonlinearity was due to the reversible opening of the pleated morphology. Allen and Roche [1989] modeled the nonlinear deformation of Kevlar fibers using a shear coupling analysis. This analysis predicts an exponential increase of the modulus with applied stress and shows good agreement with experimental results. An extension of this analysis to compressive loading also predicts an increase of the pleat-angle and a concurrent decrease of the modulus. Further evidence for the nonlinear elastic behavior of HM-fibers comes from the stress-strain curves obtained by direct compression of PBO fibers [Fawaz et al., 1989], carbon fibers [Macturk et al., 1991], and hollow PBZT fibers [Pottick, 1986]. In agreement with Allen and Roche's results [1989], Galiotis et al. [1984] showed an essentially linear stress-strain response for the
tensile deformation of single crystalline polydiacetylenes, with the exception of a small decrease in modulus at high strains attributed to a decrease in the bond force "constants". This observed modulus decrease is in contradiction with the predictions of molecular simulations performed by Klunzinger et al. [1991], which indicated a molecular origin of the nonlinearity in PBZT and carbon fibers not explained by crystalline reorientation [Jiang et al., 1991].

Yet, the nonlinearity of the elastic response in itself is not a sufficient explanation of why the elastic modulus for small deformations should be significantly different in tension and compression. Calculations for Kevlar 49 fibers based on Allen and Roche's analysis [1989] give initial moduli of 111 and 115 GPa in compression and tension, respectively. This difference, while real, is certainly negligible within experimental errors and the initial tensile modulus should be an acceptable approximation for the compressive modulus at small strains.

The studies reviewed above revealed compressive failure strains of approximately 0.5% for Kevlar filaments and 0.2% for PBZT filaments. Evaluation of the compressive strength by the tensile recoil method gave 360 and 280 MPa for these fibers and 200 MPa for PBO fibers, respectively, in good agreement with data obtained from the compression of uniaxial composites of these fibers [Allen, 1987]. Direct compression of fibers gave a compressive strength of 210 MPa for Kevlar™ and 300 MPa for PBO [Macturk et al., 1991]. Compressive strengths obtained as the product of compressive modulus and strain at failure measured by laser Raman spectroscopy are: 420, 380, 290, and 330 MPa for Kevlar 29, 49, 149, and PBZT fibers, respectively [Vlattas and Galiotis, 1990].

X-ray and electron microscopy studies have shown that intermicrofibrillar slip is involved in kink formation and that molecular kinking has to occur to give the sharp kink band boundaries observed. But even for severe compressive damage, the only
effect of kinking on the mechanical properties of polymer fibers is a small decrease of the tensile strength. Limited compressive damage has no noticeable effect on tensile fiber properties showing that only limited microstructural damage is caused. Tensile and compressive deformation of HM-polymer fibers elicit nonlinear elastic responses, but for small deformations the nonlinear effect is small and linear elasticity is a good approximation for the mechanical behavior.

2.2.2.3 Correlations between Fiber Compressive Strength and Other Fiber Properties

In order to improve the understanding of compressive failure in HM-polymer fibers, correlations between the compressive strength and other mechanical properties as well as with the morphology of the respective fibers have been considered:

For PAN-based carbon fibers the compressive strength decreases as the tensile modulus increases [Kumar et al., 1986; Dobb et al., 1990; Melanitis and Galiotis, 1990], but for organic fibers there appears to be no such correlation. Kevlar 29 and Kevlar 149 with respective tensile moduli of about 80 and 160 GPa fail both in compression at approximately the same stress of 360 to 400 MPa. PBZT fibers show also little or no improvement of the compressive strength after heat-treatment, which increases its modulus from 150 to 300 GPa and its tensile strength from 1.6 to 3 GPa [Allen et al., 1985]. Also, chemically different fibers: aramid, aromatic polyester, and polyethylene, with practically identical tensile properties fail in compression at very different strains [van der Zwaag and Kampschoer, 1988].

Kumar et al. [1986] found a correlation between density and compressive strength of PAN-based carbon fibers: lower density fibers had higher compressive strength. They reasoned that more entanglements of carbon "ribbons" [Diefendorf and Tokarsky, 1975] - the equivalent of microfibrils in linear, organic polymer fibers - or a voided,
folded sheet packing, would cause lower tensile moduli, lower densities, higher torsional moduli and, thus, higher compressive strengths. Unfortunately, the torsional moduli of the various fibers were not reported.

Dobb et al. [1990] found the compressive strength to increase along with the tensile strength in PAN-based carbon fibers. But aramid fibers with tensile strengths ranging from 2 to 4 GPa all have the same compressive failure strain [van der Zwaag and Kampschoer, 1988].

Norita et al. [1988] noticed a small effect of fiber diameter on composite compressive strength, but attributed the improved compressive strength to better alignment of the thicker fibers. Kumar and Helminiak [1989] argued that some carbon fibers failed by Euler-buckling. Larger fiber diameters and non-circular cross-sections would increase the fiber’s moment of inertia and, thus, the Euler-buckling stress. For PPTA and PBO fibers, on the other hand, the compressive strength is independent of the tensile modulus and the diameter, as noted earlier. In the course of this dissertation, measurements of the compressive strength of PPTA fibers with diameters from approximately 20 to 40 µm all gave similar results and identical to that for a control of Kevlar 29. This confirms that PPTA fibers do not fail by an Euler-buckling mechanism.

For PBZT and PPTA fibers the crystallite size has been shown to increase during heat-treatment but, as mentioned before, no increase of the compressive strength results [Allen, 1992]. In carbon fibers, the compressive strength decreased with increasing crystallite size [Kumar and Helminiak, 1989].

The observed axial crack formation within kink bands is sometimes used to argue for a possible correlation of transverse strength and compressive strength. No systematic studies of this correlation have been published yet, likely due to the experimental difficulty of measuring the transverse strength of small-diameter (=10 µm)
filaments. And, analogous to the matrix yield or ultimate strength determined compressive strength of uniaxial composites, the fiber transverse strength can probably not be varied independently of other mechanical properties, notably the longitudinal shear modulus, so that a straightforward evaluation of the correlation would be impossible. It is also likely, that the axial cracking observed in the kinked regions of HM-polymer fibers, as in uniaxial composites, is a postbuckling phenomenon due to the absence of transverse stresses in a fiber under pure compression.

A correlation between longitudinal shear modulus and compressive strength is predicted by the microbuckling theories reviewed in section 2.2.2.1, together with the experimental results confirming this correlation. A further illustration of the coupling between axial and shear stresses is also provided by the internal compressive failure caused by twisting of single filaments [DeTeresa, 1985].

The compressive strengths of various materials have also been empirically correlated with the materials' glass transition temperatures [Northolt, 1981] based on the hypothesis that both properties are manifestations of the molecular rigidity. The overall trend showed materials with high glass transition temperatures ($T_g$'s) to be more likely to have also high compressive strength, but the scatter was too large to permit a meaningful quantification of the data or even a prediction of compressive strength based on a material's $T_g$.

The pleated-sheet morphology of PPTA fibers has no effect on their compressive strength. This is demonstrated by the equality of compressive strength of Kevlar 29, which shows the pleated structure, and Kevlar 149, which does not.

The fibrillar character of HM-polymer fibers is detrimental to the compressive strength [DeTeresa et al., 1984, 1988] due to the lack of material continuity at microfibril interfaces. This view is supported by the observations of intermicrofibrillar slip during kink formation [Robertson, 1969; Takahashi et al., 1983; Martin and
Thomas, 1991]. The experimental verification of a correlation between compressive strength and microfibrillar diameter in otherwise identical fibers would be of great interest, but at least at present a control that precise of the fiber morphology during processing is not possible. There is also a fundamental limit inherent in the respective fiber forming and solidification process to the range of microfibrillar diameters achievable.

An interesting way to study the effect of a microfibrillar morphology on mechanical properties is offered by the availability of highly oriented, but non-fibrillar macroscopic model systems: single-crystalline polydiacetylenes (cf. Appendix A).

The kink bands in polydiacetylene (PDA) single crystals were identified as crystallographic twins [Robinson et al., 1986], unlike those in polycrystalline, highly oriented fibers. The difference between twins and "ordinary" kink bands in poly-crystalline fibers is the stringent symmetry observed in twins.

The critical compressive strain for polyDCHD (1,6-di(N-carbazolyl)-2,4-hexadiyne) single crystals, measured by optical microscopy and laser Raman spectroscopy, was found to be 0.22%. It was demonstrated by Fan and Hsu [1989] using polyPUHD (1,6-bis(phenyl urethane)-2,4-hexadiyne), that the tensile and compressive moduli of polydiacetylene single crystals are identical. Thus, the compressive strength of polyDCHD crystals can be estimated as the product of tensile modulus (45 GPa) [Galiotis et al., 1984] and compressive failure strain (0.22%) [Robinson et al., 1986]. One obtains a compressive strength of 99 MPa. The corresponding estimate for polyPUHD gives a compressive strength of 135 MPa (E = 45 GPa [Baughman et al., 1975], ε_c = 0.3% [Fan and Hsu, 1989]). The only shear moduli of a PDA single crystal that have been published to date were obtained by sound velocity measurements on polyTSHD (1,6-bis(p-toluene sulfonate)-2,4-hexadiyne) single crystals [Rehwald et al., 1983]. The tensile modulus of polyTSHD in chain direction was measured to equal 43
GPa, practically the same as the moduli for polyDCHD and polyPUHD. Similar lateral interactions can also be assumed for the molecules in these three polymer crystals. Both shear moduli in polyTSHD, and assumed to be of comparable magnitude in polyDCHD and polyPUHD, for deformation parallel to the chain direction equal 1.0 GPa. This number is roughly an order of magnitude larger than the compressive strengths estimated above. A difference of this size was also observed for gel-spun polyethylene fibers [DeTeresa, 1985]. The explanation offered in that case was the presence of molecular entanglements that are not represented by a model considering a collection of rods. Clearly, this explanation is not applicable to polymer single crystals. This suggests that other factors than the fibrillar microstructure of HM-polymer fibers are the origin of their lower-than-predicted compressive strengths. These other factors could be very localized crystal defects, like partial dislocations [Martin and Thomas, 1991], as suggested by Fan and Hsu [1989] to explain the large scatter of their Raman spectroscopy data at compressive strains in the range of 0.3 to 0.7%.

The cylindrical orthotropy of some highly oriented polymer fibers adds to the difficulty of interpreting the failure mechanisms in tension as well as in compression. Coupling between axial and transverse stresses occurs as a consequence of the anisotropy and, thus, the fiber can fail due to the applied axial stress, the coupled transverse stress, or a combination of both. The application of the theory of elasticity of anisotropic materials [Lekhnitskii, 1981] to the calculation of the stress distribution in model carbon and PPTA fibers has illustrated the presence of transverse stresses of the order 0.5% of the applied axial stress [Allen and Farris, 1990]. Also, these transverse stresses are not only, like the axial stress, a function of radial position, but can also change sign along the surface. Thus, a compressive axial stress can cause a tensile radial stress and a hoop stress that changes from tension to compression when
approaching the fiber radius. The anisotropy is also manifest in a large difference of axial and transverse mechanical properties: Phoenix and Skelton [1974] measured the transverse modulus and strength of Kevlar 49 fibers by transverse compression to be 0.76 and 0.45 GPa, respectively. Farris [1993] obtained an even smaller transverse strength of only 10 MPa by inflation of hollow PPTA fibers. The small transverse stresses caused by axial loading are, therefore, not negligible and should be kept in mind when studying the effects of axial loading.

2.3 Attempted Routes to Improving the Compressive Strength of Polymer Fibers and Uniaxial Composites

In this section, some of the attempts to improve the compressive strength of high-modulus polymers and of uniaxial composites will be reviewed. The literature review on the impregnation and coating of high-modulus (and other) polymers and their effects on compressive strength and other mechanical properties will be presented in Chapters 4 and 5, respectively.

2.3.1 Improving the Compressive Strength of Uniaxial Composites

The most extensively used approach to raise the compressive strength of uniaxial HM-polymer fiber composites is the fabrication of hybrid composites by blending of the polymer fibers with compressively stronger carbon or boron fibers [Moore and Sturgeon, 1973]. Such hybrid composites have compressive strengths that follow a rule-of-mixture type equation using the respective volume fractions and compressive strengths of all-HM-polymer and all-carbon fiber composites. A variation of this approach is the preparation of asymmetric hybrid composites in which carbon fiber plies are used specifically in those locations of a structure that will be predominantly
stressed in compression [Marom and Chen, 1987]. This hybridization brings along other problems, though, such as delamination between plies of different fibers and is merely the best, presently available, but not an ideal solution.

Kulkarni et al. [1975] conducted an extensive study of the effects of various composite modifications on the compressive strength of uniaxial Kevlar 49/epoxy laminates. They obtained improved composite compressive strength by blending Kevlar 49 and carbon fibers or glass fiber fabric. In another experiment, filling the matrix with metal oxides raised the matrix stiffness and lead to higher ultimate compressive stresses in the fibers, but these were not reflected in improved composite compressive strengths due to practical limitations on the volume fraction of fiber that could be incorporated in the filled matrix.

Ledbetter and Kneibel [1992] presented new textile geometries consisting of tight helical wrappings of high-modulus fibers around core fiber bundles of the same or a different polymeric reinforcing fiber. They applied this new technology to composites of Kevlar 49, Spectra 1000, and cis-PBO fibers improving the compressive strength by up to 100%.

2.3.2 Improving the Compressive Strength of High-Modulus Polymer Fibers

The most often cited reason for the poor compressive properties of highly oriented polymers is the weak lateral interactions between macromolecules and/or microfibrils. Accordingly, a lot of work has been done to confirm and exploit this hypothesis. One approach to investigate the effect of improved lateral interactions on compressive strength has been the crosslinking of liquid crystalline polymer fibers by various means, which will be briefly discussed in the following paragraphs. Another route to decrease the anisotropy of highly oriented polymers, thought to cause the weak lateral
interaction, has been the inclusion of bulky-substituent-comonomers in the polymerization of PBZT, which were supposed to disrupt the nematic packing, improve the lateral interaction by misorientation, and increase the compressive strength [Arnold and Burkett, 1990; Wang et al., 1989]. Though, it was found that Young's modulus, packing, and compressive strength were not affected.

If the lack of strong lateral interactions is indeed responsible for the compressive weakness, then the attempt to improve compressive strength by crosslinking of the molecules and/or the microfibrils seems to be quite intuitive, since this introduces strong covalent bonds in the lateral directions. Also, the examples of compressively strong materials, such as glass, alumina, and diamond (\( \sigma_c(\text{SiO}_2) = 1 \) GPa, \( \sigma_c(\text{Al}_2\text{O}_3) = 7 \) GPa, \( \sigma_c(\text{C}_{\text{Dia}}) = 16 \) GPa [Northolt, 1981]) support the notion that 3-dimensionality is favorable, if not necessary, for good compressive strength. At present, there is no theoretical framework to predict the effects of crosslinking on the mechanical properties of highly oriented, crystalline polymers. Though, crosslinking will only result in improved torsional stiffness, if the crosslink-density is sufficient so that fiber twisting will result in bond-stretching. At small degrees of crosslinking, shear deformation of the fiber would only cause bond angle opening, which has a much smaller force constant than bond stretching.

Figure 2.2 illustrates the various attempts to improve the compressive properties of PBZT fibers by introducing various crosslinkable groups or through other structural modifications described in the following paragraphs.

PBZT with 9-50 mole-% of crosslinkable 2,7-fluorene moieties (F-PBZT) was synthesized [Dotrong and Evers, 1989]. No difference in the swelling behavior of the crosslinked F-PBZT and not crosslinked PBZT was found [Bhattacharyya et al., 1989]. The compressive strength of F-PBZT fibers was in the range of 0.45 to 0.55 GPa and was decreasing with increasing temperature of heat treatment.
Another synthetic route to crosslinkable PBZT molecules was taken by introducing thermally labile methyl groups as substituents on the aromatic rings [Chuah et al., 1989]. Tensile modulus and strength decreased at a crosslink density of about 1/10 repeat units, while the compressive strength of these fibers improved slightly. At higher degrees of crosslinking the compressive strength was actually found to decrease. No explanation for this phenomenon was offered. Also, in neither of the two experiments above was the evidence for the presence of crosslinked moieties unambiguous and mostly derived from the reactions of small molecular model compounds.

Other efforts have focused on strengthening or introducing secondary forces between molecules. Benzobisthiazole units with pendent dihydroxy groups were incorporated in the PBZT backbone with the intent of forming intermolecular hydrogen bonds [Dang et al., 1989]. Instead it was found that strong intramolecular hydrogen bonds formed leading to a pseudo-ladder structure. This bond formation increased the coplanarity of the aromatic ring systems and restricted rotation around the molecular axis. Even though these two features, pseudo-two-dimensionality and inhibited rotation, should have improved the compressive strength according to the molecular viewpoint of the failure mechanism, the fiber compressive strength was actually much lower than for regular PBZT fibers, thus providing a first indication of a negative effect of a substituent on the compressive strength.

Sweeney [1992] achieved crosslinking and improved compressive strength by halogen elimination from brominated PBZT at the expense of reduced tensile properties. Table 2.3 shows an excerpt of his results. The samples with the highest halogen losses, indicating a high degree of crosslinking, gave the highest shear moduli. Yet, there was only a trend for increased shear moduli and improved compressive strength to coincide, but no strong correlation between the two properties is revealed
by these data. All the crosslinked Br-PBZT fibers were insoluble in methane sulfonic acid and lost their fibrillar, tensile failure characteristics when a degree of crosslinking between 22 and 30% was reached. Excessive void formation at higher degrees of crosslinking obscured any further improvements of the compressive strength. This approach did not provide similar results for PPTA fibers due to competition between crosslinking and thermolysis of the polymer backbone during the halogen elimination.

Table 2.3: Properties of PBZT and brominated PBZT (Br-PBZT) fibers after heat-treatment. T / t: temperature and time of heat-treatment, G: shear modulus, $\sigma_c$: compressive strength by tensile recoil, $\sigma_t$: tensile strength, E: modulus

<table>
<thead>
<tr>
<th>Fiber</th>
<th>T / t</th>
<th>G [GPa]</th>
<th>$\sigma_c$ [g/den]</th>
<th>$\sigma_t$ [g/den]</th>
<th>E [g/den]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBZT</td>
<td>500°C / 10 s</td>
<td>2.1</td>
<td>1.7</td>
<td>26.7</td>
<td>939</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>500°C / 10 s</td>
<td>2.1</td>
<td>-</td>
<td>16.3</td>
<td>871</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>500°C / 1h</td>
<td>3.5</td>
<td>2.7</td>
<td>29.9</td>
<td>724</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>500°C / 1h</td>
<td>4.1</td>
<td>2.7</td>
<td>7.2</td>
<td>482</td>
</tr>
<tr>
<td>PBZT</td>
<td>450°C / 1h</td>
<td>2.2</td>
<td>-</td>
<td>17.5</td>
<td>626</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>450°C / 2h</td>
<td>2.5</td>
<td>3.2</td>
<td>18.6</td>
<td>730</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>450°C / 4h</td>
<td>3.4</td>
<td>4.9</td>
<td>26.6</td>
<td>763</td>
</tr>
<tr>
<td>PBZT</td>
<td>425°C / 1h</td>
<td>1.9</td>
<td>1.7</td>
<td>25.3</td>
<td>839</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>425°C / 1h</td>
<td>2.7</td>
<td>2.7</td>
<td>20.6</td>
<td>678</td>
</tr>
<tr>
<td>Br-PBZT</td>
<td>425°C / 3h</td>
<td>3.0</td>
<td>1.8</td>
<td>16.9</td>
<td>696</td>
</tr>
<tr>
<td>Kevlar 29</td>
<td>-</td>
<td>1.7</td>
<td>2.9</td>
<td>26.8</td>
<td>629</td>
</tr>
</tbody>
</table>
Numerous other chemical modifications were carried out at Du Pont to achieve crosslinking and improved compressive strength of PPTA fibers but none has been successful [Allen, 1992]. Some of these modifications are presented in Figure 2.3.

Thermo-oxidative crosslinking [Kiyotsukuri et al., 1988] while quintupling the shear modulus of nylon-6,6, has shown only a moderate effect (20% increase) on the torsional rigidity of PPTA samples prepared from isotropic solution. Only relative rigidities, determined by torsional-braid analyses, were reported in this work.

Thermal crosslinking of PBZT fibers during prolonged heat-treatment at elevated temperatures was first demonstrated by Allen [1983]. Carried to an extreme, thermal crosslinking of polymer fibers leads ultimately to carbon fibers. The development of properties, in particular the compressive strength, in that process can give an insight as to the degree of crosslinking necessary for the achievement of improved compressive strength. Jiang et al. [1991] studied the development of morphology and properties in the carbonization of PBZT fibers. The compressive strength increased with the degree of carbonization after a large initial drop, so that only the best carbonized PBZT fiber showed an improved compressive strength (650 vs. 400 MPa) compared to the original PBZT fiber. But that fiber also exhibited greatly reduced tensile properties, which was attributed to excessive void formation during elimination of volatiles. Nevertheless, a similar study using polymers and processes designed and optimized for the conversion from polymer to carbon or even ceramic fibers should be of great fundamental interest in this respect.

Some other unsuccessful attempts by Du Pont to improve the compressive strength of PPTA fibers were: surface coatings with various polymers, low-melting glasses, etching with strong acids, ozone or electron beams, co-spinning of PPTA with graphite and metal particles, titanium dioxide, aluminum oxide, carbon black, alumina platelets, or various polyamides [Allen, 1992].
The introduction of complex-forming iodine species into PBZT fibers during the coagulation step has been another attempt to improve the lateral (secondary) interactions [Rakas, 1990]. There has been some evidence from WAXS and elemental analysis of the success of the formation of a strong complex between PBZT and iodine and the fibers' compressive strength was improved also, but this increase could not be attributed unambiguously to the complex formation. PPTA fibers also showed structural changes as a function of the coagulant or coagulant additives, but none of those changes improved the compressive strength of the fibers.

Among all the chemical modifications carried out to improve the compressive strength of HM-polymer fibers only the thermal debromination of bromine-substituted PBZT has led so far to promising results. But the debromination also decreased the tensile properties and resulted in a loss of the fibrillar tensile fracture, possibly affecting the damage tolerance of the fibers. Most physical fiber treatments, e.g., co-spinning of PPTA with various additives, also gave no improved fiber compressive strength. Those few treatments that have been at least partially successful will be presented in Chapters 4 and 5.
Crosslinking via Thermally Labile Methyl-Groups [Chuah et al., 1989]

Crosslinking through Thermal Debromination [Sweeney, 1992]

Thermal Crosslinking via Fluorene Moieties [Bhattacharya et al., 1989; Dotrong and Evers, 1989]

Pseudo-Ladder Structure through Intramolecular Hydrogen-Bonds [Dang et al., 1989]

Disruption of Molecular Packing by Bulky Substituents [Wang et al., 1989; Arnold and Burkett, 1990]

Figure 2.2: Chemical modifications of PBZT aimed at improving fiber compressive strength
Crosslinking via Thermally Labile Methyl-Groups [Allen, 1992]

Crosslinking through Thermal Debromination [Sweeney, 1992]

$X = \text{Cl, Br, I}$

Physical Crosslinking through Ionic Groups [Allen, 1992]

Chemical Crosslinking through Diazot Coupling of Nitrated PPTA [Allen, 1992]

Figure 2.3: Chemical modifications of PPTA aimed at improving fiber compressive strength


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3.1 Materials

This chapter describes the materials and experimental techniques as well as the corresponding hardware used in both the impregnation and coating studies. Experimental techniques used exclusively in one or the other approach are presented in Chapters 4 or 5, respectively.

Materials 1 and 2 listed below were used in the coating experiments described in Chapter 5. Material 3 was used as the control for fibers spun from solution (material 6) and subsequently used in impregnation experiments (cf. Chapter 4) along with fibers 4 and 5. The PPTA spinning dope was also used to prepare more dilute solutions from which PPTA films were prepared by spin-coating. The films were used in surface modification studies (Chapter 5) as well as in impregnation experiments (Chapter 4). Materials 2 and 7 were supplied for previous studies [Allen, 1983; DeTeresa, 1985; Pottick, 1986; Hwang, 1989] by the Wright-Patterson Air Force Materials Labs. All other materials were supplied by Du Pont.

1. heat-treated PPTA fiber: Kevlar 49® yarn, 380 denier, 267 filaments, no finish
2. heat-treated PBZT fiber: Aftech 1 yarn, 200 filaments, no finish
3. tension-dried PPTA fiber: Kevlar 29® yarn, 1500 denier, no finish
4. as-coagulated PBZT fiber, 100 filaments
5. as-coagulated PPTA tape (flattened hollow fiber or fused filaments)
6. PPTA spinning dope (approximately 20% PPTA in 100% sulfuric acid)
7. PBZT spinning dope (5.5% PBZT in polyphosphoric acid, [η] = 18 dl/g)
Mechanical properties of single filaments of materials 1 to 4, as determined in the course of this research, are listed in Table 3.1 and representative stress-strain curves are shown in Figure 3.1.

3.2 Microscopy

3.2.1 Optical Microscopy

Optical microscopy has been used for three purposes: 1) measuring of fiber diameters, 2) evaluation of compressive failure or the absence thereof, and 3) observation of coated filaments' surface appearance. The microscope (Olympus-BH2 polarizing microscope) was equipped with a calibrated eye-piece (10×), a set of lenses (2.5×, 10×, 20×, 50×, 80×), and a set of Bertrand lenses (1×, 1.25×, 1.5×). The microscope was used in reflection and in transmission mode. Fiber diameters were measured by taking one reading through the calibrated eye-piece every 5 mm along the filament. For the industrially prepared filaments fewer readings (1 reading/cm) gave sufficient accuracy.

3.2.2 Scanning Electron Microscopy

A JEOL-35CF was used to characterize the surfaces of glass-coated fibers as well as to study isotropic, impregnated fibers. All samples were mounted on aluminum cylinders using a conductive adhesive and sputter-coated with a few Ångstroms of gold. Accelerating voltages of 10 to 20 kV were used as required by the electrical properties of the samples.
Table 3.1: Mechanical properties of polymer filaments used in this work. d: diameter, E: elastic modulus, σ: tensile strength, ε: tensile strain at break, G: shear (torsion) modulus, σ_c: compressive strength, nm: not measured

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<td>3.3</td>
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<td>380</td>
</tr>
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<td>1.4</td>
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<td>4.0</td>
<td>1.5</td>
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<td>90</td>
<td>1.7</td>
<td>1.7</td>
<td>1.2</td>
<td>nm</td>
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Figure 3.1: Stress-strain curves of the filaments used in this research. 1: Aftech 1 (heat-treated PBZT) fiber, 2: Kevlar 49, 3: as-spun PBZT fiber, and 4: Kevlar 29
3.3 Mechanical Tests

3.3.1 Tensile Tests

Tensile tests for the determination of elastic modulus, strength at break, and strain at break were carried out on an Instron universal tester equipped with a Toyo TI 550 load cell (max. load: 550 grams). Force data were collected on a Dell 316SX personal computer at a rate of 5 Hz. Usually, 8 to 15 filaments were mounted on cardboard tabs using 5-Minute Epoxy™ or Superglue-Gel™. Gage lengths of 15 to 100 mm were used and the fibers tested at crosshead speeds of 0.05 to 0.5 cm/min, so that a single test would last approximately one minute as recommended by the ASTM D 3379 standard method.

The compliance of the load cell used was approximately 300 μm/N. This compliance caused a systematic error in the uncorrected moduli with a relative magnitude depending on sample diameter, length and true modulus. For example, in a typical case (where \( L = 3 \text{ cm} \), \( d = 12 \mu\text{m} \), \( E = 100 \text{ GPa} \)), the uncorrected, measured modulus would be 90 GPa and, thus, 10% too small. Because the moduli cited in the following sections as well as in Table 3.1 above are in comparison to each other, values have generally not been corrected for the machine compliance.

3.3.2 Torsion Test

The longitudinal shear moduli of filaments were determined using a torsion pendulum method [DeTeresa, 1985]. Aluminum gear blanks were used as pendulum disks. Their moments of inertia were determined by measuring of their dimensions and weighing. The results were also checked with respect to each other by using all three disks consecutively on each one of a set of 8 Kevlar 49 filaments. For the much thicker PPTA fibers spun from isotropic solution, a larger pendulum disk was prepared by
attaching a stainless steel disk to the largest gear blank. Its moment of inertia was evaluated as before. The period of the free oscillation of the pendulum disks was measured using a hand-held stop-watch. The pendulum was hung inside a chamber, to protect it from the effect of air currents. For each sample, 6 to 12 filaments were tested. The filaments were mounted on cardboard tabs as described in the previous section. For most torsion tests a gage length of 20 or 30 mm was chosen, but in some experiments shear moduli were measured on 15 cm-long fibers. The oscillation period for each filament was timed at least twice to verify consistency. Due to the dependence of the apparent shear modulus of anisotropic fibers on the axial stress in the sample a correction for this coupling was included in the calculation of the true shear modulus, G, [Allen, 1988]:

\[ G = \frac{8\pi I L}{p^2 r^4} - A\sigma_{zz} \]  

(3.1)

where I is the moment of inertia of the pendulum disk, L, the fiber length, p, the oscillation period, r, the fiber radius, A, the anisotropy correction factor, and \( \sigma_{zz} \), the axial stress in the fiber due to the pendulum mass. The value used for A depended on the kind of fiber tested. A = 0 was used for all fibers spun from isotropic solutions and A = 0.95 was used for heat-treated fibers [Allen, 1988]. DeTeresa [1985] obtained an anisotropy factor of 0.8 for Kevlar 49 and heat-treated PBZT filaments using fewer regression points than Allen [1988]. This may explain part of the difference in the value found for A, but real material differences are also possible. Allen [1988] determined a shear modulus of 2 GPa for Kevlar 49 filaments, while DeTeresa [1985] measured 1.5 GPa using the same technique. For Kevlar 29 and as-spun PPTA fibers a value of A = 0.75 was used [Rakas, 1989]. Because this factor depends on the properties of each individual sample, its general use for different samples is somewhat
arbitrary. Yet, the error introduced in the results is small compared to the standard deviation of the experiments.

3.3.3 Compression Tests

The axial compressive strength of filaments was measured using the tensile recoil test [Allen, 1987]. This test, which is presently the only test to measure a solid fiber's compressive failure stress rather than a compressive failure strain, involves the tensile stretching of a filament to a predetermined stress followed by severing the filament without disturbing the axial state of stress. Analysis of the stress development during the ensuing snap-back or tensile recoil shows that a compressive stress of equal magnitude as the tensile prestress is generated upon reflection at the clamped end. In the early phases of the research, the stressed fibers were cut manually using surgical scissors. To eliminate minor disturbances of the axial stress, the sample filament was stressed in series with two pieces of Lycra® fiber. If large disturbances were revealed in the force-time record of the experiment and the corresponding samples were discarded. Later on, an electric spark cutter was constructed to facilitate and improve the cutting of the fibers. It consisted of a Spectra Physics laser power supply and a set of electrodes as shown in Figure 3.2. The power supply would deliver the voltage necessary (max. 20,000 Volt) for the spark to cross through the air-gap. The electrodes were aligned and spaced in such a way that the electric spark would pass through the fiber when crossing the air-gap.

The stresses were applied using an Instron universal tester and the force in the filament was recorded on a PC at a rate of 5 Hz. The stress was sequentially increased in steps of 10 to 50 MPa with 4 to 6 filaments being cut at each stress level. A typical force-time record for a tensile recoil experiment is shown in Figure 3.3. The samples
would then be recovered from the grips and examined under the optical microscope for evidence of compressive failure. The compressive strength was determined as the average of the highest stress not leading to compressive failure and the lowest stress to always do so.

![Diagram of load cell and moving crosshead]

**Figure 3.2:** Electric spark cutter set-up for use in the tensile recoil test

Recently, there has been some debate over the actual state of stress in fibers during the tensile recoil. The most frequently reoccurring criticism of this test is that the state
of stress in the fiber is not "pure" uniaxial compression. This criticism is based on the experimental observation that some kinds of carbon fibers show fractographic evidence of shear failure instead of kinking [Dobb et al., 1990; Jiang et al., 1993]. It is argued that in addition to the compression caused by the tensile recoil, the cut fiber ends are also subjected to bending due to the cutting action or even air currents. In view of these experimental limitations, there are a few other complications and facts that should be kept in mind when analyzing recoil results:

Figure 3.3: Typical force-time record of a tensile recoil experiment

In cylindrically orthotropic fibers, the axial stress is a function of radial and hoop position so that axial compression or tension do not result in a purely uniaxial state of stress in the first place [Allen and Farris, 1990].

The recoil is extremely fast, on the order of 1 µs, and much slower displacements such as the bending of the loose fiber end should not significantly influence the events during recoil.
If the compressive strength is uniform along the fiber length, the compressive failure should occur very close to the clamped end, where the compressive stress is first applied. Failure away from the clamped end, as observed by Dobb et al. [1990], could indeed have occurred by other mechanisms than those of axial compressive failure. In this context, it is also worth considering the axial stress development, if compressive failure does not occur after the first reflection of the stress wave at the clamped end: The recoiling compressive stress wave is reflected at the loose end of the fiber without reversal of the sign of the stress. Constructive interference of the incident and reflected stress wave leads to a compressive stress of doubled magnitude propagating towards the clamped end. Obviously, attenuation of the propagating wave will also play a role as the total distance travelled increases.

It was discussed in Chapter 2.2.2.2 that for small deformations the relationship between compressive stress and strain is approximately linear. Thus, the compressive failure strain can be used instead of the actual compressive strength to characterize the onset of the microbuckling instability. The compressive failure strain can be measured using the beam bending technique [DeTeresa, 1985] illustrated in Figure 3.4. This technique is advantageous, if only small amounts of sample are available. One or a few sample filaments are bonded to one side of a transparent polycarbonate beam, which is then subjected to cantilever beam bending.
This type of bending results in a compressive strain gradient decreasing from the clamped to the unclamped beam end. The filament ends near the clamped beam end are being observed by optical microscopy for signs of compressive damage, such as kink bands. The compressive failure strain can be calculated using:

$$e_c(x) = \frac{3wt}{2L^2} \left(1 - \frac{x}{L}\right)$$  \hspace{1cm} (3.2)

where \( L \) is the beam length, \( w \), the deflection, \( t \), the beam thickness, and \( x \), the distance of the compressive damage from the clamped end (cf. Figure 3.4).
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66
CHAPTER 4

IMPREGNATED HIGH-MODULUS POLYMER FIBERS

4.1 Introduction

Impregnation of as-coagulated polymer fibers with a suitable inorganic oxide precursor is one way of physically combining a glass or ceramic with an organic polymer. The objective of impregnation in this context is the preparation of two interpenetrating and cocontinuous phases, one being the high-modulus polymer, the other an isotropic, rigid glass or ceramic. The isotropic, rigid phase serves to increase the global shear modulus of the fiber as well as to specifically enhance the interfibrillar shear modulus. Adhesion between the two dissimilar materials is not necessary due to the mechanical interlocking of the phases. While the properties of such nanocomposites are not easy to predict quantitatively, qualitatively it is still reasonable to expect an increase of torsion modulus and compressive strength with respect to those of the neat HM-polymer fiber.

The following sections in this introduction briefly review the formation of swollen networks of coagulated polymers (PPTA and PBZT fibers) as the basis for the feasibility of impregnation, also termed infiltration or imbibition, and present the existing literature concerning the impregnation of PPTA, PBZT and PBO.

4.1.1 As-Coagulated Structure of Polymers Precipitated from Lyotropic Solutions

In the spinning process of polymer fibers from lyotropic solutions, the liquid-solid transition occurs in the coagulation step. During coagulation the extruded polymer solution is usually cooled by the coagulant, while simultaneously the polymer is precipitated from the solvent and the solvent is extracted from the polymer-solvent-
coagulant system. When the polymer solution is completely changed to a polymer-coagulant system, the coagulant-swollen (as-coagulated) fibers have tensile properties, even before drying and other post-treatments, comparable to those of dried fibers, when normalized with respect to the polymer volume fraction [Pottick, 1986]. This high degree of mechanical integrity is consistent with a microfibrillar network of polymer chain bundles swollen by a continuous coagulant phase (Figure 4.1). This structure has been confirmed by electron microscopy of PBZT fibers, in which the as-coagulated structure had been preserved by exchange of the coagulant (water) for epoxy resin [Cohen and Thomas, 1985, 1988].

![Diagram of swollen network structure](image)

Figure 4.1: Schematic drawing showing swollen network structure of as-coagulated filament

The existence of this swollen network is the foundation for the approach to improved compressive strength described in this chapter. It is therefore of interest to
review some of the hypotheses on the formation mechanism of polymer-coagulant networks.

Miller et al. [1978] proposed that the formation of a mechanically self-supporting network in nonionic, rod-like polypeptide homopolymers poly(benzyl-L-glutamate) occurred by a spinodal decomposition mechanism. Cohen and Thomas [1985, 1988] argue, though, that the essentially one-dimensional mobility of rod-like molecules, such as PBZT, would not result in the observed interconnected, microfibrillar structure. Instead, they suggest a one-dimensional nucleation-and-growth mechanism, in which the density of nuclei determines microfibrillar diameter and deviations from axial orientation lead to the interconnectivity.

Both suggested mechanisms consider phase separation to occur spontaneously in a homogeneous system. Considering the fairly slow diffusion of a coagulant into a polymer solution [Hwang, 1989] that may not be a valid assumption. Xu et al. [1984] interpreted the microfibrillar structure of PPTA fibers as a consequence of diffusion-controlled hydrolysis: Hydrolysis forms nascent PPTA molecules, which collapse much faster than the water diffuses through the PPTA solution, thus forming microfibrils and leaving dilute, acid-filled microcavities behind. This largely conceptual model leaves enough room to accommodate locally occurring spinodal decomposition or 1-dimensional nucleation-and-growth as the mechanisms for the formation of the solid polymer phase in a heterogeneous system.

4.1.2 Impregnated High-Modulus Polymer Films and Fibers

The feasibility of reducing fiber anisotropy by forming an interpenetrating network of microfibrils and another polymer phase has been documented in a patent by Farris et al. [1989]. The infiltration of PBZT filaments by a solution exchange method,
demonstrated in that patent, does not only yield a composite fiber which has potentially better adhesion to a bulk matrix and favorable translation of tensile fiber properties into composite properties due to the microscopic dimensions of the reinforcing microfibrils (approximately 10 nm in diameter), but it also offers an opportunity to improve the compressive properties of the fiber by introducing a torsionally rigid substance that shifts the onset of the buckling instability to larger compressive stresses. Several possible matrix materials, such as epoxies, phenolics, polyimides, silicone resins, polyurethanes, monomers for different polymers, and organic and inorganic silicates were suggested in the patent. While impregnation with all of those materials serves its purpose in the manufacture of various fiber reinforced composite materials, only the silicates will lead after appropriate processing (e.g. sol-gel processing of organic silicates) to a matrix with sufficient rigidity to provide the desired support against a shear instability.

Hwang [1989] demonstrated that infiltration of isotropic PBZT fibers with polyamides does not result in improved compressive strength, confirming that a more rigid matrix is required for this purpose. Preliminary results on the impregnation of PBZT fibers with tetraethyl orthosilicate (TEOS) showed improved tensile and shear modulus, but the compressive strength could not be measured due to shrinkage induced kinkbands [Rakas, 1990]. These improvements have to be judged with care since the properties were only modestly raised: The tensile modulus increased from 150 to 200 GPa and the shear modulus from 580 to 900 MPa.

It should be noted at this point, that a cocontinuous network of HM-polymer and fully densified silica glass will have smaller tensile modulus and strength than the not-impregnated HM-polymer fiber, due to the inherently lower properties of the silica glass and the induced misorientation in the polymer phase.
PBZT films showed a 4-fold increase in compressive strength upon infiltration with and curing of a silica sol-gel precursor [Kovar et al., 1989, 1990]. Though, this same approach did not result in improved compressive strength for PBZT fibers. That of PBO fibers, by contrast, was improved from 210 to 280 MPa upon impregnation with silica [Kovar et al., 1989, 1990]. Despite these promising first results, follow-up experiments in this direction have not led to additional publications on this subject. There have also been experiments evaluating other glass compositions, e.g., borosilicate glasses, sodium borate and lead borate glasses, etc. [Kovar et al., 1989, 1990]. Compared to pure silica glass these other formulations offer the advantage of having lower melting points (< 650°C vs. 1200°C), thus allowing a densification by fusion of the glass phase within the limits of thermal stability of PBZT in nitrogen or in vacuum. Some lead borate formulations have been found to form small particles (10 to 100 nm) in the PBZT matrix rather than a continuous network and are, therefore, considered inappropriate [Schaffer, 1989]. The tensile modulus is affected only insignificantly by the impregnation with a glass phase, while elongation at break and tensile strength decrease noticeably and the flexural modulus increases [Schaffer, 1989].

The earliest published account of impregnated PPTA fibers can be found in a patent which has as primary subject the impregnation of poly(m-phenylene isophthalamide) (Nomex® by Du Pont), with the goal of improved flame resistance [Baird and Sherbeck, 1977]. It was reported in the disclosure that PPTA fiber had been impregnated with melamine-formaldehyde (MF) resin and a phosphor-containing compound to permit a comparison of the flame resistance of these two impregnated aramid fibers. Mechanical properties of these impregnated fibers were not reported.

More recent investigations used the impregnation of PPTA fibers to prepare electrically conductive, processible hybrid materials with good mechanical properties
Cospinning of PPTA and metal-phthalocyanines from isotropic solution (approximately 5% PPTA) in trifluoro methane sulfonic acid resulted in quasi-impregnated fibers. In addition, the fibers were doped with halogen either by addition to the spinning solution, by coagulating the fibers in an aqueous halogen/halide solution, or by immersing the as-coagulated fibers in a solution of halogen in benzene. These fibers had tensile moduli of 3 to 4 GPa depending on phthalocyanine concentration in the fiber, a tensile strength of approximately 22 MPa, and an elongation at break of approximately 10% [Wynne et al., 1985].

PPTA fibers spun from isotropic solution have mechanical properties inherently inferior to those of fibers spun from lyotropic solution and their morphology and structure in the dried and as-coagulated state defer considerably. Therefore, a comparison of the properties of anisotropic and impregnated isotropic polymers is not possible.

Solution exchange of water with sol-gel silica solution, inorganic silicates, a titanate, or epoxy did not significantly alter the mechanical properties of PPTA fibers [Rakas, 1990]. Unfortunately, the success of the impregnation procedure was not verified by chemical analysis of the fibers.

Allen [1992] reported that research at Du Pont had shown some improvements of flexural strength for composites of PPTA fibers, which had been impregnated with Epon 828® epoxy resin. Impregnation with 1.2 wt-% of silica or 14 wt-% of titanium dioxide did not have any effect on the fibers compressive strength.

Ueta et al. [1993] prepared PPTA/silica composite films by soaking PPTA films, which had been coagulated under controlled temperature and relative humidity to give a voided film, in a sol-gel glass solution. They report glass contents up to approximately 35 wt-%, but with maximum tensile properties occurring at concentrations of 5-10 wt-% silica. The as-spun film had a modulus of 3.5 GPa and a
tensile strength of 160 MPa, while the PPTA/silica (8 wt-% SiO$_2$) composite film had a modulus of 5.3 GPa and a strength of 220 MPa. These low numbers as well as the large strains at break (= 55 and 40%, respectively) suggest that the films were spun from isotropic PPTA solutions. Decreasing tensile properties at higher silica concentrations are possibly a consequence of polymer degradation during the prolonged soaking times in the nitric acid catalyzed sol-gel solution. The improvement of the tensile properties of the composite PPTA films should also be regarded with caution, because the heat-treatment temperature of 370°C is not sufficient to provide highly densified silica, but only a high degree of densification would explain the large relative increase of tensile properties at the small silica volume fraction. Also, it was observed in the course of this dissertation that isotropic PPTA fibers exhibit generally a much wider range of tensile properties within the same batch than do PPTA fibers spun from anisotropic solution.

4.2 Experimental

As-coagulated PPTA films were prepared for diffusion experiments by spin-coating of an isotropic solution of 5% PPTA in sulfuric acid onto glass slides followed by coagulation, washing and storage in deionized water. PPTA films were prepared from nematic solution by doctor-blading molten spinning dope (= 20 wt-% polymer) onto a glass slide, coagulating, washing and storing in deionized water.

For the impregnation studies, as-coagulated PPTA fibers were obtained by dry-jet wet-spinning and wet-spinning of nematic and isotropic PPTA solutions in 100% sulfuric acid. The isotropic solutions were prepared by dissolving pieces of the nematic PPTA dope in 100% sulfuric acid at 65 to 70°C under nitrogen atmosphere. The solution was then stored in a refrigerator until spinning it into fibers. For the spinning,
the isotropic solution was poured into the chamber of the spinning cell, which was then completely assembled and mounted on the spinning rig. The nematic dope was prepared for spinning in the following way: In a nitrogen-purged glove bag, pieces of the refrigerated dope were broken out of the Nalgene® jar in which it was stored. The pieces were then filled into a PTFE-lined glass tube (ID = 25 mm) with two 29/42 joint ends, one of which was closed with the appropriate glass stopper. The tube was then placed upright into a vacuum oven at 90°C. When the dope had melted, the tube was removed, capped with a second glass stopper and placed in a refrigerator. After cooling, the glass tube was placed again in a glove bag, the PPTA dope plug was pushed out of the tube and cut into 5-7 cm-long pieces, which were stored in a Nalgene® jar in the refrigerator until spinning. This procedure was intended - and seemed to be effective - to remove as much air as possible from the dope prior to spinning to avoid frequent fiber line breakage. Spinning conditions giving optimal spinnability and best fiber properties are summarized in Table 4.1. The spinning apparatus is represented schematically in Figure 4.2. The as-coagulated PPTA tape and as-coagulated PBZT fiber, both spun from nematic solution, were used as received from Du Pont.

The compositions of impregnated fibers and films were evaluated using elemental analysis (ash content, elemental composition) and thermogravimetric analysis. The elemental analyses were performed by the Microanalysis Lab of the chemistry department using high-temperature combustion in oxygen followed by gas analysis (for carbon, hydrogen, nitrogen, and sulfur) or gravimetry (for ash content). Thermogravimetric analysis was done on a Du Pont Instruments (now TA Instruments) Thermogravimetric Analyzer 2950. For the TGA, fiber samples were prepared in form of coils with diameters of approximately 5 to 8 mm. This was done by winding the fiber onto a quartz or copper tube, removing it carefully and tying it together using 2 to 4 short segments of the same fiber.
In order to determine which solvents and solutes would permit the infiltration of as-coagulated PPTA, a few simple diffusion experiments were carried out. The experimental set-up consisted of two legs of a U-tube separated by a piece of PPTA film (Figure 4.3). Either water or ethanol were filled to different levels into the two legs or one leg was filled with a solution of sodium hydroxide, sulfuric acid, or TEOS, the other one with pure solvent (water and/or ethanol). Then it was observed whether or not mass transport between the two legs occurred over a period of 2 to 3 days. Equilibrating solvent levels, pH changes in the initially deionized water, and the presence of orthosilicate species in the originally pure solvent demonstrated that mass transport was taking place. Presence of orthosilicate was tested by removing small amounts from the solvent tube and adding a few drops of alcoholic sodium hydroxide, which precipitated dissolved orthosilicate as silica.

Table 4.1: Spinning parameters for wet-spinning of isotropic and dry-jet wet-spinning of nematic solutions of PPTA in sulfuric acid

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nematic Solution</th>
<th>Isotropic Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Temperature</td>
<td>82 to 85°C</td>
<td>≈20°C (room temp.)</td>
</tr>
<tr>
<td>Solution Concentration</td>
<td>≈20%</td>
<td>≈8%</td>
</tr>
<tr>
<td>Coagulant Temperature</td>
<td>≈5°C</td>
<td>≈15°C</td>
</tr>
<tr>
<td>Air Gap Length</td>
<td>≈1 cm</td>
<td>0</td>
</tr>
<tr>
<td>Spinneret Diameter</td>
<td>75 or 100 μm</td>
<td>150 or 200 μm</td>
</tr>
<tr>
<td>Extrusion Speed</td>
<td>&gt;100 m/min</td>
<td>≈100 m/min</td>
</tr>
<tr>
<td>Take-Up Speed</td>
<td>&gt; 400 m/min</td>
<td>≈200 m/min</td>
</tr>
</tbody>
</table>
Figure 4.2: Schematic of fiber spinning apparatus. a) heatable spinning cell, b) polymer solution, c) coagulant stream, d) take-up wheel, e) tub to collect spent coagulant and keep as-coagulated fiber wet, f) polymer fiber

Figure 4.3: Schematic of U-tube diffusion experiments. a) liquid-filled U-tube legs, b) as-coagulated PPTA film, c) water-filled dish to prevent drying of PPTA film
Impregnation of isotropic films and fibers was carried out in a batch process, i.e., the as-coagulated film or fiber samples were simply immersed and soaked in the impregnator solutions for 1 to 14 days. Initially, anisotropic PPTA fibers were impregnated with melamine-formaldehyde (MF) resin, because the feasibility of this impregnation had been reported in Baird's and Sherbeck's patent [1977]. In addition, MF-resins are highly crosslinkable and may, in fact, have better shear moduli than anisotropic HM-polymer fibers. The predominant use of this kind of MF-resin in hard coatings may be the reason why no elastic properties have been reported for these materials. As described in the patent, impregnation was carried out in a batch process by immersing spools of as-coagulated PPTA fiber or tape into aqueous solutions of a melamine-formaldehyde resin. Different resin concentrations were used to study the effect of concentration on the final resin content in the impregnated fibers. The melamine-formaldehyde resin used was Cymel® 385 supplied by American Cyanamid. The generic structure of this resin is shown in Figure 4.4.

\[
\begin{align*}
\text{NR-XX-R}_2\text{N} & \quad \text{NR}_2 \\
\text{R}_2\text{N} & \quad \text{R} \\
\text{R} & = \text{H, CH}_2\text{OH, or CH}_2\text{OCH}_3 \\
\end{align*}
\]

Figure 4.4: Generic structure of melamine-formaldehyde resin used for impregnation

The impregnation of anisotropic fibers with sodium silicate in a batch process was not successful possibly due to osmotic collapse of the swollen network induced by the
large concentration gradient between impregnating solution and as-coagulated fiber [Allen, 1992]. Therefore, the impregnator concentration was increased very gradually in the impregnating solution using a stirred container with a syphon (Figure 4.5) draining excess liquid as concentrated sodium silicate solution was dropped into the stirred container at a rate of =100 g/day over a 3-day period. This rate of addition lead to a complete exchange of the initially present water for concentrated sodium silicate solution. The sodium silicate solution (grade F) used was obtained from Power Silicates, Inc.. It had a silica concentration of 28.3 wt-% and a molar silica-to-sodium oxide ratio of 3.23.

![Figure 4.5: Schematic of set-up used for continuous solution exchange in impregnation experiments. a) container with overflow-syphon, b) inlet tube for concentrated sodium silicate solution, c) magnetic stir-bar, d) sample-holding PTFE-spools](image)

78
After completion of the impregnation by either the batch process or the continuous solution exchange, fibers were thoroughly rinsed and wiped to reduce surface contaminations as much as possible. To verify surface cleanliness, samples of the impregnated fibers were examined under the optical microscope. In neither case were surface contaminations observed. All cleaned, impregnated fibers were first air-dried for 24 hours and then dried in a vacuum oven at 110 - 120°C for another 24 hours. This temperature range had been found sufficient to cure the neat melamine-formaldehyde precursor resin into a colorless transparent, brittle, and hard solid.

In an experiment related to the impregnation of as-coagulated filaments, the accessibility of the network was evaluated by running a reaction on as-coagulated PPTA tape or fiber. The water in the as-coagulated samples was first exchanged for 1% acetic acid in water. The exchange procedure was continued in approximately 8 hour-intervals with replacements by 3, 10, 20, 40, 75 and 100% acetic acid, followed by 50 and 26% acetic acid in acetic anhydride. Finally, nitration of as-coagulated PPTA fibers and tape was carried out in an ice bath using the following reagents: 20.0 g acetic anhydride, 7.2 g 100% acetic acid, 0.4 g 96% sulfuric acid, and 5.0 ml fuming (90%) nitric acid. This is the same nitrating solution used for the surface nitration described in Chapter 5. Control samples of dried PPTA fiber and tape were submitted to the same treatment. The reaction was terminated by placing the spool holding the swollen and control fiber/tape samples into a large amount (=1 liter) of deionized water. After thoroughly washing and drying the nitrated fibers they were redissolved in concentrated sulfuric acid and films were spin-coated onto glass plates followed by coagulation in deionized water. After thorough washing and drying, the films were examined by X-ray photoelectron spectroscopy to obtain a semi-quantitative measure of the relative extent of nitration in the as-coagulated and dried fibers/tapes, respectively.
4.3 Results

4.3.1 Diffusion through Isotropic and Anisotropic PPTA Films

Table 4.2 reports the observations made in the different diffusion experiments. Isotropic PPTA film was permeable to all kinds of solvents and substances tried, while the anisotropic films were not permeable to base, ethanol, or ethanol-based solutions. One explanation of this absence of diffusion is the possible collapse of the swollen network due to the large water-concentration gradient across the film-solvent interface, which withdraws water from the swollen film. A slow, gradual solution exchange was used later on to prevent the collapse of fibers spun from nematic solution.

Table 4.2: Results of U-tube diffusion experiment

<table>
<thead>
<tr>
<th>Left Leg / Right Leg</th>
<th>Isotropic PPTA</th>
<th>Anisotropic PPTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water / Water</td>
<td>Diffusion</td>
<td>Diffusion</td>
</tr>
<tr>
<td>1% Sulfuric Acid / Water</td>
<td>Diffusion</td>
<td>Diffusion</td>
</tr>
<tr>
<td>1% Sodium Hydroxide / Water</td>
<td>Diffusion</td>
<td>No Diffusion</td>
</tr>
<tr>
<td>Ethanol / Ethanol</td>
<td>Diffusion</td>
<td>No Diffusion</td>
</tr>
<tr>
<td>Silica Sol / Water-Ethanol</td>
<td>Diffusion</td>
<td>No Diffusion</td>
</tr>
</tbody>
</table>

4.3.2 Impregnation of PPTA Films and Fibers

In the absence of special interactions a swollen polymer with a dry density \( \rho \) and solvent volume fraction \( \phi \), impregnated with a solution of concentration \( c \) will after drying contain a weight fraction \( w \) of the solute given by equation 4.1:

80
The solvent volume fractions $\phi$ were evaluated using equation 4.2:

$$
\phi = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{wet}}} = \frac{L_{\text{wet}} d_{\text{wet}}^2 - L_{\text{dry}} d_{\text{dry}}^2}{L_{\text{wet}} d_{\text{wet}}^2} = 1 - \frac{L_{\text{dry}} d_{\text{dry}}^2}{L_{\text{wet}} d_{\text{wet}}^2}
$$

where, $V$ is the volume of as-coagulated ("wet") or dried ("dry") filaments, $L$, the length of as-coagulated ("wet") or dried ("dry") filaments, and $d$, the diameter of as-coagulated ("wet") or dried ("dry") filaments. Lengths of as-coagulated and dried fibers were measured using a ruler and diameters were obtained by optical microscopy. As-coagulated fibers were kept in the respective liquids during microscopy measurements to prevent drying and collapse.

Length changes upon drying were negligible for the anisotropic fibers, but considerable for the isotropic PPTA fibers. Table 4.3 lists the observed dimensional changes and the solvent volume fractions calculated from those observations.

Table 4.3: Dimensional changes observed upon drying of polymer filaments. $d$: diameter, $L$: length, $\phi$: water volume fraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>PPTA Fiber</th>
<th>PPTA Tape</th>
<th>PBZT Fiber</th>
<th>Iso PPTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{wet}}$ [(\mu\text{m})]</td>
<td>23.0</td>
<td>140</td>
<td>20.8</td>
<td>244</td>
</tr>
<tr>
<td>$d_{\text{dry}}$ [(\mu\text{m})]</td>
<td>18.0</td>
<td>115</td>
<td>17.9</td>
<td>92</td>
</tr>
<tr>
<td>$L_{\text{wet}}$ [cm]</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>$L_{\text{dry}}$ [cm]</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>18.0</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.39</td>
<td>0.33</td>
<td>0.26</td>
<td>0.92</td>
</tr>
</tbody>
</table>
There are reasons to believe that the apparent solvent volume fraction or the degree of dimensional change may depend on other variables than the polymer concentration in the spinning dope. These other parameters are short-term exposure to ambient air, coagulation temperature, draw ratio, drying temperature and tension.

Table 4.4 compares the observed and expected silicate weight fractions for the impregnation of as-coagulated filaments with sodium silicate solution. It is interesting to note that all the observed silicate contents are lower than the theoretically calculated numbers. Possible interpretations of this observation are: a) impregnated samples have been excessively rinsed with water and lost some of the silicate in the process, b) the water volume fraction in the swollen fiber is larger than the volume fraction of the silicate solution once the exchange is completed, or c) the silicate concentration inside the swollen network is smaller than in the bulk solution. The second interpretation has been refuted by measuring the dimensional changes of swollen PBZT and PPTA after the solution exchange was completed, but before drying the samples. The diameters of the filaments did not change as a consequence of the solution exchange showing the liquid volume fraction to be constant.

An ash content of approximately 3 to 5% has been found in all neat PBZT samples: heat-treated Aftech 1 fibers, as-spun fibers, and films prepared in this lab. Residual phosphate from the polyphosphoric acid polymerization and spinning medium seems one possible source of incombustible material in these samples and would also explain some of the surface oxygen observed by XPS (Chapter 5.3.1), but in this case XPS should have revealed the presence of phosphorous along with the oxygen, which was not the case.
Table 4.4: Composition of various sodium silicate impregnated fibers as determined by elemental analysis. AC: as-coagulated (swollen), % G (C, N, Ash): silicate glass content calculated based on carbon, nitrogen, or ash content, respectively. % G (#): glass content calculated from solvent volume fraction and concentration of impregnating solution, PPTA, PBZT: fibers spun from nematic solutions, Tape: PPTA tape spun from nematic solution, ISO: PPTA fiber spun from isotropic solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% N</th>
<th>% Ash</th>
<th>% G (C)</th>
<th>% G (N)</th>
<th>% G (Ash)</th>
<th>% G (#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dried PPTA</td>
<td>69.6</td>
<td>11.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AC-PPTA</td>
<td>67.2</td>
<td>11.1</td>
<td>3.2</td>
<td>3.3</td>
<td>4.5</td>
<td>3.2</td>
<td>18.5</td>
</tr>
<tr>
<td>Dried Tape</td>
<td>69.8</td>
<td>11.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AC-Tape</td>
<td>66.4</td>
<td>11.0</td>
<td>4.6</td>
<td>4.5</td>
<td>5.6</td>
<td>4.6</td>
<td>14.7</td>
</tr>
<tr>
<td>Dried PBZT</td>
<td>61.3</td>
<td>10.0</td>
<td>4.7</td>
<td>2.9</td>
<td>4.5</td>
<td>4.7</td>
<td>0</td>
</tr>
<tr>
<td>AC-PBZT</td>
<td>59.8</td>
<td>9.5</td>
<td>4.6</td>
<td>5.2</td>
<td>9.9</td>
<td>4.6</td>
<td>11.1</td>
</tr>
<tr>
<td>Dried ISO</td>
<td>69.8</td>
<td>11.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AC-ISO</td>
<td>43.9</td>
<td>7.0</td>
<td>22.2</td>
<td>36.2</td>
<td>39.3</td>
<td>22.2</td>
<td>79.4</td>
</tr>
</tbody>
</table>

Table 4.5 lists the elemental compositions of as-coagulated PPTA fibers spun from nematic solution and soaked in MF-resin solutions of different concentrations. Figure 4.6 illustrates that consistently more resin is found by elemental analysis than predicted by the theoretical calculations.
Figure 4.6: Melamine-formaldehyde content in impregnated PPTA fibers as a function of resin content in the solution

An explanation for the results of the resin impregnation could be preferential wetting of PPTA by the melamine-formaldehyde monomers and oligomers as the consequence of some effect like hydrophobic interactions. Table 4.5 shows that the average resin composition is not constant, but depends for equal curing conditions on the concentration of the starting resin solution. Carbon/nitrogen weight percent ratios increase steadily from 0.85 for 1% solutions to 1.06 for 75% solutions. The development of formaldehyde during cure in vacuum at 90°C was noticed and it is proposed that different amounts of lost formaldehyde in the samples account for the compositional differences.

Figures 4.7 and 4.8 illustrate the use of thermogravimetric analysis (TGA) for the determination of impregnator contents. The agreement with the corresponding results from elemental analysis was satisfactory in both cases as shown in Table 4.6.

The sodium silicate contents determined by the Microanalysis Lab as ash content and in our lab by TGA were expected to agree, because both techniques are principally
identical and defer only in some experimental details such as the kind of sample holder (quartz tube vs. platinum pan), maximum temperature (1000 vs 900°C) and pyrolysis atmosphere (oxygen vs. air). TGA curves for MF-resin impregnated PPTA fiber samples looked qualitatively like superpositions of TGA curves of the neat MF-resin and PPTA fiber. Though, comparison of relative mass losses at temperatures below the onset of fast degradation was not expected to give the generally good agreement with results obtained through elemental analysis. The pyrolysis reactions for resin and fiber can not a priori be assumed to be independent from each other and the use of transient mass loss data is also less reliable than the comparison of residual masses.

Table 4.5: Compositions of as-coagulated PPTA fiber, spun from nematic solution and impregnated with melamine-formaldehyde resin in aqueous solution by soaking for 10 days. x% Resin: resin obtained by drying and curing an x% solution, x%-PPTA: PPTA tape impregnated with x% solution, % R (C, N): resin content calculated based on carbon or nitrogen, respectively. % R (#): resin content calculated from solvent volume fraction and concentration of resin solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% N</th>
<th>% R (C)</th>
<th>% R (N)</th>
<th>% R (#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPTA</td>
<td>69.5</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Resin</td>
<td>38.3</td>
<td>45.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Resin</td>
<td>40.4</td>
<td>41.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% Resin</td>
<td>41.0</td>
<td>41.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% Resin</td>
<td>39.7</td>
<td>37.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%-PPTA</td>
<td>67.1</td>
<td>14.3</td>
<td>7.7</td>
<td>8.1</td>
<td>0.3</td>
</tr>
<tr>
<td>10%-PPTA</td>
<td>65.1</td>
<td>16.3</td>
<td>15.1</td>
<td>15.5</td>
<td>3.2</td>
</tr>
<tr>
<td>40%-PPTA</td>
<td>63.4</td>
<td>17.2</td>
<td>21.4</td>
<td>19.0</td>
<td>11.7</td>
</tr>
<tr>
<td>75%-PPTA</td>
<td>63.3</td>
<td>17.6</td>
<td>20.8</td>
<td>23.1</td>
<td>22.5</td>
</tr>
</tbody>
</table>

85
Table 4.6: Resin and silicate contents in impregnated PPTA fiber determined by elemental analysis, ash content, or thermogravimetric analysis. (*: cf. Table 4.5)

<table>
<thead>
<tr>
<th>Impregnated PPTA Fiber Samples</th>
<th>Contents [%] by Elemental Analysis/Ash Content</th>
<th>Contents [%] by Thermogravimetric Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic Fiber/Na-Silicate</td>
<td>7.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Isotropic Fiber/Na-Silicate</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>Isotropic Film/Na-Silicate</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td>1%-PPTA*</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>10%-PPTA*</td>
<td>15-16</td>
<td>15-17</td>
</tr>
<tr>
<td>40%-PPTA*</td>
<td>19-21</td>
<td>15</td>
</tr>
<tr>
<td>75%-PPTA*</td>
<td>21-23</td>
<td>20</td>
</tr>
</tbody>
</table>

Impregnation of as-coagulated PPTA with silica sols prepared from tetraethyl orthosilicate (TEOS) in ethanol-based solutions has been successful with films and fibers prepared from isotropic solutions, but was not observed for fibers spun from anisotropic solution. A problem of this method was the rapid deterioration of tensile fiber properties under the reaction conditions (HCl, reflux overnight in ethanol). The low solid content of sol-gel solutions (< 15% SiO₂) is another drawback.
Figure 4.7: Overlays of thermogravimetric analysis plots of as-spun (1) and sodium silicate impregnated (2) isotropic PPTA fibers heated in air.

Figure 4.8: Overlays of thermogravimetric analysis plots of as-spun and melamine-formaldehyde resin impregnated, anisotropic PPTA tape heated in nitrogen.
But one definite advantage of the sol-gel approach is the small-molecular size of the silica precursor compared to the two other silicate precursors. The size of the colloid in both aqueous solutions is on the order of 10 nm, which may be too large to diffuse into the swollen, but tight networks of fibers spun from anisotropic solutions.

In the nitration experiment of swollen, anisotropic PPTA fiber and tape the swollen fiber darkened almost instantaneously while the dried control sample did not noticeably change in color over the 5 minute reaction period. The mechanical properties of these fibers were not tested. Qualitatively, no embrittlement of the fibers had occurred, i.e. they handled as well as the untreated PPTA fibers. With the modified PPTA tape it was attempted to continue the reaction sequence described in section 5.2.1, but upon addition of basic sodium hydrosulfite to the water-swollen, nitrated PPTA tape an immediate darkening of the sample occurred followed within one minute by the disintegration of the tape into short segments. The segments were recovered for analysis, but could not be recast as films with sufficient mechanical integrity.

Films were prepared from approximately 2.5% solution of the nitrated, as-coagulated and dried control PPTA fibers in 98% sulfuric acid for analysis by X-ray photoelectron spectroscopy. XPS was used to quantify the extent of nitration of the two fibers, respectively. The scans of the N-region for both films are shown in Figure 4.9. There is no observable signal for the nitro-group in the scan of the control PPTA fiber, while there is a nitro-peak approximately one tenth the size of the amide-peak. Assuming random distribution of nitrated repeat units throughout the bulk of the recast PPTA film, this would correspond to a conversion of 20% based on a homogeneous reaction. In other words, at least one fifth of all PPTA repeat units was accessible to the nitrating solution in the as-coagulated state. The speed of the nitration also deserves some further consideration. Besides the obvious effect of a larger surface on the bulk extent of nitration, it is also likely that the orientation of PPTA molecules with
respect to the accessible surface in the core of the as-coagulated fiber is different from that in the skin, exclusively accessible during the nitration of dried fibers. Differences in this orientation and the associated steric conditions may also help to accelerate nitration of as-coagulated fibers. But many more experiments are necessary to explore the merit of these speculations.

Elemental analysis did not confirm this considerable increase in nitrogen content in the polymer, possibly due to differences in bulk and surface composition, or due to the insufficiently large sample size (1.6 mg) submitted for analysis.

![Figure 4.9: Overlay of XPS high resolution scans of films cast from solutions of PPTA nitrated in the swollen (1) or collapsed state (2)](image)

These data can also be used to estimate some interesting properties of the as-coagulated PPTA fibers. Based on the XPS results for the films prepared from nitrated, as-coagulated fiber and for nitrated, as-received Kevlar 49 fibers one can
calculate the specific surface area and the average microfibrillar diameter in as-coagulated fibers. The details and assumptions used in these estimates are given in Appendix B. As-coagulated PPTA fiber has a specific surface area of approximately 400,000 m²/kg. Based on this specific surface area, a microfibrillar diameter of about 6 nm was estimated. For comparison, Kevlar 49 filament with a diameter of 12.2 μm has a specific surface area of 225 m²/kg.

4.3.3 Mechanical Properties of Impregnated Fibers

Table 4.7 lists the average mechanical properties of the filaments with the composition reported in Table 4.4. The fibers that are designated in Table 4.4 with "Dried" are identical to those in Table 4.7 labeled "AS" (as-spun) since no impregnation has occurred. The designation "AC" (as-coagulated) is changed to "Imp" because impregnation has been supposedly successful to some degree. The properties of the impregnated tape have not been evaluated.

Table 4.7: Average mechanical properties of as-spun (AS) and with sodium silicate impregnated (Imp) polymer fibers. ISO: isotropic PPTA fiber

<table>
<thead>
<tr>
<th></th>
<th>AS-PPTA</th>
<th>ImpPPTA</th>
<th>AS-PBZT</th>
<th>ImpPBZT</th>
<th>AS-ISO</th>
<th>ImpISO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d [μm]</td>
<td>19</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>G [GPa]</td>
<td>2.1</td>
<td>2.1</td>
<td>1.2</td>
<td>1.3</td>
<td>1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>E [GPa]</td>
<td>58</td>
<td>57</td>
<td>88</td>
<td>67</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>σ [GPa]</td>
<td>2.1</td>
<td>2.3</td>
<td>1.7</td>
<td>1.3</td>
<td>0.21</td>
<td>0.09</td>
</tr>
<tr>
<td>ε [%]</td>
<td>3.5</td>
<td>4.2</td>
<td>1.7</td>
<td>1.8</td>
<td>17</td>
<td>12</td>
</tr>
</tbody>
</table>

90
The properties of the impregnated and as-spun PPTA fibers are practically identical, due to the small amount of glass in the sample. By contrast, there is some difference and even a large difference between the properties of impregnated and as-spun PBZT and isotropic PPTA fibers, respectively. In the latter case, these differences are almost perfectly accounted for by the larger diameter of the impregnated fiber. If properties are recalculated based on the diameter of the as-spun fiber the properties are identical within the standard deviations of the mechanical test results. This suggests that the glass is present in the fiber merely as a passive filler, not bearing any of the load nor stiffening the sample. Another possibility is that a continuous silicate network was formed in the impregnated and subsequently dried fiber, but the mechanical properties of this network are small compared to the fiber properties and have, therefore, a deleterious effect. SEM was carried out to characterize the morphological differences between the as-spun and sodium silicate impregnated, isotropic PPTA fibers. Figure 4.10 shows the fiber surfaces of the two kinds of fiber, respectively. The structure on the impregnated fiber's surface is attributed to sodium silicate exuded from the fiber during drying. The roughness of the as-spun fiber's surface can be due to features of the spinneret or the crystallization of larger structures from an isotropic solution than from a nematic one. Fracture faces of these two kinds of fiber are shown in Figures 4.11 and 4.12. The differences are much more subtle than for the fiber surfaces. The fracture faces of the impregnated fibers seem to be smoother than those of the as-spun fibers. This is consistent with the observed increased brittleness of the impregnated fibers, which is possibly due to silicate particles acting as stress concentrators initiating cracks in the fiber. The decrease of the tensile properties of the impregnated PBZT fibers cannot be explained in the same way because the diameters of the impregnated filaments are not noticably different. The disruption of microfibrillar packing and orientation in the impregnated PBZT fiber might be responsible for the observed effect,
but in absence of detailed morphological information this is a merely speculative explanation. Average mechanical properties of melamine-formaldehyde resin impregnated fibers (cf. Table 4.5) are reported in Table 4.8. The properties remain essentially unchanged within the standard deviations of the tests despite the apparent inclusion of up to 20% cured resin.

Because no change in properties was induced by impregnation with melamine-formaldehyde resin, it was attempted to deliberately decrease the properties by impregnation with a "lubricant", a low-molecular, moderately volatile liquid. Glycerol was chosen as that liquid and as-coagulated PPTA fibers were soaked in a 25% solution of glycerol in water. Elemental analysis showed the presence of 6% glycerol in fibers, which had been vacuum-dried at room temperature. The mechanical properties of these fibers are shown in Table 4.9: All mechanical properties have been decreased, similar to the sodium silicate impregnated isotropic PPTA fibers. The compressive strength decreases also and in approximate proportion to the shear modulus, as was expected.

Table 4.8: Mechanical properties of melamine-formaldehyde impregnated PPTA fibers. x%-PPTA: PPTA fiber impregnated by soaking in an x% solution of the resin

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PPTA</td>
<td>41</td>
<td>2.1</td>
<td>63</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td>1%-PPTA</td>
<td>42</td>
<td>2.1</td>
<td>60</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td>10%-PPTA</td>
<td>44</td>
<td>2.2</td>
<td>64</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td>40%-PPTA</td>
<td>41</td>
<td>2.1</td>
<td>51</td>
<td>1.5</td>
<td>3.1</td>
</tr>
<tr>
<td>75%-PPTA</td>
<td>44</td>
<td>2.2</td>
<td>61</td>
<td>1.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Figure 4.10: SEM micrographs of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber
Figure 4.11: SEM micrographs (low magnification) of the fracture faces of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber.
Figure 4.12: SEM micrographs (higher magnification) of the fracture faces of a) isotropic PPTA fiber and b) sodium silicate impregnated, isotropic PPTA fiber
Table 4.9: Mechanical properties of glycerol impregnated PPTA fibers. d: diameter, G: shear modulus, E: tensile modulus, σ: tensile strength, ε: elongation at break, σc: compressive strength

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Spun</td>
<td>40</td>
<td>1.9</td>
<td>73</td>
<td>2.0</td>
<td>3.4</td>
<td>400</td>
</tr>
<tr>
<td>Impreg.</td>
<td>49</td>
<td>0.9</td>
<td>43</td>
<td>1.4</td>
<td>3.6</td>
<td>290</td>
</tr>
</tbody>
</table>

The shear moduli of PPTA fibers spun in this lab (Tables 4.7, 4.8, and 4.9) are noticeably larger than those of the Kevlar 29 and 49 fibers supplied by Du Pont (Table 3.1). This is likely due to differences in the exact spinning conditions used in the preparation of the respective fibers. But the differences mentioned here between the industrial grade fibers and the "lab grade" fibers is not important for all fundamental purposes of this research, because properties of impregnated or coated fibers (Chapter 5) are compared only to those of as-spun or as-received PPTA fibers of the same origin and not to those of fibers that have different properties in the first place.

4.4 Summary of Impregnation Results

As-coagulated PPTA fibers spun from nematic solution have been successfully impregnated with small-molecular melamine-formaldehyde resin dimers. The resin contents in PPTA fibers obtained by soaking in differently concentrated, aqueous MF solutions were all, except at the highest resin concentrations, larger than estimated based on a simple coagulant-solution exchange. The relative excess (experimental/estimated content) diminished with increasing resin concentration. This is consistent with preferential wetting and saturation of the microfibrillar network by the MF-resin.
Though, this impregnation had no effect on the mechanical properties of the resulting fibers.

As-coagulated PPTA and PBZT fibers spun from nematic solutions and as-coagulated PPTA fiber spun from isotropic solution have been impregnated with sodium silicate from an aqueous solution by a slow solution exchange. In all cases, a smaller than estimated amount of silicate was determined in the dried fibers. This is attributed to an exclusion effect caused by the small "mesh" of the microfibrillar network and the larger size of the colloidal silicate particles. Surprisingly, a considerable decrease of the mechanical properties resulted from the incorporation of approximately 20% sodium silicate into isotropic PPTA fibers. The cause of this property reduction is not clear. It seems as if the silicate acts only to enlarge the fiber diameter, but does not carry any load. SEM showed different morphologies for neat and impregnated, isotropic fibers, but none that explain the observed differences in diameter and mechanical properties.

While the study of the microfibrillar network of as-coagulated PPTA fibers was not an objective of this dissertation, the specific surface area of the network and the average microfibrillar diameter were estimated to be 400,000 m²/kg and 6 nm, respectively.
REFERENCES

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Hwang, R.C., "Molecular" and "In-Situ Network" Composite Fibers of Poly(p-phenylene Benzobisthiazole) and Nylons, Amherst, MA: University of Massachusetts, 1989; dissertation


Schaffer, K.R., University of Massachusetts, private communication, 1989


CHAPTER 5
GLASS COATED HIGH-MODULUS POLYMER FIBERS

5.1 Introduction

The coating of HM-polymer fibers with suitable glass or ceramic precursors followed by their conversion is another way of physically combining inorganic materials and HM-polymers into a microcomposite fiber with balanced tensile and compressive properties. In contrast to the complex geometry of interpenetrating networks, the simple geometry of a coating on a cylindrical fiber permits an easy analysis of the mechanical properties of the coated fibers. A few of those predictions will be presented in the following paragraphs, before reviewing the literature on glass or ceramic coated polymers. The derivation of equations 5.1 to 5.4 is given in Appendix C.

The tensile modulus, $E$, of coated fibers (subscript: CF) can be predicted from a simple parallel model of mechanical elements one representing the HM-polymer fiber (subscript: F), the other the inorganic coating (subscript: C) of thickness, $t$. This model does not require adhesion between coating and fiber.

$$E_{CF} = E_C + (E_F - E_C)\left(\frac{R_F}{R_F + t}\right)^2$$
or,

$$E_{CF} = E_F + (E_C - E_F)V_C$$

(5.1)

where $V_C$ is the coating volume fraction.

Neglecting effects due to surface flaws in the coating and stipulating only coatings sufficiently thin so as not to affect the fibrillar, tensile failure mode of HM-polymer fibers, there are two different scenarios for the tensile failure of a coated fiber: 1) fiber and coating fail simultaneously, or 2) the coating fails at a smaller strain than the fiber, so that the ultimate failure load is the same as for the uncoated fiber. For these two
cases, the ultimate tensile strength for a coated fiber, $\sigma_{t,CF}$, is given by one or the other of the equations 5.2, where $\varepsilon$ is the tensile strain at break, in addition to the previously defined symbols.

$$
\varepsilon_C = \varepsilon_F = \varepsilon_{CF} \Rightarrow \sigma_{t,CF} = \varepsilon_{CF} E_{CF} = \sigma_{t,F} \left[ 1 - \left( \frac{R_F}{R_F + t} \right)^2 \right] + \sigma_{t,F} \left( \frac{R_F}{R_F + t} \right)^2
$$

$$
\varepsilon_C < \varepsilon_F = \varepsilon_{CF} \Rightarrow \sigma_{t,CF} = \sigma_{t,F} \left( \frac{R_F}{R_F + t} \right)^2
$$

Equation 5.3 for the shear modulus of coated fibers, $G_{CF}$, is based on the assumption of perfect adhesion between coating and fiber.

$$
G_{CF} = G_C - (G_C - G_F) \left( 1 - \frac{t}{R_F + t} \right)^4
$$

The compressive strength of coated fibers, $\sigma_{c,CF}$, is expected to increase as shown in equation 5.4 over the compressive strength of the uncoated fiber, $\sigma_{c,F}$.

$$
\sigma_{c,CF} = \frac{G_{CF}}{G_F} \sigma_{c,F}
$$

The biggest obstacle to coating polymers with metals, glasses or ceramics are the very high processing temperatures of the inorganic materials, which are usually far in excess of the polymers' degradation temperatures. The following literature review covers some of the low-temperature processes that might be suitable for the coating of polymer fibers as well as the results of those studies where coatings have actually been applied to polymer fibers.

Fischer et al. [1991] give a brief review of approaches involving the use of preceramic polymers, e.g., polysilazanes, and chemical vapor deposition (CVD) of molecular precursors of inorganic oxides. These approaches result in ceramic coatings at temperatures between 200 and 800°C, which overlaps with the maximum
temperatures supported by some organic polymers. One disadvantage of these processes is the grain size increase (≥1μm) in the ceramic coatings at low deposition temperatures, thus making the preparation of uniform and thin coatings (<1μm) impossible. It is also reasonable to assume a reduction in strength of the material as the grain size increases. The strength of the coating is not of importance for its effect to increase the fiber's compressive strength - only its rigidity is - but some strength is required for the coating to withstand the polymers thermal expansion during heat-treatment and/or curing. Mechanical properties have also not been a focus or objective of the studies reviewed, most of which are concerned with optical properties, corrosion resistance and matrix adhesion of the applied coatings. The substrates used in those studies were also exclusively inorganic in nature.

Another approach of depositing glass or ceramic coatings at low temperatures is the use of solution-borne precursors. These solutions include simple colloidal solutions of alumina, silica [Allen, 1992] or sodium silicate, for example, or make use of the sol-gel technology. Numerous examples of glass/ceramic coatings prepared using the sol-gel approach are presented in several volumes of the MRS symposia proceedings [Brinker et al., 1984, 1986, 1988]. While very thin and homogeneous coatings can be prepared using this method, they are initially very porous and densification, requiring usually temperatures in excess of 500°C, is necessary to obtain mechanical properties approaching those of the bulk material. Sol-gel technology has not been used yet to produce coatings on polymer fibers.

Electroless plating of metal coatings on polymer fibers [Thibodeaux and Baril, 1973] or sputter coating have been mostly used to improve electrical and thermal conductivity of textile fabrics. Electroless plating generally leads to coarse metal grains not suitable for the deposition of smooth coatings or the achievement of good mechanical properties.
McGarry and Moalli [1991] published the first study in which high-modulus polymer fibers have been coated with a high-rigidity ceramic in order to improve the balance between tensile and compressive properties. They obtained a compressive strength of 430 MPa for a PBO fiber with a 0.7 μm-thick coating of the unspecified ceramic. Their uncoated PBO fiber had a compressive strength of 207(± 35) MPa. Adhesion was found to be important for the reinforcing effect and only fortuitously achieved with Kevlar 49 fibers. No compressive strength of coated Kevlar 49 fibers have been reported (uncoated Kevlar 49: 345 ± 35 MPa) and neither have other mechanical properties of the coated fibers.

Allen [1992] reports on efforts by Du Pont to improve fiber compressive strength by plating PPTA fibers with alumina and silica by treatment with colloidal solutions of these oxides, followed by heat-treatment of the fibers. Thus treated yarns showed a weight increase of 4 to 8% and composite beams prepared from these yarns had a flexural yield point which increased from 330 to 400 MPa. No coating thickness or individual coated filament properties were measured.

Newman et al. [1991] report the feasibility of coating PBZT fibers directly with low-melting aluminum-silicon alloys, but do not concern themselves with the uniformity of the coating or mechanical properties of the metal-coated fibers.

From all these options, the coating of fibers from solution was chosen as the apparently technologically most simple and least costly process. Though, one necessary condition for the coating of fibers from solution is the formers' wettability.

In the existing literature, the wetting of PPTA fibers by epoxy resin is of primary concern due to its pertinence in composite manufacturing. Water wettability is of more interest here for fibers to be coated from aqueous solutions. Fortunately, water is one of the most often used "gage" liquids to measure and compare contact angles. Hsieh et al. [1991] report advancing and receding water contact angles for Kevlar 49 fibers of
65 and 33°, respectively. For dip-coating, the receding contact angle is of greater practical significance than the advancing contact angle. The 33° measured for Kevlar 49 fiber indicate relatively poor wettability when compared to a receding contact angle of 0° observed for glass fibers [Allred et al., 1984]. The wettability can be improved considerably by appropriate surface modification.

Previous work has focused on chemical surface modification of PPTA fiber as a means to improve wettability by epoxy resins and adhesion to increase the composite's interlaminar shear strength. The chemical surface modification of other HM-polymer fibers, e.g., PBZT or PBO, has not been reported at all. In the following, commercial fiber surface treatments such as sizings or finishes are not reviewed, even though some of these proprietary processes might involve chemical surface modifications.

Treatment of Kevlar fibers with an ammonia-plasma gave surface-aminated fibers which exhibited improved adhesion to epoxy resin and an essentially unaffected tensile strength [Allred et al., 1984].

Glow discharge in an argon atmosphere improved the water wettability of Kevlar 49 fibers, but was detrimental to the wetting by epoxy resin [Hsieh et al., 1991]. The improved water wettability was attributed to an increased surface polarity due to unspecified chemical changes. The improved water wettability also degraded over time (≈ 2 days) back to the value for untreated fiber. Surface rearrangements seem unlikely due to PPTA's high glass transition temperature.

Keller et al. [1983] proposed the surface hydrolysis of Kevlar 49 fibers by sodium hydroxide (50%) or sulfuric acid (50%) followed by reaction of the newly formed amine and carboxylate groups with multifunctional epoxy monomers. Using reaction temperatures between 100 and 165°C and reaction times up to 55 hours lead to large decreases (-30 to -60%) of the fiber's tensile strength.
Chatzi et al. [1988] determined by attenuated total internal reflectance infrared spectroscopy (ATR-IR) that much milder reaction conditions, i.e., less than 20 minutes at room temperature in 10% aqueous sodium hydroxide will result in a maximum surface concentration of carboxylate groups without destroying the fiber's skin. No mechanical properties or microscopy studies of surface morphology or topology were reported in addition to the IR spectra to support this claim.

Takayanagi et al. [1981, 1983] developed a procedure for the functionalization of PPTA in homogeneous solution by metalation and electrophilc substitution at the amide-nitrogen. They applied the same procedure to modify only the PPTA fiber surface by shortening the reaction time and decreasing the reaction temperature [Takayanagi et al., 1987]. This surface metalation caused only a small (7%) loss of tensile strength in the modified Kevlar 49 filaments and would be well suited for the purpose of the research presented here. But this reaction can not be applied to the surface modification of PBZT which lacks the "active" hydrogen required for the metalation.

Wu and Tesoro [1986] and Tesoro et al. [1988] presented several nitration and reduction reactions leading to surface-aminated PPTA fibers. Some of these reactions did not noticeably affect the tensile strength of Kevlar filaments while giving a high surface density of amino-groups comparable to those obtained by treatment in an ammonia-plasma [Allred et al., 1984]. In addition, these reactions are principally applicable to all polymers containing phenylene moieties. Because of these features as well as the relative simplicity of and possible control over the reactions employed in this method, it was chosen for the necessary surface modifications in this dissertation work and is detailed in the following section.
5.2 Experimental

5.2.1 Surface Modification

Coating of as-received Kevlar 49 and Aftech 1 fibers with aqueous sodium silicate solutions was not possible due to their low surface energies. Therefore, the fibers have been surface modified with siloxane/silicate groups that would increase their surface energies, making them wettable by aqueous solutions, and would have the potential to give good adhesion to the glass coating by formation of covalent bonds.

The sequence of reactions employed to modify PPTA and PBZT fibers and films is shown in Figure 5.1. Kevlar 49 and Aftech 1 were the PPTA and PBZT fibers modified.

![Diagram of reactions](image)

Figure 5.1: Reactions used to modify PPTA and PBZT fibers, exemplified here showing PPTA
The nitrating solution was prepared by cooling a mixture of 40.0 g acetic anhydride, 14.3 g glacial acetic acid, and 0.8 g 98% sulfuric acid in an ice bath, while slowly adding 10 ml of 90% fuming nitric acid using vigorous stirring. PPTA samples were immersed in the nitrating solution at ice-bath temperature (0 to 5°C) for 30 minutes to 3 hours. The nitrating solution retained the same light yellow color over the entire period. PBZT samples were immersed into the nitrating solution for up to 4 hours after it had been warmed to room temperature. The temperature during the nitration was approximately 25 to 35°C, slightly above room temperature. In this case, the color of the nitrating solution changed from light yellow to dark red-brown, indicating the development of nitrous oxides and the occurrence of oxidation as a side-reaction. Reduction of the surface-nitro groups on nitrated fibers to amino groups was carried out for all samples on a waterbath at 55 to 60°C. The reducing solution was prepared by dissolving 1.0 g sodium hydrosulfite and 2.0 g sodium hydroxide in 160 g water. Reaction time was always 3 hours. The reaction of the aminated fibers with 3-glycidoxypropyltrimethoxysilane (GPTMS) was carried out by placing washed and dried aminated samples in bulk GPTMS at 100 to 120°C under a slow stream of nitrogen. The reaction time was 24 hours. An initial attempt to run this reaction in refluxing, dry THF containing 20% GPTMS did not result in a measurable increase in the surface silicon concentration. The amount of surface-silica functionalities could be increased considerably by reaction of GPTMS-modified fibers with colloidal silica. For that purpose a 30% solution of colloidal silica (Ludox HS-40® by Du Pont) was adjusted to pH = 5.0 using 2.5% sulfuric acid. At that pH, condensation proceeds fastest [Du Pont, 1988]. Reaction time with modified fibers at room temperature was 30 to 40 minutes and the time to "gelation" of the silica solution was 45 to 60 minutes. The reaction with colloidal silica was optional in the case of PPTA fibers. The wettability of the GPTMS-modified fibers was sufficient to allow the coating with
aqueous sodium silicate solution. Due to a lower degree of modification, this step was necessary, though, for PBZT fibers to obtain a sufficient wettability. Originally, tetraethyl orthosilicate (TEOS) was used instead of colloidal silica to increase the surface concentration of silica, but it was found that the conditions for condensation - refluxing in ethanol overnight with hydrochloric acid as a catalyst - were very detrimental to the tensile properties of the fiber, probably due to partial hydrolysis of PPTA by HCl.

To assure that only real, permanent changes of the surface composition were achieved and observed by XPS surface analysis, PPTA films were modified in two control experiments. The first one was to modify PPTA films along with Kevlar 49 yarn and to compare the resulting surface compositions. Differences could have been due to different surface morphologies or inadequate rinsing and cleaning procedures that left reagents, in particular hydrolyzed GPTMS or silica, in the yarn interstices. In the other control experiment, silication was carried out on PPTA film samples which had been subjected to either all three previous modification steps, any two or one or none at all. The films were obtained by spin-coating films from 5 and 2% solutions in sulfuric acid and methane sulfonic acid, respectively, followed by coagulation in deionized water. Handling of film samples during modification, cleaning and surface analysis was easiest, if they were prepared by placing small (= 2×2 cm) pieces of as-coagulated film on a sheet of lint-free paper, placing a circular microscopy coverglass (d = 18 mm) on top of it, weighting the coverglass down with a light casting weight (= 5 g) and folding the corners of the film on the back of the coverglass. This way the polymer film shrinks around the coverglass during air-drying and can be handled easily, regardless of its mechanical robustness. A glass tube (OD = 20 mm) with several partial diagonal cuts was a useful holder for the coverglass-mounted film samples in all preparation steps.
5.2.2 Analysis

In order to verify the success and extent of each modification step, X-ray photoelectron spectroscopy (XPS) was carried out using a Perkin Elmer PHI 5000 ESCA System. Survey spectra were used to qualitatively identify the elements present at and near the surface. The spectra were obtained by scanning the energy range from 1000 to 0 eV with a resolution of 1.0 eV/step and a pass energy of 89.45 eV. Acquisition time was set to three minutes. The multiplex mode was used to obtain spectra with better resolution and quantitative determinations of the relative amounts of the surface elements. Relative amounts were obtained using the areas under the unsmoothed peaks weighted by the individual atomic sensitivity factors. The instrument settings for the multiplex scans are shown in Table 5.1. Prior to analysis, films and fibers were washed overnight with acetone in a Soxhlet extractor followed by drying in a vacuum oven at 120°C for one day or by purging in a stream of dry nitrogen at 150°C also for one day. The results of these two different drying methods are reported in the next section.

Table 5.1: Parameters for XPS multiplex scans of PPTA and PBZT fibers and films

<table>
<thead>
<tr>
<th>Element</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Nitrogen</th>
<th>Silicon</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Range [eV]</td>
<td>276-296</td>
<td>525-545</td>
<td>395-415</td>
<td>94-114</td>
<td>158-178</td>
</tr>
<tr>
<td>Resolution [eV/step]</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Pass Energy [eV]</td>
<td>35.75</td>
<td>35.75</td>
<td>35.75</td>
<td>35.75</td>
<td>35.75</td>
</tr>
<tr>
<td>Numbers of Sweeps</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Sensitivity Factor</td>
<td>0.203</td>
<td>0.540</td>
<td>0.380</td>
<td>0.270</td>
<td>0.540</td>
</tr>
</tbody>
</table>
5.2.3 Coating of Filaments

Silica- or GPTMS-modified filaments were then mounted on metal frames using Superglue™ cyanoacrylate adhesive, dipped into and withdrawn from a sodium silicate solution. The frames were made from square steel rod (=4×4 mm) bent into a rectangular shape with inside dimensions of approximately 15.5×4.5 cm. After mounting the fibers, the frames were coated with paraffin wax to prevent coating by the silicate solution. The coating solution was prepared by adding 10% by weight of water to the as-received solution, which had the following specifications: SiO$_2$/Na$_2$O = 3.23, $\rho = 1.34$ g/ml, 28.3% SiO$_2$, 8.8% Na$_2$O (Power Silicates Inc., sodium silicate solution, Grade F). The water was added to prevent film formation at the solution surface due to evaporation.

The fibers were coated initially by hanging the fiber-holding frame from a thread attached to a spool (d = 3 cm), manually dipping the frame into the silicate solution and then withdrawing it slowly by winding the thread onto the spool using an electromotor and a speed-reducing gear (APCOR multiratio gear motor, model-# 2202-25, and APCOR multiratio speed reducer, model-# 2415, Geartronics Corp.). The great number of dipping-withdrawing-drying cycles made it desirable to automate this process. For that purpose a hydraulic/pneumatic setup, as schematically shown in Figure 5.2, was designed. The following components were used: 2 Clippard Minimatic cylinders (H9C-6D) with a stroke of 6", a Clippard Eagle 4-way-valve with single solenoid and spring return, operated with 120 VAC, a Clippard Minimatic flow control valve (MFC-2) and hose fittings (11752-1). Polyethylene tubing (d = ¼") was used for all connections. Silicone oil was used as the hydraulic fluid. The pneumatic pressure was supplied by a nitrogen gas tank equipped with a reducer valve. The 4-way-valve was actuated by a cam timer (Newark Electronics) so that it was switched on for 1 to 2 minutes while the fiber-holding frame, attached to one of the cylinders' piston, was
lowered into the solution. During the remaining 28 to 29 minutes, the valve directed the pressure such that the fibers were first withdrawn from the solution and then held above it for intermediate air-drying before the cycle was repeated.

Figure 5.2: Schematic of pneumatic/hydraulic fiber coating setup

A withdrawal speed of 5 cm/min from the solution described above was found to result in very uniform coatings. Air-drying time was approximately 30 minutes between dips. After the desired number of coatings was applied, usually about 50, the
frame was taken off the set-up, dried under ambient conditions for 24 hours before starting a schedule of more thorough drying, such as vacuum-drying and atmospheric drying at temperatures up to 200°C.

5.3 Results

5.3.1 X-Ray Photoelectron Spectroscopy (XPS)

Surprisingly few XPS studies have been published, despite the frequently expressed interest in the surface chemistry of HM-polymer fibers and its importance for adhesion and interfacial shear strength in composite applications. The results obtained in this work will be compared with those of the other published studies.

Figures 5.3 and 5.4 show some examples of XPS survey spectra and how they change for modified fiber surface compositions. Even at this low resolution, one can distinguish the appearance of a second peak next to the original nitrogen signal in the nitrated PPTA and PBZT samples. The decreased and increased intensities of carbon, nitrogen, sulfur, oxygen and silicon peaks in silicated samples are also clearly visible.

The elemental surface compositions presented in this section should be considered semi-quantitative and not as absolute numbers, but in comparison to each other. The pitfalls of "quantitative" XPS have been discussed in detail by Dias [1987]. In addition to these fundamental limitations to the accuracy of the data, errors are introduced by the arbitrariness of the baseline definition for each peak and, in particular at small elemental concentrations, by the use of unfitted and unsmoothed data with a low signal-to-noise ratio. Thus, the precision of surface concentrations should be taken to be within a few percent for high concentrations (>10%) and worse for smaller ones. Small concentrations (<1%) should be read as "non-zero".
Nitration was the reaction most readily quantifiable due to the appearance of a distinct peak in the nitrogen spectrum shifted to higher binding energies with respect to the nitrogen peak in the respective polymer backbones (Figure 5.5). The areas under the "nitro"-peaks ranged from 35 to 48% of the areas under the corresponding "amide"-peaks in the case of PPTA. Because of the low reactivity of the diacid moiety only the diamino moieties are expected to be nitrated under the conditions used [Wu and Tesoro, 1986]. The surface compositions obtained for unmodified and nitrated Kevlar 49 fibers are not significantly dependent on the take-off angle (cf. Table 5.6) and the elemental composition can, therefore, be considered uniform throughout the sampling depth of the XPS. Thus, above mentioned area percentages correspond to yields of 70 to 96% or 0.8 to 1.1 NH₂/100Å². The 96% yield was achieved on isotropic PPTA film while the modification of Kevlar 49 fibers gave a maximum yield of 85% (1.0 NH₂/100Å²). These numbers compare well with the 0.8 to 0.9 NH₂/100Å² measured by Tesoro et al. [1988] using a dye assay/UV-VIS spectroscopy method. All amino-area densities have been estimated based on an average lateral area of the PPTA repeat unit (84 Å²) [Tesoro et al., 1988].

The XP spectrum of nitrated PBZT film (reaction time = 3.5 h) showed a ratio of nitro groups to phenylene units of 1, while the spectra of Aftech 1 PBZT fiber nitrated for 50, 100, and 150 minutes give ratios of 0.17, 0.34, and 0.37, respectively (Figure 5.3). Reduction of the nitro group to an amino group was virtually quantitative in all cases; the XP spectra of aminated fibers and films of PPTA and PBZT showed no more "nitro"-peaks after reaction with basic sodium hydrosulfite solution. The yield of the ring-opening condensation of GPTMS with the pendant amino groups can not be reliably determined due to the presence of silicon contaminants in some of the samples. Elemental surface compositions of modified PPTA film, Kevlar 49, and Aftech 1 fibers are shown in Tables 5.2, 5.3, and 5.4.
Figure 5.3: XPS survey spectra of modified PPTA fibers
Figure 5.4: XPS survey spectra of modified PBZT fibers
Figure 5.5: Overlay of XPS high-resolution scans of as-received and nitrated Kevlar 49 fiber showing a new peak for the nitrated sample due to the nitro-group.

Figure 5.6: Overlay of XPS high-resolution scans of Aftech 1 fiber nitratated for 1) 0, 2) 50, 3) 100, and 4) 150 minutes.
In these tables the samples are described in the following way: Theoretical: calculated from repeat unit, None: unmodified sample, Nitrated: sample treated with nitric acid, Aminated: nitrated samples reduced with sodium hydrosulfite, Siloxated: aminated sample treated with glycidoxypropyltrimethoxysilane (GPTMS), Silicated: silanated samples treated with 30% colloidal silica adjusted to pH = 5.0.

Table 5.2: Elemental surface composition of modified Kevlar 49 fibers in mole-% as determined by XPS (take-off angle = 85°)

<table>
<thead>
<tr>
<th>Modification</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
<th>% Si</th>
<th>N/O</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>77.8</td>
<td>11.1</td>
<td>11.1</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>70.3</td>
<td>20.3</td>
<td>8.1</td>
<td>1.4</td>
<td>0.40</td>
<td>0.02</td>
</tr>
<tr>
<td>Nitrated</td>
<td>64.2</td>
<td>25.4</td>
<td>10.4</td>
<td>0</td>
<td>0.41</td>
<td>0</td>
</tr>
<tr>
<td>Aminated</td>
<td>71.3</td>
<td>20.0</td>
<td>8.5</td>
<td>0.2</td>
<td>0.43</td>
<td>0.003</td>
</tr>
<tr>
<td>Silanated</td>
<td>63.6</td>
<td>28.7</td>
<td>3.8</td>
<td>3.9</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>Silicated</td>
<td>23.5</td>
<td>60.0</td>
<td>0</td>
<td>16.5</td>
<td>0</td>
<td>0.70</td>
</tr>
<tr>
<td>Chappell et al. [1990]</td>
<td>75.4</td>
<td>14.4</td>
<td>10.2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Allred et al. [1984]</td>
<td>73</td>
<td>22</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Penn and Larsen [1975]</td>
<td>62-71</td>
<td>15-27</td>
<td>5-12</td>
<td>0-2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wang et al. [1993]</td>
<td>76.1</td>
<td>14.4</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.2 shows the presence of silicon contaminations and a marked increase in the silicon concentration after the GPTMS and colloidal silica treatments. The elemental ratios given in the last two columns illustrate the progression through the reaction sequence. The ratios change essentially as expected for the respective modified fibers.
with exception of the low N/O-ratio for the aminated samples. Ideally, this ratio should be slightly larger than 1 or at least increase to the value observed in unmodified fiber. A possible explanation is the presence of other oxidized groups on the fiber surface, which have not been reduced by sodium hydrosulfite. A definite answer, though, requires more detailed studies of the reactions occurring during the modification and higher resolution of the XP spectra to allow identification of the oxygens chemical environment. The high oxygen concentration in the unmodified fiber samples is very likely due to residual surface water which was not removed by vacuum-drying at 120°C for two days. This hypothesis is supported by the results shown in Table 5.3. It compares the elemental surface compositions of unmodified samples dried for two days in vacuum at 120°C or dried by purging with dry nitrogen on an oil-bath at 150°C. Silicon contaminations of 1.4 and 0.6% have been ignored in this comparison.

Takayanagi et al. [1987], while not reporting absolute atomic surface concentrations of their Kevlar 49 fiber samples, have also observed larger than theoretical C/N- (12.5 vs. 7.0) and O/N-ratios (5.0 vs. 1.0), but did not offer an explanation.

Table 5.3: Elemental surface composition of Kevlar 49 fibers in mole-% as determined by XPS (take-off angle = 85°) dried by two different drying methods

<table>
<thead>
<tr>
<th>Drying Method</th>
<th>% Carbon</th>
<th>% Oxygen</th>
<th>% Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>77.8</td>
<td>11.1</td>
<td>11.1</td>
</tr>
<tr>
<td>Vacuum at 120°C</td>
<td>70.3</td>
<td>20.3</td>
<td>8.1</td>
</tr>
<tr>
<td>N₂-Purged at 150°C</td>
<td>75.4</td>
<td>12.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Table 5.4 shows again the presence of silicon contaminations and a reduction of the carbon and nitrogen concentrations at the surface concurrent with an increase of the
silicon and oxygen concentrations. Comparison of the entries in Tables 5.2 and 5.4 shows comparable compositions and elemental ratios for equally modified Kevlar 49 fibers and PPTA films. This demonstrates that the geometric form of the samples does not affect the XPS analysis results.

Table 5.4: Elemental surface composition of modified PPTA films in mole-% as determined by XPS (take-off angle = 60°)

<table>
<thead>
<tr>
<th>Modification</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
<th>% Si</th>
<th>N/O</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>77.8</td>
<td>11.1</td>
<td>11.1</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>75.3</td>
<td>12.8</td>
<td>11.4</td>
<td>0.5</td>
<td>0.89</td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrated</td>
<td>71.2</td>
<td>19.2</td>
<td>8.6</td>
<td>1.0</td>
<td>0.45</td>
<td>0.01</td>
</tr>
<tr>
<td>Aminated</td>
<td>70.8</td>
<td>16.8</td>
<td>9.7</td>
<td>2.7</td>
<td>0.58</td>
<td>0.04</td>
</tr>
<tr>
<td>Silanated</td>
<td>66.6</td>
<td>26.6</td>
<td>2.9</td>
<td>3.9</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>Silicated</td>
<td>24.4</td>
<td>53.2</td>
<td>0.4</td>
<td>22.1</td>
<td>0.01</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 5.5 shows that the same reactions used for the surface modification of PPTA can also be successfully employed for the surface modification of PBZT fibers. In addition to the features analogous to those in the results for surface-modified Kevlar 49 fibers, it is of interest to note the high level of surface oxygen in the unmodified fiber, despite purging with nitrogen and the absence of oxygen from the polymer backbone. Other workers [Newman et al., 1991] have interpreted this observation as possible surface oxidation during heat-treatment, but in the present study this phenomenon was also observed for freshly prepared, not heat-treated films and as-spun PBZT fiber (Table 5.6). The contaminated samples contain oxygen as well as silicon. But despite
the fairly large amount of silicon, it can not explain all of the oxygen found in the surface. While intriguing, it was chosen to not further investigate the nature and origin of this oxygen excess. It seems reasonable to assume a connection with the ash content of the bulk PBZT fibers. A bulk oxygen analysis of the fibers would show, whether the surface oxygen concentration is representative of the bulk composition or whether it is introduced after formation of the surface. The latter case could then be verified by surface analysis of PBZT film or fiber prepared under strict exclusion of oxygen. If the oxygen is part of the bulk composition, NMR spectroscopy would be an appropriate method to identify the chemical nature of the oxygen containing moieties.

Table 5.5: Elemental surface composition of modified Aftech 1 fibers in mole-% as determined by XPS (take-off angle = 75°)

<table>
<thead>
<tr>
<th>Modification</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
<th>% S</th>
<th>% Si</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>77.8</td>
<td>0</td>
<td>11.1</td>
<td>11.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>70.8</td>
<td>14.1</td>
<td>6.1</td>
<td>5.0</td>
<td>3.9</td>
<td>0.06</td>
</tr>
<tr>
<td>Nitrated</td>
<td>67.8</td>
<td>17.1</td>
<td>7.2</td>
<td>4.4</td>
<td>3.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Aminated</td>
<td>70.1</td>
<td>15.2</td>
<td>9.3</td>
<td>4.2</td>
<td>1.2</td>
<td>0.02</td>
</tr>
<tr>
<td>Silanated</td>
<td>58.0</td>
<td>32.3</td>
<td>1.1</td>
<td>0.7</td>
<td>7.9</td>
<td>0.14</td>
</tr>
<tr>
<td>Silicated</td>
<td>25.6</td>
<td>56.0</td>
<td>0.4</td>
<td>-</td>
<td>18.0</td>
<td>0.70</td>
</tr>
<tr>
<td>Newman et al. [1991]</td>
<td>76</td>
<td>17</td>
<td>5</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 5.6: Elemental surface composition of as-prepared PBZT film and fiber in mole-
% as determined by XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
<th>% S</th>
<th>% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>77.8</td>
<td>0</td>
<td>11.1</td>
<td>11.1</td>
<td>0</td>
</tr>
<tr>
<td>Film (80°)</td>
<td>67.9</td>
<td>19.5</td>
<td>6.1</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>Fiber (75°)</td>
<td>69.1</td>
<td>21.0</td>
<td>5.4</td>
<td>2.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

By varying the take-off angle between the detector entrance lens and the sample surface it is possible to collect spectra of electrons escaping from different sample depths. At near-normal angles, electrons originating at the maximum escape depth can still reach the detector and the resulting spectrum will therefore reflect the average composition of an approximately 5 nm-thick region. By contrast, at very low detector angles only electrons originating much closer to the surface than 5 nm will enter the detector. In either case, the fraction of photoelectrons that reach the detector out of all those generated decreases exponentially with the depths of their origination in the sample [Andrade, 1985].

Table 5.7 shows the surface composition of Kevlar 49 fiber as a function of the take-off angle. The importance of the oxygen containing surface contamination, possibly water, decreases with a larger angle. As a consequence, oxygen levels decrease, while carbon and nitrogen levels increase upon changing the angle from 10 to 85°. There is practically no angle dependence of the results of the nitrated sample suggesting a reaction depth of at least 5 nm. On the other hand, the reaction depth during the silanation of aminated Kevlar 49 fibers with GPTMS appears to be less than 5 nm, since there is a marked shift towards the composition of hydrolyzed GPTMS (50.0% C, 41.7% O, 0% N, 8.3% Si) upon changing the angle from 85 to 10°.
Table 5.7: Elemental surface composition of some modified and vacuum-dried Kevlar 49 by XPS as a function of take-off angle.

<table>
<thead>
<tr>
<th>Modification</th>
<th>% Carbon</th>
<th>% Oxygen</th>
<th>% Nitrogen</th>
<th>% Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>None - 10°</td>
<td>74.1</td>
<td>18.1</td>
<td>7.2</td>
<td>0.6</td>
</tr>
<tr>
<td>None - 85°</td>
<td>74.6</td>
<td>16.4</td>
<td>8.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrated - 10°</td>
<td>66.9</td>
<td>23.4</td>
<td>9.7</td>
<td>-</td>
</tr>
<tr>
<td>Nitrated - 85°</td>
<td>67.0</td>
<td>22.9</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>Siloxated - 10°</td>
<td>59.3</td>
<td>27.9</td>
<td>4.6</td>
<td>8.3</td>
</tr>
<tr>
<td>Siloxated - 85°</td>
<td>64.6</td>
<td>24.3</td>
<td>6.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

5.3.2 Appearance of Coated Fibers

The first evidence of the presence of a coating on the dip-coated fibers was the observation of colored fringes on the filament surface (Figure 5.7), but the filament diameter did not increase noticeably within the resolution of the optical microscope. These colors are interpreted as due to interference. While the presence of different colors reveals a slightly changing thickness of the coating, further application of sodium silicate did not result in an amplification of these thickness variations.

Large variations in thickness, shown in Figure 5.8, occurred when the withdrawal speed during dip-coating was too fast (> 5 cm/min). This critical speed depends among other factors on the concentration of the sodium silicate solution, but the latter was kept constant throughout most of the experiments.

The application of thick glass coatings led to the formation of kink bands in the filaments (Figure 5.9) as a consequence of the shrinkage developed by the coating.
during drying. This can be prevented by keeping the filaments under sufficiently high tension during the coating and drying steps.

While air-dried coatings are usually free of visible defects, after drying at elevated temperatures (>150°C) cracks, such as those shown in Figures 5.10 and 5.11, appear in the coating. The helical shape of these cracks suggests the mismatch of thermal expansion coefficients of polymer fiber and glass coating to be the reason for this type of coating failure.

Figure 5.7: Optical micrograph of interference fringes on thinly glass-coated Kevlar 49 filament
Figure 5.8: Optical micrograph showing silicate glass beads formed during rapid dip-coating

Figure 5.9: Optical micrograph showing kink bands formed in a thickly coated Kevlar 49 filament due to coating drying stresses
Figure 5.10: Optical micrograph showing helical crack in heat-treated coating on Kevlar 49

Figure 5.11: Electron micrograph showing helical crack in heat-treated coating on Kevlar 49
5.3.3 Mechanical Properties of Modified and Coated Fibers

The nitration with fuming nitric acid and the subsequent reduction in approximately 1% sodium hydroxide at 55-60°C are the harshest conditions used during the modification. The force at break was measured for all modified filaments on samples with 1.5 cm gage length and at a crosshead speed of 0.05 cm/min. The tensile strength of Kevlar 49 is not measurably affected by either the nitration or the reduction steps as demonstrated in Table 5.8. The tensile strength of Aftech 1 filaments decreases by approximately 15%, even though PBZT is chemically more inert than PPTA. But for that very reason harsher nitration conditions (30°C vs. 0°C, 3.5 hours vs. 1-3 hours) had to be chosen to achieve modification, probably resulting in the observed loss in tensile strength by oxidative degradation.

Table 5.8: Tensile strength of modified Kevlar 49 and Aftech 1 filaments

<table>
<thead>
<tr>
<th>Filament</th>
<th>$\sigma$ [GPa]</th>
<th>Filament</th>
<th>$\sigma$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified Kevlar 49</td>
<td>3.2 ± 0.3</td>
<td>Unmodified Aftech 1</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>Nitrated Kevlar 49</td>
<td>3.0 ± 0.3</td>
<td>Nitrated Aftech 1</td>
<td>2.2 ± 0.5</td>
</tr>
<tr>
<td>Aminated Kevlar 49</td>
<td>3.1 ± 0.3</td>
<td>Aminated Aftech 1</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>Silanated Kevlar 49</td>
<td>3.2 ± 0.2</td>
<td>Silanated Aftech 1</td>
<td>2.2 ± 0.4</td>
</tr>
<tr>
<td>Silicated Kevlar 49</td>
<td>2.7 ± 0.4</td>
<td>Silicated Aftech 1</td>
<td>1.9 ± 0.3</td>
</tr>
</tbody>
</table>

Silanated and silicated fibers were stored in water to prevent condensation of the silanol functionalities, which would have bonded individual filaments together making their gentle extraction from the fiber bundle very difficult. The tensile strength of the
filaments was observed to decrease significantly, down to approximately 1 GPa, after storage in water for a number of weeks.

Table 5.9: Diameter and shear modulus of as-received (*) and glass-coated Aftech 1 and Kevlar 49 fibers

<table>
<thead>
<tr>
<th>Aftech 1</th>
<th>Kevlar 49</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.0*</td>
<td>1.2</td>
</tr>
<tr>
<td>14.2</td>
<td>2.1</td>
</tr>
<tr>
<td>14.5</td>
<td>2.3</td>
</tr>
<tr>
<td>15.0</td>
<td>2.6</td>
</tr>
<tr>
<td>15.0</td>
<td>2.4</td>
</tr>
<tr>
<td>13.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 5.9 shows typical diameter and corresponding shear moduli of coated and air-dried Aftech 1 and Kevlar 49 filaments. Rearranging equation 5.3 to give,

$$G_c = \frac{G_{CF} - G_F \left(1 - \frac{t}{R_F + t}\right)^4}{1 - \left(1 - \frac{t}{R_F + t}\right)^4}$$  (5.5)

one can calculate from the data listed in Table 5.9 a shear modulus for the glass coating of 4-5 GPa. Alternately, one can also plot the raw data listed in Table 5.9 as shown in Figure 5.12 to obtain the coating's shear modulus as the intercept of the regression line through the data. This also gives a coating shear modulus of 4-5 GPa. A direct method of determining the properties of the air-dried glass coating would be preferable,
but could not be realized due to difficulties in obtaining macroscopic samples which were not warped, bent or cracked.

![Graph](image)

Figure 5.12: Regression plot of data for Kevlar 49 fibers from Table 5.9 for determination of the coating's shear modulus

The coated filament defects shown in Figures 5.7 and 5.8 also pose a problem in the evaluation of their compressive strength. Compressive failure as a consequence of tensile recoil or bending can not be identified in coated filaments kinked prior to testing. And while a cracked coating may still increase the global average of the shear modulus of an individual filament, that same filament will fail locally in compression where it is weakest, i.e., where it has the smallest local shear modulus. In fact, examination of coated filaments before and after tensile recoil tests show compressive failure to occur where the coating was cracked prior to the test. The obvious solution to this problem is to use only defect-free coated filaments for compressive tests. Because only few defect-free coated filaments were available from each batch, the
beam bending technique was the more practical technique to study the compressive behavior of these filaments in direct comparison with as-received, uncoated fibers.

Table 5.10: Compressive failure strains of uncoated and sodium silicate-coated (t = 0.5μm) Kevlar 49 fibers

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>d (μm)</th>
<th>ε_c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Kevlar 49</td>
<td>12.2</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>Coated Kevlar 49</td>
<td>13.2</td>
<td>0.6 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5.10 shows the results of one set of cantilever beam bending experiments. The compressive failure strains are the averages of about 12 observations for each of the two fibers. The coated fiber had merely been air-dried at 60°C to avoid cracking of the coating. A shear modulus for coated filament was not measured, but is estimated using equation (5.3) to be approximately 2.2 GPa compared to 1.4 GPa for the uncoated Kevlar 49 filament. The increase of the compressive failure strain is, thus, approximately proportional to the increase of the shear modulus as predicted by equation (5.4). But for a reliable study of the correlation between compressive strengths and shear moduli of coated fibers, a much larger number of fibers with differently thick coatings, i.e. different shear moduli, is required.

5.4 Other Fiber Coating Experiments

Because of the potentially detrimental effect of chemical surface modification on fibers' tensile properties and the time and expense involved in running those reactions, methods to apply a coating directly to as-received filaments are considered more practical. Two such methods have been tried in this research: 1) Coating of
unmodified filaments with metal by electroless plating or sputter-coating and 2) Coating of filaments with a glass precursor solution of lowered surface energy.

Unmodified Kevlar 49 filaments were coated with silver using an electroless plating procedure commonly employed for the silvering of glassware. Figure 5.13 shows that silver was readily deposited onto the filament, but also its very coarse structure.

The smoothness of the coating could possibly be improved by lowering the concentration of the silvering solution and depositing multiple, thinner coatings instead of a single, thick one, but because even the thickly coated filaments showed no improved torsional rigidity this technique was abandoned.

Aftech 1 filaments, sputter coated with a gold layer approximately 0.3 μm thick, also showed no improved torsional rigidity. This is possibly also due to the granularity and the lack of mechanical integrity of the gold coating.

Four different experiments were carried out to examine the feasibility of coating unmodified polymer fibers with glass precursor solutions of lower surface energies compared to aqueous sodium silicate solutions. The easiest approach is the addition of a surfactant, here sodium dodecylsulfate (SDS), to an aqueous sodium silicate solution. While a solution containing 0.1% SDS based on silicate wets both Kevlar and Aftech 1 filaments, the solution is unstable and the silicate flocculates within a few hours, too rapid to be useful for a day-long dip-coating process. A few percent of a nonionic surfactant, poly(ethylene glycol) with MW = 2000, were added to sodium silicate solution of different concentrations (15-25% silica). None of the solutions was stable for a period of at least 24 hours.
Ethanol-based silica sol-gel solutions have been found to wet isotropic PPTA and PBZT films well but not filaments during dip-coating. The very low viscosity of these silica sols, the volatility of the solvent, and the low silica content (≤15%) are other difficulties of this approach. Even when all these factors are brought under control through sufficient experimentation, the resulting coating on the fibers would be very porous and require heat-treatment at temperatures above 700°C, beyond the thermal stability even of PBZT, to densify the coating and achieve bulk silica mechanical properties. The formulation of a sol-gel glass composition suitable for coating and with a low densification temperature were outside of the scope of this research.

In a feasibility experiment, Dr. Ben Gong coated Aftech 1 fiber with alumina by controlled pyrolysis/oxidation of a precursor aluminum-polymer complex coating showed no increased torsional rigidity, but the tensile strength had decreased as a consequence of the pyrolysis conditions. The coating thickness in this case was less
than approximately 0.3 µm. The continuity and structure of the coating was not examined.

The last approach taken for the coating of unmodified polymer filaments was inspired by the mold-making technique used in ceramic shell investment casting [ASM, 1970]: In this metallurgical process, a paraffin wax or polymer (e.g., PE, PP, PS) pattern is repeatedly dip-coated in a slurry of refractory grains (e.g., alumina, zirconia, silica,) in surfactant-containing aqueous, colloidal silica and stuccoed with additional, usually coarser grain during the drying process. After thorough air-drying, the coated pattern is then heated to remove the pattern and to fuse the coating into a strong shell to be used as the mold.

The modifications of this process to suit the purpose of the current research are the following: Alumina polishing powders with nominal sizes of 0.3, 0.1, and 0.05 µm (Microgrit™ GB, Micro Abrasives Corporation) have been used as the grain in a slurry containing 30% colloidal silica as the binder and 0.1% SDS as surfactant. A slurry containing 35% alumina (total solids: 54%) was prepared by stirring 80 g of the two smallest-grained polishing powders into 150 g of the colloidal silica using a magnetic stirrer.

A paraffin wax rod (d = 1 cm) was manually dip-coated in the slurry to test the wetting and to obtain a macroscopic sample for assessment of the coating properties. After air-drying at room temperature for several days, the coated rod was placed in an oven at 90 to 100°C to melt out the wax and to further dry the coating. The resulting shell appeared stiffer and stronger than macroscopic samples of sodium silicate dried under identical conditions. As-received Kevlar 49 fibers were pre-treated by a single dipping in 30% colloidal silica containing 1% SDS. These fibers were then coated with the alumina slurry in an analogous fashion to the coating with sodium silicate. While the fibers were readily coated by the slurry, the resulting coating was very non-uniform
in thickness. Microscopic observations suggest that one of the causes of this non-uniformity is the "structure" of the slurry, which seems to contain larger aggregates of alumina grains instead of finely dispersed ones.

5.5 Summary of Modification and Coating Experiments

Coating of as-received Kevlar 49 and Aftech 1 fibers with aqueous sodium silicate solutions was not possible due to their low surface energies. Therefore, the fibers have been surface modified with siloxane/silicate groups that increased their surface energies, making them wettable by aqueous solutions, and gave good adhesion to the glass coating, likely by formation of covalent bonds. The success and extent of the surface reactions was characterized by X-ray photoelectron spectroscopy (XPS).

Modified fibers were repeatedly and slowly dip-coated in aqueous sodium silicate solution, until a uniform coating of the desired thickness was obtained. A small pretension (50-100 MPa) was applied on the fibers prior to coating to prevent their kinking due to coating shrinkage stresses. If too thin coatings were applied or temperatures in excess of 120°C were used in the drying schedule, the coatings failed by helical cracking due to the thermal expansion of the fibers.

The tensile load at break of Kevlar filaments was not affected by the surface modification or the coating. The tensile strength of the PBZT fibers decreased by approximately 15% as a consequence of more severe reaction conditions.

The moderate drying temperatures gave a sodium silicate glass coating with a torsional modulus between 4 and 5 GPa. While this is only about 20% of the shear modulus of a fully densified silicate glass, it is 2- to 3-times larger than that of the HM-polymer fibers and better than the shear modulus of any organic polymer. The coating
led to a shear modulus increase for Kevlar 49 and Aftech 1 (PBZT) fibers from approximately 1.5 and 1 GPa to >2.5 and >2 GPa, respectively.

Additional experiments showed the feasibility of other coating methods, such as the electroless plating of fibers with silver or the coating with alumina-colloidal silica slurries, for example. But it was chosen to not further pursue these approaches in this dissertation.
Allen, S.R., Du Pont Company, private communication, 1992


Dias, A.J., Modification of Synthetic Polymers: Surface Modification of Poly(vinylidene fluoride) and Poly(chlorotrifluoroethylene), and Preparation of Semiconducting Polymers by Bulk Modification of Poly(vinylidene fluoride), Polybutadiene and Poly(trifluoroethylene), Amherst, MA: University of Massachusetts, 1987; dissertation

Du Pont, "Ludox® Colloidal Silica - Properties Uses, Storage and Handling", technical brochure, Wilmington, DE: Du Pont, 1988; trade brochure


135


6.1 Summary and Conclusions

Chapter 2 reviewed work detailing the present understanding of materials' compressive strength, in particular that of anisotropic materials such as uniaxial fiber composites and high-modulus polymer fibers. There is much evidence suggesting that compressive failure in high-modulus polymer fibers, as in most uniaxial fiber composites, occurs by a shear microbuckling instability. For that case, the minimum shear modulus determines the compressive strength. In fact, the compressive strength of any material has its minimum shear modulus as a fundamental upper bound. It was also reviewed in Chapter 2 that so far chemical changes of polymer structure, most notably crosslinking, have not lead to consistent improvements of fiber compressive strength.

The approaches to improve the compressive strength of HM-polymer fibers via their shear moduli presented in this dissertation rely on the physical combination of the HM-polymer with a torsionally more rigid material.

Chapter 4 presented the impregnation of the swollen, as-coagulated structure of polymer fibers with solution-based precursors for highly crosslinkable and torsionally rigid materials. Water-based melamine-formaldehyde resin has been impregnated into PPTA fibers spun from nematic solution. Elemental analysis showed a larger than expected amount of resin in all fibers impregnated with solutions of different concentrations. This is attributed to adsorption phenomena at the swollen fibers' surface leading to preferential wetting and a breach of the assumption of equal resin concentrations in the aqueous phases inside and outside the swollen fiber. Yet, despite cured resin contents of over 20% in the impregnated fibers, their mechanical properties...
were not greatly, if at all, affected. Films and fibers of PPTA prepared from isotropic solutions have been impregnated with up to 40% of sodium silicate, but PPTA and PBZT fibers spun from nematic solution picked up only a few percent of sodium silicate during a continuous solution exchange process. It is believed that this is a consequence of the tighter interfibrillar spaces in the fibers spun from the more concentrated, nematic solutions as compared to films and fibers prepared from isotropic solution. The tighter spaces act as a filter for larger particles. This was not a problem for the impregnation with melamine-formaldehyde resin precursor due to its small-molecular size, but the colloidal particles in the sodium silicate solution apparently were too large for a successful impregnation. Small-molecular silica glass precursors are possibly an answer to this problem, but under the conditions used in this study the basic or acidic catalysts needed for the sol-gel reactions reduce the tensile properties of PPTA fibers dramatically. Mechanical properties of anisotropic fibers were practically unaffected by impregnation with a small amount of sodium silicate. The mechanical properties of isotropic, sodium silicate impregnated fibers were decreased with respect to not impregnated fibers in approximately inverse proportion to their increased cross-sectional area. The poor mechanical properties are attributed to a lack of integrity of the glass phase, which could not be densified using elevated temperatures due to the lower thermal stability of the polymer.

In a related experiment, the microfibrillar network of as-coagulated PPTA tape and fiber was nitrated after an appropriate solvent exchange. The speed of the reaction and the large extent of nitration achieved showed the very good accessibility of the as-coagulated network to small-molecular reagents. The specific surface area and average microfibrillar diameter were estimated to be approximately 400,000 m²/kg and 6 nm, respectively, based on the extent of the nitration.
Chapter 5 presented the surface-functionalization of Kevlar 49 (PPTA) and Aftech 1 (PBZT) fibers with silica-groups or even colloidal particles, in order to achieve good water wettability and adhesion to sodium silicate coatings. The surface modifications were followed by X-ray photoelectron spectroscopy (XPS). It was found in the course of these experiments, that heat-treated and as-spun PBZT fibers have a considerable amount of surface oxygen, the origin of which can not be explained with the presently available data. XPS confirmed the nitration of the fibers, as well as the reduction of the nitro groups to amino groups and the large increase in the surface silicon concentration upon silanation and treatment with colloidal silica. Tensile strength of Kevlar 49 fibers remained unchanged within experimental variations during the surface modification.

Harsher reaction conditions had to be employed for PBZT fibers resulting in a loss of tensile strength in the nitration reaction. The surface modified fibers were dip-coated in aqueous sodium silicate solution. The air-dried coatings had torsional moduli of about 5 GPa, far below the bulk materials' shear modulus but still more than twice that achievable by organic polymers. Coated fibers had slightly reduced tensile properties, mostly due to the increased diameter of the coated fibers, but their shear moduli were increased up to 200 or 300% depending on the thickness of the silicate coatings. Coated Kevlar 49 fibers with an average shear modulus of 2.3 GPa had a compressive strain at failure of 0.6% compared to 0.4% for uncoated fibers.

This demonstrates that the use of 3-dimensionally crosslinked, inorganic coatings can overcome the limitations to material properties inherent in anisotropic materials made up from 1-dimensional molecules of rather uniform orientation.

The simpler preparation technique and resulting morphology of coated fibers gives this approach an edge over the realization of interpenetrating phases of an inorganic glass and a HM-polymer microfibrillar network.
6.2 Suggested Future Work

One immediate objective of future research should be to increase the rigidity of coatings applied to HM-polymer fibers. The conceptually easiest way is heat-treatment at temperatures, where the glass-coating will densify and essentially achieve bulk properties. But thermal stresses generated in the process will severely limit its practicality. A more promising way may be the use of coating solutions with higher solids contents or slurries, which exhibit increased rigidity after drying at low to moderate temperatures. The higher solid content would also reduce the shrinkage preventing some of the cracking observed in thin coatings. Another way of preparing essentially identical coated fibers is their coating as described in Chapter 5 followed by placement in a fluidized bed of very fine refractory particles. The fluidized bed would simultaneously accelerate the drying and decorate the precoated fiber surface with particles.

The very high thermal stability of PBZT and PBO fibers even makes the coating with aluminum alloys or low-melting, yet water-resistant, phosphate or tin oxide glasses possible [Beall and Quinn, 1990; Bahn and Quinn, 1991; Bahn et al., 1991; Quinn and Beall, 1991; Tick, 1983]. The elimination of the drying steps and the need for densification for property maximization would be a great advantage in the preparation of coated fibers, but other technical challenges associated with cooling stresses are certain to emerge instead.

Considering the small number of published, systematic studies of HM-polymer fiber surfaces, compared to studies of carbon fiber surfaces, and their importance in composite technology, it seems obvious to dedicate some effort to the fundamental characterization of fiber surface properties using XPS, contact angle measurements and surface profiling techniques.
For future attempts to utilize the as-coagulated, swollen structure of lyotropic polymers as the starting template for nanocomposites, it would be very helpful to have an improved fundamental, quantitative understanding of the as-coagulated structure and how its architecture can be influenced by spinning or post-spinning conditions. Electron microscopy has been used to measure microfibrillar diameter in as-coagulated PBZT fibers impregnated with an epoxy resin, but little information has been obtained about the effective size of the intermicrofibrillar spaces. That size is critical for impregnation by limiting the size of the molecules that can be introduced into the microfibrillar network. Diffusion experiments similar to those presented in Chapter 4 using probe molecules of various and uniform sizes as well as detection methods like liquid or gas chromatography would permit the determination of the effective pore size and how it varies with environmental conditions (solvent, pH, temperature, etc.), polymer concentration in the spinning solution and other variables. In this context, specific interactions between impregnators and swollen HM-polymer fiber should also be taken into account. Small angle X-ray scattering of as-coagulated fibers would also provide some of the information sought in the above mentioned experiments.

"Internal" modification of the microfibrillar surfaces, as presented in Chapter 4, presents a feasible approach to improved compressive properties by combining features of structural chemical modifications, such as crosslinking, with the concept of cocontinuous composites. In this case, one of the two phases would be the modified "interphase". The challenge of this approach lies in finding the appropriate reagents, which would modify microfibrillar surfaces, but would not cause any polymer degradation. This second condition is particularly important because of the large surface-to-volume ratio of the swollen fibers. The objective of the internal surface modification would be to increase interfibrillar interactions and, thus, the interfibrillar shear modulus, without completely changing the chemical nature of the polymer in
question, as has been the case with a priori chemical modifications of PPTA and PBZT. In that respect, one could say that with this approach it is possible to prepare fibers with properties that mimic those of a fiber without a microfibrillar morphology - with all the desired and certainly a few undesired consequences.

Another intriguing possibility of preparing nanocomposites of inorganic glasses and high-modulus polymers has been opened by the development of the low melting glass compositions mentioned above, which can be coprocessed with thermotropic liquid crystalline polymers to give various morphologies including interpenetrating glass and polymer phases. Basic evaluations of various composition-processing-property relationships provide ample subjects for extensive research.

In order to understand the reasons for the apparent failure of chemical crosslinking to significantly improve the compressive strength of HM-polymer fiber, mechanical modelling of the effect of crosslinking on the shear modulus and buckling load of anisotropic, semi-crystalline polymers should prove insightful.

One way of experimentally verifying such modelling results would be to monitor the shear modulus/compressive strength development during carbonization or ceramization of appropriate precursor polymers. Polyacrylonitrile and polysilanes as precursors for carbon and silicon carbide fibers, respectively, would be such appropriate precursors. The "degree of crosslinking" can possibly be determined by solid-state NMR or inferred from the ratios of axial and transverse moduli. The challenge in these experiments would be to change only the crosslink density but not, for example, the defect concentration which could also play a role in the compressive failure of brittle fibers. Similar experiments actually seem to be already in progress [Jiang et al., 1993].

An interesting extension of the experimental verification of the shear-normal coupling analysis by Allen [1988] would be the determination of the apparent shear modulus of a thick-walled, hollow fiber under compression by the torsion pendulum
method. In this case the compressive load could be applied by a wire of known torsional rigidity threaded through the hollow fiber and fixed along with the fiber to the torsion pendulum at one end, while the free end would be mechanically clamped down after the desired compressive load is applied to the fiber by pulling on the free end of the wire. With this set-up any occurring nonlinearities in the shear modulus-normal stress behavior could be easily observed. It may even be possible to evaluate the apparent shear modulus at normal stresses very close to the onset of compressive failure and, thus, settle some disputes concerning the microbuckling theory.

The one-dimensionality of high-modulus polymers is the molecular origin of their mechanical anisotropy, which results in tremendous axial properties and orders of magnitude smaller transverse properties. The compressive failure of HM-polymer fibers by kinking is a manifestation of the latter and it can be overcome only by decreasing the mechanical anisotropy. This can be done by combination with isotropic, rigid, inorganic materials, as shown in this dissertation, or possibly by chemical crosslinking. A third fundamental possibility to reduce mechanical anisotropy, which is not yet within the reach of technology, is the "ultra-processing" of fibers, that is the preparation of fibers with a specific "lay-up" sequence, a designed radial profile of molecular orientation (e.g., fibers in which the molecules in the surface layers, the "skin", are oriented in the hoop direction to provide torsional stiffness and transverse strength). New organic, inorganic and hybrid materials will offer more parameters to balance tensile and compressive properties, damage tolerance and density, but understanding the physical origins and interdependence of those properties will not become simpler.
REFERENCES


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APPENDIX A

SINGLE CRYSTALLINE POLYDIACETYLENES

Introduction

Single crystals are prototypical anisotropic materials. Unlike other anisotropic materials, including high-modulus polymer fibers, single crystals are a single, homogeneous phase. The absence of intermediate structural units with dimensions in-between those of the whole single crystal and the constituting molecules, such as microfibrils, entails that the molecular and intermolecular properties are identical to those of the whole single crystal. In single crystals, there is no morphology that could complicate the determination of molecular structure-property correlations. For these reasons, single crystalline polydiacetylenes present a great opportunity not only to test the computational prediction of thermoelastic and crystallographic properties of polymers based on atomistic concepts, but also to verify some of the analytically predicted correlations between different material properties. The one of particular interest here is, of course, the correlation of the smallest shear modulus with the compressive strength. The direct determination of both of these properties for single crystalline polydiacetylenes would be a good and quantitative test of the microbuckling theory, especially if the crystals' shear moduli could be widely varied by the choice of different substituents on the polydiacetylene main chain [Baughman et al., 1976]. This experiment was the motivation for the synthesis described in the following section and carried out in the progress of this dissertation research.
Figure A.1: Reaction scheme for the syntheses of 2,4-hexadiyne-1,6-diol (HDD), 1,6-bis(phenylurethane)-2,4-hexadiyne (PUHD) and poly PUHD.
Experimental

Poly(1,6-bis(phenyl urethane)-2,4-hexadiyne) (polyPUHD) was chosen as the PDA to be synthesized first, because of its well documented synthesis and known ability to form long, fiber-like crystals [Wegner, 1969]. The reactions involved in the monomer synthesis and polymerization are shown in Figure A.1.

Propargyl alcohol was oxidatively coupled at room temperature to give 2,4-hexadiyne-1,6-diol using a method based on the one described by Hay [1962]: 240 g of reagent grade acetone were placed in a 3-neck 500 ml round bottom equipped with reflux condenser, dropping funnel and gas inlet tube. After dissolving 1.7 g copper(I) chloride (CuCl) and 2.8 ml tetramethylethylenediamine (TMEDA) in the acetone, oxygen was bubbled vigorously through the solution and 20.0 g of propargyl alcohol were added drop-wise over a period of 30 minutes. After completed addition, the mixture was kept stirring overnight under an oxygen atmosphere. The acetone was then distilled off under vacuum. The residue was stirred with 35 ml of 2% hydrochloric acid, filtered, washed 5-times with 5 ml of ice water, and dried in a dessicator over concentrated sulfuric acid for one week in the dark. The resulting raw 2,4-hexadiyne-1,6-diol (HDD) was recrystallized from 8-times its weight of water and dried as before. Interestingly, it was observed that HDD would sublime under vacuum at approximately 90°C giving long and flat, white needles of HDD (This property is not referenced in the Beilstein Handbook of Organic Chemistry.). Unfortunately, the sublimation appeared to be competing with thermal polymerization/degradation of the raw HDD so that sublimation yields were typically less than 10%.

The bis(phenyl urethane) of hexadiynediol (PUHD) was synthesized by adding 47.0 g of freshly distilled phenylisocyanate to a solution of 11.0 g recrystallized HDD in 140 ml anhydrous THF (distilled over calcium hydride). After addition of 1.0 ml triethylamine and 0.5 ml dibutyltin dilaurate, the solution was heated in a water-bath to
50°C for 3 hours [Wegner, 1969]. After cooling to room temperature, the solution was slowly stirred into 2 liters of n-heptane. The precipitate was filtered off, washed with 50 ml n-heptane and air-dried in a dark location. The raw PUHD was recrystallized form 100% ethanol and stored in the refrigerator.

The melting points of HDD and PUHD were determined by DSC and their compositions verified by elemental analysis. The results are listed in Table A.1. The raw yields of the oxidative coupling and of the addition of phenylisocyanate were approximately 90%.

<table>
<thead>
<tr>
<th></th>
<th>% Carbon</th>
<th>% Hydrogen</th>
<th>% Nitrogen</th>
<th>Mp [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDD (calc.)</td>
<td>65.45</td>
<td>5.49</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>HDD (found)</td>
<td>64.43</td>
<td>5.49</td>
<td>0.14</td>
<td>112</td>
</tr>
<tr>
<td>PUHD (calc.)</td>
<td>68.79</td>
<td>4.63</td>
<td>8.04</td>
<td></td>
</tr>
<tr>
<td>PUHD (found)</td>
<td>68.80</td>
<td>4.62</td>
<td>7.90</td>
<td>168</td>
</tr>
</tbody>
</table>

2.0 g recrystallized PUHD were dissolved in 200 ml boiling 1,4-dioxane in a 500 ml-Dewar container and 200 ml of boiling water were added. The container was then capped with a rubber stopper and the solution cooled over a period of ∼ 24 hours to room temperature. This crystallization resulted in a mat of short (= 0.5 cm), needle-shaped monomer crystals which was filtered from the dioxane-water solution and washed with 50 ml of fresh, refrigerated dioxane-water mixture. The crystals turned rapidly blue due to polymerization initiated by ambient light. The polymerization of the vacuum-dried monomer crystals was carried out using a high-energy UV-lamp.
followed by annealing at 120°C in a vacuum oven. The resulting polymer crystals were bronze colored and had a metallic luster.

Results

The obtained polyPUHD single crystals were too short for any mechanical testing. Professor David Bloor from the University of Durham, England, has prepared large quantities of long (5-6 cm), fiber-like polyPUHD by uncontrolled cooling of 10 liter batches of PUHD solution initially heated to 50°C [1992]. He suggested that rapid cooling of somewhat smaller batches of 1 to 2 liters of monomer solution from an elevated temperature may also result in the desired, long dendritic crystals. This crystallization technique, though, has not been tried in the course of this research before this project was abandoned altogether for the following reasons:

Data reported in the literature show the practical identity of the longitudinal shear moduli for different polymers having similar intermolecular interactions. All the single crystalline polydiacetylenes reported in the literature have differently bulky, but chemically similar side groups. It would, therefore, have been very unlikely to obtain a series of PDAs covering a range of shear moduli which to correlate with the different PDAs' compressive strength (assuming there would have been only one compressive strength value for all PDAs of equal shear modulus).

The single data point in a compressive strength-shear modulus correlation study which would have been obtained by the planned experiment was calculated based on literature data: $G = 1$ GPa, $\sigma_c = 0.1$ GPa (cf. section 2.2.2.3). The reproduction or verification of this result was not the objective of this dissertation.

BLOOR, D., University of Durham, England, private communication, 1992


ESTIMATE OF SPECIFIC SURFACE AREA AND AVERAGE MICROFIBRILLAR DIAMETER OF AS-COAGULATED PPTA FIBERS

An as-coagulated PPTA fiber was nitrated in the swollen state as presented in section 4.2. A PPTA film prepared by spin-coating a solution of that nitrated fiber in sulfuric acid was analyzed by X-ray photoelectron spectroscopy. XPS showed that one fifth of all PPTA repeat units had been nitrated. Using the following assumptions, the specific surface area, $A_{sp}$, and microfibrillar diameter, $d_m$, was estimated from this result as shown below.

- Microfibrils are essentially 100% crystalline and impenetrable by any reagent.
- All repeat units on the surface of the microfibrillar network were substituted with a single nitro group.
- The shape of microfibrils is well approximated by a cylinder.
- The concentration of nitrated PPTA repeat units in the bulk and at/near the surface are identical.

$$ A_{sp} = \frac{x \cdot N_A \cdot A_{RU}}{M_{RU}} $$  \hspace{1cm} (B.1)

where $x$ is the molar fraction of nitrated PPTA repeat units in the bulk, $N_A$ is Avogadro's number, $A_{RU}$ is the average lateral area of a PPTA repeat unit, and $M_{RU}$ is the molecular weight of one PPTA repeat unit. Dimensions of the pseudo-orthorhombic unit cell containing two PPTA repeat units are: $a = 5.18\text{Å}$, $b = 7.87\text{Å}$, and $c = 12.9\text{Å}$ [Northolt]. From these dimensions, $A_{RU}$ is approximated as the arithmetic mean of both lateral faces - $ac$ and $bc$ - of the PPTA unit cell. Thus

$$ A_{sp} = \frac{0.2 \cdot 6.0221 \cdot 10^{23} \text{mole}^{-1} \cdot 84 \cdot 10^{-20} \text{m}^2}{238.25 \cdot 10^{-3} \text{kg mole}^{-1}} = 424,643 \text{m}^2\text{kg}^{-1} $$
Treating the microfibrillar network as a collection of thin, cylindrical rods, one can calculate the average microfibrillar diameter, $d_{\mu}$, from the specific surface area, $A_{sp}$, and the volumetric density, $\rho_{\mu}$, of the microfibrils, which are here assumed to be perfectly crystalline.

$$d_{\mu} = \frac{4}{\rho_{\mu} \cdot A_{sp}}$$  \hspace{1cm} \text{(B.2)}

$$d_{\mu} = \frac{4}{1503 \text{ kg m}^{-3} \cdot 424,643 \text{ m}^2 \text{kg}^{-1}} = 6.1 \cdot 10^{-9} m$$

Using nitration yields of less than 100% would increase the specific surface area in inverse proportion and decrease the microfibrillar diameter proportionately. For example, assuming a nitration yield of approximately 85%, as determined for the nitration of as-received Kevlar 49 fibers (cf. section 5.3.1), one obtains a specific surface area of 499,580 m$^2$/kg and a microfibrillar diameter of 5.3 nm.
APPENDIX C

ANALYTICAL MODELS FOR MECHANICAL PROPERTIES OF COATED FIBERS

Elastic Modulus of a Coated Fiber

Using a simple parallel model of two elastic elements to represent the contributions of the coating and the fiber, respectively, is an intuitive way to calculate the global elastic response of the coated fiber.

\[
E_{CF} = \frac{\sigma}{\varepsilon} = \frac{F}{\varepsilon A_{CF}} \quad \text{and} \quad F = \sigma_F A_F + \sigma_C A_C \quad \text{where}
\]

\[
A_F = \pi R_F^2
\]

\[
A_C = \pi \left( (R_F + t)^2 - R_F^2 \right)
\]

\[
A_{CF} = A_F + A_C = \pi (R_F + t)^2
\]

Division by \( A_{CF} \) and \( \varepsilon \) leads to an expression for the elastic modulus of the coated fiber as a function of coating thickness, \( t \), uncoated fiber radius, \( R_{CF} \), and the elastic moduli of coating and fiber, \( E_C \) and \( E_F \):

\[
E_{CF} = E_F \left( \frac{R_F}{R_F + t} \right)^2 + E_C \left[ 1 - \left( \frac{R_F}{R_F + t} \right)^2 \right] = E_C + \left( E_F - E_C \right) \left( \frac{R_F}{R_F + t} \right)^2
\]

or - introducing the coating volume fraction, \( V_C = 1 - \left( \frac{R_F}{R_F + t} \right)^2 \) \hfill (C.1)

\[
E_{CF} = E_F + (E_C - E_F) V_C
\]
Tensile Strength of a Coated Fiber

For the estimate of the resulting tensile strength it is assumed that for all practical coating thicknesses and moduli the fiber will be bearing more load than the coating. Thus, there are two possible cases for tensile failure: 1) coating and fiber fail simultaneously or 2) the coating fails prior to the fiber which will subsequently fail at a load corresponding to the failure load of an uncoated fiber. In these two cases one obtains the two following estimates of coated fiber tensile strength:

\[ \sigma_{t,CF} = E_{CF} \varepsilon_{CF} = \sigma_{t,C} \left[ 1 - \left( \frac{R_F}{R_F + t} \right)^2 \right] + \sigma_{t,F} \left( \frac{R_F}{R_F + t} \right)^2 \] (C.2)

\[ \sigma_{t,CF} = \sigma_{t,F} \left( \frac{R_F}{R_F + t} \right)^2 \]

where subscripts F, C, and CF designate properties of the uncoated fiber, the coating, and the coated fiber, respectively; \( R_F \) is the uncoated fiber's radius, \( t \) is the coating thickness, \( \varepsilon \), the elongation at break, and \( \sigma_t \) is the tensile strength.

Shear Modulus of a Coated Fiber

For the estimate of the torsional modulus again a parallel mechanical model is assumed such that the torsional rigidity of the coated fiber, \( D_{CF} \), is the sum of the torsional rigidities of the fiber and the coating, \( D_F \) and \( D_C \). This assumption implies in this case, unlike in the case of the parallel elements modeling the tensile modulus, that adhesion between fiber and coating is perfect.

\[ D_{CF} = D_C + D_F \]

\[ D_X = G_X J_X \] where \( X = C, F \) or \( CF \)
For circular cross-sections, the polar moments of inertia, \( I \), are given by:

\[
I_F = \frac{\pi R_F^4}{4} \\
I_C = \frac{\pi (R_{CF}^4 - R_F^4)}{4} \\
I_{CF} = \frac{\pi R_{CF}^4}{4}
\]

such that

\[
G_{CF} = G_C - (G_C - G_F) \left( \frac{R_F}{R_F + t} \right)^4
\]  

(C.3)

where \( G \) is the shear or torsion modulus of fiber, coating or coated fiber, respectively.

Compressive Strength of a Coated Fiber

Shear microbuckling theory predicts the equality of the magnitudes of longitudinal shear modulus, \( G \), and axial compressive strength, \( \sigma_c \). Strict application to coated fibers thus leads to:

\[
\sigma_{c,CF} = G_{CF}
\]

Using the experimentally observed proportionality, but not equality of compressive strength and torsional modulus, and applying it to coated polymer fibers yields:

\[
\sigma_{c,CF} = \frac{G_{CF}}{G_F} \sigma_{c,F}
\]  

(C.4)
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