TRANSIENT MOISTURE EFFECTS ON THE VISCOELASTICITY OF SYNTHETIC FIBERS AND COMPOSITES

by

Zhiqiang Wang

Dissertation submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
in
Engineering Mechanics

APPROVED:

David A. Dillard
D. A. Dillard, Chairman

T. C. Ward
T. C. Ward

J. P. Wightman
J. P. Wightman

R. A. Heller
R. A. Heller

A. C. Loos
A. C. Loos

August, 1990

Blacksburg, Virginia

TRANSIENT MOISTURE EFFECTS ON THE VISCOELASTICITY OF SYNTHETIC FIBERS AND COMPOSITES

by

Zhiqiang Wang

Committee Chairman: D. A. Dillard

Engineering Science and Mechanics

(ABSTRACT)

Transient moisture conditions can accelerate the viscoelastic behavior of certain materials over that of constant moisture conditions. This is termed the mechano-sorptive phenomenon. The thrust of this research effort is to study the mechano-sorptive effects on the creep behavior of synthetic fibers and composite materials. This study consisted of two main parts: 1). a phenomenological investigation of the transient moisture effects in synthetic fibers and composite materials and 2). mechanistic studies of the observed phenomenon. The materials studied included Kevlar® fibers, Kevlar® fiber reinforced composites, Technora fibers, poly(methyl methacrylate) (PMMA) fibers, and Nylon 6,6 fibers.

Unidirectional (0°) Kevlar® 49/7714 epoxy coupons undergoing desorption exhibited an increase in tensile and bending creep deformations, a decrease in storage modulus, and an increase in the loss tangent (Tan δ) when compared to coupons maintained at a constant

(saturated) moisture content. However, the transient moisture effects were not seen in composite coupons along the matrix direction. Experimental results showed that aramid fibers exhibited logarithmic creep behavior under tensile load. Even though different constant moisture conditions did not have appreciable effects on the creep behavior of aramid fibers, the creep process increased substantially under transient moisture conditions. The logarithmic creep rates and the mechano-sorptive effects increased with temperature. The creep activation energies of Kevlar® fibers are: 4.84 Kcal/mole for the cyclic moisture conditions and 1.04 Kcal/mole for the constant (saturated) moisture condition. Increases in stress may increase the logarithmic creep rates but may reduce the mechano-sorptive effect. In addition, the creep behavior under transient moisture conditions was nonlinearly dependent on stress. The fiber elastic compliance was observed to increase after creep deformation. Moreover, it was found that the fiber elastic compliance has correlation with the logarithmic creep rates.

Aramid fibers contain hydrogen bonds between rod-like crystallites oriented at small angles relative to the fiber axis. These hydrogen bonds may be disrupted during a transient moisture process. The breakage of these hydrogen bonds may cause slippage of hydrogen bonded crystallites and result in accelerated crystallite rotations, thus causing increases in logarithmic creep rate. Analysis indicated that the obtained activation energy (4.84 Kcal/mole) and the reduction in fiber elastic compliance due to creep deformation support the proposed mechanisms.

ACKNOWLEDGEMENTS

My sincerest thanks go to my advisor, Dr. David A. Dillard, for abundantly supporting me with direction, opportunity, encouragement, and friendship throughout the course of the study. I am also grateful to Drs. Tom Ward, James Wightman, Robert Heller, and Alfred Loos for being on my graduate committee. I am indebted to the helpful discussions on this interdisciplinary subject with my graduate committee members and Drs. Garth L. Wilkes, Fred A. Kamke, and Michael P. Wolcott. The technical support of Mr. Danny Reed is also appreciated.

In addition, I would also like to acknowledge the generous financial and technical support from Du Pont Corporation as monitored by Drs. H. Y. Loken, Paul Riewald, and George Zahr. I also appreciate the National Science Foundation's Center on High Performance Polymeric Adhesives & Composites at Virginia Polytechnic Institute and State University and the Virginia Institute for Materials Systems for funds to continue this work and develop an interdisciplinary approach to this study.

I would like to express my heartily thanks to Dr. and Mrs. Robinson for their genuine friendship during the entire course of my study. Above all, I would like to thank my parents and all of my family members for the vote of confidence they cast in my direction over the years, and for the interest they have taken in my education. Especially, I wish to thank my wife and my son for their support and understanding.

TABLE OF CONTENTS

Chapter 1

INTRODUCTION 1

References 6

Chapter 2

LITERATURE REVIEW 8

2.1 **Introduction** 8

2.2 **Phenomenological Aspects** 10

2.2.1 Behavior of Solid Wood 10

2.2.2 Behavior of Wood-based Products 25

2.2.3 Behavior of Natural Fibers 30

2.3 **Mechanistic Aspects** 32

2.3.1 Hydrogen Bond Mechanism 33

2.3.2 Slip Plane Mechanism 36

2.3.3 Other Mechanisms 37

2.4 **Summary** 38

References 41

Illustrations 49

Chapter 3

TRANSIENT MOISTURE EFFECTS IN SYNTHETIC FIBERS AND COMPOSITES .. 65

3.1 **Introduction** 65

3.2 **Experimental** 67

3.2.1 Tensile Creep Tests 67

3.2.2 Bending Creep Tests 69

3.2.3 DMA Tests 70

3.2.4 Kevlar® 49 Yarn Tests 70

3.2.5 Single Fiber Tests 71

3.3 **Results and Discussions** 76

3.3.1 Tensile Creep Tests 76
3.3.2 Bending Creep Tests 77
3.3.3 DMA Tests 77
3.3.4 Kevlar® 49 Yarn Tests 79
3.3.5 Single Kevlar® Fiber Tests 80
3.3.6 Single Technora® Fiber Tests 83
3.3.7 Single Nylon 6,6 Fiber Tests 84
3.3.8 Single PMMA Fiber Tests 84
3.4 **Conclusions** 85
References 88
Tables 90
Illustrations 93

Chapter 4
PARAMETRIC AND MECHANISTIC STUDIES OF MECHANO-SORPTIVE PHENOMENON IN ARAMID FIBERS 113
4.1 **Introduction** 113
4.2 **Experimental** 114
4.2.1 Tests at Different Temperature Levels 115
4.2.2 Tests at Different Stress Levels 115
4.2.3 Changes of Fiber Elastic Compliance Due to Creep 116
4.2.4 Tests at a Constant (Low) Moisture Condition ... 116
4.3 **Experimental Results** 117
4.3.1 Tests at Different Temperature Levels 117
4.3.2 Tests at Different Stress Levels 117
4.3.3 Changes of Elastic Compliance due to Creep 119
4.3.4 Creep Under a Constant (Low) Moisture Condition 119
4.4 **Discussions** 120
4.4.1 Microscopic Structures of Aramid Fibers 120
4.4.2 Water in Aramid Fibers 123
4.4.3 Creep Mechanisms under Transient Moisture

Conditions 125
4.4.4 Creep Activation Energies of Kevlar® 49 Fibers.. 126
4.4.5 Crystallite Rotation, Fiber Elastic Compliance, and Creep 128
4.4.6 Stress Effects on the Creep Behavior of Aramid Fibers 133
4.5 **Conclusions** 134
4.5.1 Creep under Constant Moisture Conditions 134
4.5.2 Creep under Cyclic Moisture Conditions 134
4.5.3 Mechanisms 135
References 137
Illustrations 141

Chapter 5
SUMMARY AND RECOMMENDATIONS 153

Appendix
CREEP AT A CONSTANT MOISTURE CONDITION AFTER MECHANO-SORPTIVE PROCESS 158

VITA 161

LIST OF TABLES

Table 3.1 Properties of aramid fibers 90

Table 3.2 Mechano-sorptive creep test results of Kevlar® fibers 91

Table 3.3 Mechano-sorptive creep test results of Technora® fibers 92

LIST OF FIGURES

Fig. 2.1 Relative creep of wood beams [5] 49

Fig. 2.2 Creep of wood beams under cyclic moisture conditions [15] 50

Fig. 2.3 Creep level vs. creep oscillation amplitude [24] 51

Fig. 2.4 Creep strain vs. moisture content at different stresses [26] 52

Fig. 2.5 Zero-load corrected loops from Fig. 2.4 [26] 53

Fig. 2.6 The effects of moisture desorption rate on the creep of wood beams [5] 54

Fig. 2.7 The effects of transient temperature in the creep of wood beams [34] 55

Fig. 2.8 Creep of wood beams in pyridine environment [17] 56

Fig. 2.9 Creep recovery of wood beams under transient moisture conditions [36] 57

Fig. 2.10 Residual deformation at the end of each moisture cycle [4] 58

Fig. 2.11 Effects of relative humidity range on the creep of particleboards [39] 59

Fig. 2.12 Effects of material constituents on the creep of particleboards [45] 60

Fig. 2.13 Creep of corrugated pasteboard under compression [51] 61

Fig. 2.14 Transient moisture effects in the dynamic modulus of wool fiber [52] 62

Fig. 2.15 Correlation between swelling and phase angle of a horse hair [57] 63

Fig. 2.16 Relaxation behavior of a wool fiber [58] 64

Fig. 3.1 Kevlar® applications on an aircraft fuselage section [1] 93

Fig. 3.2 Moisture absorption curve of Kevlar/Fiberite 7714 epoxy coupons 94

Fig. 3.3 Stress-strain curve of Kevlar cloth 95

Fig. 3.4 Diagram of the fiber creep test fixture 96

Fig. 3.5 Diagram of the central test system in the fiber test fixture 97

Fig. 3.6 Relative humidity profile in the fiber creep tests 98

Fig. 3.7 Tensile creep of Kevlar® 49/Fiberite 7714 epoxy coupons $[0^0]_8$ 99

Fig. 3.8 Tensile creep of Kevlar cloth 100

Fig. 3.9 Bending creep of Kevlar® 49/Fiberite 7714 epoxy coupons $[0^0]_8$ 101

Fig. 3.10 DMA test results 102

Fig. 3.11 Creep of Kevlar® 49 yarn at 57.9 Newtons (13 lbs) 103

Fig. 3.12 Creep of Kevlar® 49 yarn at 66.8 Newtons (15 lbs) 104

Fig. 3.13 Creep of Kevlar® 49 yarn at 89.1 Newtons (20 lbs) 105

Fig. 3.14 Creep of Kevlar® 29 fiber 106

Fig. 3.15 Creep of Kevlar® 49 fiber 107

Fig. 3.16 Creep of Kevlar® 149 fiber 108

Fig. 3.17 Creep of Technora® Fiber 109

Fig. 3.18 Creep of Nylon 6,6 fiber 110

Fig. 3.19 Creep of PMMA fiber under a constant (saturated) moisture condition 111

Fig. 3.20 Creep of PMMA fiber 112

Fig. 4.1 Creep rates of Kevlar® 49 fibers at different temperatures 141

Fig. 4.2 Mechano-sorptive ratios of Kevlar® 49 fibers at different temperatures 142

Fig. 4.3 Creep rates of Kevlar® 49 fibers at different stresses 143

Fig. 4.4 Logarithmic creep compliance rates of Kevlar® 49 fibers at different stresses 144

Fig. 4.5 Mechano-sorptive ratio of Kevlar® 49 fibers at different stresses 145

Fig. 4.6 The structure of PPTA molecules and their hydrogen bonding [16] 146

Fig. 4.7 A unit crystal cell of PPTA fibers [13, 15, 17] 147

Fig. 4.8 Pleated structure of PPTA fibers [13, 19, 22] 148

Fig. 4.9 The structure and dimension of a water molecule [25] 149

Fig. 4.10 Bonding of water molecules between crystallites 150

Fig. 4.11 Arrhenius plots of the creep of Kevlar® 49 fibers 151

Fig. 4.12 Creep rates vs. fiber elastic compliance of Kevlar® fibers 152

Chapter 1

INTRODUCTION

It is well known that environmental conditions, such as moisture and temperature, have a profound effect on the viscoelastic properties of polymeric and composite materials. For hydrophillic materials, moisture is often found to reduce stiffness and increase creep, presumably through a plasticization effect. The effects of constant moisture content on the mechanical properties of polymers and composite materials have been widely studied and are fairly well understood. However, in reality, many materials and structures experience a changing moisture environment [1 - 7]. For outdoor structures, the moisture content in the structures varies with the climatic conditions such as precipitation and solar radiation, the time of the day, and the season of the year [1 - 6]. Besides these factors, for moving structures, the moisture content and the sorption rate of the structure also depends on the moving speed of the structure and the geographical locations the structure is traveling through. For example, the environment an airplane experiences could involve substantial humidity and hence moisture sorption fluctuations [1, 2, 7]. Therefore, the mechanical response of hydrophillic materials concurrently undergoing sorption is of interest.

Armstrong and Kingston first observed that creep of wood undergoing sorption process is greatly accelerated over creep at any constant moisture content [8]. Since their original work, this topic area has been studied by many researchers on wood, wood products, and natural fibers. Due to the importance of the phenomenon, the term "mechano-sorptive" has been coined to describe this behavior [9]. The main feature of the phenomenon is that the effect of moisture on the performance of materials depends not only on its content level but also on the sorption of moisture content. Often, the dependency of material performance on sorption is very strong. For example, for wood, delayed failures have been observed to occur at relatively low loads and for short periods of time duration upon moisture cycling [10].

Independent from the discovery of mechano-sorptive behavior in wood materials, Mackay and Downes observed that, during the process of moisture absorption in a wool fiber, the dynamic torsional rigidity of the wool fiber experienced a pronounced undershoot followed by a gradual recovery toward its equilibrium value long after the moisture regain had reached a saturation level [11]. Following this pioneer work, several researchers have furthered the results primarily on wool and cotton fibers [12 - 16]. The results obtained by these researchers confirmed those of Mackay and Downes.

Despite the mechano-sorptive research on wood, wood products, and

natural fibers, the significance of mechano-sorptive effects in composite materials was unknown prior to this research effort. For example, in predicting performance under transient moisture conditions, one technique widely used in designing composite structures is based on an "average" moisture content or a "worst case" at constant moisture condition. This practice automatically assumes that the material properties and behavior are only functions of moisture content, and not of moisture history. For certain materials, this design concept is not justified, and may also be grossly nonconservative.

To develop an understanding of transient moisture effects in the areas of composite materials and synthetic fibers, research efforts have been focused on two related aspects. The first one is to identify whether or not the mechano-sorptive phenomenon is exhibited in composite materials and its constituent fibers. The second one is to investigate the mechanisms responsible for the phenomenon. To conduct the tests, a fiber test fixture has been designed and built. The fixture has the ability to change the test humidities under constant temperatures and the ability to measure the viscoelastic deformation of a single filament.

To accomplish these objectives, tensile creep tests, bending creep tests, and dynamic mechanical analysis (DMA) tests have been performed under transient moisture conditions and constant moisture

conditions. The tested materials include unidirectional Kevlar® 49/Fiberite 7714 epoxy coupons, and single Kevlar® 29, Kevlar® 49, Kevlar® 149, Technora®, Nylon 6,6, and PMMA fibers. The effects of load levels and temperature levels on the mechano-sorptive behavior of Kevlar® 49 fibers have been studied. The relationship between the creep process and the fiber elastic compliance was also investigated. The study of the parametric influences on mechano-sorptive behavior has its practical importance as well as its theoretical value. For example, the understanding of these effects could provide engineers with a correct design concept in an application which involves transient moisture environment. The insight of these parametric influences could also form a background to establish a mechanistic explanation of the phenomenon.

In Chapter 2, the research progress in the area of transient moisture effects on the materials such as wood, wood boards, paper, paper boards, wool, and cotton fibers has been reviewed. This chapter is based on a paper written by the author, Dr. D. A. Dillard, and Dr. F. A. Kamke, which is entitled "Transient Moisture Effects in Materials - A Review" (accepted, *J. of Materials Science*). In Chapter 3, the experimental results on the transient moisture effects in Kevlar® fiber reinforced composite coupons, Kevlar® fibers, Technora® fibers, Nylon 6,6 fibers, and PMMA fibers have been presented. This chapter is partially based on a paper written by the author, Dr. D. A. Dillard, Dr. M. P. Wolcott, Dr. F. A. Kamke, and Dr. G. L. Wilkes,

which is entitled "Transient Moisture Effects in Fibers and Composite Materials" (in print, *J. of Composite Materials*). In Chapter 4, the influence of various parameters, such as temperature and stress, on the mechano-sorptive phenomenon of Kevlar® fibers and the possible mechanisms responsible for the phenomenon have been studied and discussed. This chapter is based on a paper written by the author, Dr. D. A. Dillard, and Dr. T. Ward, which is entitled "Temperature and Stress Effects in the Creep of Aramid Fibers Under Transient Moisture Conditions and Discussions on the Mechanisms" (in review, *J. of Polymer Science: Physics Edition*). Finally, Chapter 5 is the summary of the work and recommendations for future studies. Because this dissertation is based on several journal papers, each chapter contains its own set of references and figures.

References

1. Tenny, D. R. and Unnam J., "Analytical Prediction of Moisture Absorption in Composites", *Journal of Aircraft,* 15(3):148-54 (March 1978)
2. Tompkins, S. S., Tenny, D. R. and Unnam J., "Prediction of Moisture and Temperature Changes in Composites During Atmospheric Exposure", *Composite Materials : Testing and Design (Fifth Conference),* ASTM STP 674, American Society for Testing and Materials, pp. 368-80 (1979)
3. Dvoskin, N. et al, "Collaborative BAe/GAC Environmental Fatigue Test Program: Environmental Definition", *Technical report AC-79.5* Under Contract No. PO WMD 1173/8/W by Grumman Aerospace Corporation, Bethpage, New York 11714 (Nov. 1979)
4. Considine, J.M., "Compressive Creep Behavior of Paperboard in a Cyclic Humidity Environment - Exploratory Experiment", *Mechanics of Cellulosic and Polymeric Materials*, Perkins, R.W. (Editor), The Third Joint ASCE/ASME Mechanics Conference, AMD-Vol. 99, MD-Vol. 13, pp. 149-56, (1989).
5. Collings, T.A., "The Effect of Observed Climatic Conditions on the Moisture Equilibrium Level of Fiber-reinforced Plastics", *Composites,* 17(1):33-41, (1986).
6. Springer, G.S., "Moisture Content of Composites Under Transient Conditions", *Environmental Effects on composite Materials*, Springer, G.S. (Editor), Technomic, Westport, Connecticut, (1981).
7. McKague, E.L. et al, "Moisture in Composites: The Effect of

Supersonic Service on Diffusion", *J. Composite Materials,* 9:2-9 (Jan. 1975)

8. Armstrong, L.D. and Kingston, R.S.T., "Effect of Moisture Changes on Creep in Wood," *Nature,* 185(4716):862-3, (1960)
9. Grossman, P.U.A., "Requirements for A Model that Exhibits Mechano-sorptive Behavior", *Wood Sci. Technol.* 10:163-8 (1976)
10. Hearmon, R. F. S. and Paton, J. M., " Moisture Content Changes and Creep of Wood," *Forest Products Journal*, August1964, pp. 357-359.
11. Mackay, B.H. and Downes, J. G., "The Effect of the Sorption Process on the Dynamic Rigidity Modulus of the Wool Fiber", *J. of Applied Polymer Science,* II (4):32-8 (1959).
12. Nordon, P.,"Some Torsional Properties of Wool Fibers", *Textile Research Journal*, 32:560-8, (July 1962).
13. Jentzen, C. A., "The Effect of Stress Applied During Drying on Some of the Properties of Individual Pulp Fibers", *Tappi,* 47(7):412-8, (1964)
14. Shishoo, R., "Load Deformation Behavior of Wool at High Temperatures in Different Media, Part I: Creep of Wool Fibers and Yarns in Steam", *Textile Research Journal*, 42:33-44, (Jan, 1972).
15. Danilatos, G. and Feughelman, M., "The Internal Dynamic Mechanical Loss in α-Keratin Fibers During Moisture Sorption", *Textile Research Journal,* 46:845-6, (1976).
16. Feughelman, M., "A Note on Mechanical Weakening in a Stretched Wool Fiber During Moisture Sorption", *Textile Research Journal*, 32:788-9 (1962).

Chapter 2

LITERATURE REVIEW

2.1 Introduction

Numerous studies have shown that transient moisture conditions have additional effects on the mechanical properties of hygroscopic materials over any constant moisture condition. The interaction of moisture sorption processes and mechanical properties is referred to as the mechano-sorptive phenomenon. This phenomenon has been a research topic for more than thirty years since Armstrong and Kingston, and Mackay and Downes first discovered this phenomenon in wood materials and wool fibers. As a result of these studies, a large body of literature has accumulated in this area. A detailed review on these published papers reveal that the materials studied included wood, wood-based products, natural fibers. The studied properties included creep, delayed failure, dynamic mechanical moduli, and dimensional stability.

Relative humidity (R.H.) and temperature variations may result in moisture changes in materials. A variety of factors influence the level of humidity, for example, the time of the day; the season of the year; precipitation; location changes for long distance moving

structures; and elevation changes for flying vehicles. There are many structures and materials which could experience humidity changes, such as: airplane wings and fuselage; bridge structures; exposed beams in restaurant kitchens, boiler rooms, and cooling towers; roofing decks; fruit packs; paper during unwinding and converting operations or paper-based packaging; and books in long term storage in places without relative humidity control equipment. The effects of transient moisture conditions in materials are frequently dramatic, complex, and difficult to interpret. Yet, in a very practical sense, these effects are so influential that they cannot be ignored. Transient moisture effects could affect the long term performance of materials in many ways and the effects could cause concern to a variety of industries. For example, in wood and wood-based panels, transient moisture conditions have been found to increase creep, and reduce creep rupture life substantially, thus degrading their stability and durability. In the transportation industry, apple packs have been found to distort severely after being unloaded from the refrigerated holds on to the wharf and stored under relatively light load. In the textile industry, transient moisture conditions may result in excessive dimensional instability or wrinkles in textile products. In the paper industry, surface wrinkles and baggy edges were found in rolls of paper formed during unwinding and converting operations or due to the difference in producer's packing environment and customer's unpacking environment. In homes, the warping and delaminating of decorative paper from walls

is a more domestic example.

The purpose of this review is to bring together the existing knowledge on this common subject and highlight the fundamentals of the phenomenon. The review is grouped into two parts. Part one is focused on the phenomenological aspect of the behavior. The experimental results from many researchers have been related and discussed so that a coherent picture of the phenomenon may be appreciated. Part two is focused on the mechanistic aspect. Fundamentals of the phenomenon and proposed mechanisms are discussed so that one can gain a deeper insight into the phenomenon.

2.2. **Phenomenological Aspects**

2.2.1. Behavior of Solid Wood

One of the first reports indicating the interaction between moisture sorption and creep behavior of wood was published in 1960 by two Australian researchers, Armstrong and Kingston [1]. Their results showed that even though the relative creep (creep expressed as percentage of the initial elastic deformation) of wood materials was not affected by constant moisture content, it was increased to a large extent by moisture sorption processes. For example, as shown in Figure 2.1, the relative creep of wood allowed to dry while under load was about three times of that occurring in wood maintained at a constant

moisture condition. Later, Grossman termed this the mechano-sorptive phenomenon [2].

Studies have shown that both softwoods and hardwoods exhibit mechano-sorptive phenomenon. A relative comprehensive but non-exhaustive list of studied species may include: among softwood species, klinki pine (*Araucaria klinkii* Lauterb) [3, 4], hoop pine (*Araucaria cunninghamii* Ait) [5, 6], radiata pine (*Pinus radiata* D. Don) [5], bunya pine (*Araucaria bidwillii*) [7], ponderosa pine (*Pinus ponderosa*) and scots pine (*Pinus sylvestris*) [8, 9, 10], yellow poplar (*Liriodendron tulipifera* L.) [11], and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) [12 - 14]; among hardwood species, beech (*Fagus sylvatica*) [10, 15 - 19], alpine ash (*Eucalyptus gigantea* Hook. f.), mountain ash (*Eucalyptus regnans* F. Muell) and blackbutt (*Eucalyptus pilularis* Sm.) [5], buna (*Fagus crenata Blume)* [20], redwood (*Sequoia sempervirens*) [21], and messmate stringybark (*Eucalyptus obliqua*) [22, 23]. Among the properties studied, most tests were performed to examine the creep behavior of the materials. Experimental results showed that all of these species exhibited mechano-sorptive phenomenon. While detailed comparison may reveal quantitative differences which may be associated with the structural differences among species, there are no qualitative differences between these species. Therefore, the primary effect may be due to a structure level and/or material system which are common to all wood

species.

The phenomenon is exhibited under both absorption and desorption* conditions. Whether the material is allowed to absorb or desorb moisture, the creep levels are higher than those at any constant moisture content [5, 7]. However, as indicated in Figure 2.1, a desorption process has a larger effect on relative creep than an absorption process [5, 7, 11].

When moisture content is allowed to change between absorption and desorption in a cyclic manner, the creep level accumulates over the moisture cycles. Figure 2.2 is a typical example of the cyclic moisture effect on creep [15]. Detailed observations of the creep during a cyclic moisture process reveal three aspects of the effect [4, 5, 15, 16]. First, during any desorption steps, the creep level increases. Secondly, during an absorption step, at moisture levels reached for the first time since the load was applied (the first wetting cycle in Figure 2.2), the creep level increases. And thirdly, during a moisture absorption step at levels reached for the second and

---

* The term *absorption* in this dissertation refers to the event that moisture or solvents diffuse into a solid, while the term *desorption* refers to the event that moisture or solvents diffuse out of a solid.

the subsequent steps since the load was applied, the creep level decreases. However, the recovery in the absorption step is less than the increase in the desorption step and, therefore, the resultant creep level continues to increase over moisture cycles. Hoffmeyer and Davidson have examined the amplitude of oscillation of the mechano-sorptive creep under cyclic moisture conditions from the results of several researchers [15, 16, 24, 25]. As indicated in Figure 2.3 [24], when the amplitude was plotted against total creep, a fairly linear relationship was found.

Mechano-sorption could lead to delayed failures in shorter times and at lower load levels than specimens held at constant moisture conditions. The results of Hearmon and Paton, as indicated in Figure 2.2, showed that beech beams (2 X 2 X 60 mm) failed at 3/8 of the static strength after only fourteen moisture cycles, which corresponded to about a twenty-eight day time duration [15]. However, when maintained at high constant moisture content and under the same load level, a specimen of the same material crept only 1/12 of the failure strain and showed no evidence of future failure. Armstrong and Kingston also noticed minute compression failures in their mechano-sorption specimens (12.5 X 38 X 102 mm) [5]. However, they reported that no failure was observed on specimens (10 X 10 X 102 mm) under a tension loading mode in mechano-sorptive experiments. Humphries and Schniewind have studied the behavior of Douglas-fir

columns (6.4 X 9.5 X 280 mm) under cyclic relative humidities [12]. Creep levels of specimens under cyclic moisture conditions (R.H. between 35% and 87%) were about two orders of magnitude higher than those of the specimens kept at highest constant moisture condition (R.H. ≅ 87%). Of the 34 specimens tested under cyclic moisture conditions, 5 failed in less than 3 days, 10 failed after 3 but less than 14 days, and 19 specimens had not failed after 14 days, when the tests were discontinued. Schniewind [14], and Schniewind and Lyon [13] have studied the creep-rupture life of Douglas-fir beams (10 X 10 X 200 mm and 50.8 X 50.8 X 1016 mm respectively) under cyclic moisture conditions. Their results showed that the mean creep-rupture life under cyclic moisture conditions could be less than that under constant moisture conditions by an order of magnitude. Among the eighteen specimens tested by Schniewind and Lyon, about half of the specimens failed when the relative humidity was high and the other half of the specimens failed when the relative humidity was low. Therefore, it seems that the surface conditions at the moment of failure were not an important factor. [13].

Under certain conditions, there may be a process of exhaustion of available deformation in repeated moisture cycles. Hunt and Shelton have investigated the possibility to obtain a stable-state creep during a cyclic moisture process [9, 26]. They found that a stable-state could be produced by loading scots pine beams at a higher

load level and at a high humidity level, making one absorption-desorption cycle, and then reducing the load followed by another absorption-desorption cycle. Thereafter, any subsequent moisture cycles caused the creep to follow a loop on a moisture content versus creep strain curve. In the tests when the creep strains were measured, the load levels were kept below 10% of the rupture load. The results are shown in Figure 2.4. [26]. Moreover, if the creep loops under tension and compression in Figure 2.4 are corrected by the loop under zero load, the resulting loops will appear more closed and the shapes of the loops for tension, compression, and bending will resemble each other as shown in Figure 2.5 [26]. It needs to be noted that relatively low stress levels may be necessary in obtaining a stable-state creep under cyclic moisture conditions.

Mechano-sorptive creep rate is dependent on the rate of change in moisture content. Armstrong has measured the creep of alpine ash and blackbutt under a bending load at different desorption rates. Figure 2.6 shows the results obtained on alpine ash specimens [5]. The results showed that the rate of change in creep was related to the rate of change in moisture content. Especially, as shown in curve B, the creep rate closely followed the rate of moisture changes. Christensen [4] tested small klinki pine specimens (1.5 X 1.5 X 80 mm) under bending load at different absorption conditions. His results confirmed this rate dependency. The rate dependency suggests that the

phenomenon is not directly time dependent, but moisture rate dependent.

Even though the creep rate is dependent on the rate of change in moisture content, the creep magnitude is unlikely to be affected by the rate of moisture change but is a function of the total change of moisture content [4, 5, 13, 27]. Schniewind found that the mechano-sorptive creep is related linearly to the extent of moisture change in beech. [27]. From the results on alpine ash, Armstrong reached the same conclusion [5]. Schniewind and Lyon have shown that the creep rupture life is linearly dependent on the square root of the extent of moisture change [13].

In the literature, most mechano-sorptive studies were performed on specimens with the cross sectional dimensions on the order of a few millimeters [3, 4, 8-11, 15, 17-20, 26]. Therefore, before the results can be incorporated into design codes, the influence of size effects has to be addressed. The size of a specimen strongly influences its moisture change rate [28], and consequently, within a given period of time, affects the magnitude of moisture change [13]. Armstrong and Christensen compared the creep behavior of two beams, 1 X 1 X 60 mm and 20 X 20 X 900 mm, under cyclic moisture conditions. They concluded that the behavior of the two specimen sizes was qualitatively similar. However, no numerical comparison was given [3]. Schniewind and Lyon

have studied the size effect on the creep rupture life of Douglas-fir specimens [13]. On an average basis, the creep rupture life increased by more than one order of magnitude when the cross sectional area of specimens increased from 10 X 20 mm to 50.8 X 50.8 mm. However, the creep rupture life even for the larger specimens is still much less than that recorded at the same load level under constant moisture conditions [13]. Some researchers believe that for large structural members, mechano-sorptive effects may be insignificant. For example, based on the comparison of the trend lines obtained from the results of Schniewind [14] and Schniewind and Lyon [13] with the trend line for tests under constant moisture conditions from Wood [29], Barrett concluded that environmental cycling would have "probably little or no effect on the behavior of large timbers and glued-laminated members." [30]. Before approaching such a conclusion, however, caution needs to be taken. As reported by Schniewind and Lyon [13], for their large specimens (50.8 X 50.8 X 1016 mm), the moisture changes actually took place at the outer surface layers, while the moisture content at the inner part occupying 2/3 of the specimen thickness remained relatively constant. Because the outer surface layers of bending specimens carry most of the load, the failure may occur at the surface layers due to moisture changes. As the failure develops, moisture changes could occur at a deeper location around the failed spot, thus resulting in a progressive failure mode. The results of Schniewind and Lyon showed that their specimens indeed failed in this fashion [13].

The effect of the initial moisture content on mechano-sorptive creep has been studied also [5, 27]. Schniewind reported that, for beech material, the effect was independent of the position of the moisture content at which the test had begun [27]. However, Armstrong noted that, for hoop pine specimens, the mechano-sorptive effect increased with increasing initial moisture content for equal moisture increments [5].

Evidence suggests that mechano-sorptive behavior may be not present over the entire range of moisture content, There may be a moisture content threshold, above which the phenomenon is less pronounced. For example, Armstrong repòrted that for hoop pine specimens with a saturation level of 110% moisture content, moisture change above about 35 to 55% did not affect creep behavior [5]. It is interesting to note that this moisture threshold is about the same as the fiber saturation point. Above the fiber saturation point, absorbed moisture is mainly present within the wood cells as free water. Below the fiber saturation point, water molecules are primarily contained within the cell walls where they could contribute to the hydrogen bonds between molecular chains or otherwise influence the material.

Even though quantitative differences may be involved, mechano-sorptive phenomenon was found to be present under all loading

modes. For example, Armstrong and Kingston have identified the phenomenon under compression, bending, and tension [5], Hearmon and Paton have identified the phenomenon under shear [15], and Humphries and Schniewind under buckling loading [12]. In comparing mechano-sorptive behavior under bending, compression, and tension, Armstrong and Kingston concluded that the phenomenon was most pronounced under compression, and then in descending order, under bending and tension [5]. Ellwood also reported that beech specimens, when drying, showed larger creep in compression than in tension [31]. However, Hunt and Kingston have shown that, for pine materials, bending, compression, and tension under low stresses (3.8% and 7.5% of the static strength) give similar results when corrected by the zero-load deformations [26]. Shrinkage, as present in a desorption process, will tend to cause increases in compressive deformation and decreases in tensile deformation. Similarly, swelling, as present in an absorption process, will cause increase in tensile strain and decrease in compressive strain. The effects of shrinkage and swelling may, at least partly, contribute to the differences between the creep levels under different loading modes.

Except for a few exclusions, most mechano-sorptive tests were conducted under constant temperature. The effect of temperature during mechano-sorptive processes has been assessed by several researchers [15, 21, 27, 32, 33]. From their results it seems that temperature

below about 60 °C does not have appreciable influence on the mechano-sorptive creep level. For example, Hearmon and Paton have studied the mechano-sorptive effects on beech at 20, 25, 30 and 40 °C. They reported that temperature did not have much effect on the relative mechano-sorptive creep [15]. Schniewind also had the same conclusion on beech material [27]. However, influences of temperature have been observed above 60 °C. For most wood materials, this temperature is within the range of glass transition associated with the softening of hemicellulose [34]. Erickson et al measured mechano-sorptive creep under desorption on redwood at 40°C and 65°C. They found that relative creep was several times greater at 65 °C than at 45°C [21, 32]. Arima has studied the effect of temperature on the recovery behavior of specimens after mechano-sorptive processes [33]. Initially green wood beams (mountain ash and radiata pine, 15 X 15 X 600 mm) were clamped in place along tangential and radial directions to produce a fixed deformation, and then were subjected to drying conditions at different temperatures (25, 40, 50, 65, and 80 °C). After about 12 days of clamping, the specimens were released from clamps and their recovery levels were recorded. According to the recovery levels, the results fell into two groups, one was at 25 and 40 °C, and the other one was at 65 and 80 °C. The results at 50 °C along the radial direction fell into the former group while along tangential direction the latter group. The latter group recovered to a larger extent. Based on these observations, Arima concluded "it may

be considered that some components of wood have begun to change to their softened state between 50 °C and 65 °C".

Even though the scope of this review has been focused on the behavior of materials under transient moisture conditions, a brief discussion about the effect of transient temperature is relevant at this point. Kitahara and Yukawa have compared creep levels of hinoki bending specimens under transient thermal conditions and constant temperature conditions [34]. As indicated in Figure 2.7, test results showed that when the specimens were heated up from either 20, 30 or 40 °C to 50 °C while under a constant load, the creep levels of the specimens were much higher than that at constant 50 °C. Moreover, the creep level had an increasing trend when the difference between the two temperature levels increased. However, when the specimens were cooled down from 50 °C to 40 °C, the creep level of the specimen was lower than those at both 50 °C and 40 °C. Arima also conducted similar tests on hinoki bending specimens [35]. His results showed that when the temperature was increased from one level (20 °C) to another level (either 40, 50, 60 or 75°C), the creep levels were higher than the creep levels at either of the constant temperatures. The phenomenon is especially conspicuous when the higher temperature was above 60°C. Because the equilibrium moisture content or the fiber saturation point decreases as the temperature increases at a given relative humidity, the question as to how much the moisture content changes would affect

the creep level remains. Schniewind and Lyon have conducted creep rupture tests on Douglas-fir specimens under cyclic temperature and moisture conditions. The temperature and relative humidity were cycled sinusoidally and with 180° out of phase. Their results indicated that temperature cycling has little or no effect on time-to-failure, since the average of time-to-failure is about what would be expected on the basis of the concurrent moisture changes alone. [13].

Gardner et al have studied the effect of solvents other than water on the mechano-sorptive behavior in beech material [17]. Some solvents such as methanol, ethanol, and pyridine were found to cause mechano-sorptive phenomenon, while others, such as dioxan, n-propanol, and benzene did not produce mechano-sorptive phenomenon. The results in Figure 2.8 indicate the mechano-sorptive behavior of a beech specimen when pyridine was used. The difference of these solvents in the ability to produce mechano-sorptive phenomenon was found to relate to their polarity, their swelling kinetics, and their own molecular sizes. For example, n-propanol has only about half of the swelling power of methanol and ethanol, and also, its larger molecular size may hinder n-propanol from entering the material quickly enough to cause the phenomenon. In the case of dioxan, the swelling rate of a beech-dioxan system was found to be very slow and it has been conjectured that the time window in the experiment might not be long enough to cover the time sufficient for the phenomenon to be observed

[17]. Benzene is a nonpolar solvent and, consequently it does not have any swelling power. Swelling is related to hydrogen bonding. When polar solvents enter a material with hydrogen bonds, the solvent tends to break the original hydrogen bonds and insert between the broken hydrogen bonds to form new bonds, therefore moving the molecular chains further apart. This microscopic process is manifested as swelling behavior macroscopically. Swelling may be a good indicator of whether a solvent will cause mechano-sorptive phenomenon.

When a specimen is unloaded after mechano-sorptive cycling, some recovery may be observed, but it appears that a large permanent deformation will remain. However, the permanent deformation could be reduced by moisture cycling after unloading [3, - 5, 33, 36]. Experimental results on klinki pine [3, 4], eucalyptus gigantea [3], hoop pine [5], and radiata pine and eucalypt [33, 36] have shown that the absorption steps are much more effective than desorption steps in reducing the permanent deformation. Actually, most recovery occurred during the first absorption step after unloading [3 - 5], and nearly 100% recovery was obtained after specimens were immersed in water [33, 36]. An example of the influence of the moisture cycling is shown is Figure 2.9 [36]. Arima has studied the influence of various parameters on the moisture-cycling-induced recovery. He found that moisture-cycling-induced recovery was not influenced by a delay of two weeks before subjecting specimens to moisture absorption, nor by a

temporary increase of moisture content before unloading [33, 36]. However, the temperature during the loading period influenced the recovery to a large extent. For example, when radiata pine was subjected to 80°C and eucalypt was subjected to 50°C during a mechano-sorptive process, they lost some of the recovery capacity [33, 36]. This is explained by the formation of a new stable configuration above a critical temperature, namely, the glass transition, which reduces recovery potential during subsequent moisture cycles after unloading [33, 36].

It must be noted that even though moisture cycling can accelerate the recovery process after unloading a mechano-sorptive specimen, it appears that there is still an irrecoverable portion of the deformation after the cycling treatment. Christensen has studied the cycling treatment on klinki pine specimens. He found that the cycling treatment did not result in a complete recovery but reduced the residual deformation to a value which tended to increase over previous mechano-sorption cycles when the specimen was under loading. The results are shown in Figure 2.10 [4].

Although the major stream of the research has been along the path of understanding the phenomenon, there have been efforts to find the methods for reducing the effects of the phenomenon. Besides the previously mentioned loading schemes as discovered by Hunt in order to

produce a stable-state deformation under cyclic moisture conditions [9, 26], Erickson and Sauer [21] and Erickson, Chen, and Lehtinen [32] have found that freezing before kiln drying (prefreezing) could significantly reduce the amount of mechano-sorptive creep in redwood heartwood. The treatment was especially effective when the temperature was high and the moisture content change was rapid and large.

2.2.2. Behavior of Wood-based Products

Driven by the considerations of economy, conservation of natural forest resources, and tailoring of wood properties to end uses, wood-based panels, such as plywood, particleboard, and fiberboard, have shown increasing growth in the market. many grades of these panels are used as load-carrying materials, e.g. in construction and transportation industry. The environment of their applications often involves substantial humidity fluctuations. Therefore, the influence of transient moisture conditions must be understood to ensure satisfactory design and performance.

After discovery of mechano-sorptive phenomenon in whole wood, a number of papers has emerged addressing the transient moisture effects in particleboards [37-43], fiberboards [38, 42-45], and plywood [39, 41-43]. Not surprisingly, these studies show that mechano-sorption effects are also present in wood-based panels, and are even more pronounced than in whole wood [37, 38, 42, 43]. Also different from

whole wood, relative creep was found to increase with increasing equilibrium moisture content [37, 38].

As in whole wood, the mechano-sorptive phenomenon is present under adsorption, desorption, and cyclic moisture conditions [37, 38, 40-45]. Contrary to the experience with whole wood [5], however, Sauer and Haygreen in studying wet and dry process hardboards of aspen [44], and Bryan and Schniewind in studying urea- and phenolic-bonded particleboards of Douglas-fir [37] found that absorption conditions had greater effects than desorption conditions. On the other hand, in studying urea-bonded particleboards of radiata pine and standard and tempered hardboard of eucalypt, Armstrong and Grossman demonstrated that desorption plays a larger role than absorption in increasing creep levels under cyclic moisture conditions [38]. The discrepancy may be explained through the direct effect of constant moisture effects on creep. If constant moisture effect is not negligible in creep, the deformations arising with changes in moisture content could be overtaken.

Haygreen et al studied the effect of the extent of moisture changes on mechano-sorptive creep levels of particleboards under cyclic moisture conditions [39]. Their data have been processed and are plotted in Figure 2.11. As indicated in the graph, the creep deformations increased as the range of moisture content increased.

Mechano-sorptive phenomenon in wood-based panels were also studied under different loading modes. Hunt tested mechano-sorptive effects under tension and compression [40]. His results showed that after 21 days under cyclic moisture conditions the creep levels were about three times higher than those under constant moisture conditions. Martensson [46], and Martensson and Thelandersson [47] investigated the creep behavior of hardboards under tensile, compressive, and bending loads. They concluded that mechano-sorptive effects were most pronounced in bending, less in compression, and least in tension.

Generally speaking, the creep compliance of wood-based panels in an increasing order is in the following sequence: plywood, particleboards, and hardboards. Haygreen et al have studied the creep behavior of particleboards and plywood under absorption conditions and found that creep levels of particleboard specimens were as much as 2 to 3 times of those of plywood specimens [39]. Armstrong and Grossman have studied the creep behavior of particleboards and hardboards under cyclic moisture conditions [38]. They found that the creep deflection of hardboards (made of eucalypt species of medium and high density) are higher than those of particleboards (made of radiata pine). However, limited data suggest that when the ratios of mechano-sorptive creep level to constant moisture level are compared, the picture might

be different. The data from the experiment of Haygreen et al on plywood and particleboards suggests that the ratio may be even higher for plywood than for particleboards [39]. The data from Sauer and Haygreen on wet- and dry-process hardboard shows parallel results [44].

The processing methods in making the wood-based panels or the treatment on the panels could influence the creep deflection levels also. For example, Sauer and Haygreen found that dry-process hardboard exhibited higher creep level than wet-process hardboard [44]. Armstrong and Grossman found that the tempering treatment on hardboard could reduce the mechano-sorptive creep level [38]. Byrd and Koning found that surface sizing treatment with starch on corrugated fiberboards could reduce mechano-sorptive creep level [45]. The influence of these factors may be through their influence on the moisture absorption capacity or rate.

The constituent materials of the boards may affect the extent of the mechano-sorptive creep. Byrd and Koning have investigated the compressive mechano-sorptive creep behavior of fiberboards with different constituents or proportion of constituents [45]. Their results have been reprocessed and are shown in Figure 2.12. From the results we may see that bark content and high yield of pulp could cause increase in the mechano-sorptive creep rate. Several interesting

points may drawn from the graph. 1). The yield of fiber content has a greater effect on the mechano-sorptive creep than the content of bark; 2). Factors affecting mechano-sorptive creep may not affect the creep behavior under constant moisture condition as much; 3).The characteristic in 2) resulted in the fact that higher mechano-sorptive creep rate had a higher creep rate ratio (the ratio of creep rate under transient moisture condition to that under constant moisture condition); and 4). Higher creep rate under constant moisture condition does not necessarily mean a higher mechano-sorptive creep rate. McNatt and Hunt have studied the creep behavior of flakeboards and plywood specimens under cyclic moisture conditions [41]. Their results indicate that the mechano-sorptive creep level of oak flakeboard is higher than that of aspen flakeboard, and that of Douglas-fir plywood is higher than that of southern pine plywood.

Results from some researchers suggest that the binders used in bonding the constituents do not significantly affect the mechano-sorptive behavior [39, 48]. The results of Haygreen et al indicated that the mechano-sorptive creep of urea and phenolic bonded particleboards were very similar both qualitatively and quantitatively [39]. The results of Gressel also indicated that even though different binders could affect the equilibrium moisture content in particleboards, they do not cause different creep rates [48]. However, Byrd has shown that different adhesives could result in different

levels of compressive mechano-sorptive creep in corrugated fiberboard [49].

Byrd has studied the cyclic moisture effects on tensile and compressive creep of kraft paper handsheets [50]. As indicated in Figure 2.13, when papersheets were subjected to cyclic relative humidity from 35% to 90%, the creep level was 4.6 to 9 times higher than that when the papersheet was subjected to a constant 90% R.H.. Under compressive load, the creep obeyed a linear relationship in the time domain. As a result of this increased creep rate, the creep rupture time under cyclic moisture condition was much less than that under constant moisture conditions [51].

2.2.3. Behavior of Natural Fibers

Natural fibers such as wool and cotton fibers are mainly used in the garment industry. The wrinkling behavior of garments under transient conditions, such as washing and drying, is an important factor in influencing their appearance. Natural fibers are also used in ropes, where rigidity and strength under transient moisture conditions are important.

Mackay and Downes measured the effect of sorption processes on the dynamic rigidity modulus of wool fibers [52]. Their results showed

that, when a large increase was made in the relative humidity surrounding a wool fiber, its dynamic torsional rigidity was found to pass through a minimum value considerably less than the final equilibrium value. The more abrupt the increase in relative humidity, the more pronounced was the effect. Furthermore, the recovery from minimum to the equilibrium value of rigidity takes a much longer time than the time to reach moisture equilibrium. This phenomenon is shown in Figure 2.14 [52]. Nordon [53] confirmed this finding by a more detailed study. He concluded that any changes in the relative humidity surrounding the fiber first led to a reduction and then led to a partial recovery of the rigidity. The effect was most pronounced at the higher humidities [53]. Jentzen has performed creep tests under a drying environment on holocellulose pulp fibers made from longleaf pine. The diameter of the fibers was about 10 μm. A fiber was taken out from water immersion and then was subjected to a tensile creep test. He found that while the surface of the fiber was still covered by water droplets, no appreciable deformation was apparent. However, at the instant when the water droplets disappeared and the fiber began to dry, a sudden increase in deformation was observed [54].

Test results indicated that cotton fabrics wrinkled more during moisture changes than at moisture equilibrium. If the fabrics, however, are treated with a process known as wet crosslinking, the sensitivity of wrinkling during transient moisture conditions could be

reduced [55]. Shishoo has measured the creep behavior of dry wool fibers in a steam environment. Samples were subjected to the action of steam before loading. It was found that pre-steaming from 0 to 60 seconds markedly influenced the subsequent creep in steam, and maxima in creep were obtained at a pre-steaming time of ca. 30 seconds (fiber diameter was 47 μm) [56]. Danilatos and Feughelman have studied the dynamic damping behavior of wool fibers and horse hair during moisture absorption processes. They found that, as indicated in Figure 2.15, the damping reached a maximum at the point in time when the swelling of the fiber reached an equilibrium plateau [57]. This phenomenon parallels others and confirms the general picture that during sorption the molecular structure of keratin fibers have a maximum mobility. Feughelman has noted that, in a relaxation tests on wool fibers, as indicated in Figure 2.16, the force had an additional decrease over constant x% R.H ($x > 0$). after a moisture cycle from x% R.H. to 0% R.H. and then back to x% R.H.. The additional decrease reached a maximum when x is about 40. When x is about 80, the phenomenon disappeared [58].

2.3. **Mechanistic Aspects**

In order to model and predict the phenomenon rigorously, a comprehensive understanding about the cause of the mechano-sorptive

effect is necessary. Although the topic has been the subject of numerous investigations for over 30 years, a fully satisfactory explanation of the phenomenon has not been advanced. Nevertheless, several mechanisms have been proposed. These mechanisms are mainly based on the argument of hydrogen bonding, molecular mobility, and internal stress gradient due to the presence of moisture gradient. It is possible that different mechanisms or a combination of several mechanisms to be responsible for observed behavior in various materials.

2.3.1. Hydrogen Bond Mechanism

Gibson proposed that the mechano-sorptive phenomenon is caused by the continual making and breaking of hydrogen bonds due to the change in moisture content. During the temporary disruption of the hydrogen bonds, a stress bias will favor additional deformation [16]. This explanation is based on the consideration that adjacent cellulose chains in wood materials are held together by hydrogen bonds (with a strength of 5-8 kcal/mole). The bonds are formed between the hydrogen atoms of hydroxyl groups and suitably situated oxygen atoms in an adjacent chain. The hydrogen bonds play an important role in determining the mechanical properties, such as stiffness and strength, of wood materials. When water molecules are absorbed into the material, some water molecules, being small and polar, may disrupt the original bonds and bridge in between to form new hydrogen bonds.

Similarly, when water molecules are desorbed from the material, some of the water molecules which acted as bridges between the molecular chains will leave the sites and cause a temporary breakage of the hydrogen bond linkages.

A logical development of the hydrogen bond explanation would be that if other polar solvents are used, mechano-sorptive effects would be manifested also. Gardner et al has found that, besides water, methanol, ethanol, and pyridine also cause mechano-sorption effects in beech wood material [17]. However, besides the polarity, the effects of solvents may also depend on such factors as molecular size and the swelling kinetics of the solvents [17].

Armstrong has questioned the hydrogen bond mechanism based on his constant moisture flux experiment [7]. In this experiment, a constant flux of moisture was produced by imposing different humidity levels on the inside and outside of a hollow bunya pine specimen. The results of the experiment indicated that the relative creep, determined for wood under compressive load parallel to the grain, were similar in wood subjected to constant moisture flux conditions and to constant moisture conditions without moisture flux [7]. However, a constant moisture flux may not cause hydrogen bond change. Under a constant moisture flux condition, the number of water molecules will be the same at any time within any infinitesimal volume of the wood material.

In order to have disruption of hydrogen bonds, in the context of the hydrogen bond mechanism, the number of water molecules may need to change to induce the disruption. The movement of water molecules inside the material could be accomplished through the movement of free water molecules. Because the free water molecules are not associated with the wood molecular chains, their movement would not cause any change in the hydrogen bonds. Actually, when water molecules are in equilibrium inside the material, there is a constant rate of exchange of water molecules between free and bound water. So the equilibrium is actually a rate equilibrium or dynamic equilibrium. Only when this equilibrium of exchange is upset, say, by a change in external environment, is a statistical disruption of hydrogen bonds possible. Therefore, the mechanism more accurately may be considered as a disturbance in the exchange rates between the breaking and reforming of hydrogen bonds between the wood molecules. In this sense, the mechano-sorption mechanism may be treated as a special form of a chemical reaction.

Although the breaking and remaking of hydrogen bonds during a transient moisture conditions may provide a general explanation to mechano-sorptive phenomenon, it does not provide a detailed explanation for the quantitative differences between different materials or under different conditions. Therefore, to explain the phenomenon to a full extent and to provide analytical models, the

incorporation of material structure in the mechanism is necessary.

2.3.2. Slip Plane Mechanism

Based on SEM microscopic observations, Hoffmeyer and Davidson have proposed a "slip zone" model to explain mechano-sorptive phenomenon in wood under compression and bending [24]. Polarized microscopy revealed zones of minute failures as distinct planes extending through the S2 layer of the cell wall. The angle between the slip plane and the longitudinal axis of the cell wall is typically on the order of 60 degrees. The number of slip planes is known to be a function of stress level, moisture content and duration of load. To relate the formation of slip planes to the mechano-sorptive creep, Hoffmeyer and Davidson hypothesized that the change of the elastic, viscoelastic, and plastic properties of wood are in proportion to the number of slip planes, and the number of slip planes is in proportion to the amount of moisture change.

Because slip planes only form under compression and bending and at relatively high stress levels, this model is insufficient to explain the mechano-sorptive phenomenon under tension and at low stress levels. However, it is possible that different mechanisms prevail under tension and under compression and bending, or at low stresses versus moderate stresses and high stresses.

2.3.3. Other Mechanisms

In explaining the behavior of wool fibers in a transient moisture environment, Mackay and Downes proposed that the temporary reduction and the later recovery in rigidity modulus is due to the transient stresses produced as a result of differential swelling during the penetration of the water front into the fiber and that these stresses cause temporary rupture of bonds, which contributes to the drop of rigidity [52]. Nordon suggested that there are two competing factors in influencing the observed behavior. The rigidity is decreased during a sorption process when interchain hydrogen bonds are broken and one or more water molecules are inserted between the chains, forming a much weaker and more flexible links between chains. The other process responsible for the increase of rigidity is time dependent and is more effective in the later stage of the experiment. It was assumed that for each equilibrium moisture content there is a corresponding molecular configuration in the lowest free energy state. At this state, the rigidity is a maximum. When this state is upset by moisture sorption, molecular chains will reorient themselves to constitute a new energy state so that the condition of a minimum free energy for the system can be satisfied. However, the sorption rate is much faster than the rate the molecular chains reorient themselves, so one first observes a reduction in rigidity followed by a slower recovery after the moisture equilibrium has been attained [53].

In studying the mechano-sorptive behavior of wood materials, Mukudai and Yata proposed that slippage between the S_1 and S_2 layers of the secondary wall results in a redistribution of stress. Since each cell wall layer has different molecular orientations and chemical makeup, each layer will exhibit a different viscoelastic response and swelling characteristics [59, 60, 61]. Van de Put has employed molecular deformation kinetics to describe the mechano-sorptive behavior in wood. Accelerated deformation is caused by an increase of "holes", called flow units, which allow an increase of molecular mobility. The flow of the polymer is then analogous to a quasi-first-order chemical reaction [62, 63].

2.4. **Summary**

Compared to constant moisture conditions, changes in moisture content accelerate creep [5, 7, 11, 15, 38, 50, 54, 56, 59], creep recovery [3-5, 33, 36], and relaxation processes [58], cause reductions in creep rupture life [13, 14, 15, 51] and dynamic modulus [52, 53, 56] and increases in damping [57], and influence the wrinkle behavior of fabrics [56, 57].

The influences of moisture changes in materials behavior have been found to be present in wood [1-27, 29-33], wood-based panels [37-49], paper [50-51], natural fibers [52-54, 56-58, 65], fabrics

[55], high strength synthetic fibers and composite materials [59-61]. It is interesting to note that all of these materials contain hydrogen bonds on a molecular level. Another common characteristics of these materials is that they all possess anisotropic responses to moisture effects such as swelling strains along different material directions. While their common molecular structure may relate to the origin of the phenomenon, it is also important, however, to note that there are quantitative differences in the mechano-sorptive behavior among different materials which may be explained through the differences in their material structures.

For a given material system, factors which may directly influence mechano-sorptive effects are the direction of moisture changes [5, 7, 11], the history of moisture changes [4, 5, 15, 16, 9, 26, 39, 56], the rate of moisture changes [4, 5,], and the magnitude of moisture changes [4, 5, 13, 27, 39, 53]. The factors may indirectly, or to a second order degree, influence the mechano-sorptive phenomenon are the temperature levels [15, 21, 27, 32, 33], specimen dimensions [13, 14, 30], and loading modes [5, 12, 15, 40, 46, 47]. The influences of temperature levels and specimen dimensions may be accomplished, at least partly, through their influences on the moisture rate and magnitude of moisture changes, while the loading modes may be related to the responses of materials to moisture effects along different material directions.

Recent trends of study on mechano-sorptive behavior appear to be oriented at searching for theoretical explanations to the phenomenon [24, 59], and practical assessment of parametric influences [8, 9, 19, 26, 41, 42, 43]. On the theoretical aspects, emphasis has been placed on the incorporation of material structures to the phenomenon. On the practical aspects, focal points are on the design levels such as more practical environmental factors, effects in larger members, temperature levels, etc..

As a retrospection, even though the research in the area has been ongoing for more than thirty years, no reliable quantitative predictions of the phenomenon are available. The lack of understanding of the phenomenon may be due largely to the complexity of the phenomenon. However, the lack of a consistent test method and data presentation has contributed to the inability to devise a plausible theory. In light of the cost and effort in conducting these tests, in the opinion of the author, it is necessary to establish a standard test method and, at least a standard definition of test parameters and the format of presenting the results.

References

1 Armstrong, L.D. and Kingston, R.S.T., "Effect of Moisture Changes on Creep in Wood, *Nature,* 1185(4716):862-3, ((1960)

2. Grossman, P.U.A., "Requirements for A Model that Exhibits Mechano-sorptive Behavior", *Wood Sci. Technol.* 10:163-8 (1976)

3. Armstrong, L.D. and Christensen, G.N., "Influence of Moisture Changes on Deformation of Wood Under Stress," *Nature*, 191(4791):869-870 (1961)

4. Christensen, G.N., "The Use of Small Specimen for Studying the Effect of Moisture Content Changes on the Deformation of Wood," *Australia Journal of Applied Science,* 13(4):242-57, (1962)

5. Armstrong, L. D. and Kingston, R. S., " The Effect of Moisture Changes on The Deformation of Wood Under Stress," *Australia Journal of Applied Science*, 13:257-76, (1962)

6. Grossman, P. U. A., "Use of Leicester's Rheological Model for Mechano-sorptive Deflections of Beams", *Wood Science and Technology*, 5:232-5, (1971)

7. Armstrong, L. D., "Deformation of Wood in Compression During Moisture Movement", *Wood Science,* 5(2):81-6, (1972)

8. Hunt, D. G., "The Mechano-sorptive Creep Susceptibility of Two Softwoods and Its Relation to Some Other Materials Properties", *J. of Materials Science,* 21:2088-96, (1986)

9. Hunt, David G; Shelton, C.F., "Stable -state Creep Limit of

Softwood", *J. of Material Science*, 22(1):313-20, (1987)

10. Hunt, David G; Shelton, C.F., "Progress in the Analysis of Creep in Wood During Concurrent Moisture Changes", *J of Material Science*, 22(1):313-20, (1987)
11. Szabo, T. and Ifju, G., "Influence of Stress on Creep and Moisture distribution in Wooden Beams Under Sorption Conditions", *Wood Sci.*, 2(3):159-67, (1970)
12. Humphries, M. and Schniewind, A. P., "Behavior of Wood Columns Under Cyclic Relative Humidity", Wood Science, 15(1):44-8 (1982).
13. Schniewind, A. P. and Lyon, D, E., "Further Experiments on Creep-rupture Life Under Cyclic Environmental Conditions", *Wood and Fiber*, 4(4):334-41, (1973)
14. Schniewind, A. P., "Creep-rupture Life of Douglas-fir Under Cyclic Environmental Conditions", Wood Sci. and Tech., 1(4):278-88 (1967).
15. Hearmon, R. F. S. and Paton, J. M., " Moisture Content Changes and Creep of Wood," *Forest Products Journal*, August 1964, pp. 357-359.
16. Gibson, E. J., "Creep of Wood: Role of Water and Effect of a Changing Moisture Content," *Nature,* 206(4980):213-4, (1965)
17. Gardner, R., Gibson, E. J., and Laidlaw, R. A., " Effects of Organic Vapors on the Swelling of Wood and on Its Deformation Under Load," *Forest Products Journal,* 17(4):50-1, (1967)
18. Hunt, D., " A Preliminary Study of Tensile Creep of Beech With Concurrent Moisture Changes," *ICM 3*, 3:299-308, (1979)
19. Hunt, D.G., "Creep Trajectories for Beech During Moisture Changes

Under Load", *J. Material Sci.* 19(5):1456-67, (1984)

20. Takemura, T.; "Plastic Properties of Wood in Relation to the Non-equilibrium States of Moisture Content", *Mem. Coll. Agric.; Kyoto University* 88:31-48, (1966)
21. Erickson, R.W. and Sauer, D.J., "Flexural Creep Behavior of Redwood Heartwood During Drying from the Green State", *For. Prod. J.*, 19(12):45-51, (1969)
22. Leicester, R.H., "A Rheological Model for Mechano-sorptive Deflections of Beams", *Wood Sci. Technol.* 5:211-20, (1971)
23. Leicester, R.H., "Lateral Deflection of Timber Beam-columns During Drying", *Wood Sci. Technol.* 5:221-31 (1971)
24. Hoffmeyer, P. and Davidson, R. W., "Mechano-sorptive Creep Mechanism of Wood in Compression and Bending", *Wood Sci Technol.*, 23:215-27, (1989)
25. Mohager, S., "Studier av Krypning Hos Trä", Doctoral Dissertation, Kungliga Tekniska Högskolan, Stockholm
26. Hunt, D. G. and Shelton, C. F., "Longitudinal Moisture-shrinkage Coefficients of Softwood at the Mechano-sorptive Creep Limit", *Wood Sci. Technol.*, 22:199-210, (1988)
27. Schniewind, A. P., "Über den Einfluß von Feuchtigkeitsänderungen auf das Kriechen von Buchenholz quer zur Faser unter Berücksichtigung von Temperatur und Temperaturänderungen", *Holz als Rohund Werkstoff*, 24(3):87-98 (1966)
28. J. Crank, in "Diffusion in Solids", (Oxford Press, London, 1976)

29. Wood, L. W., "Relation of Strength of Wood to Duration of Load", U.S. Forest Service, Forest Products Lab, Report No. R1916.

30. Barret, J. D., "Effects of Loading Time on Design", in Structural Use of Wood in Adverse Environments, edited by Meyer, R. W., and Kellogg, R. M. (Van Nostrand Reinhold Company, New York, 1982), p. 307.

31. Ellwood, E.L., "Properties of American Beech in Tension and Compression Perpendicular to the Grain and Their Relation of Drying", *Yale University, School of Forestry Bulletin No. 61* (1954).

32. Erickson, R. et al, "The Effect of Unidirectional Diffusion and Prefreezing Upon Flexural Creep in Redwood", *Forest Products Journal*, 22(10):56-60, (1972)

33. Arima, T., "Recovery of Wood After Mechano-sorptive Deformation. II. effects of drying conditions while clamped", *Mokuzai Gakkaishi (J. Jpn. Wood Res. Soc.)*, 25(7):469-75, (1979)

34. Kitahara, K. anf Yukawa, K., "The Influence of the Change of Temperature on Creep in Bending", Journal of Jap. Wood Research Society, 10(3):169-75 (1964).

35. Arima, T., "Creep in Process of Temperature Changes. I. Creep in Process of Constant, Elevated, and Decreased Temperature", Journal of Japanese Wood Research Society, 18(7):349-53 (1972).

36. Arima, T. and Grossman, P.U.A., "Recovery of Wood After Mechano-sorptive Deformation", *J. Inst. Wood Sci.*, 8(2):47-52, (1978)

37. Bryan, E. L. and Schniewind, A. P., "Strength and Rheological Properties of Particleboard", *Forest Products Journal,* 15(4):143-8, (1965)

38. Armstrong, L. D. and Grossman, P. U. A., "The Behavior of Particle Board and Hardboard Beams During Moisture Cycling", *Wood Science and Technology*, 6:128-37, (1972)

39. Haygreen, J., Hall, H., Yang, K.N. and Sawicki, R., "Studies of Flexural Creep Behavior in Particleboard Under Changing Humidity Conditions", *Wood and Fiber* 7:74-90, (1975)

40. Hunt, D., "Measurement of Elastic and Creep Properties of Particleboard in Tension and Compression", Wood Science, 2(4):212-20 (1970)

41. McNatt, J.D., and Hunt, M. O., "Creep of Thick Structural Flakeboards in Constant and Cyclic Humidity", Forest Products Journal, 32(5):49-54 (1982)

42. McNatt, J. D. and Laufenburg, T.L., "How Moisture Changes Affect Long-term-load Performance of Wood-base Panels in I-beams and Other Structural Composite Members", in "Mechanics of Cellulosic and Polymeric Materials" AMD-Vol. 99, MD-Vol. 13., Edited by Perkins, R.W. (ASME, New York, 1989)

43. Laufenburg, T. L., "Creep Testing of Structural Composite Panels: A Literature Review and Proposed Standard", In *Proceedings of the Twenty-first Washington State University International Particleboard/Composite Materials Symposium*, T. M. Maloney, Ed.

Washington State University, Pullman, WA; March 1987, (Washington State University, 1987) pp. 297-313

44. Sauer, D.J. and Haygreen, J.G., "Effects of Sorption on the Flexural Creep Behavior of Hardboard", Forest Products Journal, 18(10):57-63 (1968)

45. Byrd, V.L., and Koning, J. W. Jr., "Corrugated Fiberboards", Tappi, 60(6):35-37 (1978)

46. Martensson, A., "Tensile Behavior of Hardboard Under Combined Mechanical and Moisture Loading", *Wood Sci. Technol.*, 22:129-42, (1988)

47. Martensson, A., and Thelandersson, S., "Behavior of Wooden Structural Elements Under Combined Mechanical and Hygral Loading", In Proceedings of International Conference on Timber Engineering, Seattle, WA, September 19-22 1988, Vol. 2, Edited by Rasik Y. Itani, (Forest Products Research Society of Madison Wisconsin, 1988) pp. 384-394

48. Gressel, V.P., "The Effect of Time, Climate and Loading on the Bending Behavior of Wood-base Materials", Holz als Roh- und Werkstoff, 30:259-66; 347-55; 479-88, 1972

49. Byrd, V.L., "Adhesive's Influence on Edgewise Compression Creep in a Cyclic Relative Humidity Environment", Tappi Journal, pp. 98-100, October 1986

50. Byrd, V.L., "Effect of Relative Humidity Changes During Creep on Handsheet Paper Properties", *Tappi* , 55(2):247-52, (1972)

51. Byrd, V.L., "Effect of Relative Humidity Changes on Compressive Creep Response of Paper", *Tappi* , 55(11):1612-3, (1972)

52. Mackay, B.H. and Downes, J. G., "The Effect of the Sorption Process on the Dynamic Rigidity Modulus of the Wool Fiber", *J. of Applied Polymer Science,* II (4):32-8 (1959).

53. Nordon, P.,"Some Torsional Properties of Wool Fibers", *Textile Research Journal*, 32:560-8, (July 1962).

54. Jentzen, C. A., "The Effect of Stress Applied During Drying on Some of the Properties of Individual Pulp Fibers", *Tappi,* 47(7):412-8, (1964)

55. Liljemark, N. T. et al, "The Sensitivity of Cotton Fabrics to Wrinkling During Changing Moisture Regain and in Its Dependence on Setting and Cross-linking Parameters", *Textile Research Journal*, 41:526-33 (June, 1971).

56. Shishoo, R., "Load Deformation Behavior of Wool at High Temperatures in Different Media, Part I: Creep of Wool Fibers and Yarns in Steam", *Textile Research Journal*, 42:33-44, (Jan, 1972).

57. Danilatos, G. and Feughelman, M., "The Internal Dynamic Mechanical Loss in α-Keratin Fibers During Moisture Sorption", *Textile Research Journal,* 46:845-6, (1976).

58. Feughelman, M., "A Note on Mechanical Weakening in a Stretched Wool Fiber During Moisture Sorption", *Textile Research Journal*, 32:788-9 (1962).

59. Mukudai, J. and Yata, S.; "modeling and Simulation of Viscoelastic

Behavior (Tensile Strain) of Wood Under Moisture Change"; Wood Sci. Technol. 20:335-48, (1986)

60. Mukudai, J. and Yata, S.; "Further Modeling and Simulation of Viscoelastic Behavior (Bending Deflection) of Wood Under Moisture Change"; Wood Sci. Technol. 21:49-63, (1987)

61. Mukudai, J. and Yata, S.; "Verification of Mukudai's Mechano-sorptive Model"; Wood Sci. Technol. 22:43-58 (1988)

62. Van de Put, T. A. C. M.; "Reaction Kinetics of BOnd Exchange of Deformation and Damage Processes in Wood"; Proceedings IUFRO conference, Firenze, Italy, September 1986

63. Van de Put, T. A. C. M.; Theoretical Explanation of the Mechano-sorptive Effect in Wood"; Wood and Fiber Science 21(3):219-30, (1989)

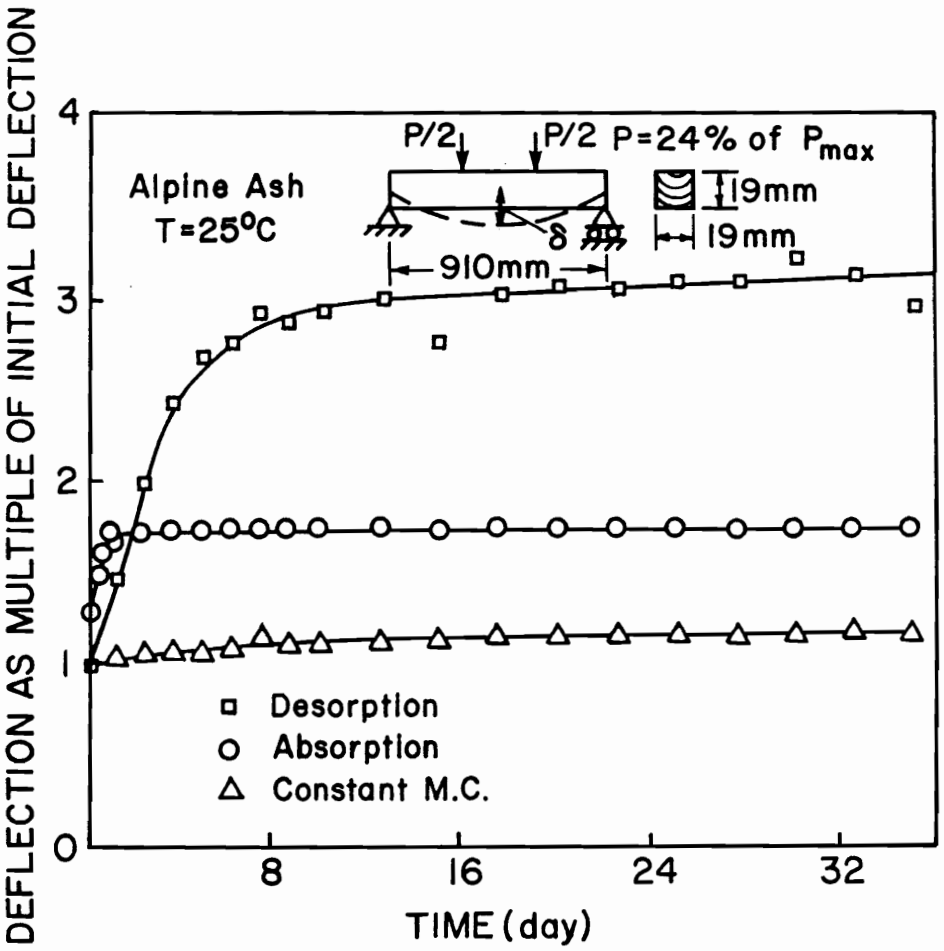

Fig. 2.1 Relative creep of wood beams [5]

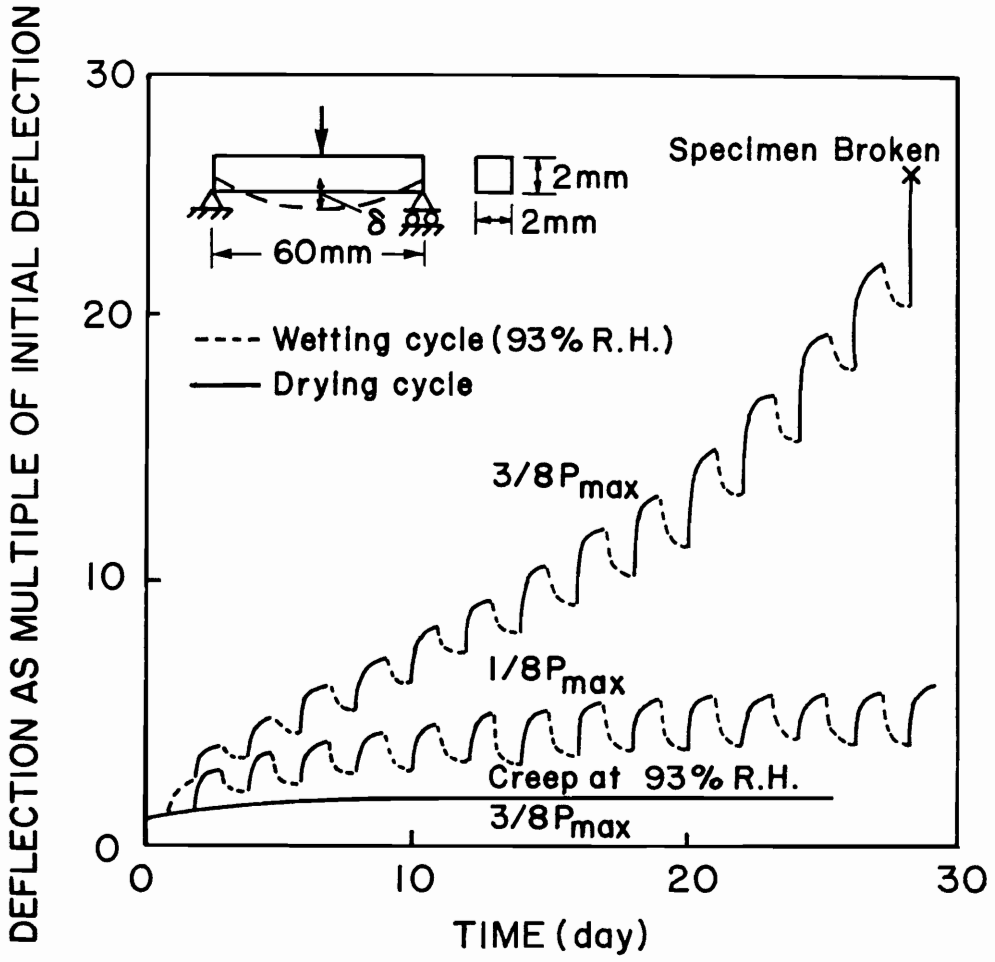

Fig. 2.2 Creep of wood beams under cyclic moisture conditions [15]

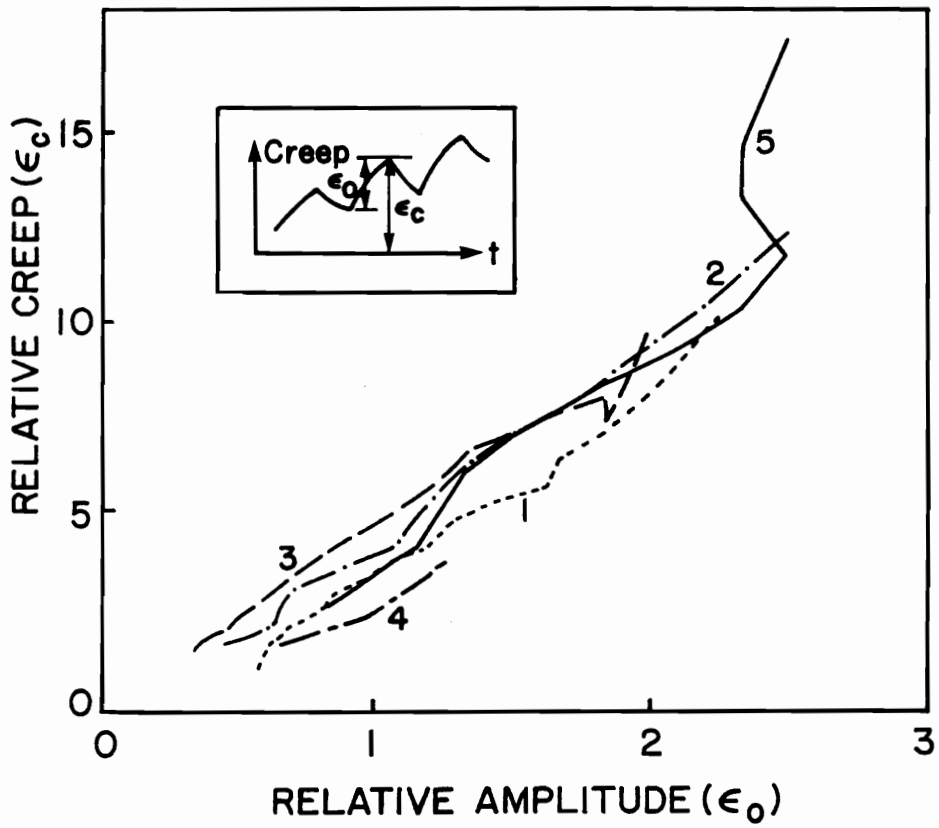

Fig. 2.3 Creep level vs. creep oscillation amplitude for moisture content variations of the order of 15% - 18% [24]

1: In [25]: E=16.0 GPa; stress=20 MPa
2: In [25]: E=14.5 GPa; stress=20 MPa
3: In [25]: E=12.0 GPa; stress=20 MPa
4: In [16]: Fig. 1
5: In [15]: Fig. 1

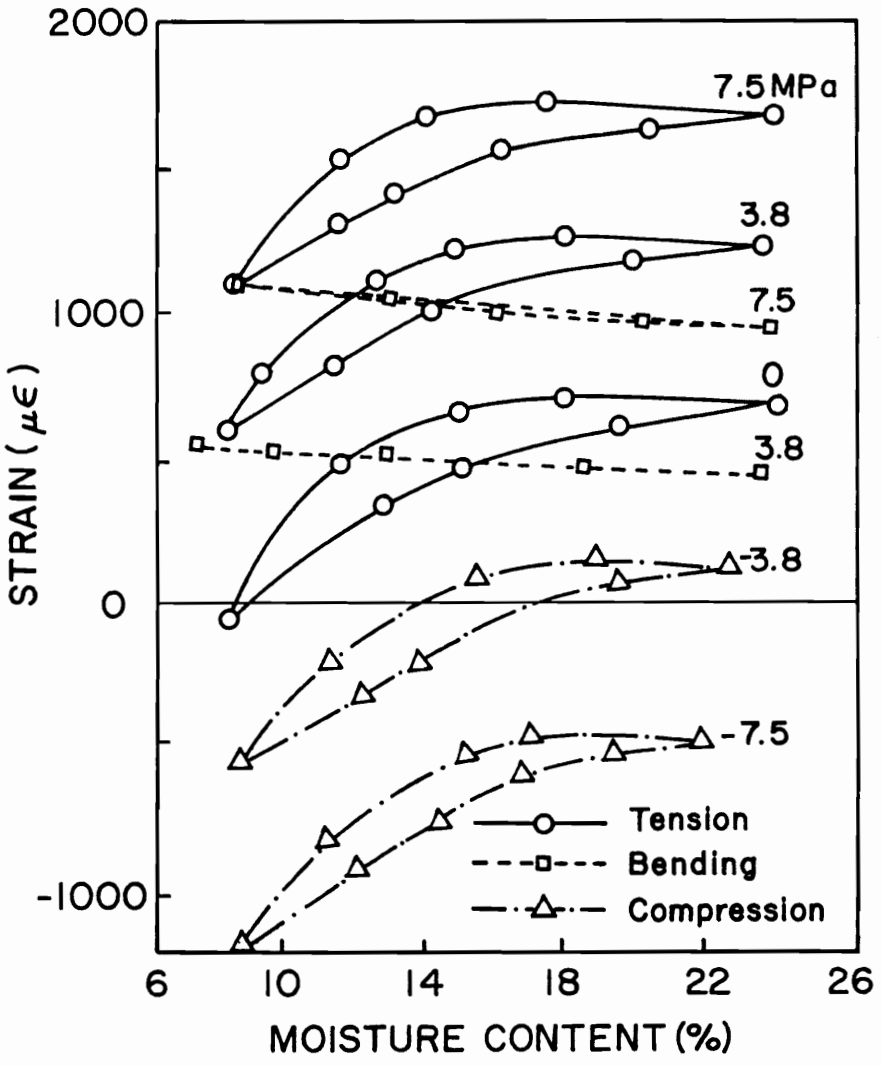

Fig. 2.4 Creep strain vs. moisture content at different stresses [26]

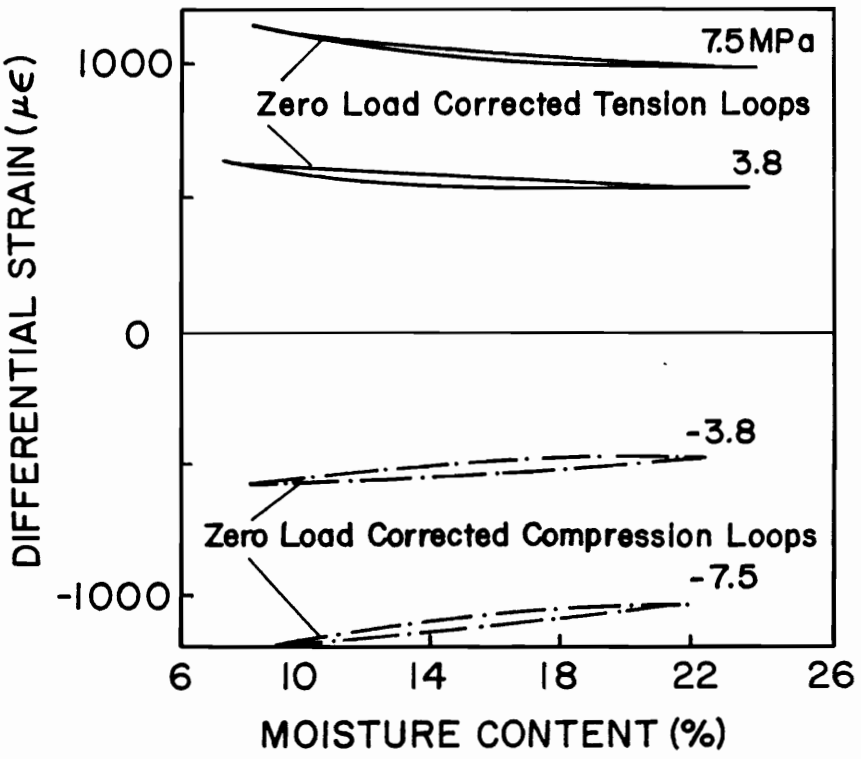

Fig. 2.5 Zero-load corrected loops from Fig. 2.4 [26]

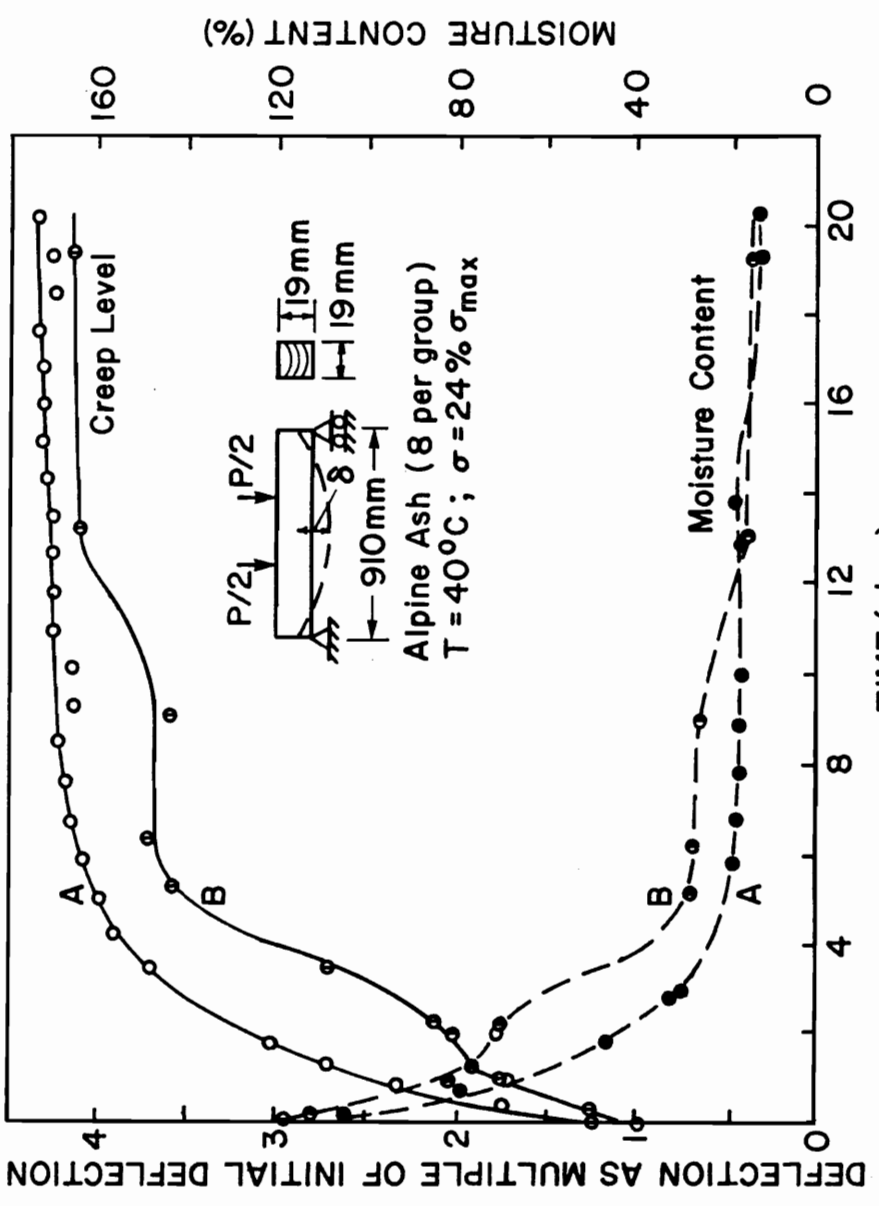

Fig. 2.6 The effects of moisture desorption rate on the creep of wood beams [5]

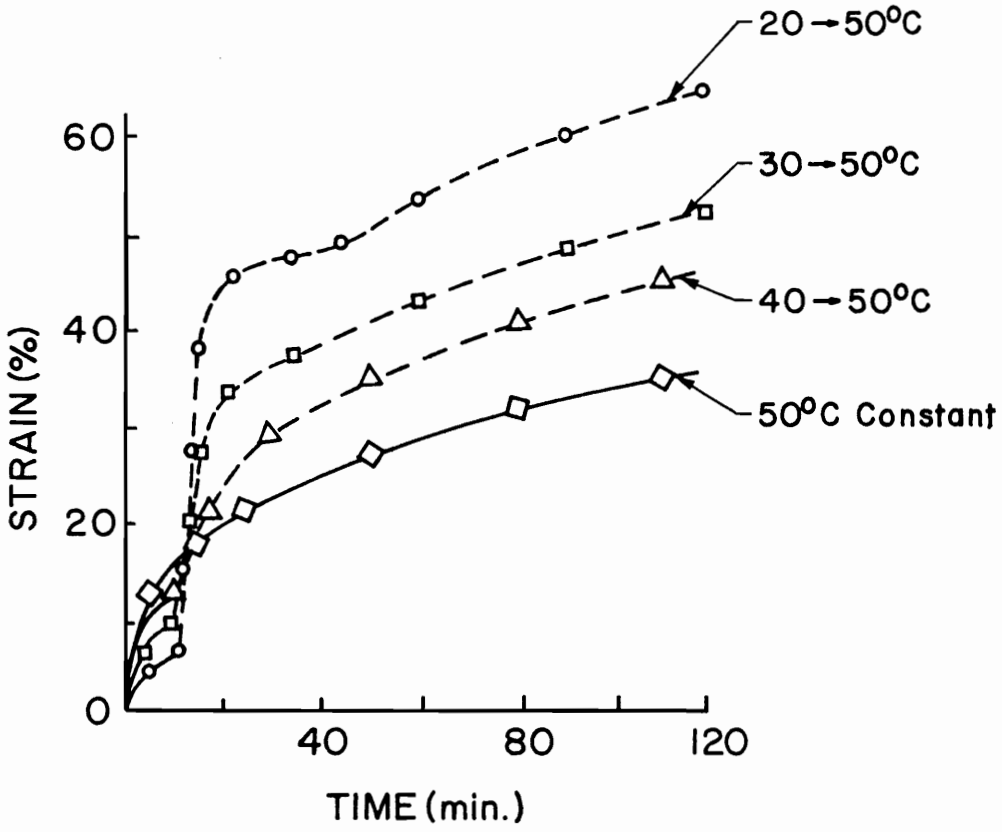

Fig. 2.7 The effects of transient temperature in the creep of wood beams [34]

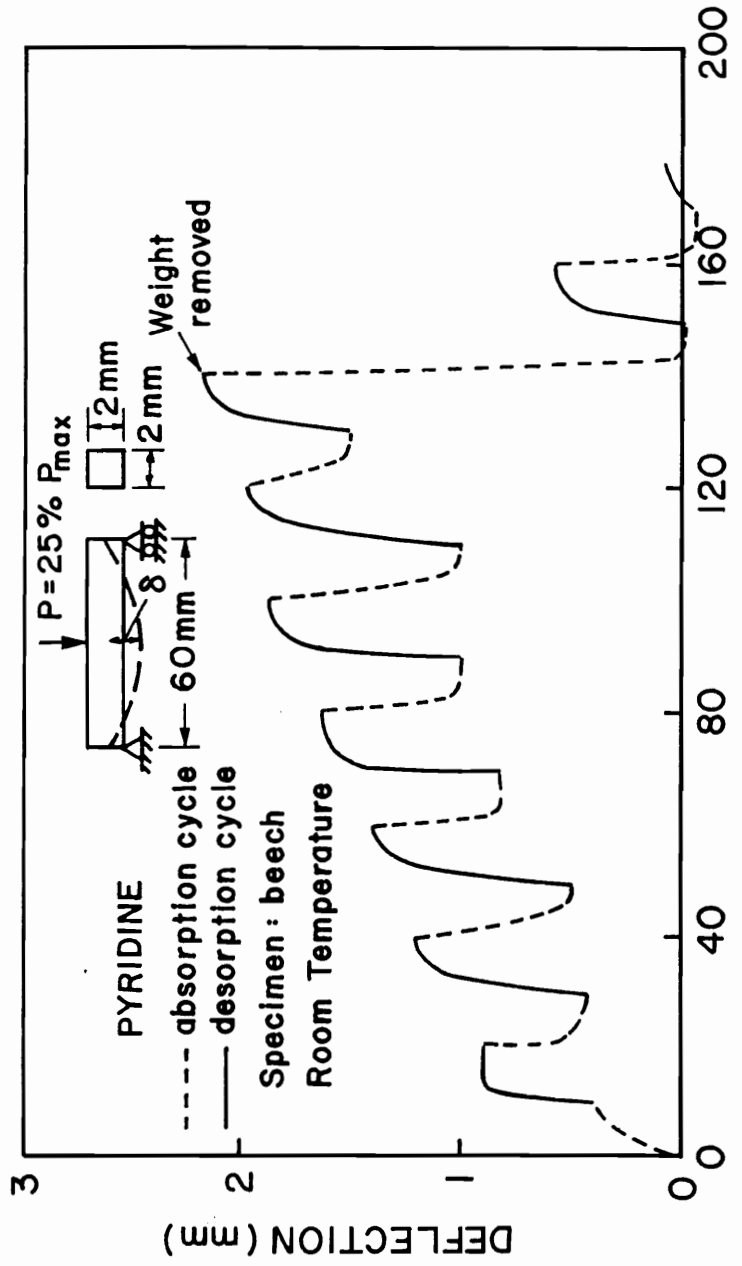

Fig. 2.8 Creep of wood beams in pyridine environment [17]

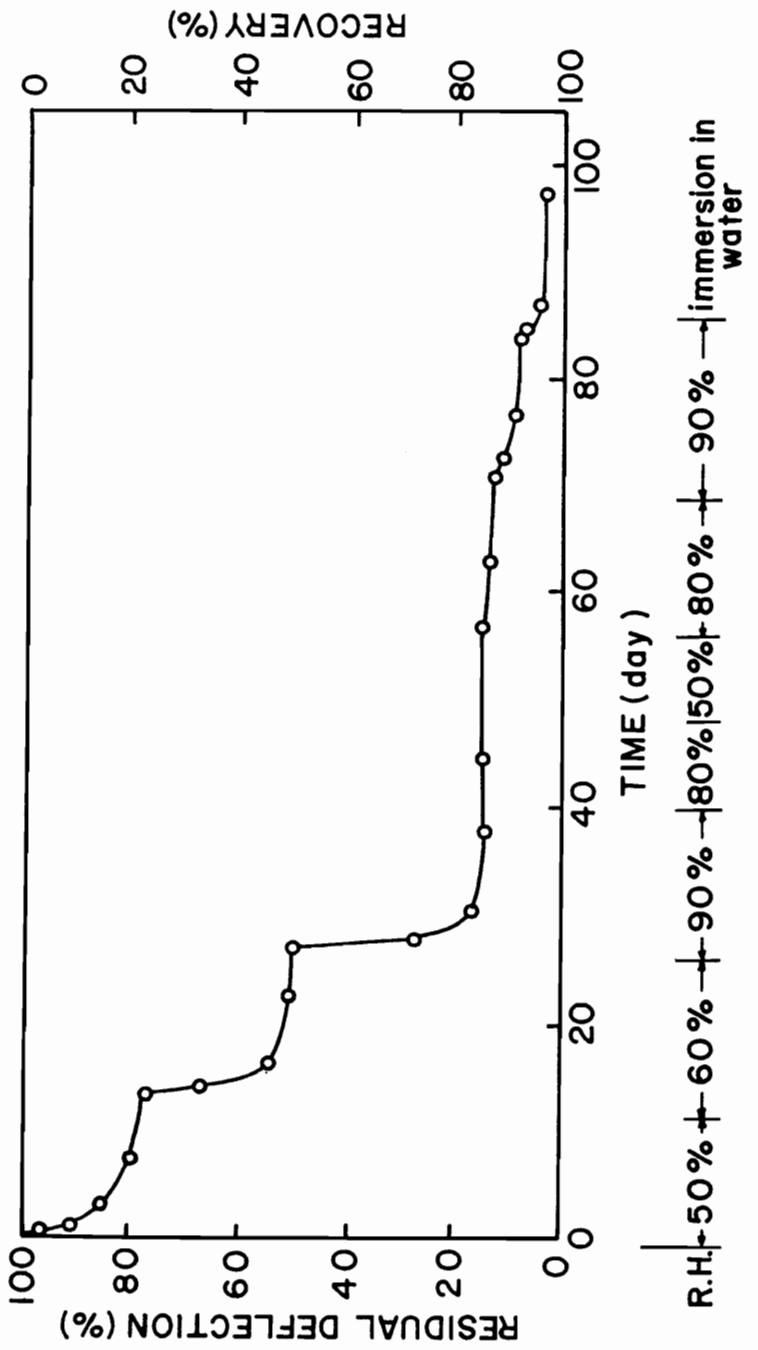

Fig. 2.9 Creep recovery of wood beams under transient moisture conditions [36]

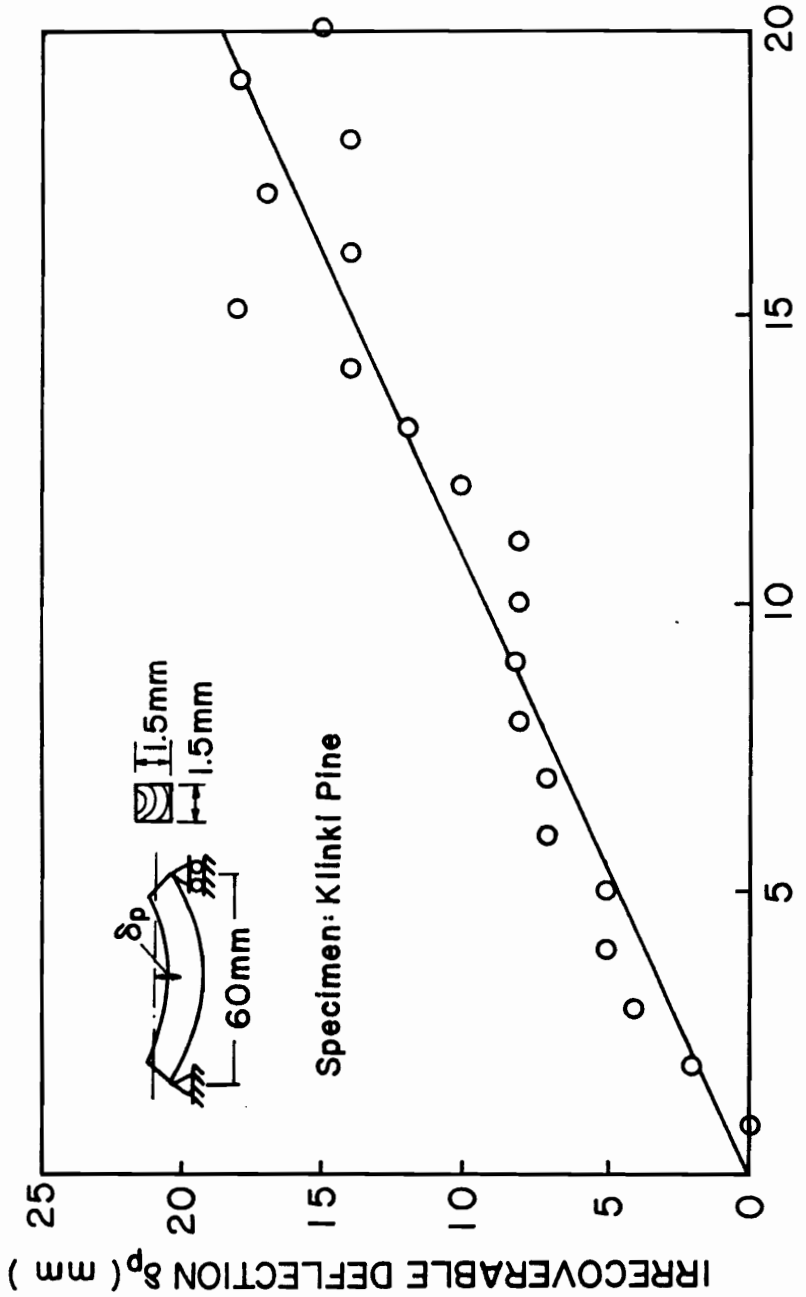

Fig. 2.10 Residual deformation at the end of each moisture cycle [4]

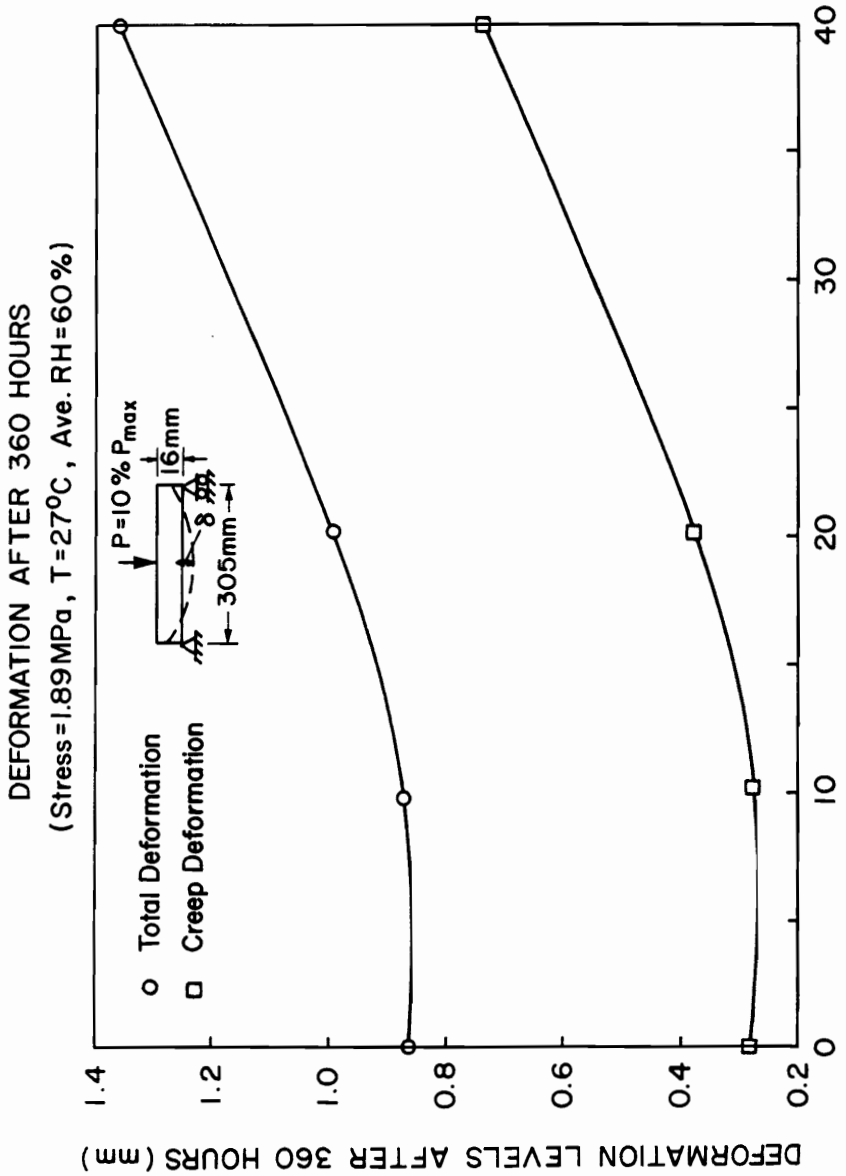

Fig. 2.11 Effects of relative humidity range on the creep of particlebaord [39]

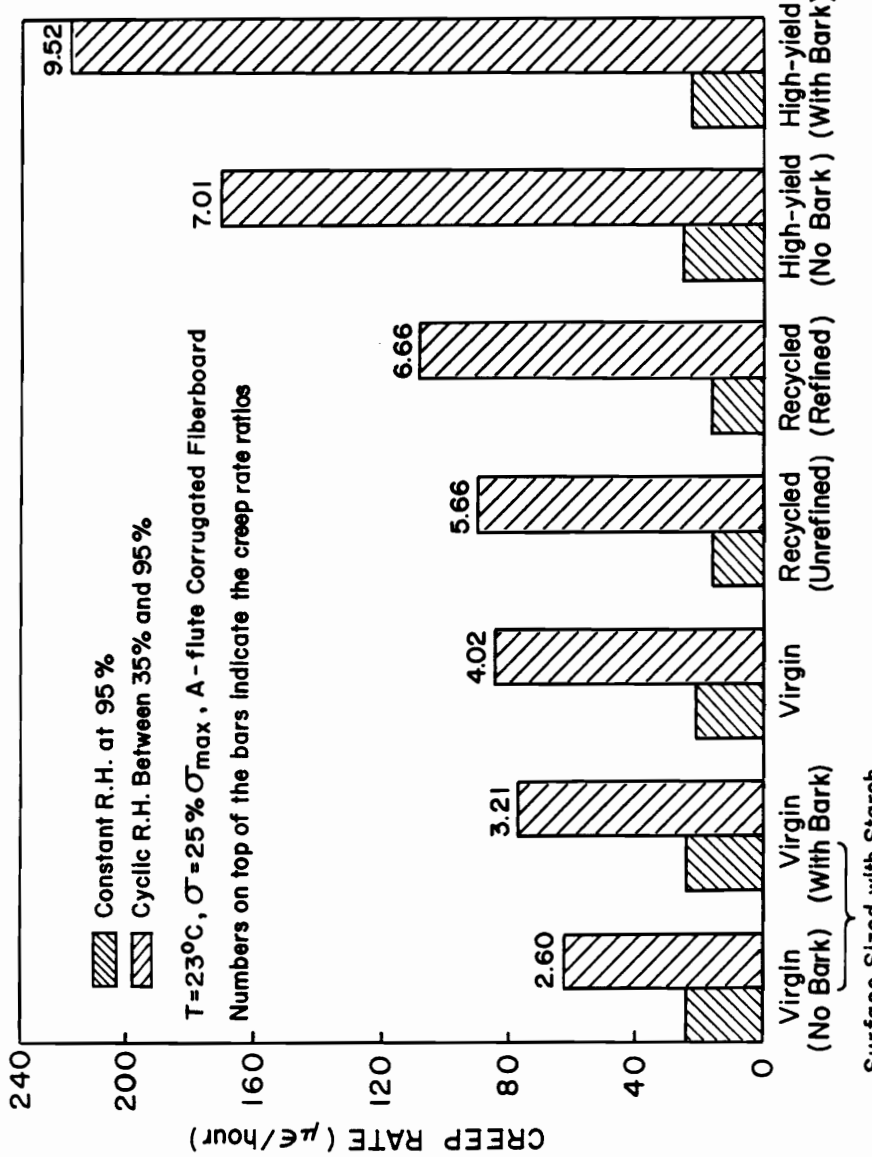

Fig. 2.12 Effects of material constituents on the creep of particlebaord [45]

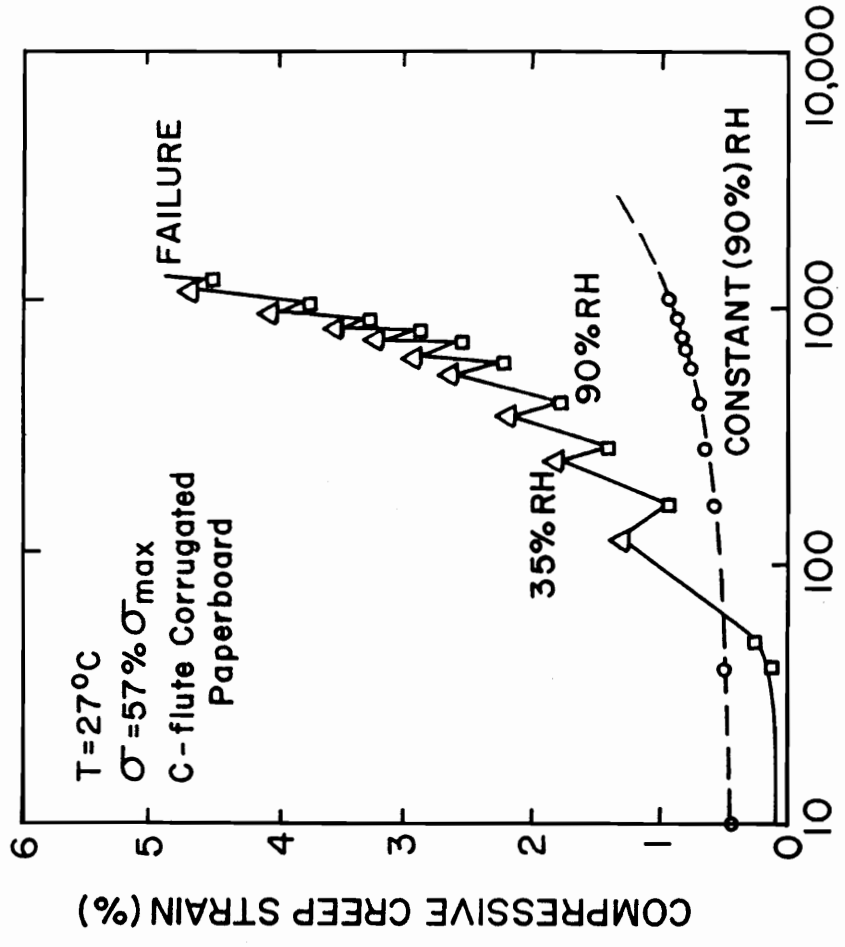

Fig. 2.13 Creep of corrugated paperboard under compression [51]

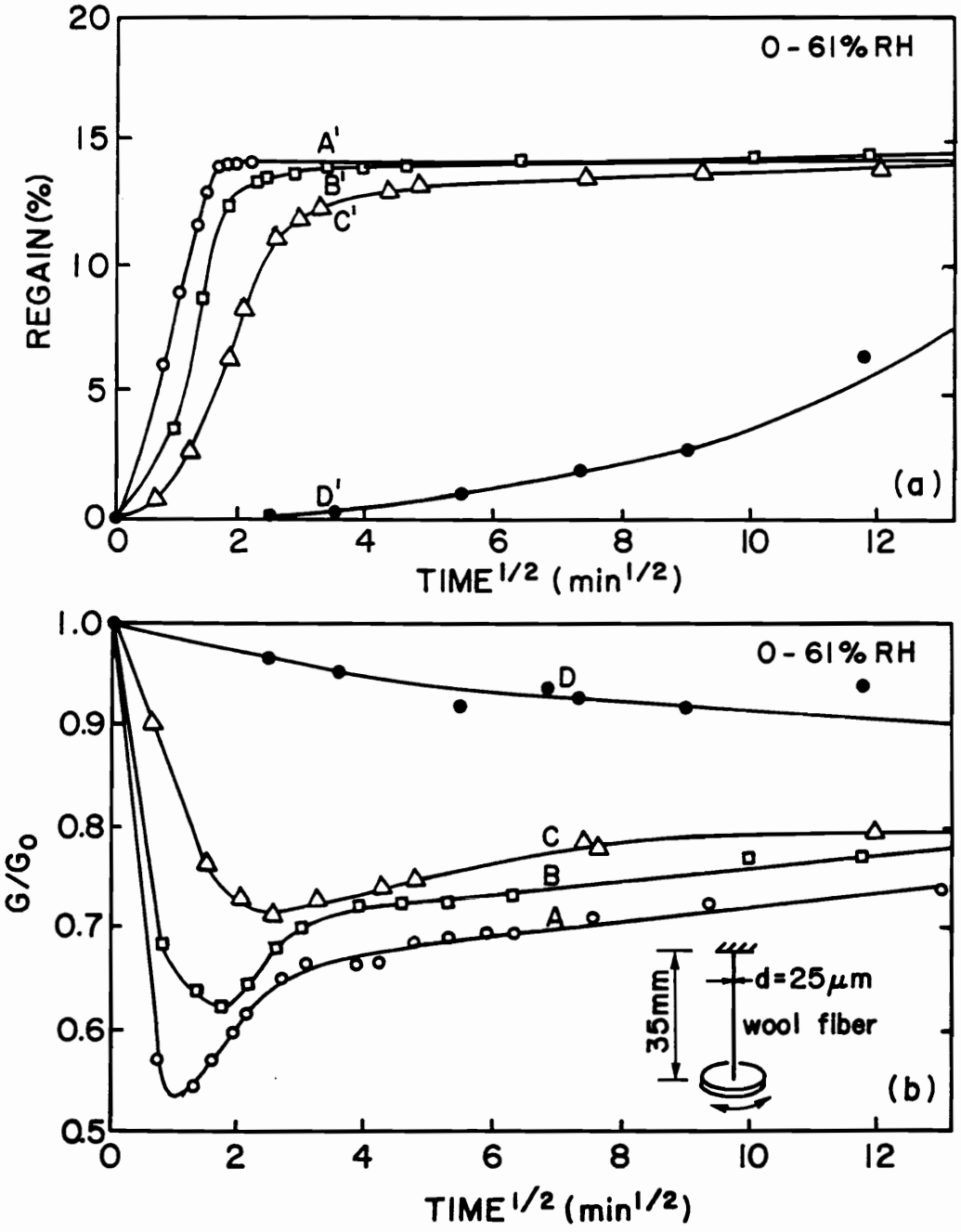

Fig. 2.14 Transient moisture effects in the dynamic modulus of wool fibers [52]

Fig. 2.14(a) shows the moisture conditions under which the curves in Fig 2.14(b) were obtained (e.g. curve A in (b) was obtained under the moisture condition as shown in curve A in (a))

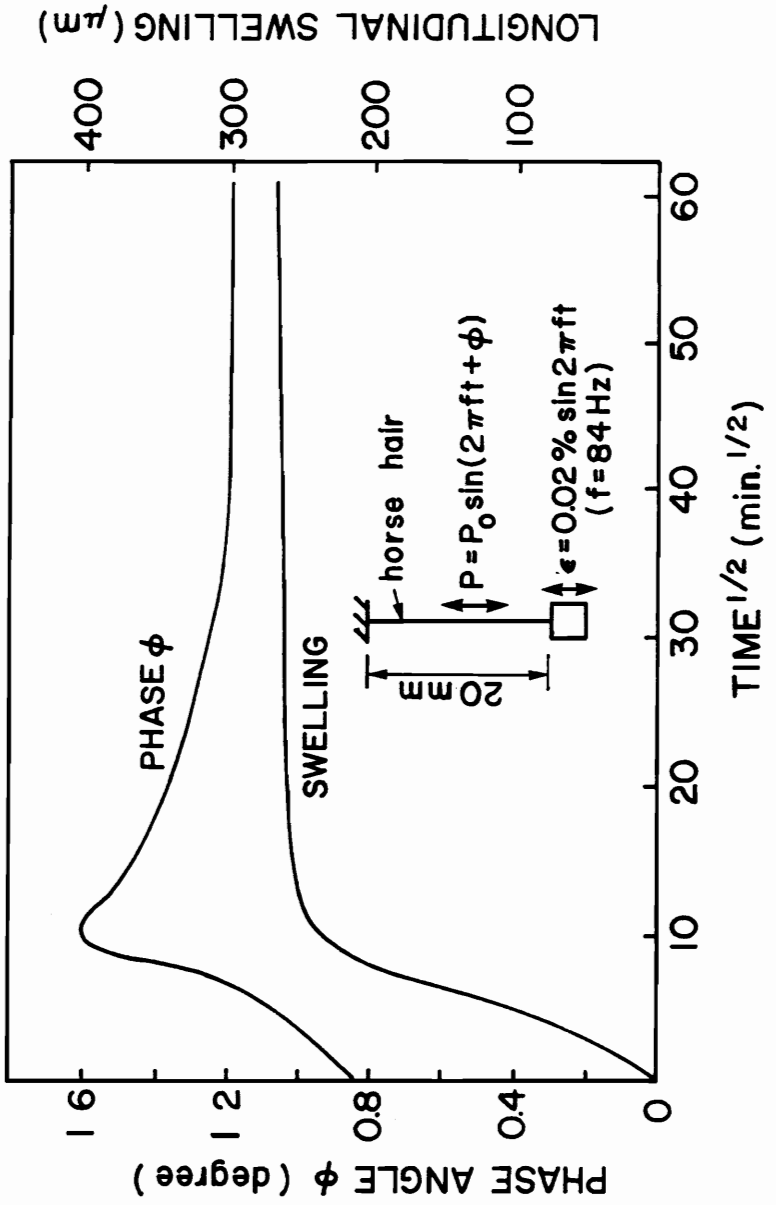

Fig. 2.15 Correlation between swelling and phase angle of a horse hair [57]

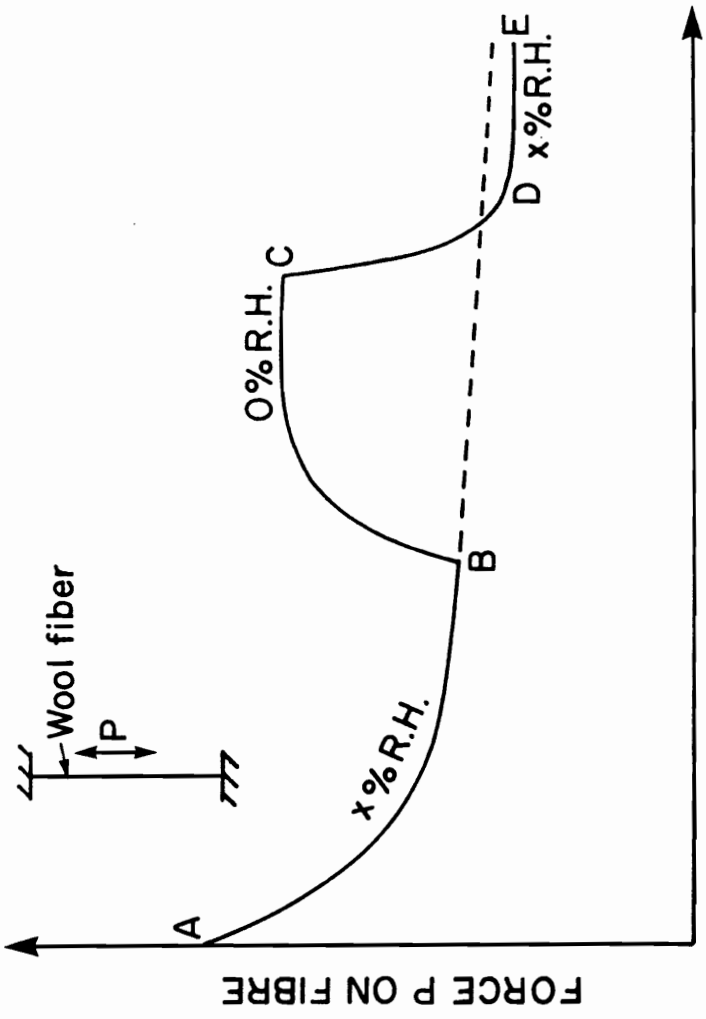

Fig. 2.16 Relaxation behavior of a wool fiber [58]

Chapter 3

TRANSIENT MOISTURE EFFECTS IN SYNTHETIC FIBERS AND COMPOSITES

3.1 Introduction

Kevlar® fibers, produced by Du Pont, are aromatic materials. Since the commercial availability of Kevlar® fibers in the early 1970s, they have been increasingly used in such structures as, to name a few, aircraft wings and helicopter blades, submarine structures, ballistic protection clothes, sporting goods, offshore cables, fiber optic cables, etc. The adoption of Kevlar® fibers are primarily due to their high specific strength and modulus or high specific toughness. Figure 3.1 illustrates an application of Kevlar® 49 fibers on an aircraft (AVTEK 400) fuselage section [1]. On such an aircraft, Kevlar® 49 fibers are estimated to be 72% of the total airframe fiber portion [1].

The creep behavior of Kevlar® fibers have been studied to some extent [2, 3]. In testing the creep behavior of single Kevlar® 29, Kevlar® 49, and PRD 49-III fibers, Ericksen has reported that these fibers exhibited logarithmic creep behavior at test times as long as several hours [2]. In testing Kevlar® 49 yarns, Cook et al reported that the logarithmic creep behavior usually prevail until rupture of individual fibers in the yarns [3]. However, in the studies of creep

behavior in Kevlar® fibers, the moisture effect is less known. Clearly, such studies will facilitate the understanding of the durability of Kevlar® and other aramid fibers.

As reviewed in Chapter 2, moisture sorption has significant effects in the creep behavior of wood, wood products, and natural fibers. Hydrogen bonding is cited as one of the few possible mechanisms responsible for such effects. It is a well established research conclusion that Kevlar® fibers contain hydrogen bonding along the radial direction of the fibers [4]. Aramid fibers are hydrollic [5, 6]. The fibers possess lateral hydrogen bonds between crystallites [4]. Preliminary tests conducted on two Kevlar® 49 fiber reinforced composite coupons suggested that transient moisture conditions could accelerate its creep process as compared even to high constant moisture conditions. Therefore, to investigate the mechano-sorptive phenomenon in Kevlar® fibers and Kevlar® fiber reinforced composites, a series of tests has been conducted on Kevlar® 49 fiber reinforced composite coupons, Kevlar® yarns, and single Kevlar® 29, Kevlar® 49, and Kevlar® 149 fibers. These tests included the fiber creep tests, bending creep tests, dynamic mechanical analysis (DMA) tests under both transient moisture conditions and constant moisture conditions. To help in ascertaining the mechano-sorptive mechanisms, tests have been also conducted on Technora® fibers, Nylon 6,6 fibers, and poly(methyl methacrylate) fibers (PMMA). In this chapter, experimental

results concerning the primary mechano-sorptive effects on these materials are reported. Further experimental results and the related mechanisms will be addressed in Chapter 4.

3.2. **Experimental**

3.2.1. Tensile Creep Tests

Tensile creep tests on Kevlar® 49/epoxy composite coupons were performed in a servo-hydraulic mechanical testing machine (MTS). Specimens were cut out of Kevlar® 49/Fiberite 7714 epoxy panels supplied by the Du Pont Company. The fiber volume fraction was 60%. The test specimens were 8-ply, 0^0 unidirectional, 1.0 mm by 12.7 mm in cross-section and 254 mm in length (0.04 in X 0.5 in X 10 in). Specimens were conditioned in an environment with 100% relative humidity (R.H.) and 60 $^{\circ}$C for about three months. The moisture absorption curve is shown in Figure 3.2. Moisture saturation level in the specimens was about 7 percent of the dry mass of the specimens. Along the fiber direction, the moisture-conditioned specimens had an ultimate strength of 760 MPa (116 ksi) and a Young's modulus of 51 GPa (7.4 msi) at 60°C.

During the test, the temperature was kept at 60°C and the load was maintained at 137.8 MPa (20 ksi). Relative humidity and

temperature were controlled by an environmental chamber attached to the testing machine. A constant moisture condition and a desorption moisture condition were used in the tests. A constant moisture condition in the specimen was imposed by maintaining a 95% R.H. in the environmental chamber. A desorption condition in the specimen was imposed by maintaining 5% R.H. in the test chamber after a moisture saturated specimen was installed on the testing machine.

Data acquisition was accomplished by recording the output signals from the MTS with a Hewlett Packard (HP) computer. To convert the electrical signals into digital signals, A/D converters were interfaced between the output signals and the HP computer. A computer program in HP Basic was written to coordinate the data acquisition.

Tensile creep tests were also performed on woven Kevlar®/epoxy specimens in a creep frame. The material used was two-layer Kevlar® cloth with $\pm 45^{\circ}$ orientation. The specimen was 0.2 mm (0.008 in.) in thickness, 12.7 mm (0.5 in.) in width, and 107.0 mm (4.2 in.) in length. Before the creep tests, specimens were conditioned in a water bath above water until saturation. The saturation level of the specimens was about 2.9% of the dry weight of the specimens. The modulus of the saturated specimen was 4.60 GPa (0.67 msi) and the strength of the saturated specimen was 220.5 MPa (32.0 ksi). A constant stress of 51.7 MPa (7.5 ksi) was applied to the specimens in

the creep tests. All tests were performed at 30° C.

In constant moisture condition tests, a thin plastic film was loosely wrapped around saturated specimens to minimize desorption. A wick was used to replenish any lost moisture. In desorption tests, moisture saturated specimens were placed in an environment of 50% R.H. and 30°C. An extensometer was used in the tests to measure the deformation of the specimens. The stress strain curves of the wet and dry woven Kevlar®/epoxy specimens are shown in Figure 3.3.

3.2.2. Bending Creep Tests

Bending creep tests were conducted in a self-designed bending fixture with two clamping ends under both desorption and constant moisture conditions at 60°C. Before the tests, the specimens were conditioned at 100% R.H. and 60 °C until saturation. The specimens were 85 mm (3.3 in) in span, 12.7 mm (0.5 in) in width, and 1.0 mm (0.04 in) in depth. A load of 16.6 Newtons (3.7 lbs) was applied at the center of the beams.

In constant moisture condition tests, a thin plastic film was loosely wrapped around saturated specimens to minimize desorption. A wick was used to replenish any lost moisture. In desorption tests, moisture saturated specimens were placed in an environment of 20% R.H. and 60°C. A dial indicator accurate to 0.0025 mm was used to measure

the deformation at the center of the specimens. Each test lasted about 24 hours.

3.2.3. DMA Tests

When a sorption process occurs during an isothermal dynamic mechanical test, mechano-sorptive behavior should be manifested as a drop in storage modulus and a corresponding increase in both loss modulus and tan δ. To investigate this possibility, tests were performed on a Du Pont 982 Dynamic Mechanical Analyzer (DMA). The specimen dimensions were 45 mm (1.77 in) in length, 12.7 mm (0.5 in) in width, and 1 mm (0.04 in) in thickness. The tests were conducted at a constant temperature of $60^{o}C$, a constant frequency of 5 Hz, and a constant peak to peak amplitude of 0.3 mm. Approximately 5 minutes after a saturated specimen was clamped in the DMA and was oscillated, dry air was introduced into the chamber at a small flow rate to impose a desorption condition. After about 70 minutes, the air was turned off. Later on, the air was turned on again at a higher flow rate. The difference in the air flow rates could result in different desorption rates, and thus the qualitative effects of the desorption rate could be observed.

3.2.4. Kevlar® 49 Yarn Tests

In studying the mechano-sorptive phenomenon on Kevlar® fibers, tensile creep tests were performed on Kevlar® 49 yarns. The tests were

performed in a MTS machine. To control the test temperature and humidity, an environmental chamber was interfaced to the testing machine. The nominal length of a yarn specimen was 235 mm (9.25 in). The average compliance of the yarns was 0.026 μm/Newton (4.56 X 10^{-6} in/lb). The average strength of the yarns was 156.0 Newtons (35 lbs). Before each test, the specimens were conditioned in 100% R.H. and 60 °C environment for about two weeks until saturation. After the start of the test, the relative humidity was changed between 10% to 100%. However, due to the difficulty in scheduling, the cycles were irregular. The applied load levels were at P = 57.9, 66.8, and 89.1 Newtons (13, 15, and 20 lbs). The test temperature was 60 °C.

3.2.5. Single Fiber Tests

In a mechano-sorptive test using yarns, questions arose as to whether the difference in tautness of each single fiber or the twisting of the yarn will affect the results. To eliminate the uncertainty and to better isolate the contribution of the fibers and matrix, a single fiber creep test was adopted.

Single fiber tests were performed at 60 °C on Kevlar® 29, Kevlar® 49, Kevlar® 149, Technora®, Nylon 6,6, and PMMA fibers using a specially designed fixture. A diagram of the fixture is shown in Figure 3.4. The fixture is composed of three systems: the central test system, the environment generating system, and the control and data

acquisition system. Most of the parts in the system can be readily purchased.

As detailed in Figure 3.5, the central test system is mainly composed of a glass tube and a loading chain. One end of the specimen is threaded through a small hole in an aluminum cup and held in place with a drop of cyanoacrylate adhesive. The cup is screwed into the upper cap of the environmental chamber. The other end of the specimen is cemented to another aluminum cup which is connected to the upper part of the core of the linear variable differential transducer (LVDT) by a nonmagnetic connecting rod. About 95% of the length of the specimen is enclosed in the environmental chamber. To maintain stable test conditions, care has been taken to ensure that the environmental chamber is airtight except for the small hole through which the lower end of the specimen passes. The loading chain is composed of an aluminum cup, one or two connecting rods, the LVDT core, and a weight pan to which additional loads can be applied to reach the desired load level used in the tests. The weight pan is attached through a nonmagnetic connecting rod which is threaded into the lower part of the LVDT core. The load (P) applied to the specimen is the sum of the weights of the aluminum cup, the upper connecting rod, the LVDT core, and, if used, the lower connecting rod and the dead load block. The smallest weight that can be applied is the weight of the connecting assembly and the LVDT core, a total of 73.5 milinewtons (7.5 grams).

The environment generating system is composed of an air pump, a solenoid valve, a desiccant column, a water reservoir, the necessary tubing, and a convection oven. Depending on the desired relative humidity level in the environmental chamber, the solenoid valve can be switched between the dry air path and the humid air path according to the control signals issued by the computer via a digital to analog card. To minimize the disturbance of the air flow to the fiber, as indicated in Figure 3.5, the lower cap is machined in such a way that the air will flow upward when it is introduced into the test chamber through six symmetrical holes in the lower cap. To maintain a constant temperature, a convection oven is used to contain the whole setup except for the air pump, which was mounted just outside of the oven in order to allow it to cool better and avoid the heat gain to the oven.

The control and data acquisition system is composed of a personal computer, a programmable data acquisition card, a relay device, a relative humidity and temperature probe, and a LVDT. The output of the LVDT signal is linearly proportional to the deformation of the specimen. Software written in Quick Basic coordinates the activities of the data acquisition and the relative humidity controlling. The output of the LVDT, the output of the probe, and the test time are stored in the computer for later analysis. Preliminary tests suggested that the fiber creep versus logarithmic time approximate a straight

line. Therefore, to minimize the number of data points, the output of the LVDT is recorded at a logarithmic rate. To monitor the progress of an ongoing test, either the recorded LVDT signals or the recorded relative humidity profile can be displayed on the computer screen according to the software option one may select at any time during the test. The LVDT signals can be either plotted in logarithmic time domain or linear time domain as one desires.

Preliminary tests performed on Kevlar® fibers showed that the creep rates varied from fiber to fiber. Ericksen's results at room conditions for single Kevlar® fibers also showed large variability in creep rates [2]. Therefore the experiment was designed so that most of the conclusions obtained would depend less on comparisons between test pieces, and more on comparisons between the results from the same fiber at different stages of the experiment.

Figure 3.6 is the humidity profile adopted during the tests under cyclic moisture conditions. Before the start of a test, a fiber was preconditioned in an environment with nominal relative humidity level of 95% and 60 $^{\circ}$C for a sufficiently long time (about 4 hours) for the fiber to be saturated. After saturation, the test was started with the same relative humidity level and temperature as in the preconditioning stage so that during the first two hour period the moisture content in the fiber was constant. After the first two hours, the humidity levels

were cycled between 5% and 95% to observe the mechano-sorptive behavior. In this way, the creep rates at constant humidity level and cyclic humidity levels could be compared on the same fiber.

The Kevlar® fibers (Kevlar® 29, Kevlar® 49, Kevlar® 149) used in the tests were provided by the Du Pont Company. The Technora® fibers were supplied by the Teijin Limited Corporation in Japan. The diameter of single Kevlar® and Technora® fibers was nominally 12 μm. The denier values of the Kevlar® fibers were measured at room conditions by Du Pont prior to shipment to our lab. Ten pieces of fibers with a length of 41.0 mm (1.61 in) were used to obtain the denier data for each type of Kevlar® fibers. The strength and the elastic compliances of the fibers were measured in our laboratory at 60°C and 95% R.H. to provide basic information for the fibers. The strength, the elastic compliance, and the denier of the fibers used in the tests are tabulated in Table 3.1. The nominal fiber length between grips in each test was 216 mm (8.5 inches). The constant stress used in the tests was 0.97 GPa (0.14 msi) which is about 35% of the ultimate tensile strength (UTS).

The Nylon 6,6 fiber was provided by the Du Pont Corporation. The diameter of a single fiber was 28 μm. The ultimate tensile strength of the moisture saturated fiber at 60°C was 930 MPa (135 ksi). The tests were conducted at 175 MPa (18.8% UTS) and 60°C.

The diameter of a single PMMA fiber was 138 μm. The strength of moisture saturated fiber at 60°C was 828 MPa (120 ksi). The tests were conducted at 7.3 MPa (0.9% UTS) and 60°C.

3.3. **Results and Discussions**

3.3.1. Tensile Creep Tests

Figure 3.7 shows the relative creep (defined as the percentage of the elastic deflection) for the constant moisture condition and the relative creep for the desorption process. The results suggest that when the moisture content of specimens is kept constant, the relative creep is lower than that of specimens undergoing a desorption process. It is worthy to note that during the tests, at any time, the moisture content of the specimens with constant moisture content is always higher than that of the specimens under desorption condition. The creep strain for the two constant moisture specimens averaged 30 percent of the elastic strain. However, the creep strain for the desorption specimens averaged 45 percent of the elastic strain.

The results for the woven Kevlar®/epoxy specimens are shown in Figure 3.8. From these results we see that during the initial phase of the test, the desorption specimen attained a higher creep level than the saturation specimen. However, after the desorption specimen was

dried, its creep did eventually fall below that of the saturated specimen.

3.3.2. Bending Creep Tests

Bending creep test results for two composite specimens are shown in Figure 3.9, suggesting that creep is more pronounced under a desorption process than when the specimen is maintained at the high (saturated) moisture content. The two specimens started with the same moisture content, therefore, during the tests, the moisture content in the desorption specimen is always less than that in the constant moisture specimen. Nevertheless, the creep of the desorption specimen was 29% higher than that of the specimen which was kept at the higher constant moisture level. The results indicate that transient moisture conditions can accelerate the creep process and magnify the creep levels of the tested composite material.

3.3.3. DMA Tests

Several tests were performed on Kevlar® 49/epoxy specimens. Figure 3.10 is the plot of typical results. As indicated in Figure 3.10, when dry air was introduced into the chamber, there was a significant decrease in the storage modulus. After about 70 minutes, the dry air was turned off. The storage modulus was found to increase accordingly. At this time, however, the storage modulus was higher than that at the beginning of the test. The increase in storage

modulus is probably due to the decrease in the moisture content after desorption. When dry air was re-introduced into the chamber at a higher flow rate, the storage modulus was found to decrease further. The greater decrease in storage modulus associated with the higher flow rate indicates that the mechano-sorptive phenomenon may be rate dependent. Rate dependency of the phenomenon is also reported elsewhere [7, 8]. Reductions in storage modulus on the order of 20% were observed.

The findings in this test indicate that transient moisture condition will reduce the dynamic storage stiffness of the Kevlar® 49/epoxy composite material along fiber direction. qualitatively agreeing with results from the tensile and bending creep tests.

It is worth noticing the corresponding change of tan δ with that of the storage modulus. From those data we can infer that the loss modulus increased during the desorption process. The result indicates that the internal damping increased during desorption. An increase in internal damping during sorption processes has also been observed in other materials [9, 10].

To check the possibility of electronic system malfunction due to the flow of air, steel samples and dry Kevlar®/epoxy specimens were used to repeat the tests. In these tests, none of the above mentioned

mechano-sorptive phenomenon was observed.

It needs to point out that when the air was turned off during the tests, temperature increased from 60°C to 68°C and decreased to about 57°C, and finally stabilized at 60°C in about 10 minutes. This temperature change caused related changes in moduli also. When presenting the results in Figure 3.10, the author has smoothed out this annoying distraction for easier interpretation of the results.

To investigate whether the mechano-sorptive phenomenon is dominated by the matrix or the fiber, 90° specimens were tested also. No mechano-sorptive behavior was observable, suggesting that the fibers may be more susceptible to mechano-sorptive behavior than the epoxy matrix. This observation led us to conduct tests on fibers.

3.3.4. Kevlar® Yarns Tests

The obtained results on Kevlar® 49 yarns are shown in Figure 3.11, 3.12, and 3.13. The results indicate that during an absorption process, the deformation decreases, while during a desorption process, the deformation increases. The total deformation increases over successive cycles. For example, if the peaks of deformation are joined together, an approximate line with positive slope could be obtained. As a comparison, a creep test was performed on a yarn at 100% constant relative humidity at 89.1 Newtons. It can be seen from Figure 3.13

that the creep level at constant relative humidity is much lower than that at the cyclic relative humidity condition. This data showed considerable scatter, but the anomalous trends provided the impetus for developing more refined test techniques.

3.3.5. Single Kevlar® Fiber Tests

To ascertain the mechano-sorptive phenomenon on Kevlar® fibers, a number of creep tests have been conducted on single Kevlar® 29 fibers, single Kevlar® 49 fibers, and single Kevlar® 149 fibers. Test results are summarized in Table 3.2. Typical results of measured creep strains (total strain - elastic strain) for Kevlar® 29, Kevlar® 49, and Kevlar® 149 were plotted in logarithmic time domain as shown in Figures 3.14 to 3.16 respectively. It was found that in such a graph, the data points approximate straight lines, therefore the creep is called logarithmic creep.

Logarithmic creep curves can be expressed as:

$$\varepsilon(t) = a_i + b_i \mathrm{Log}(t) \qquad (i=1,\ 2) \qquad (3.1)$$

where

$\varepsilon(t)$: creep strain at time t ($\mu\varepsilon$)

t: time (second)

a_i: the creep strain when t=1 second ($\mu\varepsilon$)

b_i: the logarithmic creep rate ($\mu\varepsilon$/decade of time)

i : moisture condition index; i=1 for constant moisture conditions, and i=2 for cyclic moisture conditions

The logarithmic creep rates, b_i (i=1,2) are independent of time, and generally speaking, for a given material, is a function of temperature, stress, specimen size and shape, moisture history, and possibly the moisture levels.

To quantify the mechano-sorptive effects in aramid fibers, mechano-sorptive ratio is defined as follows:

$$r = \frac{b_2}{b_1} \qquad (3.2)$$

As defined in Equation (3.2), the mechano-sorptive ratio indicates the logarithmic creep rate under cyclic moisture conditions (b_2) relative to that under constant moisture conditions. The mechano-sorptive ratio may be a function of a variety of factors. For example, for a given material, it may depend on the temperature, stress level, the rate of moisture changes, the size and shape of the specimens, and possibly the baseline constant moisture levels.

In Figure 3.14 and Figure 3.15, results for Kevlar® 29 and Kevlar® 49 fibers under cyclic moisture conditions are contrasted with those under a relatively high constant moisture condition at 95% R.H.. The results suggest that when the moisture content in the fiber is constant, the slope of logarithmic creep is significantly less than that when the moisture content was cycled. Kevlar® fibers are commonly shown [2] to exhibit the logarithmic creep for a constant moisture level as illustrated in Figures 3.14, 3.15 and 3.16. Cook [3] has indicated that the logarithmic creep may prevail until the last decade of failure occurs in Kevlar® yarns. If the data are extrapolated to model long term behavior of the fibers, estimates can be obtained for the amount of acceleration induced by the transient moisture conditions. Based on this assumption, it would take on the order of 5 years at 60°C, 95% R.H. to reach the same creep strain obtained after 2 days of cycling conditions. Nonetheless, calculations indicate that more than 100 years of 2-hour cycling under a constant load of 35% of the ultimate strength would be required for Kevlar® 49 fibers to reach 55% of the typical fiber failure strain (2.4%).

From the experimental results, one may see that mechano-sorptive phenomenon is exhibited in Kevlar® fibers. Of the three kinds of fibers, Kevlar® 29 has the largest logarithmic creep rate, Kevlar® 149 has the smallest logarithmic creep rates, and Kevlar® 49 has intermediate values. If the ratio of the slopes is taken as an

indicator of the degree of mechano-sorptive effect, the trend of the data in Table 3.2 suggests that the effect is most pronounced in Kevlar® 29 fibers, is least pronounced in Kevlar® 149 fibers, and is intermediately pronounced in Kevlar® 49 fibers.

A Kevlar® 29 fiber was taken through a recovery process for three days after a two day mechano-sorptive creep test and was loaded again to test its creep behavior. It was found that, after the three day recovery, the logarithmic creep rates and the mechano-sorptive ratio were reduced. However, the reduction in the logarithmic creep rate under cyclic moisture condition was more substantial than that under the constant moisture condition. For example, the logarithmic creep rate under cyclic moisture conditions on the second creep loading was reduced by 60.4% while that under constant moisture condition was reduced only by 10.6%. As the result of these reductions, the mechano-sorptive ratio was reduced by 56%. As discussed in detail in Chapter 4, these reductions may indicate that at least part of the creep strain is not recoverable.

3.3.6. Single Technora® Fiber Tests

The test results from single Technora® fibers are tabulated in Table 3.3. A typical result is shown in Figure 3.17. From the results one may see that the creep of the Technora® fibers is also logarithmic. The fiber is similar to Kevlar® fibers in exhibiting

mechano-sorptive behavior.

3.3.7. Single Nylon Fiber Tests

Figure 3.18 shows the results of a Nylon 6,6 fiber. The three test results shown in the figure were performed on the same fiber in the order of dry condition (5% R.H.), wet condition (95% R.H.) and cyclic moisture conditions (cyclic between 5% R.H. and 95% R.H.). After each test, the fiber was allowed to recover for at least three days. The mechano-sorptive phenomenon as observed in Kevlar® fibers and Technora® fibers was not seen in Nylon 6,6 fibers. As shown in Figure 3.18, when the relative humidity was cycled, the creep level of the fiber was merely changed between those of high relative humidity and low relative humidity. The conclusion shown here agree with those obtained by Hunt [11].

3.3.8 Single PMMA Fiber Tests

Figure 3.19 shows the results obtained from a PMMA fiber under a constant moisture condition at 95% R.H.. As shown in the figure, the data appears to approximate straight lines on a log-log graph, indicating a power law creep behavior. Figure 3.20 shows typical results of the mechano-sorptive tests on PMMA fibers. As seen in the figure, when the moisture content was cycled between high and low, the upper limit of the creep profile did not exceed what would be expected for the creep profile under constant moisture condition. Therefore, it

may be concluded that PMMA fibers do not exhibit appreciable mechano-sorptive behavior.

3.4. **Conclusions and Discussions**

Unidirectional (0°) Kevlar®/epoxy composite coupons undergoing desorption exhibit an increase in tensile and bending creep deformations, a decrease in storage modulus (E'), and an increase in the loss tangent (Tan δ) when compared to coupons maintained at a constant high (saturated) moisture content. The creep of single Kevlar® and Technora® fibers increase when exposed to cyclic moisture conditions. This phenomenon is not seen in the Nylon 6,6 and PMMA fibers. However, it needs to be noted that even though Nylon 6,6 and PMMA fibers do not exhibit mechano-sorptive behavior, their creep levels are much higher than those in Kevlar® and Technora® fibers.

There are several mechanisms have been proposed for the observed mechano-sorptive phenomenon in aramid fibers. These mechanisms include the free volume mechanism, the osmotic action induced by moisture transport and the presence of salt contaminants in the fibers, and the hydrogen bonding and crystallite rotation mechanisms.

It has been suggested that free volume increases when moisture is added to a polymer. During a desorption process, time is required for the additional free volume to dissipate [12]. Transient increases in free volume could result when the occupied volume of the water molecules is removed. The temporary increase in free volume could cause an increase in creep level. However, even though Nylon 6,6 fibers and the PMMA fibers contain free volumes, these fibers did not exhibit mechano-sorptive phenomenon. Therefore, free volume might not be the mechanism responsible for the observed increase in creep under transient moisture conditions.

Both Kevlar® and Technora® fibers are aromatic polyamide fibers with highly oriented crystallites [4, 13]. The polymeric molecule of Kevlar® fibers is poly(*p*-phenylene terephthalamide) (PPTA) [4]. The polymeric molecule of Technora® fibers is poly(*p*-phenylene/3, 4'-diphenylether terephthalamide) (PPDETA) [14]. Both of the fibers are made through a process known as dry-jet wet spinning [13, 15]. Due to the similarity in the processing techniques, these fibers are believed to possess similar crystallographic and morphological characteristics.

It is known that, during the manufacturing process of Kevlar® fibers, the polymer is dissolved in sulfuric acid which is used as orientation solvent. The filaments are subsequently washed with a solution of sodium carbonate to neutralize and remove the sulfuric

acid [4]. Therefore, there may be sodium sulfate (Na_2SO_4) salt remaining in the fibers. This has been confirmed through elemental analysis of Kevlar® fibers [15]. The content of the salt in the Kevlar® fibers and Technora® fibers are substantially different. Analysis indicates that the content of the extracted sodium ion in Technora® fibers (2.0 μg/g) is only 1.8% of that in Kevlar® fibers (110 μg/g) [14]. However, as shown in the experimental results, the mechano-sorptive effects in these two kinds of fibers are on the same order of magnitude. This comparison may, therefore, indicate that the osmotic pressure induced by the transport of moisture, if any, is not a major factor in causing the mechano-sorptive effects observed in these fibers.

It has been shown that Kevlar® fibers contain hydrogen bonds between the highly oriented crystallites [4]. The orientations of the crystallites relative to the fiber axis of Kevlar® 29, Kevlar® 49, and Kevlar® 149 have been reported to be 11.0°, 9°, and 9° respectively [4]. The diffusion of water molecules in the fibers may break these hydrogen bonds and cause the rotation of the crystallites toward the fiber axis when under the action of tensile loading. The hydrogen bonding and crystallite rotation mechanisms will be discussed in detail in Chapter 4.

References

1. Windecker, L. J., "Genesis of AVTEK 400", in Technical Symposium V, Design and Use of KEVLAR® aramid fiber in Composite Structures, MGM Grand Hotel Reno, Nevada, Sponsored by the Du Pont Company Industrial Fibers Division, E-65339
2. Ericksen, R. H., "Creep of Aromatic Polyamide Fibers", *Polymer*, May 1985, Vol 26, pp. 733-746
3. Cook, J. et al, "Creep and Static Fatigue of Aromatic Polyamide Fibers", in *Fatigue and Creep of Composite Materials,* Proceedings of the Third RISΦ International Symposium on Metallurgy and Materials Science, 6-10 September, 1982, H. Lilholt and R. Talreja, Eds, RISΦ National Laboratory, Roskild, Denmark.
4. Dobb, M. G., "High Performance Fibers", in *Handbook of Composites,* Vol. 1: Strong Fibers, Edited by W. Watt, 1985, p. 675
5. Smith, W. S., "Environmental Effects on Aramid Composites", *Du Pont Technical Paper, E-53160,* December 1979, E. I. Du Pont De Nemours & Co. (Inc.), Textile Fibers Department, Kevlar Special Products, Center Road Building, Wilmington, DE 19898.
6. Augl, J. M., "Moisture Sorption and Diffusion in Kevlar 49 Aramid Fiber", *Report NSWC TR 79-51,* March 30, 1979, Naval Surface Weapons Center, Dahlgren, Virginia 22448.
7. Christensen, G.N., "The Use of Small Specimen for Studying the Effect of Moisture Content Changes on the Deformation of Wood,"

Australia Journal of Applied Science, 13(4):242-57, (1962)

8. Armstrong, L. D. and Kingston, R. S., " The Effect of Moisture Changes on The Deformation of Wood Under Stress," *Australia Journal of Applied Science*, 13:257-76, (1962)
9. Danilatos, G. and Feughelman, M., "The Internal Dynamic Mechanical Loss in α-Keratin Fibers During Moisture Sorption", *Textile Research Journal,* 46:845-6, (1976).
10. Danilatos, G.D. and Postel, R., "Dynamic Mechanical Properties of Keratin Fibers During Water Absorption and Desorption", *Journal of Applied Polymer Science*, 26:193-200 (1981).
11. Hunt, D.G., "Creep of Nylon-6,6 During Concurrent Moisture Changes," *Polymer*, Vol. 21, 1980, pp. 502-508.
12. Gardner, R., Gibson, E. J., and Laidlaw, R. A., " Effects of Organic Vapors on the Swelling of Wood and on Its Deformation Under Load," *Forestry Products Journal,* 17(4):50-1, (1967)
13. Blackwell, J., Cageao, R.A., and Biswas, A., "X-ray Analysis of the Structure of HM-50 Copolyamide Fibers", *Macromolecules*, 20:667-71 (1987)
14. Technical Information: A New Series of Laminates and Prepregs from a New Species of Aramid Fiber, "Technora®", Teijin Limited, 1st Project Group, Fiber & Textile Research Laboratories, 3-4-1, Minohara, Ibaraki, Osaka 567, Japan
15. Penn, L., and Larsen, F., "Physiochemical Properties of Kevlar 49 Fiber", *J. of Applied Polymer Science*, 23:59-73 (1979).

Table 3.1 Aramid Fiber Properties

	Kevlar® 29	Kevlar® 49	Kevlar® 149	Technora®
Danier	1.52 (6.4%)	1.48 (11.5%)	1.41 (9.5%)	1.41 [14]
Compliance (1/TPa)	11.2	8.73	5.14	11.87
Strength (GPa)	2.56	2.63	2.80	3.15

Table 3.2 Mechano-sorptive creep test results of Kevlar® fibers

b_1 ($\frac{\mu\varepsilon}{\text{decade}}$)	b_2 ($\frac{\mu\varepsilon}{\text{decade}}$)	r (b_2 / b_1)
	Kevlar® 29 fiber	
333.8 (343.0)*	1007.6 (1035.4)	3.0
234.8 (241.3)	1154.3 (1186.1)	4.9
185.6 (190.7)	869.5 (893.5)	4.7
251.4 (258.3)	1010.5 (1038.4)	4.2
	Kevlar® 49 fiber	
150.8 (155.0)	419.5 (431.1)	2.8
173.3 (178.1)	542.2 (557.1)	3.1
103.4 (106.2)	282.5 (291.2)	2.7
142.5 (146.4)	414.7 (426.5)	2.9
	Kevlar® 149 fiber	
86.7 (89.4)	93.7 (96.6)	1.1
53.0 (54.6)	128.4 (132.4)	2.4
61.4 (63.3)	131.9 (136.0)	2.2
67.0 (69.1)	118.0 (121.7)	1.9

* Number in parenthesis indicates the logarithmic creep rate per unit stress ($\frac{\mu\varepsilon}{\text{decade}}$/GPa)

Table 3.3 Mechano-sorptive creep test results of Technora® fibers

b_1 ($\frac{\mu\varepsilon}{\text{decade}}$)	b_2 ($\frac{\mu\varepsilon}{\text{decade}}$)	r (b_2 / b_1)
300.3 (309.6)*	522.8 (539.0)	1.7
304.9 (314.3)	622.7 (642.0)	2.0
276.0 (284.5)	547.8 (564.7)	2.0
293.7 (302.8)	564.4 (581.9)	1.9

* Number in parenthesis indicates the logarithmic creep rate per unit stress ($\frac{\mu\varepsilon}{\text{decade}}$/GPa)

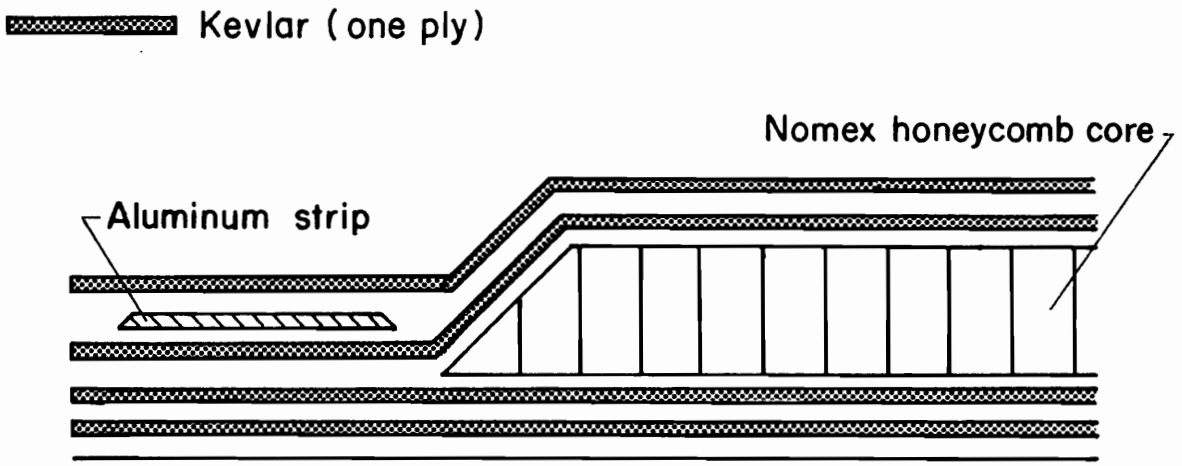

Fig 3.1 Kevlar application on an aircraft fuselage section [1]

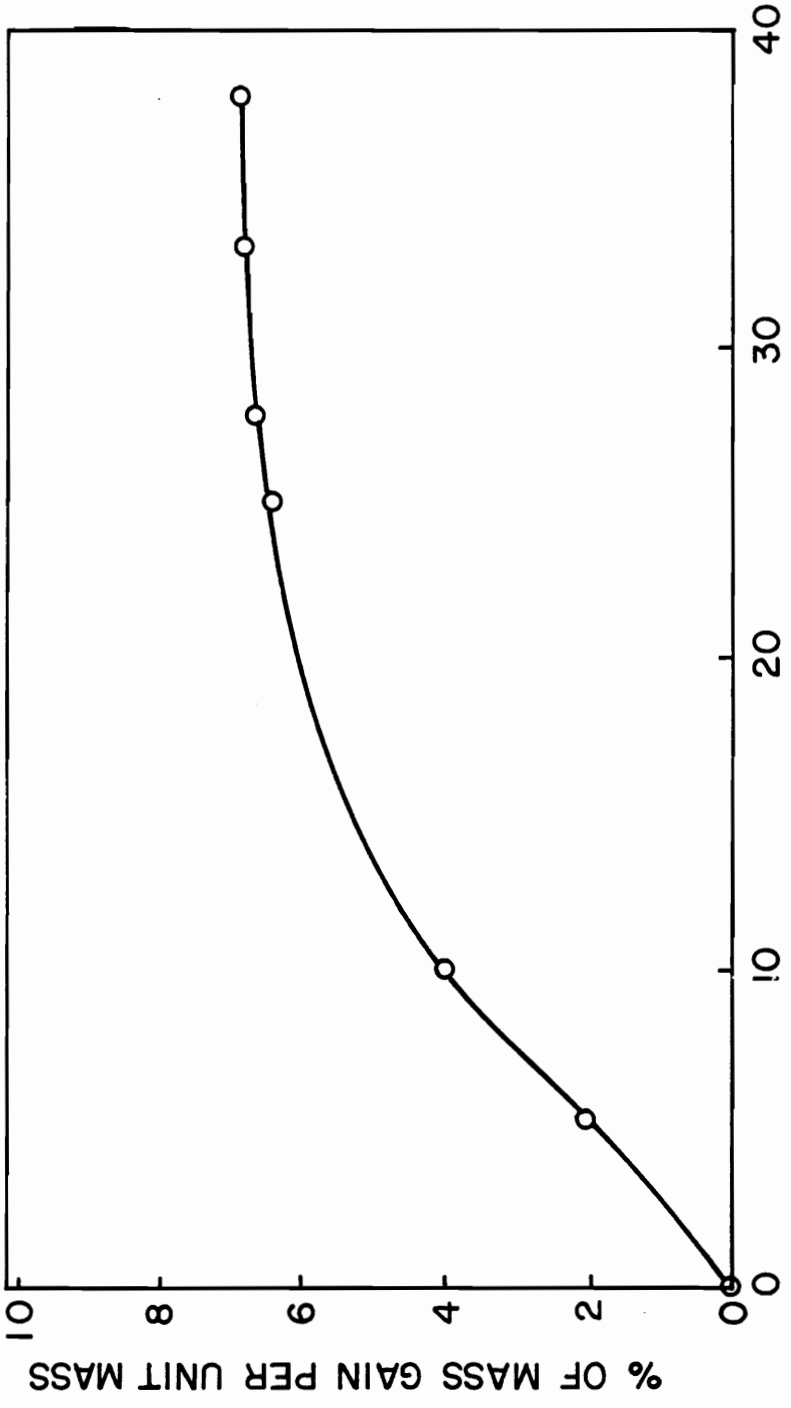

Fig. 3.2 Moisture absorption curve of Kevlar/Fiberite 7714 epoxy coupons

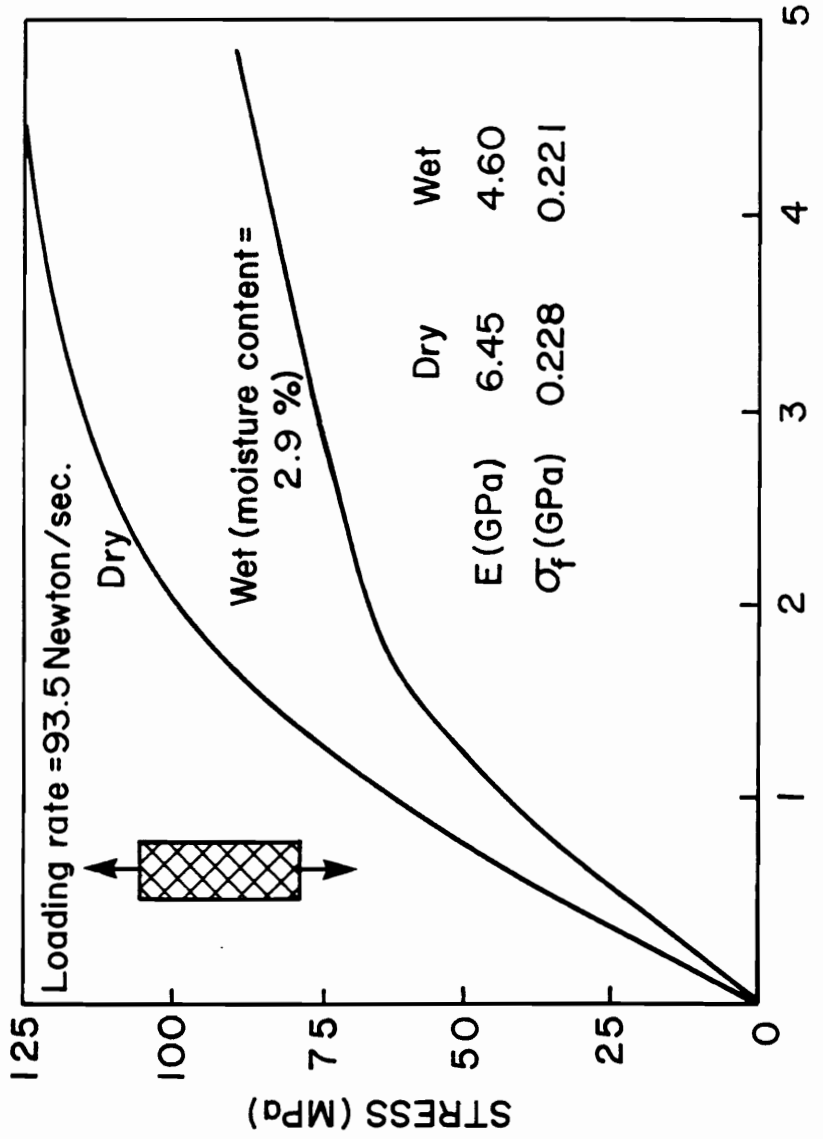

Fig. 3.3 Stress-strain curve of Kevlar cloth

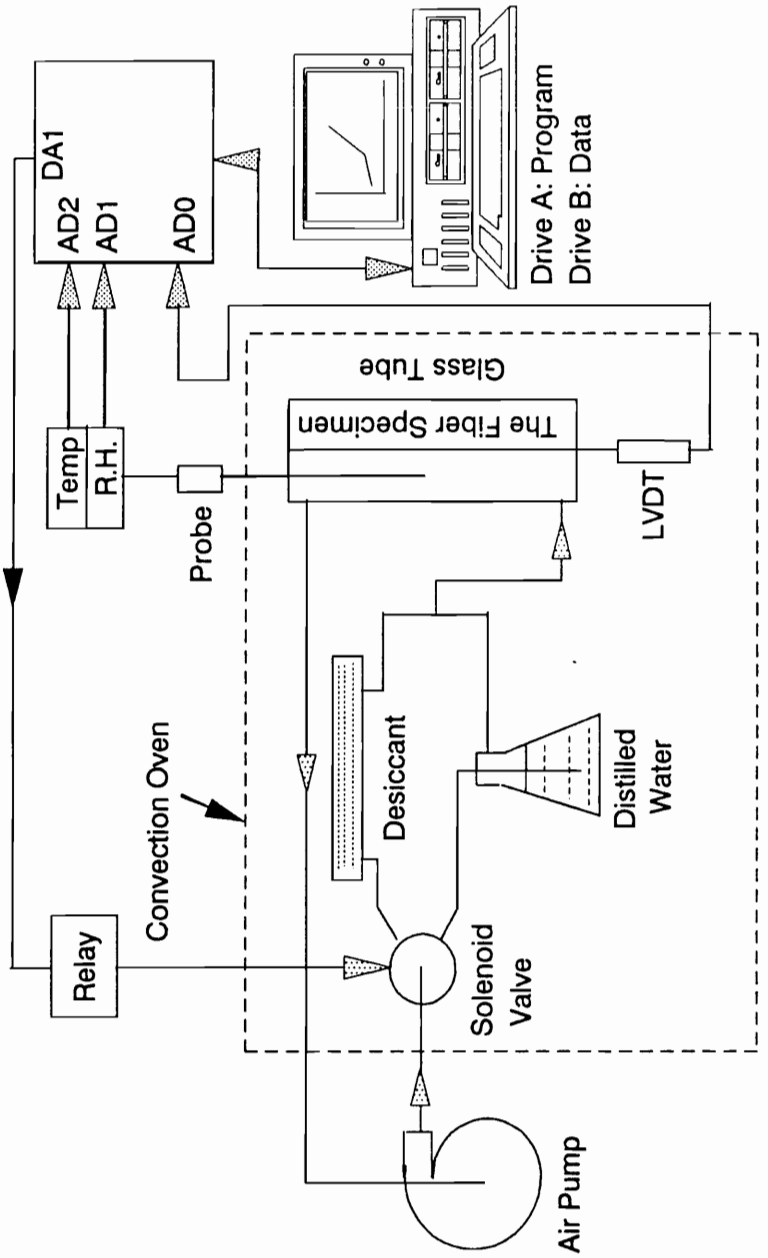

Fig. 3.4 Diagram of the fiber creep test fixture

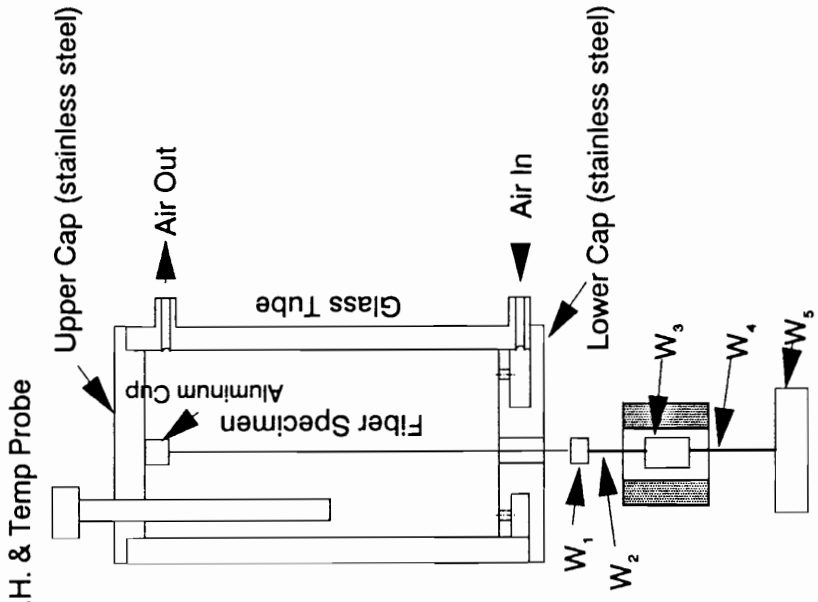

Fig. 3.5 Diagram of the central test system in fiber test

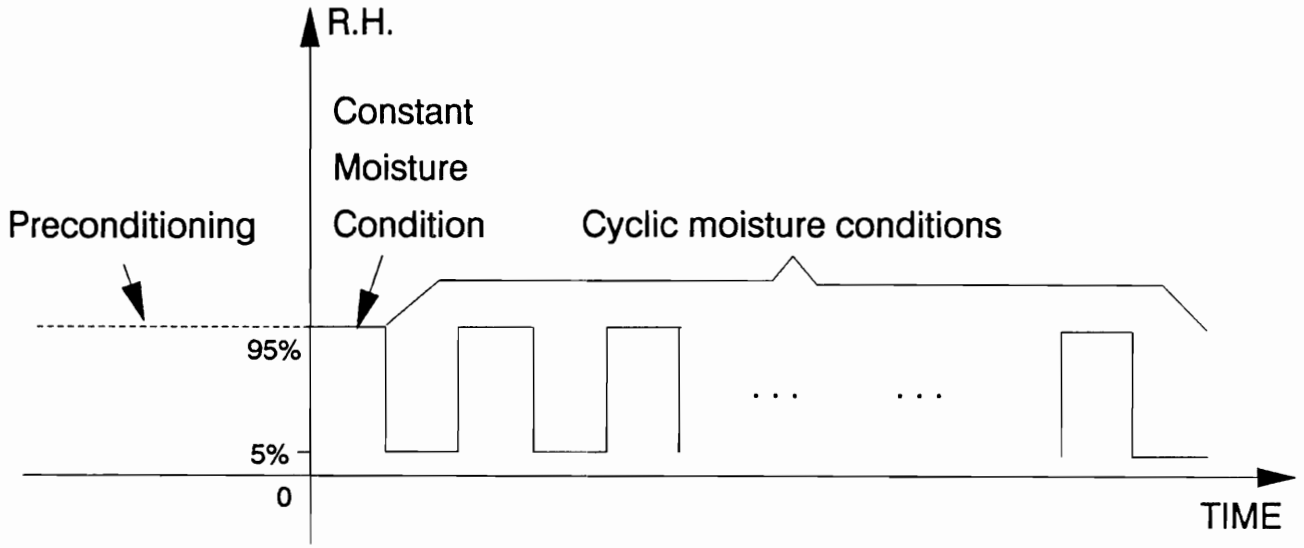

Fig. 3.6 Relative humidity profile in the fiber creep test

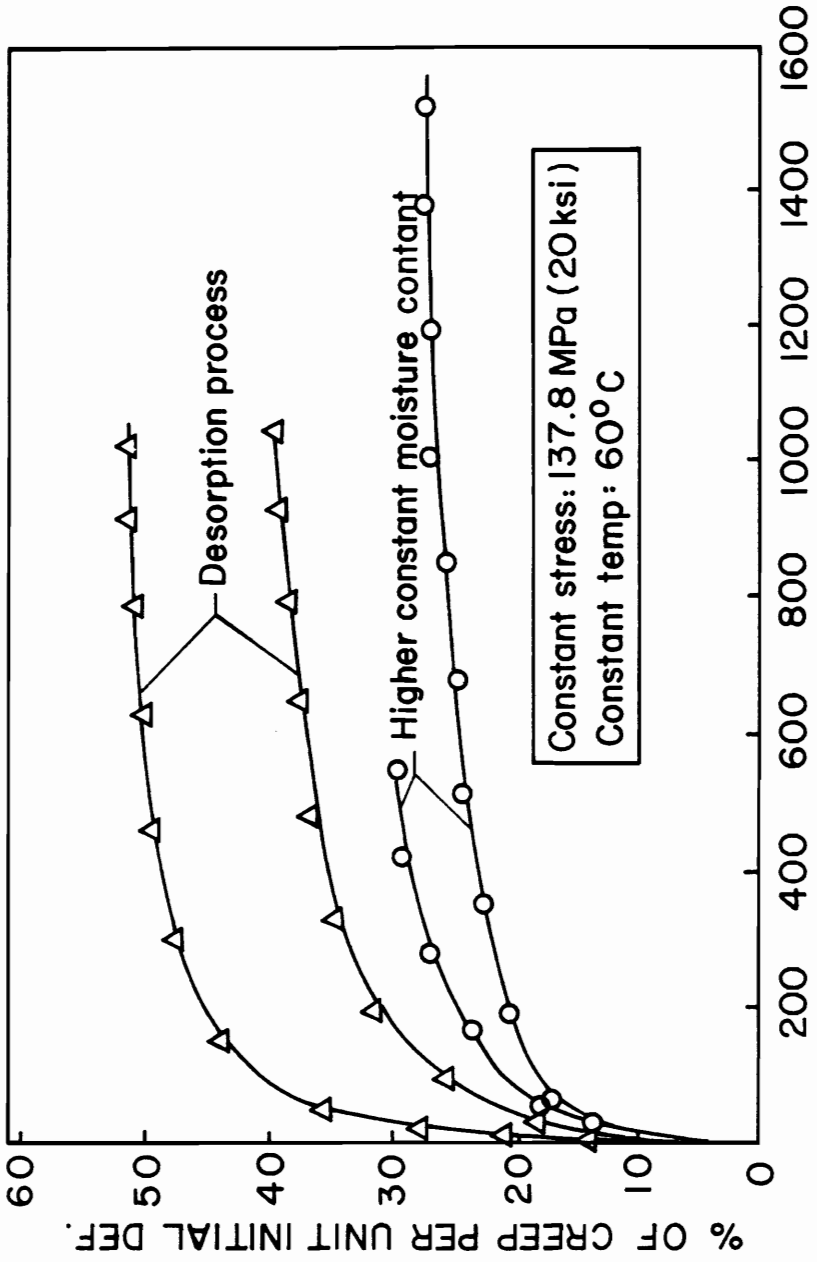

Fig. 3.7 Tensile creep of Kevlar/Fiberite 7714 epoxy coupons $[0^{\circ}]_8$

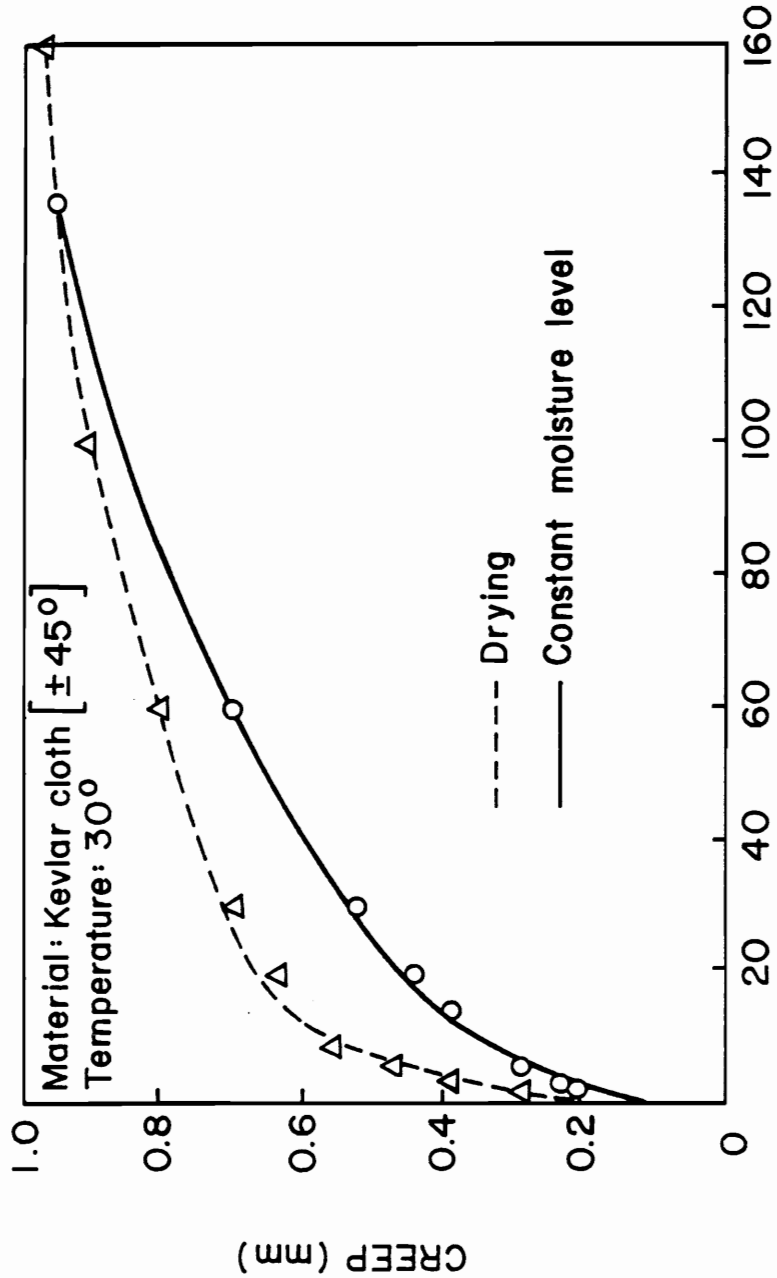

Fig. 3.8 Tensile creep of Kevlar cloth

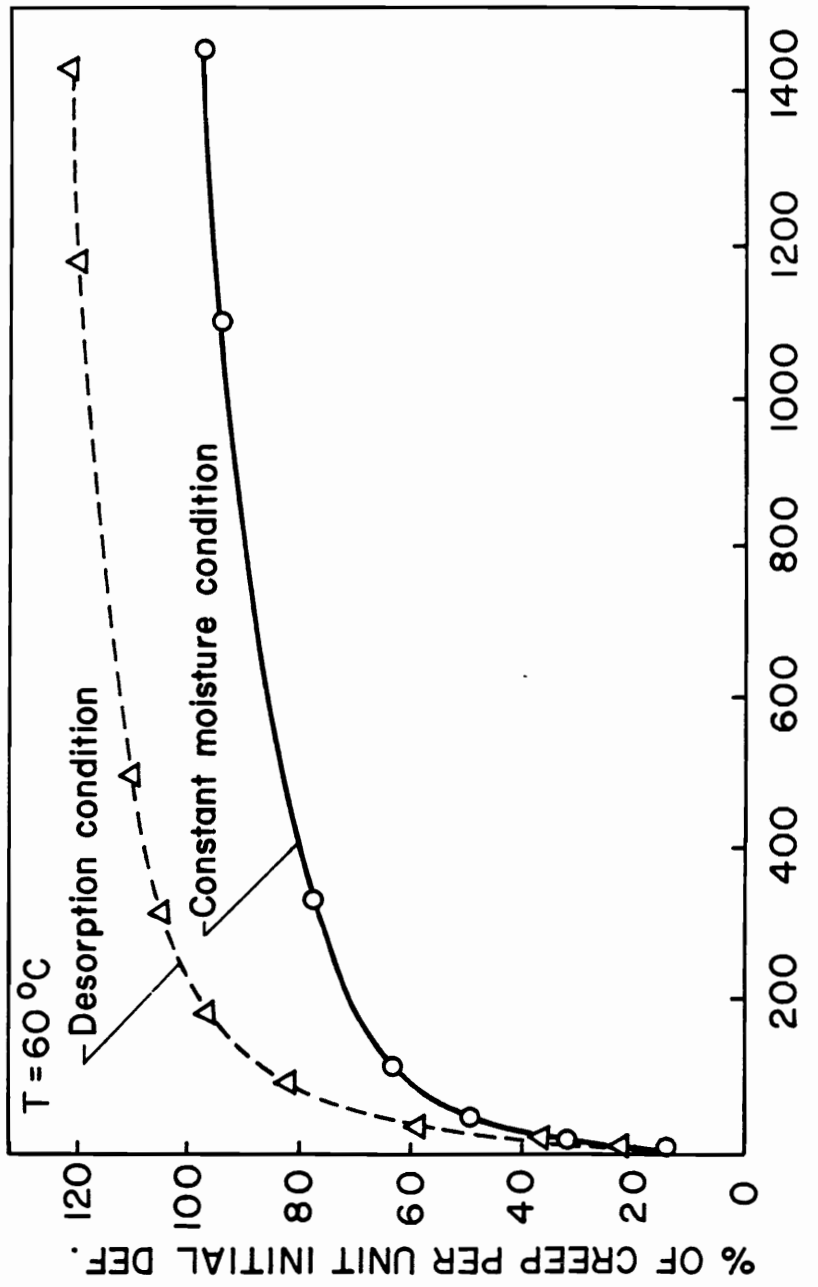

Fig. 3.9 Bending creep of Kevlar 49/Fiberite 7714 epoxy coupons $[0^{\circ}]_8$

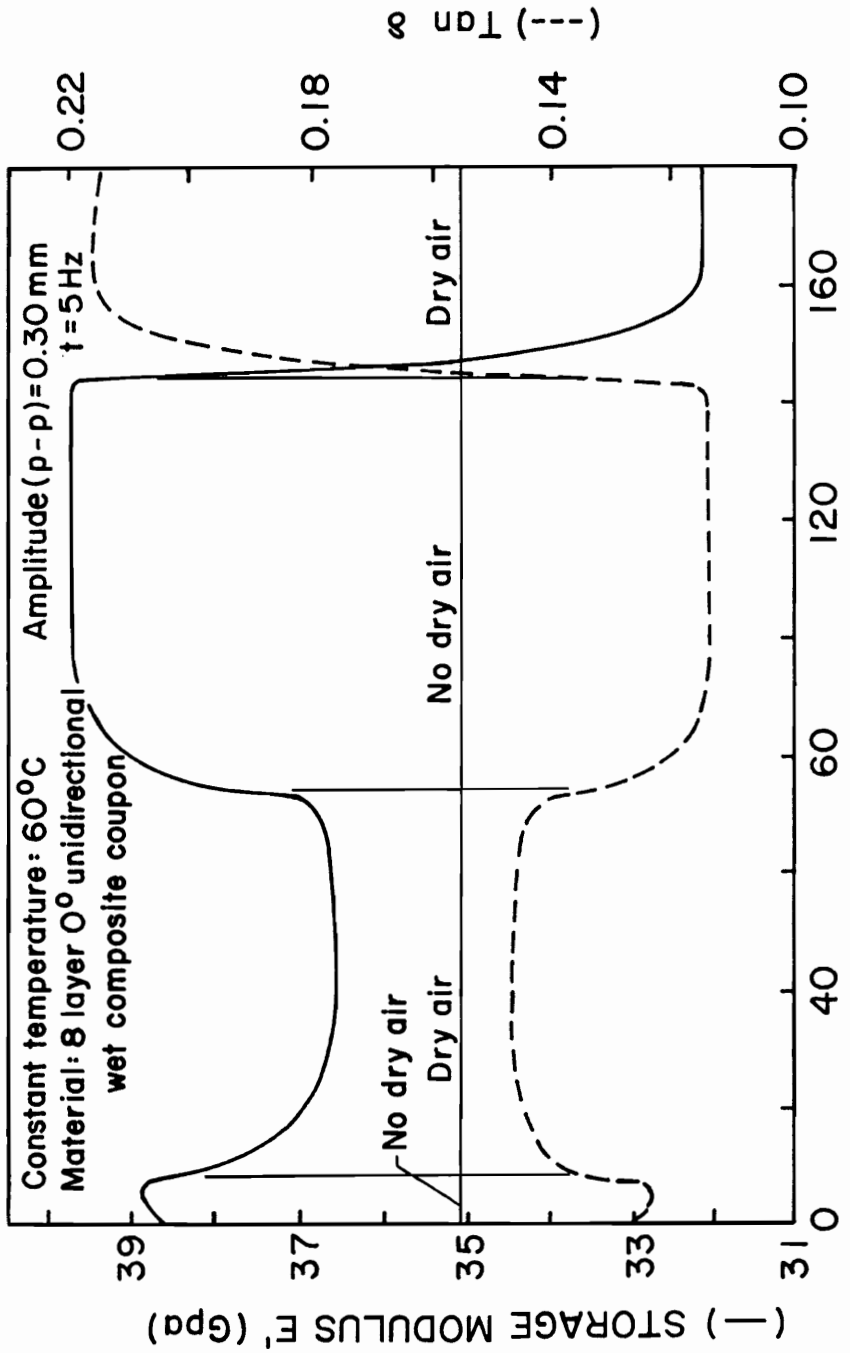

Fig. 3.10 DMA test results

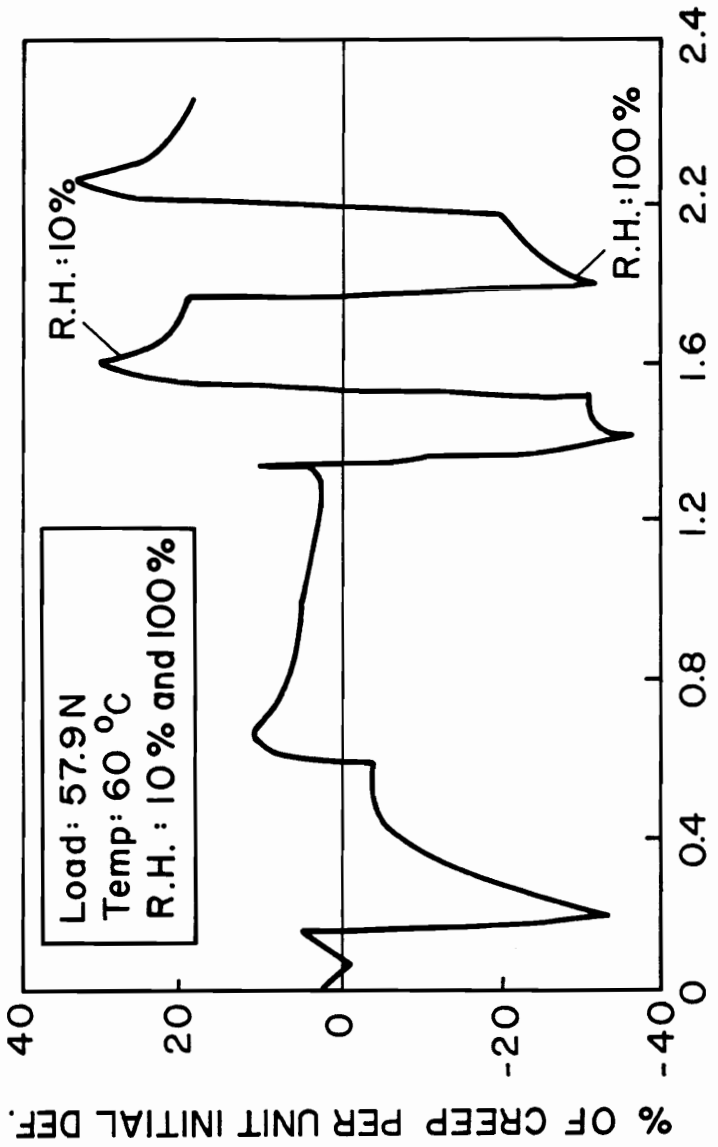

Fig. 3.11 Creep of Kevlar 49 yarn at 57.9 Newtons (13 lbs)

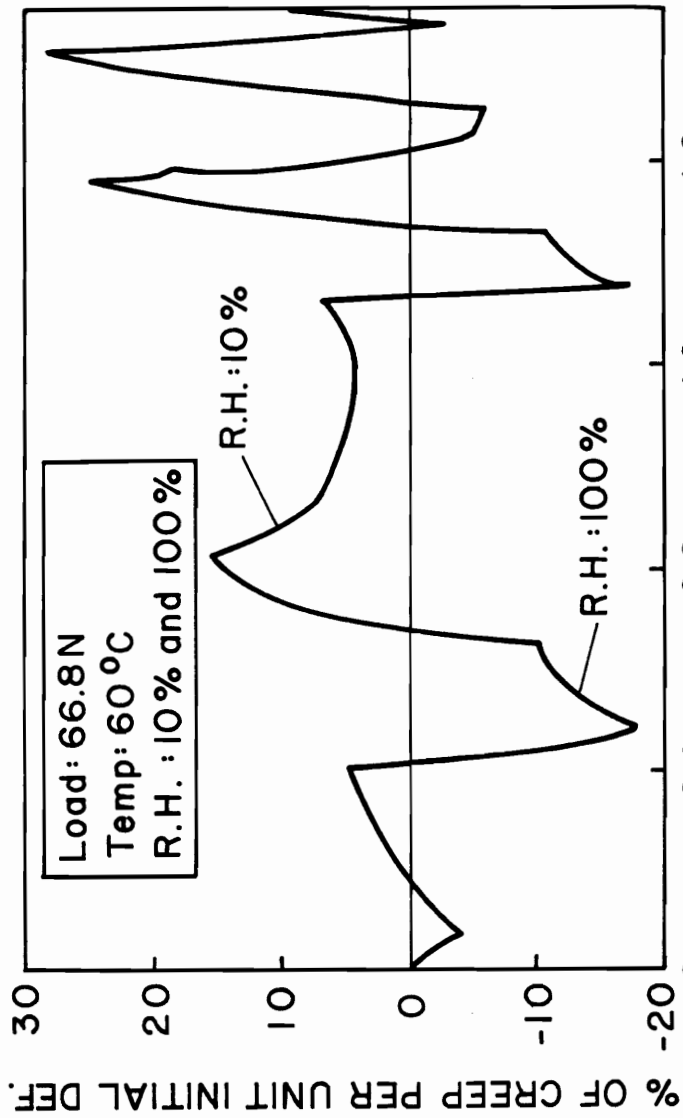

Fig. 3.12 Creep of Kevlar 49 yarn at 66.8 Newtons (15 lbs)

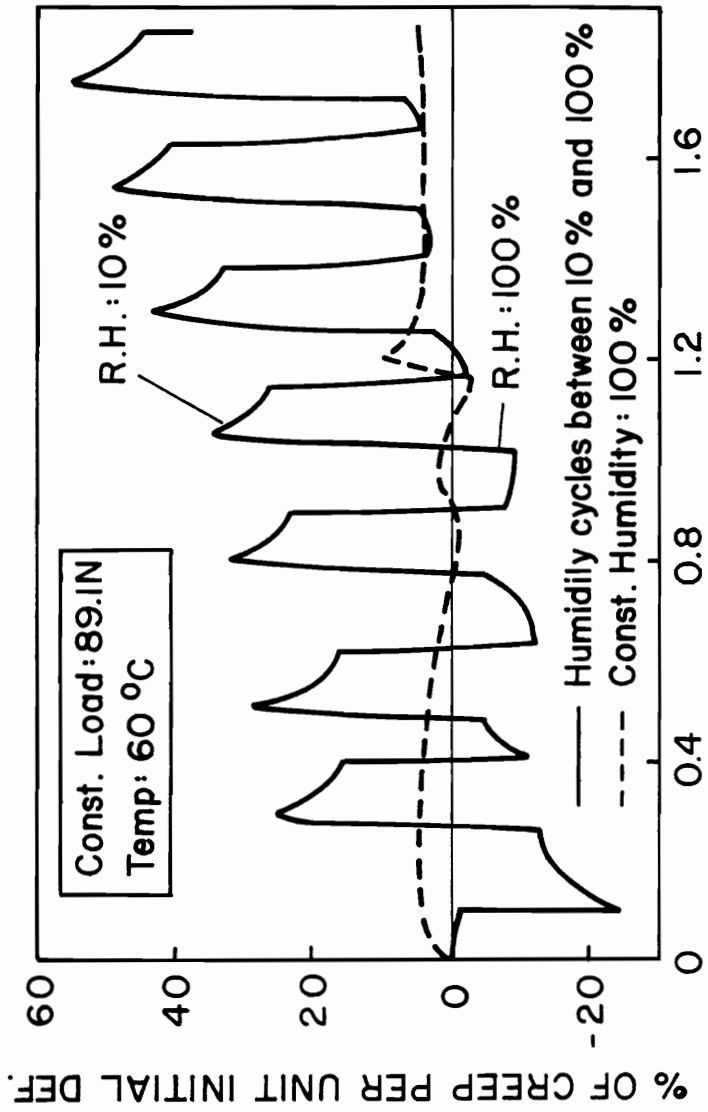

Fig. 3.13 Creep of Kevlar 49 yarn at 89.1 Newtons (20 lbs)

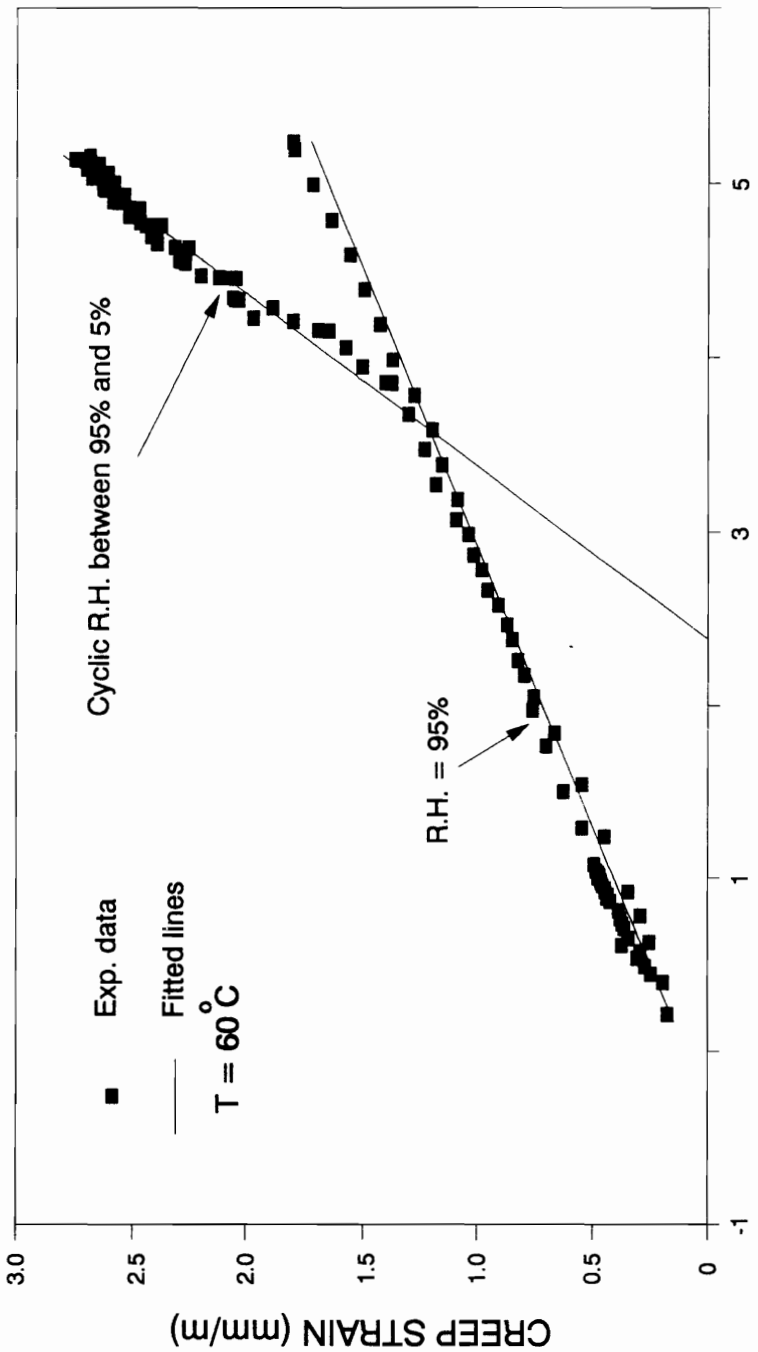

Fig. 3.14 Creep of Kevlar 29 fiber

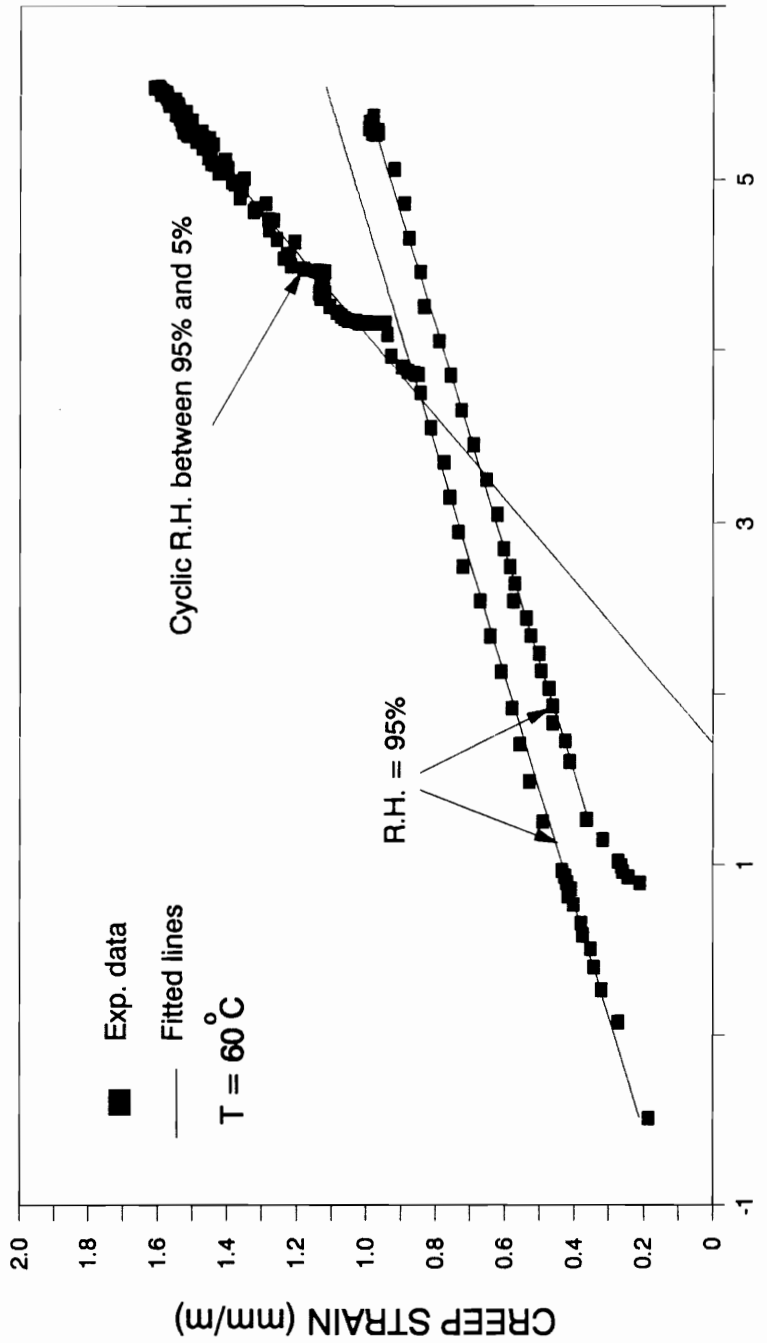

Fig. 3.15 Creep of Kevlar 49 fiber

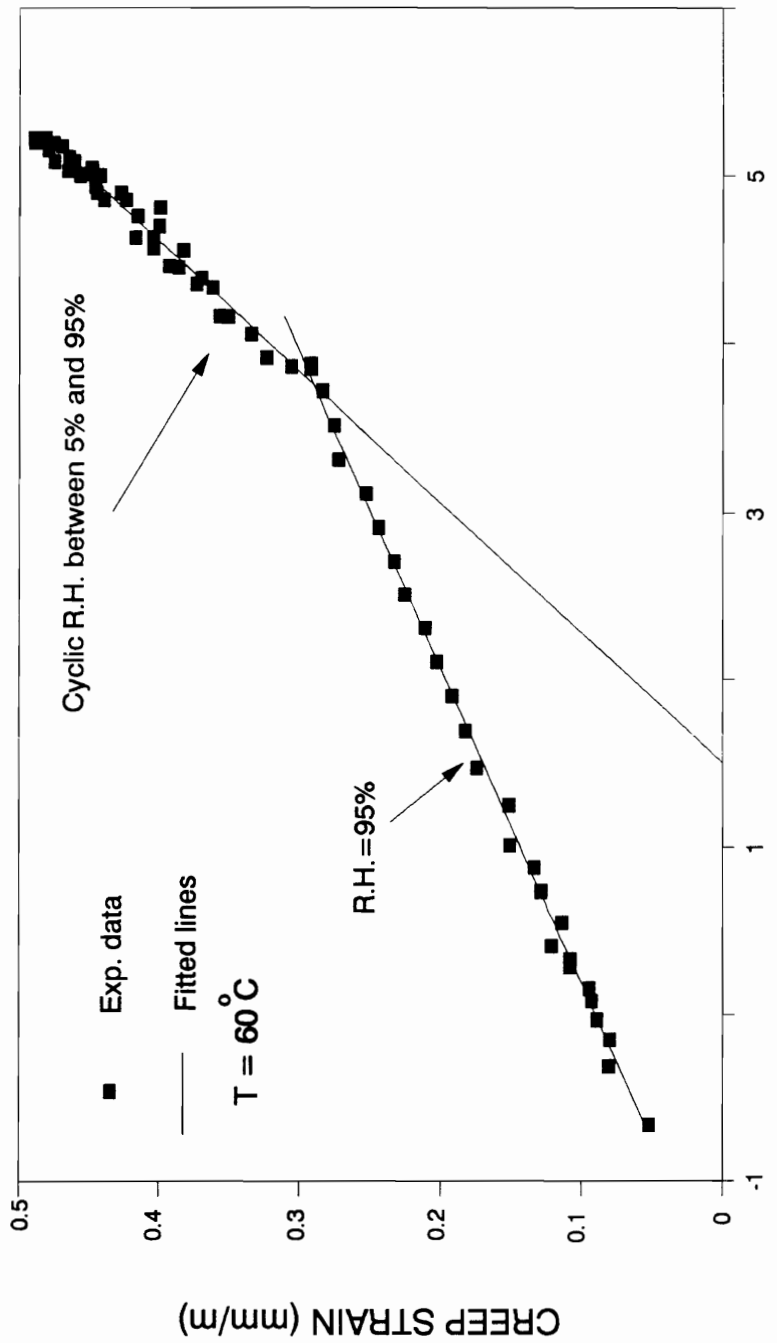

Fig. 3.16 Creep of Kevlar 149 fiber

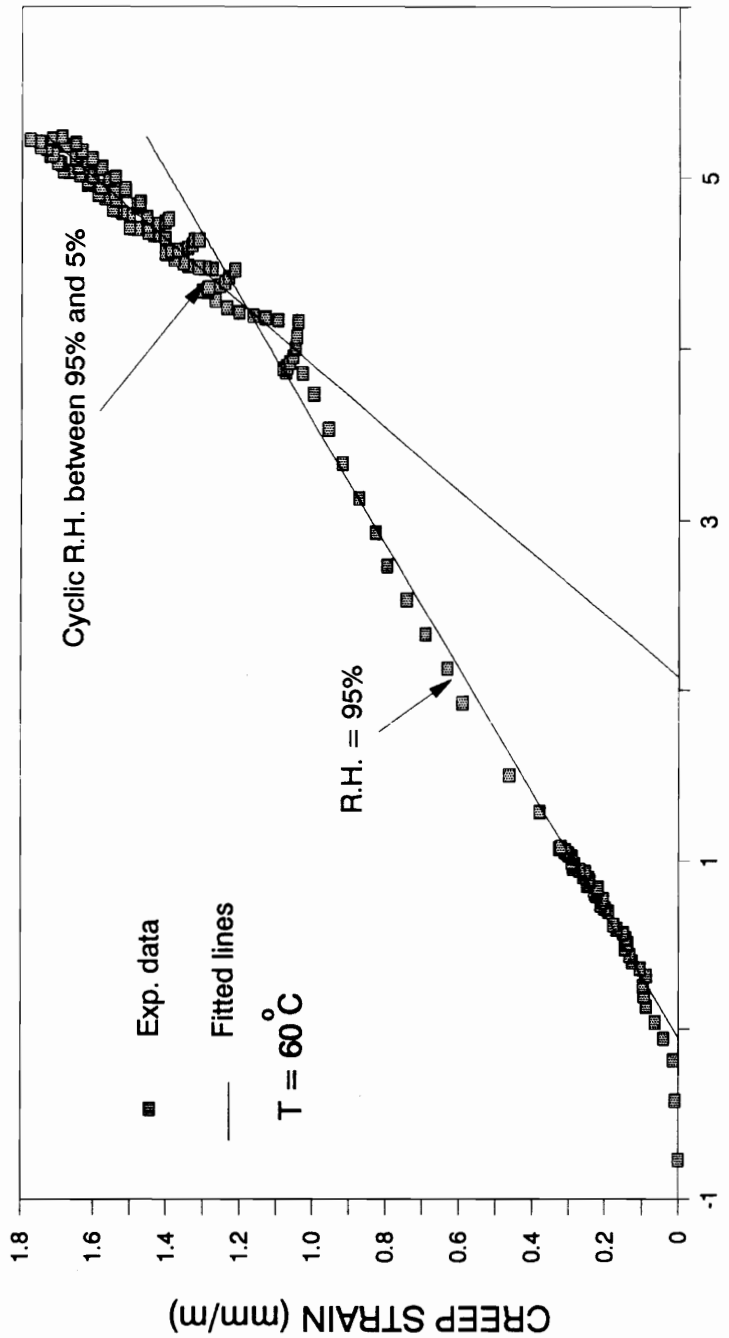

Fig. 3.17 Creep of Technora Fiber

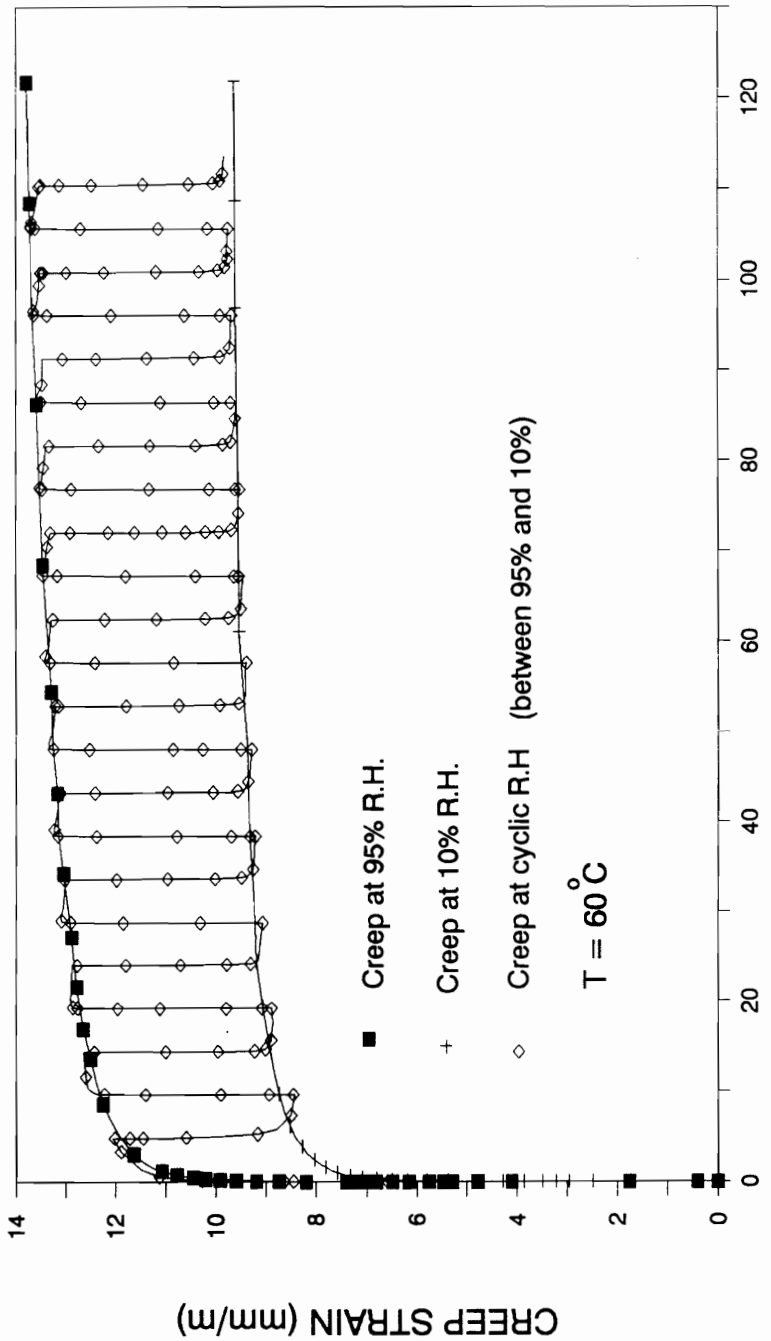

Fig. 3.18 Creep of Nylon 6,6 fibers

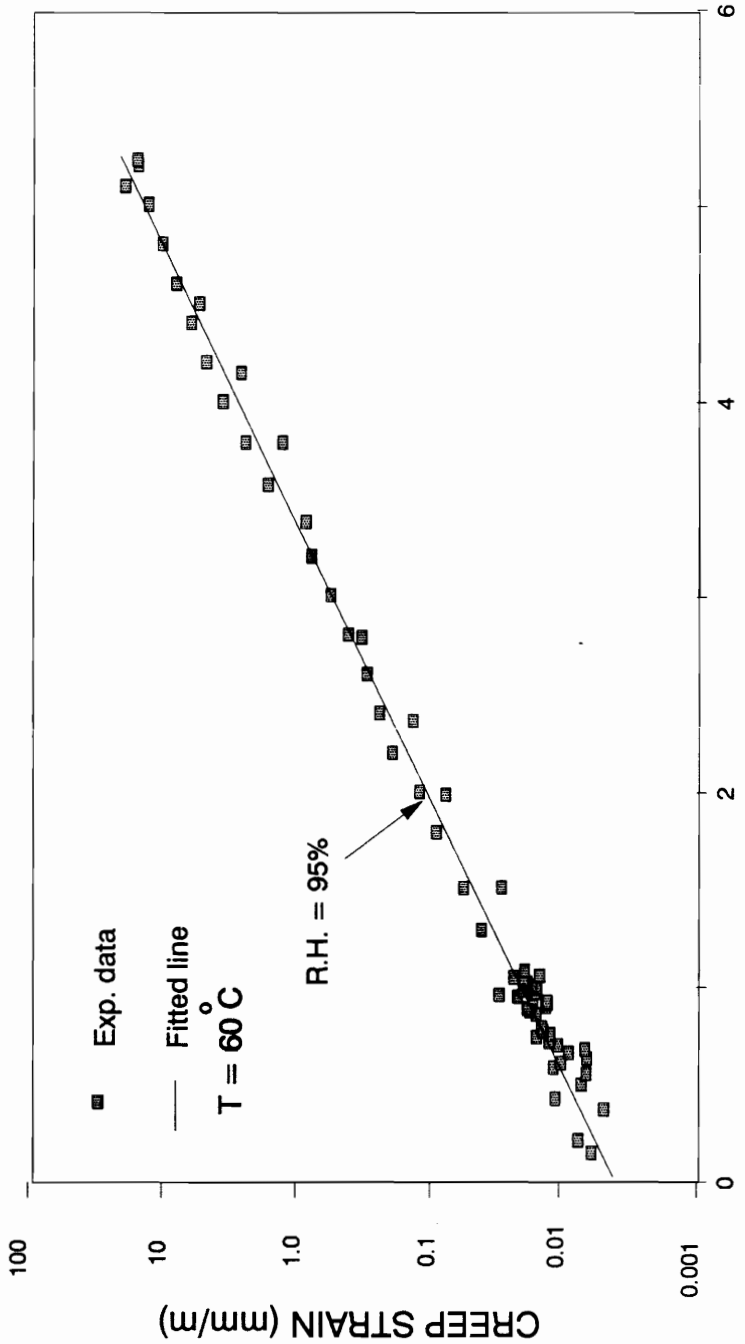

Fig. 3.19 Creep of PMMA fiber under constant moisture condition

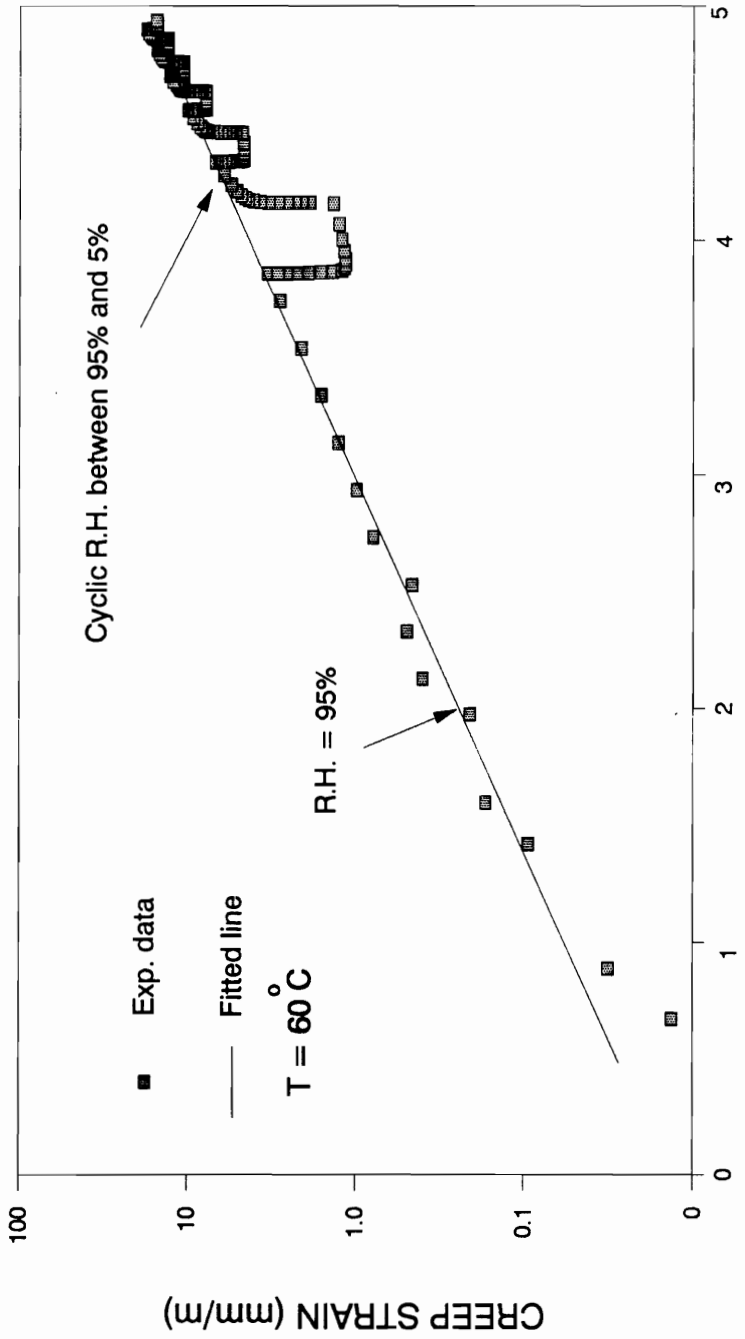

Fig. 3.20 Creep of PMMA fiber

Chapter 4

PARAMETRIC AND MECHANISTIC STUDIES OF MECHANO-SORPTIVE PHENOMENON IN ARAMID FIBERS

4.1 Introduction

In chapter 3, the experimental results of transient moisture effects in aramid fibers were presented. Experimental results on single aramid fibers and their composite have shown that transient moisture conditions could substantially accelerate the creep levels of aramid fibers and reduce the storage modulus of Kevlar®/epoxy composite specimens. It has been found that under both constant and cyclic moisture conditions, the creep strains of single aramid fibers approximate straight lines when plotted against logarithmic time. Therefore, the ratio of the slope, or logarithmic creep rate, under transient moisture conditions to that under constant moisture conditions was taken as an indicator to quantify the transient moisture effects on creep [1]. These results indicated that the additional effects of transient moisture conditions over constant moisture conditions are influential and should not be ignored.

In this chapter, attention will be focused on the further understanding of the mechano-sorptive phenomenon in aramid fibers. Particularly, effort will be devoted to the studies of 1). the

influence of various parameters, such as temperature and stress, on the creep behavior under transient moisture and constant moisture conditions, and 2). the creep mechanism under these conditions in terms of molecular, crystallographic, and morphological features of aramid fibers.

4.2 **Experimental**

The specimens used in the tests were Kevlar® 49 single filaments. Single filaments were carefully separated from a section of yarn (2160T, D968) provided by Du Pont Company. To facilitate the separation, a plate covered with a piece of black velvet was used as a work table. The nominal diameter of the single filaments was 14.7 μm and the nominal denier of the filaments was about 2.23. The nominal specimen length was 216 mm (8.5 in). The fiber strength based on six measurements at 60 °C and 95% R.H. was 2.0 GPa (290 ksi) with a standard deviation of 0.13 GPa (18.9 ksi) (2.0 ± 0.13 GPa) at a gage length of 216 mm (8.5 in). Between 30°C and 60°C, temperature did not have appreciable influence on the fiber elastic compliance. Based on 17 measurements at 95% R.H., the fiber elastic compliance was 8.61 1/TPa ± 0.10 1/TPa (59.4 1/Gsi ± 0.69 1/Gsi). The tests were conducted in a specially designed fixture which has been described in detail in chapter 3 and in [4].

4.2.1 Tests at Different Temperature Levels

Temperature levels used in the tests were 30, 40, 50, and 60 °C. At each temperature, three tests were conducted to minimize data scattering due to fiber variabilities. The stress level was kept at a constant level of 0.64 GPa (92.8 ksi) which is about 32% of the breaking strength. In each test, the first two hour creep was measured when the moisture content inside the specimen was in equilibrium at 95% relative humidity (R.H.). To ensure an equilibrium moisture condition, the specimen was pre-conditioned at 95% relative humidity under no load for a sufficient long period of time before the commencement of the creep test. The preconditioning time was selected according to the conditioning temperature which was the same as the creep test temperature. For example, at 30°C, the preconditioning time was at least 24 hours, while at 60°C, at least 4 hours. After the first two hour creep at the constant moisture condition, the relative humidity was switched between 5% and 95% to impose a cyclic moisture condition inside the specimen. Each relative humidity level was kept for a two hour period before being switched to the next level. The total time for each test was 48 hours.

4.2.2. Tests at Different Stress Levels

Three stress levels were used in the tests, namely, 0.43, 0.64, and 1.10 GPa (62.4, 92.8, and 159.9 ksi). These stress levels correspond to 22%, 32%, and 55% of the fiber strength. The test

temperature was kept at a constant level of 60°C. Three tests were conducted at each stress level to obtain a meaningful average. The other aspects of the test procedure are the same as described above in the section of temperature effects.

4.2.3. Changes of Fiber Elastic Compliance Due to Creep

The elastic compliances of each individual fiber before and immediately after a creep test were measured. After pre-conditioning each fiber, the elastic displacements at three stress levels were measured to obtain the initial fiber elastic compliance ($D_e^{(i)}$). After the measurement, at least two hours were allowed for the fiber to recover from the possible viscoelastic deformations due to loading during the measurement. After the recovery stage, the creep test was conducted under cyclic moisture conditions for 48 hours at 0.64 GPa (92.8 ksi) and 60°C. Immediately after the creep test, the final fiber elastic compliance ($D_e^{(f)}$) was measured by the same method as mentioned for the initial elastic compliance measurement. In these tests, care has been taken to ensure that the temperature and relative humidity for the two compliance measurements to be the same as the creep test temperature.

4.2.4. Tests at a Constant (Low) Moisture Condition

To examine the creep behavior of aramid fibers in response to different equilibrium moisture conditions, several tests have been

conducted under a constant moisture condition at approximately 5% R.H.. Before the conduction of each test, a fiber was conditioned in the test chamber at a nominal 5% R.H. until the attainment of a moisture equilibrium inside the fiber. During the test, the temperature was kept at 60°C and the stress level was maintained at 0.64 GPa (92.8 ksi). These results are used to compare with the corresponding results obtained in the previous tests under a constant moisture condition at 95% R.H..

4.3 **Experimental Results**

4.3.1. Tests at Different Temperature Levels

The experimental results for parameters b_i (i=1, 2) and r at different temperatures shown in Figures 4.1 and 4.2.

From these results one may see that the logarithmic creep rates and the mechano-sorptive ratio increase with increasing temperatures. However, the logarithmic creep rate under cyclic moisture conditions is more dependent on temperatures than that under constant moisture conditions.

4.3.2. Tests at Different Stress Levels

To examine the stress effect on the creep behavior of the fibers,

creep compliance could be used. Dividing Equation (3.1) by stress σ, one may obtain the following equation:

$$D(t) = A_i + B_i \, Log(t) \qquad (4.1)$$

where

D(t): The creep compliance of the fiber

A_i : $A_i = a_i / \sigma$

B_i : $B_i = b_i / \sigma$, logarithmic creep rate per unit stress or logarithmic creep compliance rate

One may see that if B_i is constant, the viscoelastic behavior is linearly dependent on the stress. However, if B_i decreases with stress, the viscoelasticity of the fiber will have negative deviation from linear behavior; and if B_i increases with stress, the viscoelasticity of the fiber will have positive deviation from linear behavior.

Test results at three stress levels are shown in Figures 4.3, 4.4, and 4.5.

From the results shown in Figures 4.3 and 4.4, one may conclude that under constant moisture conditions, the logarithmic creep rate may increase linearly with stresses at lower stress levels. However,

at higher stress levels, the increase is nonlinear and less significant. In testing Kevlar® yarns, Cook [8] reached the same conclusion. Under cyclic moisture conditions, the logarithmic creep rate increases as the stress level increases. However, the increase is nonlinear with a negative deviation (stiffening) from linear behavior.

From the results shown in Figure 4.5, one may see that, at lower stress levels, the mechano-sorptive ratio decreases slightly as the stress increases. However, at higher stress levels, the mechano-sorptive ratio appears insensitive to the stress increases.

4.3.3. Change of Elastic Compliance due to Creep

Five measurements indicated that the elastic compliance of Kevlar® 49 fibers decreased by 16% ± 0.45% after two day mechano-sorptive creep deformation. In testing single Kevlar® 49 and Kevlar® 29 fibers at room conditions, Ericksen found that the elastic modulus of the fibers increased as the creep strain increased [5].

4.3.4. Creep under a Constant (Low) Moisture Condition

Under a constant moisture condition at 5% R.H., the logarithmic creep rate of Kevlar® 49 fibers was 192 ± 14.9 με/decade. This creep rate is very close to that obtained under a constant moisture condition at 95% R.H. (192 ± 1.8 με/decade). From these results one may see that different constant moisture levels may not have

significant effects on the creep behavior of the fibers. This conclusion parallels others that constant moisture conditions do not have significant effects on the fatigue behavior and tensile properties of aramid fibers [10 - 12]. This conclusion also emphasizes the significance of transient moisture effects on the creep behavior of aramid fibers. Even though the creep behavior was not significantly different at the two constant moisture conditions, when the moisture content was cycled between these two levels, the creep level of the fibers increased significantly.

4.4. **Discussions**

4.4.1. Microscopic Structures of Aramid Fibers

Chemically, aramid Kevlar® fibers are composed of poly (*p*-phenylene terephthalamide) macromolecules and, therefore, are often referred to as PPTA fibers [13 - 16]. The structure of PPTA molecules as well as their hydrogen bonding within the fiber is shown in Figure 4.6 [16]. The aromatic rings contribute high thermal stability, and the para configuration gives high strength and modulus. Free rotation around the phenyl-carbonyl and the phenyl-nitrogen bonds is inhibited by the presence of the aromatic rings, the double bond nature of the amide group arising from resonance effects, and possibly the steric effects between the ortho hydrogen atoms on the rings and

the amide hydrogen [13]. Therefore the molecular chains must be regarded as rod-like. Actually, when dissolved in solvents, the molecular chains remain rod-like so that they can aggregate to form liquid crystals [16].

The crystallographic structure of aramid fibers have been studied by X-ray diffraction techniques [13, 15, 17, 18]. In the fibers, the molecular chains are bonded together laterally through hydrogen bonding to form crystallites. The crystallites are known to orient relative to the fiber axis at an average angle of about 10° [13]. The orientation of the crystallites has an important effect on the fiber stiffness of aramid fibers [2, 3]. The crystallite dimensions were reported to be about 50 Å in width and 250 Å in length by Northolt [2], and 20-140 Å in width and 100 Å in length by Ballou [18]. Therefore, in a typical aramid fiber, 900-6000 crystallites could be seen in a longitudinal section containing the fiber axis. The crystallinity of the fiber has been estimated to be nearly 100% [15, 19]. A schematic diagram of the unit cell of a crystallite along with its configurational dimensions is shown in Figure 4.7 [13, 15, 17].

Even though the understanding of the morphology of aramid fibers is still not complete, some results from X-ray and electron microscopic examinations do provide meaningful insights into the behavior of these fibers [2, 13, 19 - 21]. Generally, it has been

known that the fiber possesses fibrillar structures [19]. Crystallites are connected radially through hydrogen bonding to form fibrils with a diameter of about 6000 Å [19, 21]. Since the force of hydrogen bonding decreases as the bonding distance increases and since the surface of one crystallite cannot fit into the lattice positions of its neighbors, the bonding force across the interface of neighboring crystallites may be expected to be smaller than that within the crystallites. Based on the electron microscopic examination of the longitudinal sections, a pleat structure along the longitudinal direction was proposed [13, 19, 22]. As shown in Figure 4.8, the fiber is envisaged to consist of radially arranged sheets pleated along the longitudinal direction. The formation of the pleat is considered to be due to a periodic change in the direction of the fibril axis [19]. The angle between the adjacent components of the pleat is reported to be about 170° [13], and the longitudinal dimension of a pleat is reported to be 5000 Å [19]. The pleated sheets are bonded together along tangential direction possibly through van der Waals forces [5, 22]. The pleat structure, however, does not exist in isolated fibrils or in films formed by a single layer of fibrils [19]. Therefore the pleats may be able to relax when a fibril is isolated from its neighbors [19].

4.4.2. Water in Aramid Fibers

The moisture uptake of aramid fibers is Fickian [23, 24]. The equilibrium moisture content is a function of the relative humidity [23, 24]. For example, the equilibrium moisture content at 95% R.H. is about 6% and that at 10% R.H. is about 0.8% [23, 24]. The diffusion coefficient depends on both temperature and moisture concentration [24].

The structure and dimensions of a water molecule is shown in Figure 4.9 [25]. The molecule possesses two bonding and two non-bonding valence-shell electron pairs. These electron pairs are arranged in approximate tetrahedral positions with the oxygen atom at the center. The distance between the oxygen atom and a hydrogen atom is about 0.94 Å. Lone pair and lone pair-bond pair repulsions reduce the bond angle to less than 109.5°. The size of a water molecule is about 1.5 Å. Therefore, there is enough space between two crystallites for the residence of absorbed water molecules. By using Fourier transform infrared spectroscopy techniques, the presence of water molecules between the crystallites through hydrogen bonding to the amide groups has been confirmed in both Kevlar® fibers and Kevlar® films [26, 27].

At moisture equilibrium, the bonding of water molecules to the PPTA molecular chains may be illustrated as in Figure 4.10. It may be

argued that, when a moisture equilibrium is attained prior to the application of a mechanical load to a fiber, the presence of water molecules in the fiber may not significantly alter its deformation behavior upon subsequent mechanical loading. Equivalently, water plasticization in aramid fibers may not produce significant effects since a moisture equilibrated fiber and a dry fiber are both hydrogen bonded structures. The only effects, if any, may arise from the difference between the hydrogen bonding strengths of the two kinds of hydrogen bonds (refer to Figure 4.6 and Figure 4.10). Experimental results from various researchers seem to support this argument. For example, test results presented in this paper indicated that the level of constant moisture content does not have significant effects on the creep behavior of Kevlar® fibers. Experimental results from other researchers also indicated that, in aramid fibers, constant moisture conditions did not have significant effects on the fatigue behavior [10] and the tensile properties [11, 12].

However, when water molecules diffuse into or leave from the aramid fibers, the equilibrium of hydrogen bonding may be upset and at least part of the hydrogen bonded structure may be temporarily disturbed. This temporary disruption in the fiber, as discussed in detail below, may have significant influence on the time dependent behavior of the fiber.

4.4.3. Creep Mechanisms Under Transient Moisture Conditions

Because water molecules are small and polar, at the moisture diffusion front, water molecules may approach the hydrogen bonding sites in the fiber to statistically disrupt the original hydrogen bonds. After the temporary breakage of the hydrogen bonds between the bonded elements, water molecules may bridge in between them to form new hydrogen bonds (Figure 4.10). In a moisture desorption process, when water molecules leave the fiber, the hydrogen bonds previously formed by the bridged water molecules may break and the hydrogen bonds may reform in the original form but not at the original place. It is very important to notice the difference between the state of hydrogen bonding under transient moisture conditions and that under constant moisture conditions. Under transient moisture conditions, at least part of the hydrogen bonds in the fiber are temporarily disrupted. However, under constant moisture conditions, the hydrogen bonds may not break. These two states of hydrogen bonds may contribute to the observed difference between creep under cyclic moisture conditions and that under constant moisture conditions. If a fiber is under stress while experiencing a transient moisture condition, the hydrogen bonded elements may slide relative to each other due to the disrupted hydrogen bonds and the action of the stress, thus giving the increased deformation as observed in the creep tests.

The deformation of aramid fibers may not only be due to the

slippage between the hydrogen bonded elements but also due to orientation effects. Because molecular chains and therefore crystallites are rod-like structures, tensile loading may cause disoriented crystallites to rotate toward the direction of the fiber axis. Actually, crystallite rotation has been considered to be the origin of the elastic and viscoelastic deformations of aramid fibers under constant moisture conditions [2, 5]. Therefore, it is reasonable to assume that crystallite rotation is also responsible for the creep of aramid fibers under transient moisture conditions. However, the rotation may be accelerated due to the disruption of hydrogen bonds in moisture sorption processes.

These discussions may have several implications. If the creep under transient moisture conditions arises from the breakage of hydrogen bonds, the activation energy of the creep processes should be comparable to the dissociation energy of the hydrogen bonds. Additionally, if the crystallite rotates toward the fiber axis, according to Northolt [2], the fiber elastic compliance will decrease after creep deformation.

4.4.4. Creep Activation Energies of Kevlar® 49 Fibers

To obtain the activation energy of the creep processes, the average values of the logarithmic creep rates were fitted into the

Arrhenius Equation (4.2) by a least-squares curve fitting technique. The Arrhenius plots are shown in Figure 4.11.

$$\bar{b}_i = A_i \, e^{-\frac{E_a^{(i)}}{R\,T}} \qquad (i=1,\ 2) \qquad (4.2)$$

Where

$\bar{b}_i$: The average value of b_i (i=1,2)

R : Gas constant, 1.99 Cal/mole K

T: Temperature in K

$E_a^{(i)}$: Apparent activation energy (i=1,2)

A_i : The value of b_i at "infinite temperature" (i=1,2)

The results obtained are shown as follows:

$$E_a^{(1)} = 1.04 \text{ Kcal/mole};\ A_1 = 929\ \mu\varepsilon/\text{decade} \qquad (4.3a)$$

$$E_a^{(2)} = 4.84 \text{ Kcal/mole};\ A_2 = 556200\ \mu\varepsilon/\text{decade} \qquad (4.3b)$$

The values in (4.3a) were obtained under the constant moisture condition (R.H.= 95%), and those in (4.3b) were obtained under cyclic moisture condition (R.H. between 95% and 5%). The correlation coefficients in the curve fitting are not less than 0.95, indicating good fitting of the data by Arrhenius equations.

The value of $E_a^{(2)}$ may be viewed as the required energy to activate the observed creep process under the cyclic moisture conditions. If the increased creep under transient moisture conditions is due to the breakage of the hydrogen bonds in the fibers, the obtained activation energy should be comparable to the dissociation energy of the hydrogen bonds.

Rosen [31] has reported the values of hydrogen bond dissociation energy as 3 to 7 Kcal/mole. Mark [32] has pointed out that the dissociation energy of hydrogen bonds is 5 Kcal/mole at a action range of about 2.8 Å. Affsprung, Christian, and Worley [33] have measured the dissociation energy of the type of hydrogen bonding -N-H --- O = C < in γ-butyrolactam and found the value to be 3.5 ± 0.4 Kcal/mole. Kulevski and Reinecke [34] have measured the activation energy of the same type of hydrogen bonding in 2-pyridone and found the value to be 4.4 ± 0.4 Kcal/mole. The obtained activation energy for the mechano-sorptive creep is well within the ranges of these reported values, thus supporting the proposed mechanism.

4.4.5. Crystallite Rotation, Fiber Elastic Compliance, and Creep

Theoretically speaking, crystallite rotation could be detected by a technique, such as X-ray scattering, which measures the crystallite

angles. However, because the changes in crystallite angles are usually small (may be on the order of 1°), difficulty in the instrumentation and the limitation on the precision of the conventional X-ray device may not permit accurate detection of the crystallite rotation. However, crystallite angles are related to the fiber elastic compliances [2]. Therefore, the elastic compliance was used for the crystallite rotation studies.

The dependence of fiber elastic compliance on the crystallite angles have been studied by Northolt and Van Aartsen [3] and Northolt [2]. For small and intermediate crystallite angles (e.g. less than 15°) theoretical analysis [3] and experimental studies [2] produced the following equation (re-arranged form from [2]):

$$D_e = d_{33} \, (1 + k_a \langle \sin^2 \theta_o \rangle) \qquad (4.3)$$

Where

θ_o: Crystallite angle relative to the fiber axis (degree)

d_{33}: The elastic compliance of the crystallite parallel to its axis of symmetry, $d_{33} \cong 4.17$ 1/TPa

k_a: A measure of the anisotropy of the crystallites, $k_a \simeq 42$ to 100.

D_e: elastic compcompliance of the PPTA fiber (1/TPa)

The creep strain due to the crystallite rotation may be estimated as [5]:

$$\varepsilon_r = \chi \frac{\cos(\theta_o - \Delta\theta) - \cos\theta_o}{\cos\theta_o} \qquad (4.4)$$

The coefficient χ is applied to account for the possibility that only a fraction of the crystallites along a fibril participates in the rotation. Therefore, numerically, χ should be less than one. The exact value of χ may depend on the stress level, temperature level, and the strength of the involved hydrogen bonds. For a semi-crystalline polymer, it may also depend on the crystallinity of the polymer.

For a small value of $\Delta\theta/\theta_o$, (4.4) can be simplified to

$$\varepsilon_r = k \tan\theta_o \Delta\theta \qquad (4.5)$$

From (4.5), one may see that, for the same amount of change in crystallite angle, $\Delta\theta$, the logarithmic creep rate and creep strain due to crystallite rotation will decrease as θ_o decreases. From Equation (4.3), one may see that this relationship may lead to the conclusion that, under given experimental conditions, the logarithmic creep rate and creep strain will decrease as the fiber elastic compliance decreases.

Theoretical analysis and experimental results suggest that, among PPTA fibers, the relationship in Equation (4.3) does not depend on the difference in fiber types [2, 3]. Therefore, the creep behavior of Kevlar® 29, Kevlar® 49, and Kevlar® 149 have been examined in relation to their initial elastic compliances. These results are shown in Figure 4.12. From these results one may see that the logarithmic creep rates of the PPTA fibers increase as the fiber elastic compliances increase, and, therefore, may indicate the dependence of the creep strain on the initial crystallite angles.

If we assume that d_{33} and k_a in Equation (4.3) do not change during a creep deformation, the following relation may be obtained for small changes in crystallite angles:

$$\Delta\theta = \frac{1 + k_a \sin^2\theta_o}{k_a \sin 2\theta_o} \cdot \frac{\Delta D_e}{D_e^{(i)}} \qquad (4.6)$$

Where

$\Delta\theta$: Change in crystallite angle in a creep process

ΔD_e: Change in elastic compliance in a creep process

$D_e^{(i)}$: Elastic compliance of the fiber before creep deformation

The elastic compliance (D_e) of the tested fiber have been

measured before ($D_e^{(i)}$) and after ($D_e^{(f)}$) mechano-sorptive creep processes. Results from these tests indicated an average reduction of 16.0% in the elastic compliances due to the creep deformation. According to Equation (4.6), the corresponding crystallite angle change was estimated to be about 1°. In the estimation, θ_o and k_a were taken to be 8° and 55 respectively. These values will result in an initial fiber elastic compliance ($D_e^{(i)}$) of 8.61 1/TPa which is the average value from elastic compliance measurements.

The aforementioned discussions may have implications on the recoverability of creep strains. After creep takes place, as indicated above, the crystallite angles will decrease by rotation. If a fraction of the decreased crystallite angle is not reversible after recovery test, irrecoverable creep strain, reduced logarithmic creep rate in a subsequent creep test, and the reduction in fiber elastic compliance may be observed. As indicated in Chapter 3, the logarithmic creep rates tend to decrease after the initial creep and recovery. These results may, therefore, indicate that the rotated crystallite angles are not totally recoverable. Based on this conclusion, one may conjecture that creep strain may not be totally recoverable. In testing Kevlar® 49 fibers under room conditions, Ericksen [5] has measured irrecoverable creep strain after creep loading. Northolt [2] has also identified irreversible crystallite rotation after tensile extension of PPTA fibers.

4.4.6. Stress Effects on the Creep Behavior of Aramid Fibers

As indicated in the experimental results, stress has nonlinear effects on the mechano-sorptive creep of the aramid fibers. Because the numerical prediction of the viscoelastic parameters are not available at present, a quantitative discussion on the nonlinear viscoelastic behavior will not be possible. Nonetheless, some qualitative considerations based on the proposed mechanisms do provide explanation for the observed nonlinearity.

The nonlinear effects may arise, at least partly, from the effects of crystallite orientation and rotation. Stress has two competing effects in the creep of an aramid fiber. Higher load will increase the tendency of the slippage deformation between viscoelastic units. However, as shown by Northolt [2], crystallite angles may decrease instantaneously upon the application of a load. Therefore, higher stress level may result in a greater reduction in crystallite angles, thus resulting in a smaller initial crystallite angle for the subsequent creep. As previously discussed, initial crystallite angle θ_o may affect the logarithmic creep rates. This effect will cause the logarithmic creep rates of aramid fibers a negative deviation from the linear behavior.

4.5. **Conclusions**

The studies presented in this paper may lead to the following conclusions:

4.5.1. Creep under Constant Moisture Conditions

1. Various levels of constant moisture content do not have significant influence on the creep behavior of the tested fibers.

2. Generally speaking, logarithmic creep rate under constant moisture conditions increases slightly with increasing temperatures. The apparent activation energy of the creep process in Kevlar® aramid fibers under constant moisture conditions is about 1 Kcal/mole.

3. At small stresses (e.g. less than 30% of the ultimate strength), the logarithmic creep rate increases linearly with stresses (linear viscoelasticity). However, at larger stresses, the logarithmic creep rate appears to be less dependent on stress level (nonlinear (stiffening) viscoelasticity).

4.5.2 Creep under Cyclic Moisture Conditions

1. Aramid fibers exhibit mechano-sorptive phenomenon, i.e. significant increases in creep under transient moisture conditions.

2. Both the mechano-sorptive logarithmic creep rate and the mechano-sorptive ratio increase as temperature increases. The apparent activation energy of the mechano-sorptive process in Kevlar® aramid fibers is about 4.8 Kcal/mole.

3. The mechano-sorptive logarithmic creep rate increases with increasing stresses. However, the logarithmic creep rates per unit stress and the mechano-sorptive ratio decrease as stress increases, indicating that the mechano-sorptive effect is reduced at higher stress level.

4.5.3. Mechanisms

1. The main microscopic features of aramid fibers are hydrogen bonding and rod-like structures. These characteristics may be the origins of the observed mechano-sorptive phenomenon. Under transient moisture conditions, hydrogen bonds may break temporarily at the location where moisture content changes, and the crystallites may slip relative to each other under the action of stresses, thus causing increase in creep deformation. The obtained activation energy of the mechano-sorptive process is well within the range of the reported values of the hydrogen bond strength.

2. Under transient moisture conditions, the disruption of hydrogen bonds may accelerate the crystallite rotation inside the fiber, thus

resulting in a higher logarithmic creep rate. Changes in fiber elastic compliances and the dependence of logarithmic creep rates on the fiber elastic compliances may provide confirmation for the crystallite rotations.

References

1. J. Z. Wang, D. A. Dillard, et al "Transient Moisture Effects in Fibers and Composite Materials", *J. of Composite Materials*, in Press.
2. M. G. Northolt, *Polymer*, **21**, 1199 (Oct., 1980).
3. M. G. Northolt, and J. J. Van Aartsen, *J. of Polym. Sci.: Polym. Symposium*, **58**, 283 (1977).
4. J. Z. Wang, D. A. Dillard, et al, "Experimental Techniques to Measure Fibers and Composite Response to Transient Moisture Exposure", *1990 Spring Conference on Experimental Mechanics*, Albuquerque, New Mexico, June 4 - 6, 1990.
5. R. H. Ericksen, *Polymer*, **26**, 733 (May 1985). 6. A. R. Bunsell, *J. of Mater. Sci.*, **10**, 1300 (1975).
7. R. H. Ericksen, *Composites*, **26**, 189 (July 1976).
8. J. Cook, A. Howard, N. J. Parrat, and K. D. Potter, "Creep and Static Fatigue of Aromatic Polyamide Fibers", in *Fatigue and Creep of Composite Materials*, Proceedings of the Third RISΦ International Symposium on Metallurgy and Materials Science, 6 - 10 September, 1982, H. Lilholt and R. Talreja, Eds, RISΦ National Laboratory, Roskild, Denmark.
9. W. C. Guenther, *Analysis of Variance*, Englewood Cliffs, N.J., Prentice-Hall (1964).
10. M. E. Roylance and W. W. Houghton, *J. of American Helicopter*

Society, 3 (Oct. 1983).

11. C. Gourdin,"Kevlar and KRP Aging under Various Environments", *Advances in Composite Materials*, A. R. Bunsell et al, Eds., Pergmon Press, Oxford, 497.
12. W. S. Smith, "Environmental Effects on Aramid Composites", in *Proceedings of Society of Plastics Engineers Conference* (Dec. 1979).
13. M. G. Dobb, "High Performance Fibers", in *Handbook of Composites*, Vol. 1: Strong Fibers, Edited by W. Watt, 1985, p. 675.
14. R. J. Morgen, E. T. Monee, W. J. Steele, and S. B. Deutscher, *Polym. Prepr.*, **21**, 264 (Aug. 1980).
15. L. Penn, *J. of Appl. Polym. Sci.*, **23**, 59 (1979).
16. J. J. Pigliacampi, "Organic Fibers", in *Engineered Materials and Handbook,* Volume 1: Composites, ASM International, 1987, p. 54.
17. M. G. Northolt, *Eur. Poly. J.*, **10**, 799 (1974).
18. J. W. Ballou, Paper presented at the Meeting of the American Chemical Society , Division of Polymer Chemistry, New York, N.Y., April 1976, in *Polym. Prepr.* **17**, 75 (1976).
19. M. Panar, P. Avarkian, R. C. Blume, K. H. Gardner, T. D. Gierke, and H. H. Yang, *J. of Polym. Sci.: Polym. Phys. Ed.,* **21**, 1955 (1983).
20. R. Hagege, M. Jarrin, and M. Sotton, *J. of Microscopy*, **115**, 65 (Jan. 1979).
21. L-S Li, L. F. Allard, and W. C. Bigelow, *J. of Macromol. Sci.* -

Physics, **B22 (2)**, 269 (1983).

22. M. G. Dobb, D. J. Johnson, and B. P. Saville, *Phil. Trans. Roy. Soc.*, **A294**, 483 (1979).

23. W. S. Smith, "Environmental Effects on Aramid Composites", *Du Pont Technical Paper, E-53160,* December, 1979, E. I. Du Pont De Nemours & Co. (Inc.), Textile Fibers Department, Kevlar Special Products, Centre Road Building, Wilmington, DE 19898

24. J. M. Augl, "Moisture Sorption and Diffusion in Kevlar 49 Aramid Fiber", *Report NSWC TR 79-51,* March 30, 1979, Naval Surface Weapons Center, Dahlgren, Virginia 22448, or Silver Spring, Maryland 20910.

25. J. E. Fergusson, *Inorganic Chemistry and the Earth —— Chemical Resources, Their Extraction, Use and Environmental Impact*, Pergmon International Library, 1982, p. 257.

26. E. G. Chatzi, H. Ishida, and J. L. Koenig, *Applied Spectroscopy,* **40(6)**, 847 (1986).

27. K. Haragushi, T. Kajiyama, and M. Takayanagi, *J. of Applied Polym. Sci.*, **23**, 915 (1979).

28. R. E. Allard, and D. K. Roylance, *J. of Mater. Sci.*, **18**, 652 (1983). 29. S. Y. Lo, H. T. Hahn, and T. T. Chiao, "Swelling of KEVLAR 49/epoxy and S2-glass/epoxy Composites", in *Progress in Science and Engineering of Composites*, T. Hayashi, K. Kawata, and S. Umekawa, Eds., ICCM-IV, Tokyo, (1982).

30. S. N. Vinogradov, and R. H. Linnell, in *Hydrogen Bonding*, p. 12,

Van Nostrand Reinhold Company, 450 West 33rd Str. New York, N.Y. 10001, (1971).

31. S. L. Rosen, *Fundamental Principle of Polymeric Materials*, Barnes and Nobel, New York, 1971

32. H. F. Mark, in *Polymer Science and Materials*, A. V. Tobolsky and H. F. Mark, Eds., Wiley, Interscience, New York, 1971.

33: H. E. Affsprung, S. D. Christian, and J. D. Worley, Spectrochim. *Acta* **20**, 1415 (1964).

34: N. Kulevski and W. Reineke, *J. Phys. Chem.* **72**, 3339 (1968).

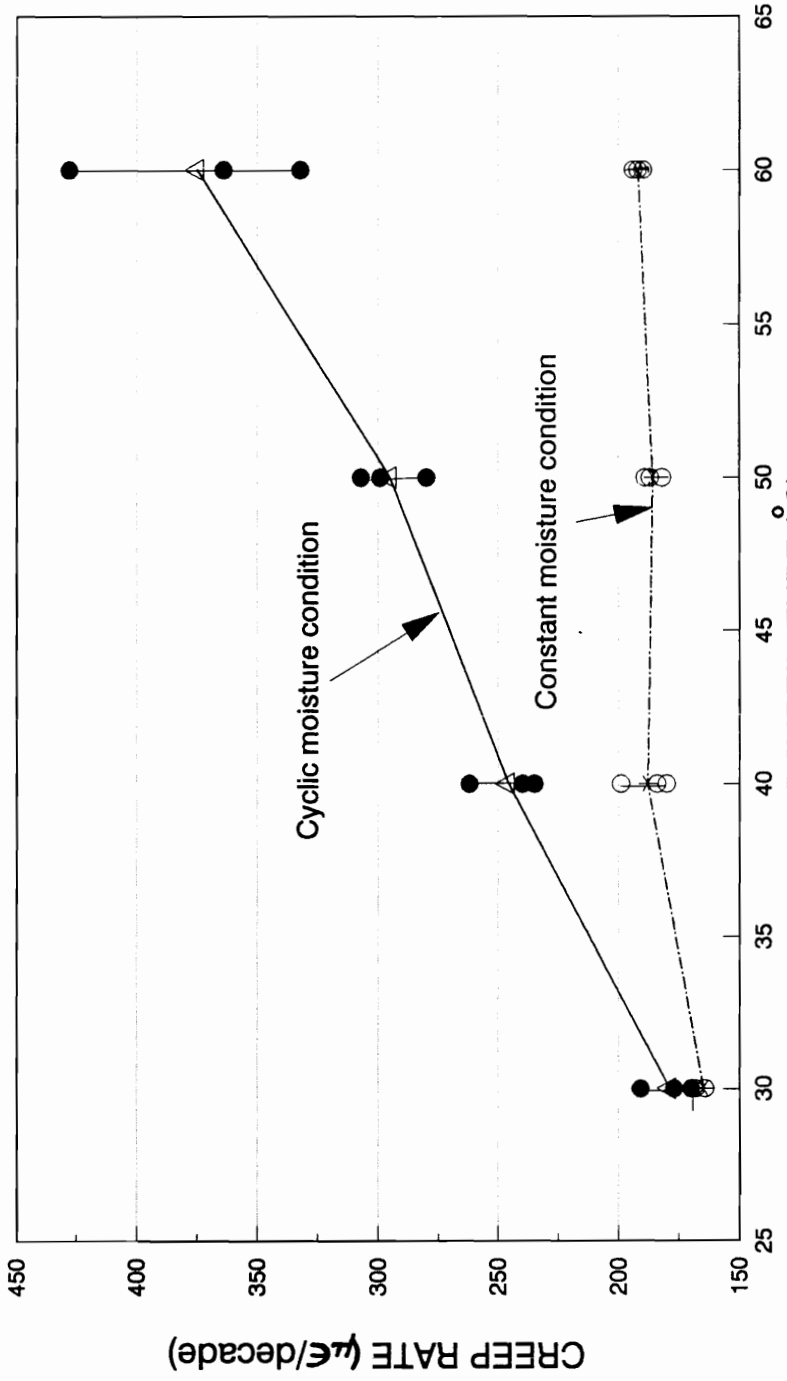

Fig. 4.1 Creep rates of Kevlar 49 fibers at different temperatures

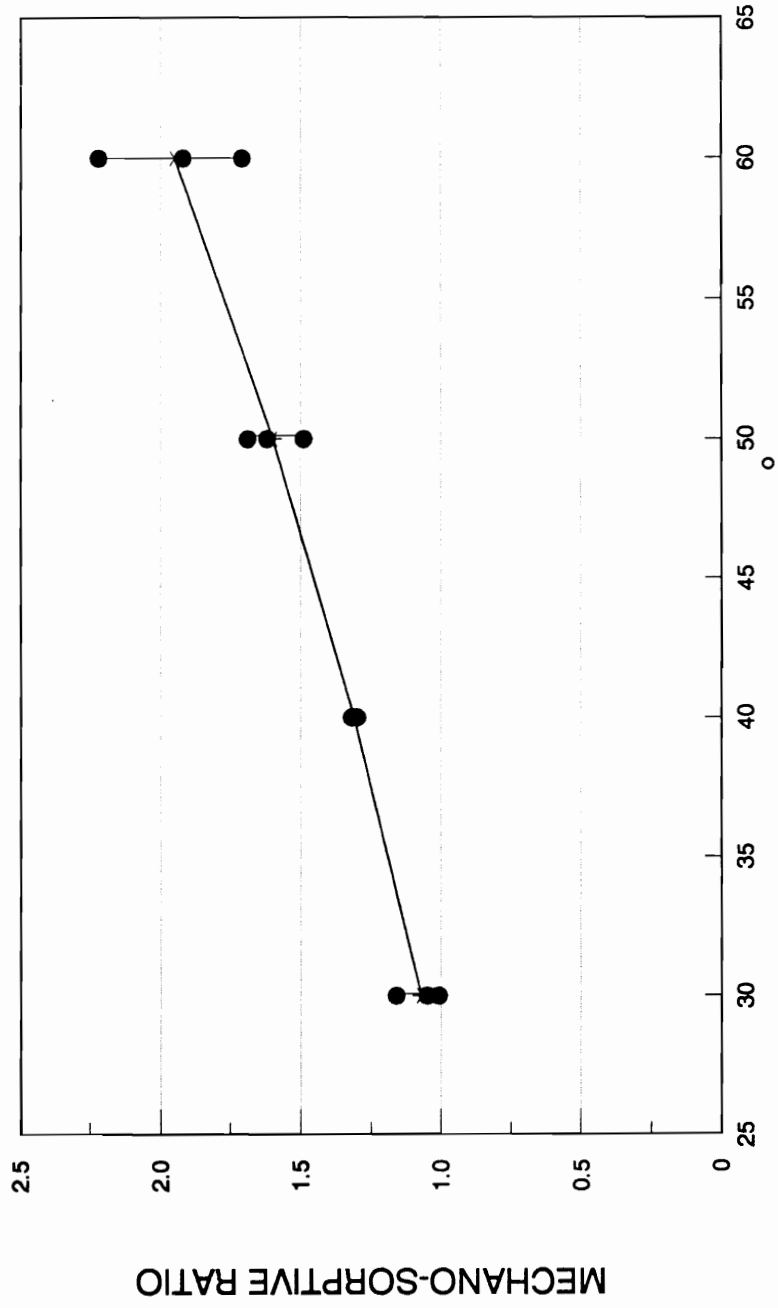

Fig. 4.2 Mechano-sorptive ratio vs. temperature

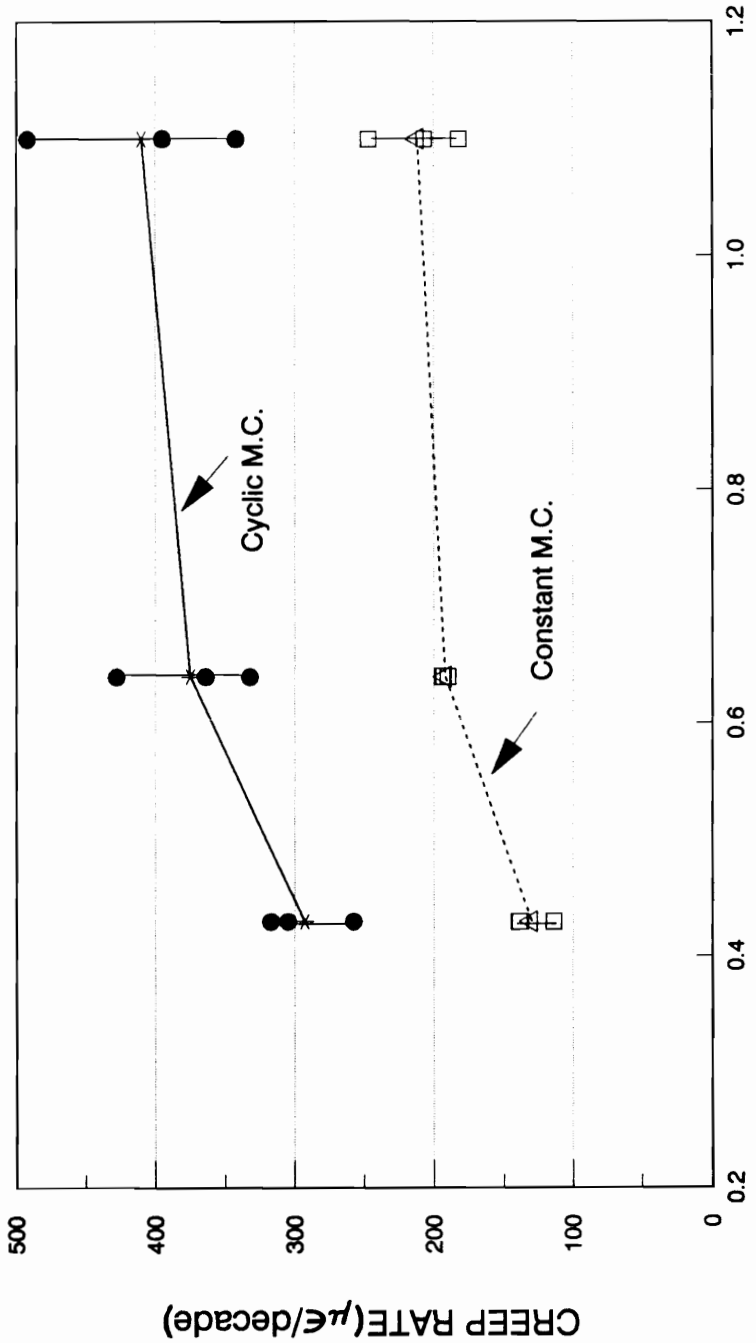

Fig. 4.3. Creep rates vs. stress

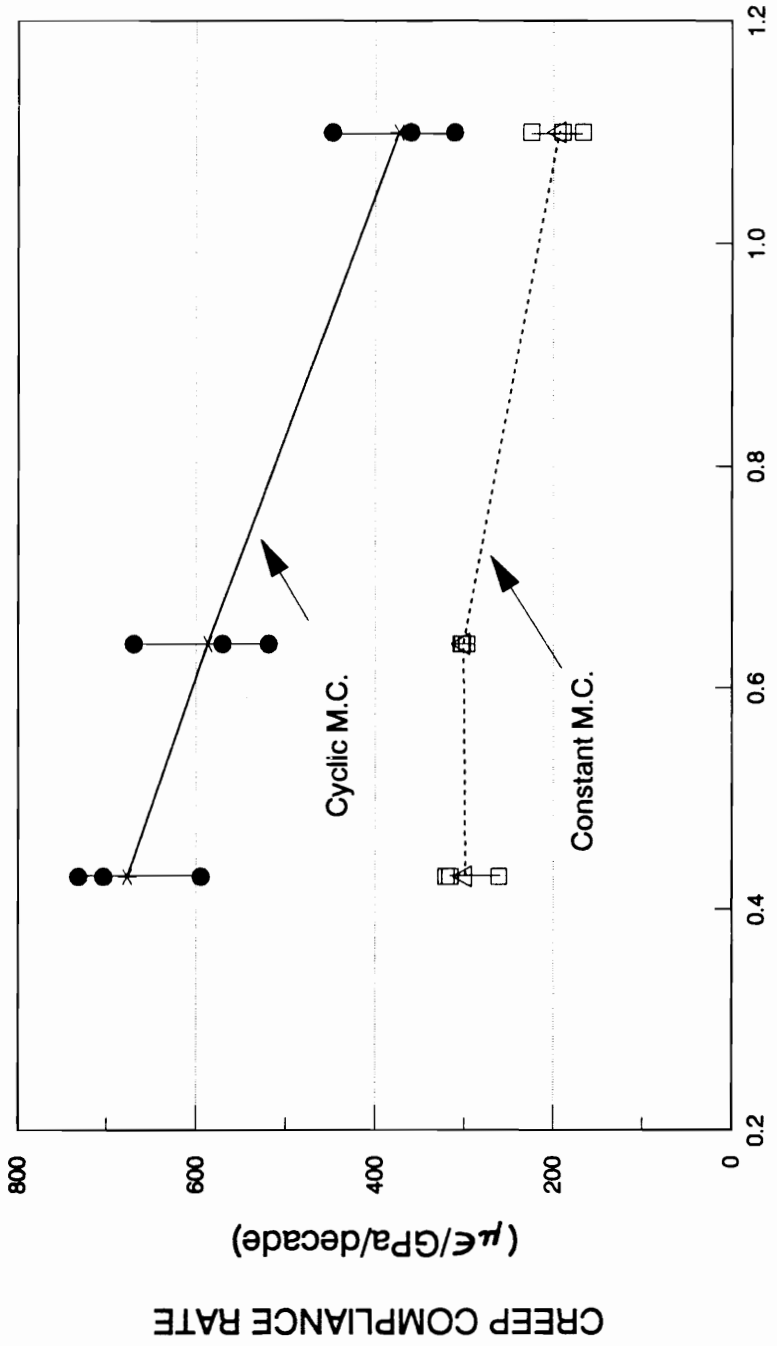

Fig. 4.4. Creep compliance rate vs. stress

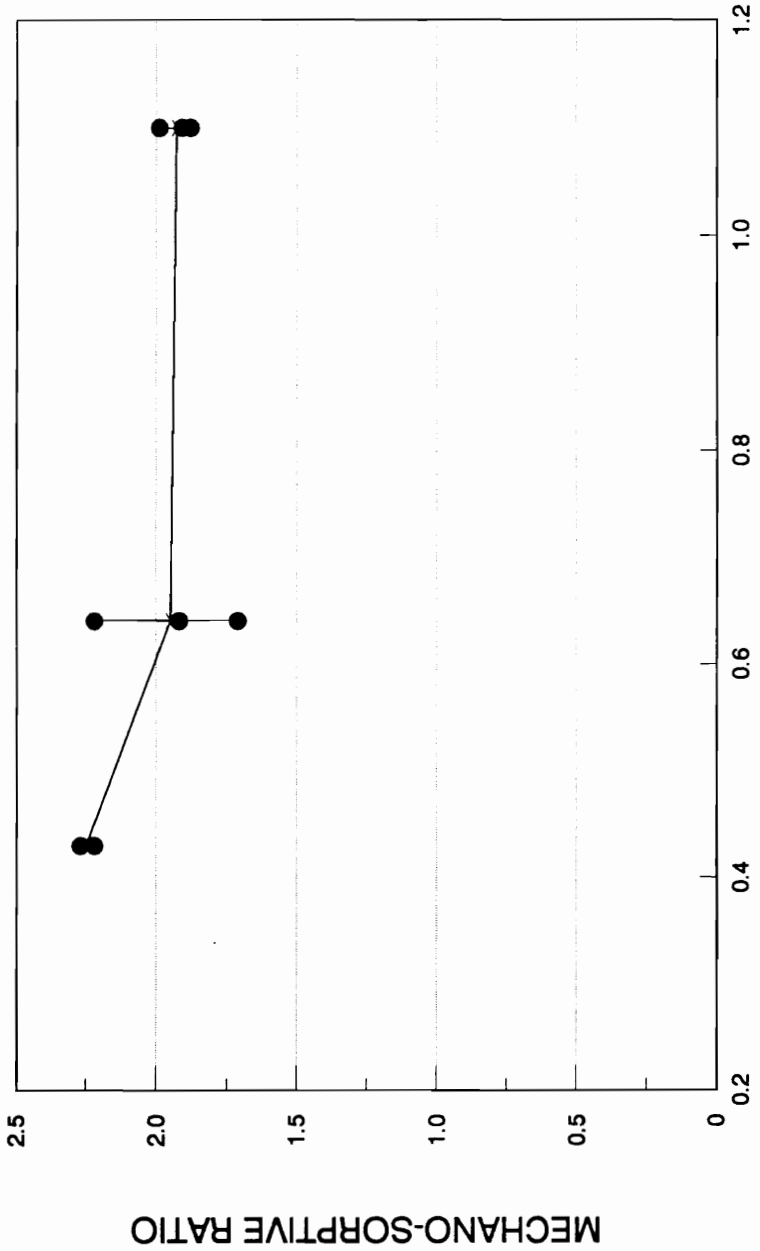

Fig. 4.5. Mechano-sorptive ratio vs. stress

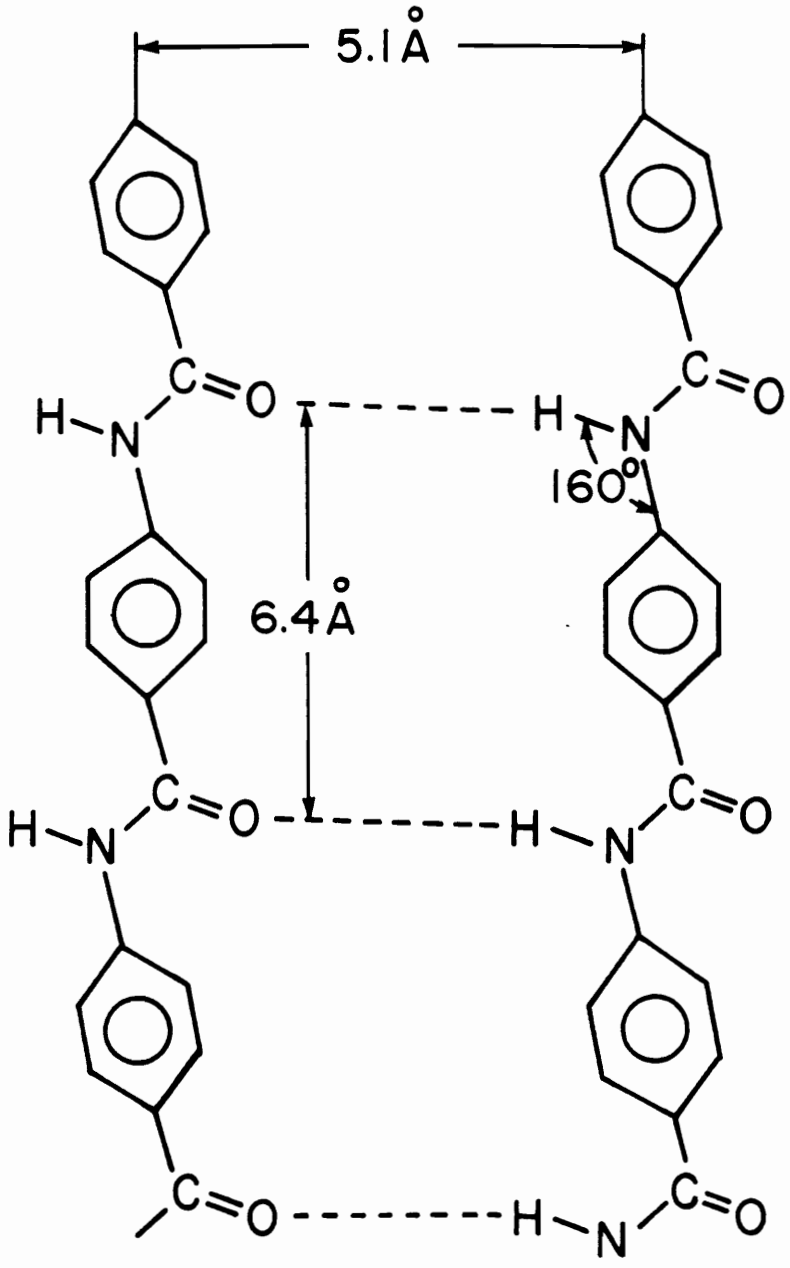

Fig. 4.6 The structure of PPTA molecules and their hydrogen bonding [16]

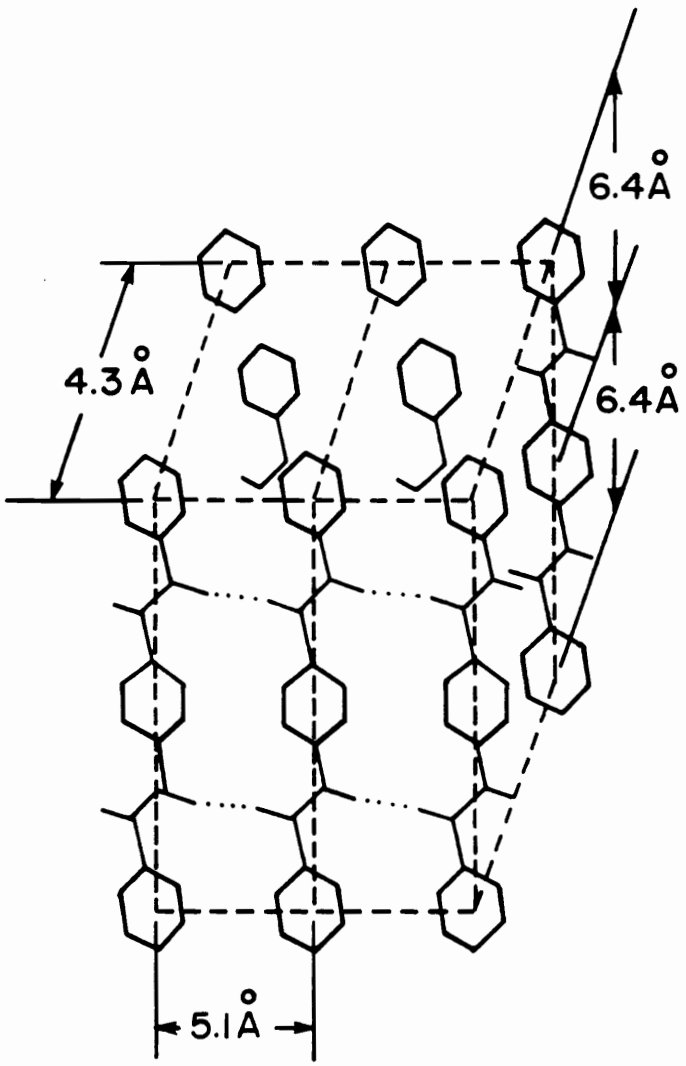

Fig. 4.7 A unit crystal cell of PPTA fibers [13, 15, 17]

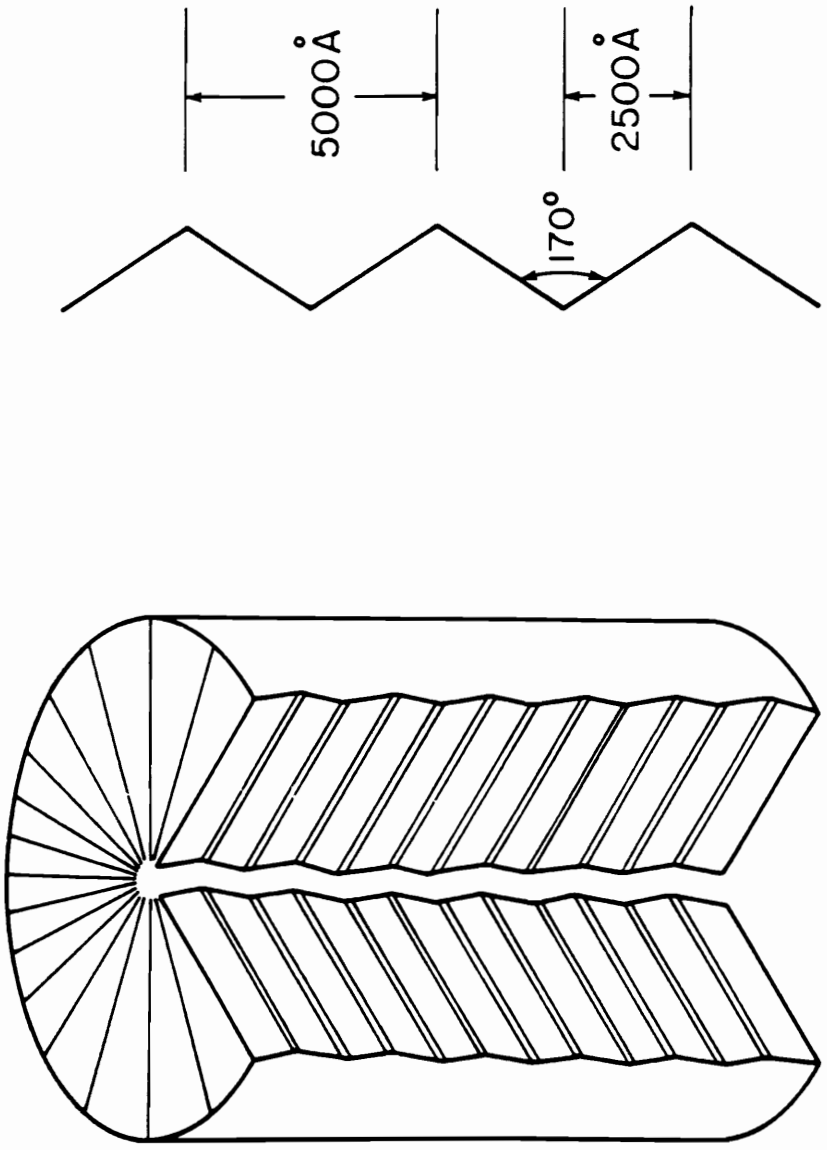

Fig. 4.8 Pleated structure of PPTA fibers [13, 19, 22]

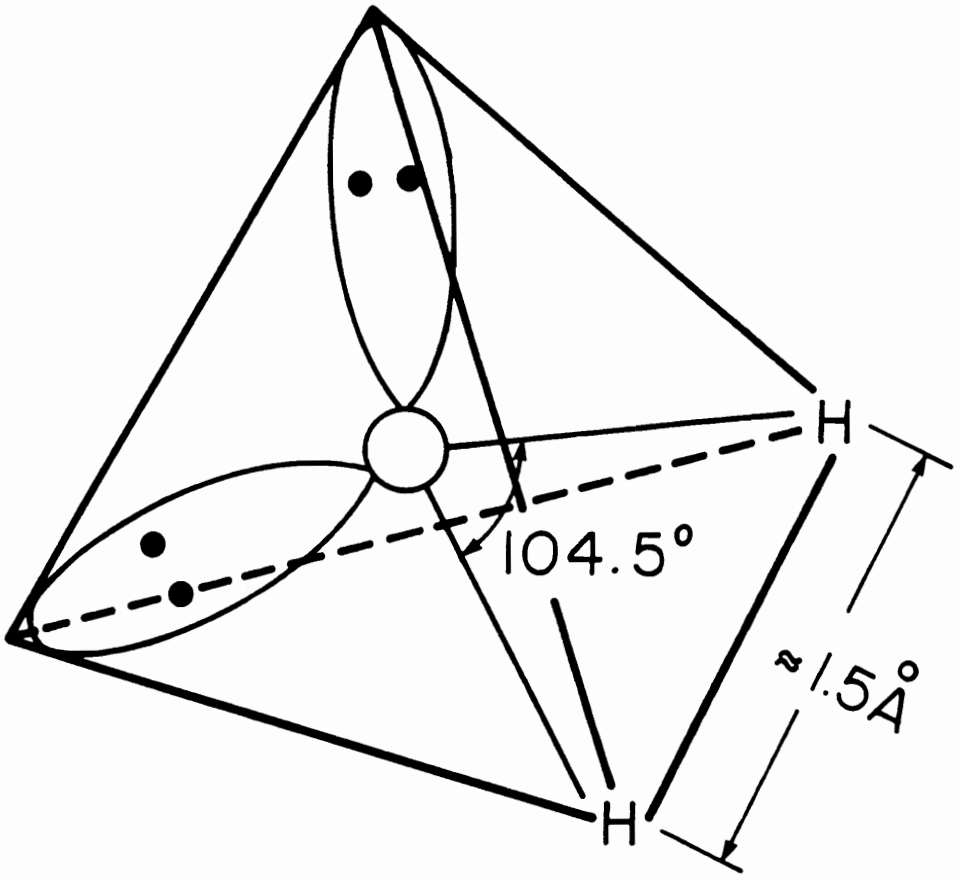

Fig. 4.9 The structure and dimension of a water molecule [25]

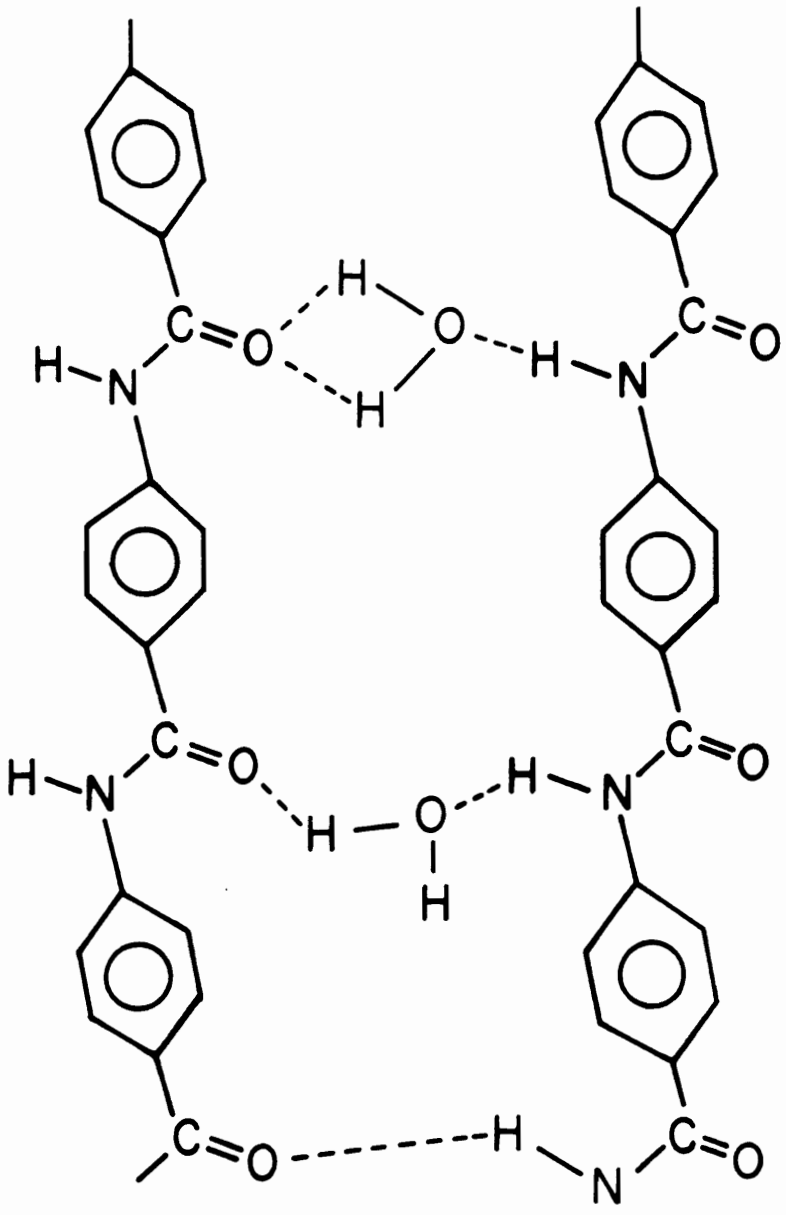

Fig. 4.10 Bonding of water molecules between crystallites

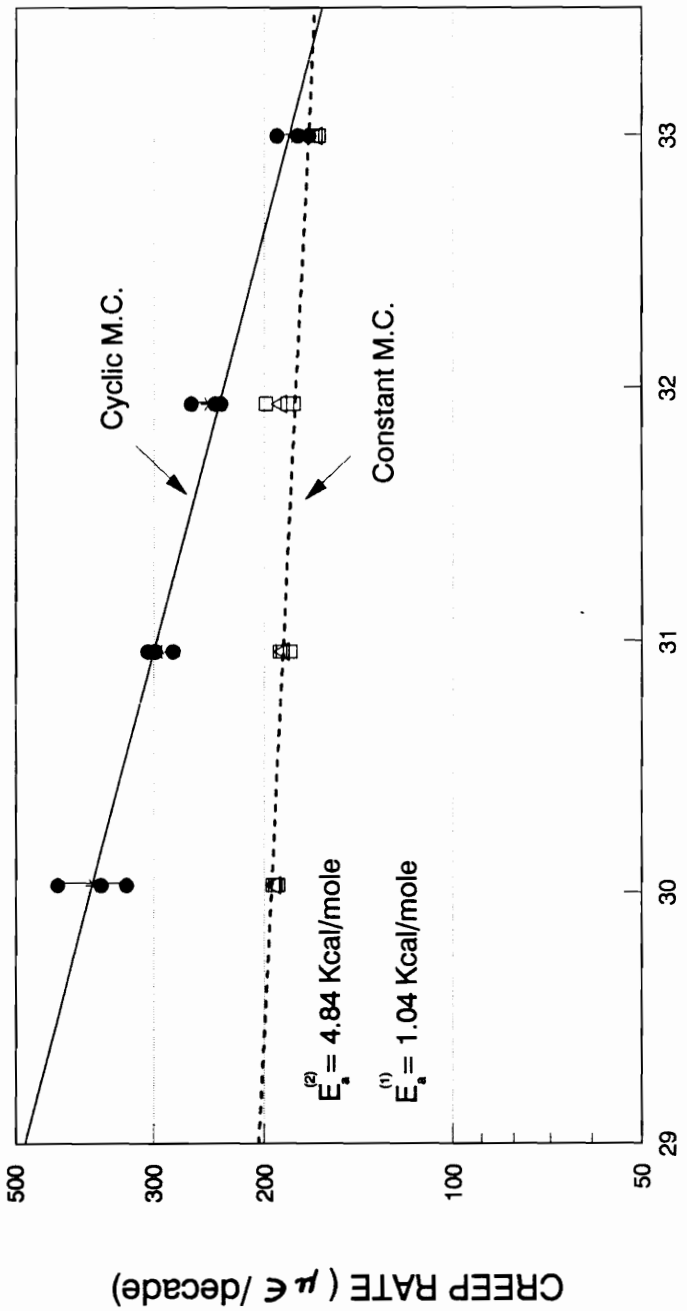

Fig. 4.11. Arrhenius plot of creep rates

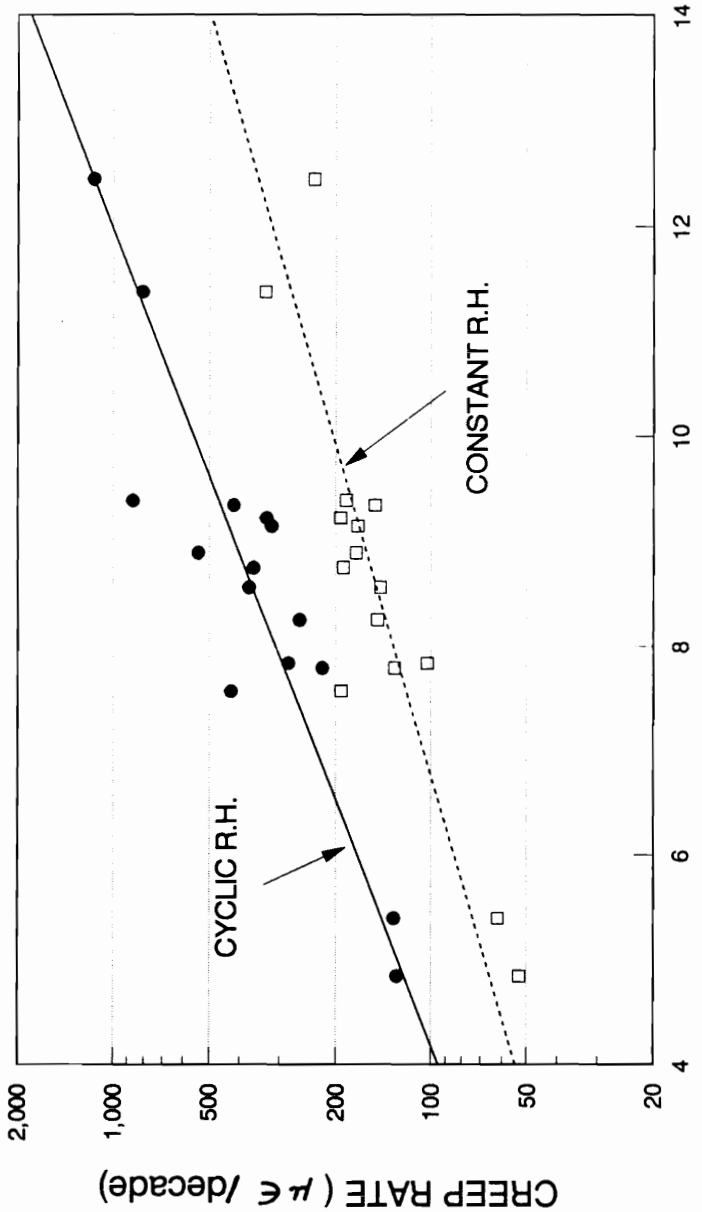

Fig. 4.12. Creep rates vs. fiber elastic compliances

Chapter 5

SUMMARY AND RECOMMENDATIONS

This interdisciplinary study investigated the transient moisture effects in Kevlar® 49/7714 epoxy composite coupons, Kevlar cloth, Kevlar® fibers, Technora® fibers, Nylon 6,6, and PMMA fibers. The effects of transient moisture conditions were compared with those of constant moisture conditions. On the Kevlar® 49/7714 epoxy composite coupons, the tensile creep, bending creep, and dynamic mechanical properties were tested. By utilizing a self designed fiber creep test fixture, the tensile creep behavior of single fibers under transient and constant moisture conditions were studied. To minimize data scattering due to fiber variabilities, behavior under the two kinds of moisture conditions were tested on the same fiber to draw more reliable conclusions. In an effort to deepen the understanding of the transient moisture effects, tensile creep tests on single Kevlar® 49 fibers were also conducted under different temperature and stress levels, and under different moisture conditions. The possible mechanisms of hydrogen bonding and crystallite rotations were discussed.

Through these efforts, it has been concluded that even though different constant moisture conditions might not have substantially

different effects on the creep behavior of aramid fibers, the transient moisture conditions had higher effects on the creep behavior than any constant moisture conditions. The mechano-sorptive phenomenon may be very well due to the breakage and remaking of hydrogen bonds and the resulting acceleration of crystallite rotations during a transient moisture process. These proposed mechanisms have been supported by the obtained creep activation energy and the relationship between creep process and the fiber elastic compliance. In testing the creep behavior of Nylon 6,6 and PMMA fibers under transient moisture conditions, however, no appreciable mechano-sorptive phenomenon was observed. These results may be also explained through the proposed mechanisms.

The research effort produced not only the above mentioned tangible results, but also new research opportunities. Therefore, we recommend further research efforts in the following areas:

1). Conduct tests using different solvents to probe into the proposed hydrogen bonding mechanism. Specific solvents may be used are: tetrahydrofuran (THF, C_4H_8O), cyclohexanone ($C_6H_{10}O$), chlorobenzene (C_6H_5Cl) , and cyclohexane (C_6H_{12}). Their polarity (μ) and boiling point (Bp) are listed as follows (data are from CRC Handbook of Chemistry and Physics, 67th Edition, 1986 - 1987, CRC Press, Inc. pp. E58-E60).

Tetrahydrofuran:	μ = 1.63D,	Bp = 67°C
Cyclohexanone:	——— ,	Bp = 155.6°C
Chlorobenzene:	μ = 1.69D,	Bp = 132°C
Cyclohexane:	——— ,	Bp = 80.7°C

Tetrahydrofuran and cyclohexanone contain oxygen capable of forming hydrogen bonds. However, compared to water (μ = 1.85D), they are slightly less polar. Therefore they should produce less mechano-sorptive phenomenon when used to test the creep behavior of aramid fibers. Chlorobenzene (polar) and cyclohexane (nonpolar) do not possess hydrogen bond forming abilities, therefore, the mechano-sorptive phenomenon should disappear when these solvents are used. As the molecular size increases, the diffusion ability of the solvents will be hindered. Because the molecules of these solvents are much bigger than the water molecule, one needs to take the size factor into account in assessing the test results.

2). Make measurements of the crystallite angle changes during the creep process under transient moisture conditions. In making these measurements, wide angle X-ray scattering technique may be used. The measurement can provide direct correlation between the crystallite angle reduction and the creep process, thus probing into the proposed crystallite angle rotation mechanism. From preliminary measurements, it has been found that the main difficulties encountered are the resolution of the equipment and the alignment of the fibers in a yarn.

From estimation as indicated in Chapter 4, the crystallite angle change in a creep process for several days may be about 1^{o}. This angle change may be at the sensitivity limit of a normal X-ray equipment. Another limitation comes from the intensity of the X-ray source. Because the intensity of the X-ray source is not strong enough to detect the crystallite angles in a single fiber, a bundle of fibers may be needed to make the measurement. Therefore, any misalignment of the fibers will introduce extra experimental error into the results.

3). Investigate the effect of salt contaminants in the fiber on the mechano-sorptive behavior. Even though the results from Kevlar® fibers and Technora® fibers may rule out this possibility. However, more dedicated effort may be needed to confirm the conclusion. It has been suggested that cellulose acetate and/or polyurethane fibers with and without Li_2SO_4 or Na_2SO_4 may be used to investigate the effects of the salt contaminants on the creep behavior under transient moisture conditions.

4). Test the recoverability of the fibers under transient moisture conditions. Due to the limitation of the single fiber creep fixture, the recoverability of the fiber after a mechano-sorptive creep process could not be directly tested because the total weight of the core of the LVDT and the connecting rod is comparable to the weight of the creep load. To circumvent this difficulty, a bundle of fiber may be tested to allow higher creep load levels.

5). Test the delayed failure behavior of the fibers under transient moisture conditions and constant moisture conditions. In the mechano-sorptive tests, because the creep deformation can be accelerated, it is important to ascertain whether the effect of the acceleration in creep is to reduce the delayed failure life as compared to constant moisture conditions. Because the comparison needs to be made on different fibers, it is necessary to conduct a number of tests to draw reliable statistical conclusions.

Appendix

CREEP AT A CONSTANT MOISTURE CONDITION AFTER MECHANO-SORPTIVE PROCESS

A test was performed to examine the creep behavior after mechano-sorptive creep. The test was conducted at 50 °C and 0.64 GPa (32% of static strength). The relative humidity profile is shown in Figure A.1 and the results are shown in Figure A.2. The creep rates obtained during the three moisture stages are as follows:

$$b_1 = 187.4\ \mu\varepsilon/\text{decade}$$

$$b_2 = 279.6\ \mu\varepsilon/\text{decade}$$

$$b_3 = 82.9\ \mu\varepsilon/\text{decade}$$

Where: b_1 : Creep rate at the initial moisture stage (R.H. = 95%)

b_2 : Creep rate at the second moisture stage (Cyclic R.H. between 5% and 95%)

b_3 : Creep rate at the third moisture stage (R.H. = 95%)

As shown in the results, at the constant moisture condition after mechano-sorptive creep, the creep rate is reduced as compared to the creep during the initial constant moisture stage moisture condition. The reduction in creep rate after mechano-sorptive creep may be due to effect of the more oriented crystallite angles in the fiber.

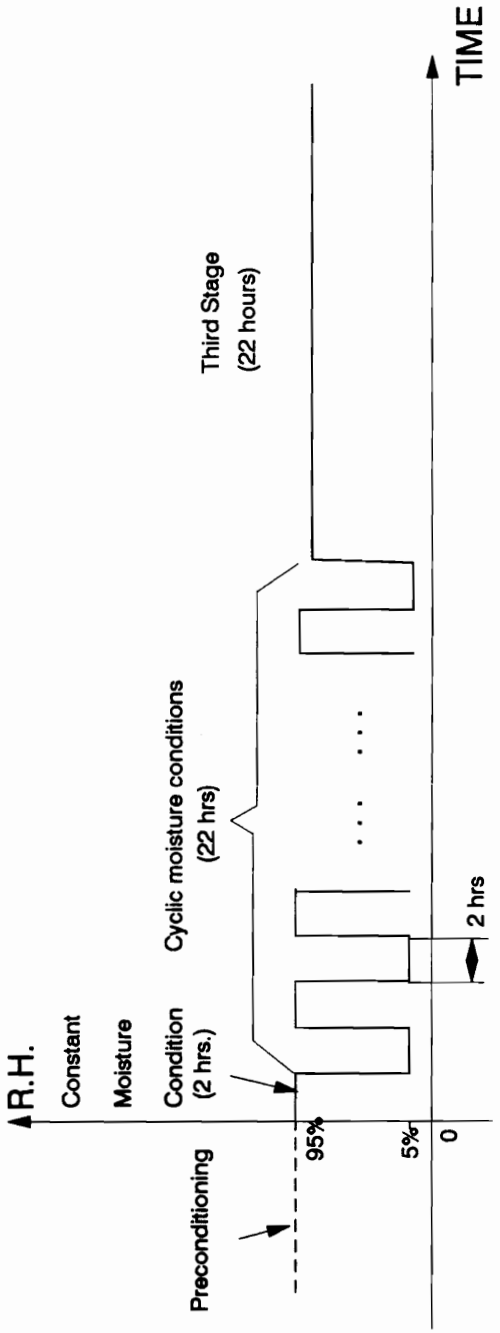

Fig. A.1 Relative humidity profile in the fiber creep test

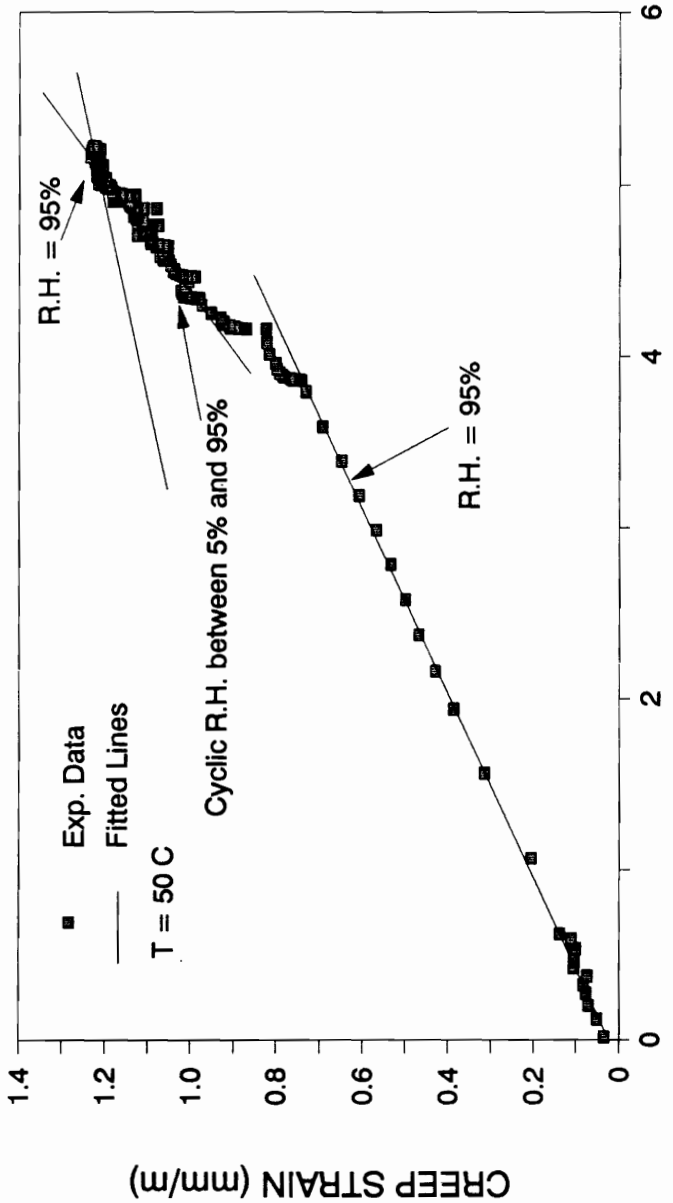

Fig. A.2 Creep of Kevlar 49 fiber

VITA

John Z. Wang was born in Lingyuan, Liaoning on July 1, 1957. He was admitted to the Northeast University of Technology in Shenyang, Liaoning in 1977, where he received his B.S. and M.S. degrees in Mechanical Engineering in 1981 and 1984, respectively. After the graduation, he taught at the Northeast University of Technology for one year. In September 1985, he came to Blacksburg, Virginia to attend Virginia Polytechnic Institute and State University to pursue his PhD. education in the Department of Engineering Science and Mechanics.