

/AGE DETERMINATION OF CELLULOSIC FIBERS FROM CREEP  
MEASUREMENTS/

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## INTRODUCTION

The physical age of a material is viewed as the time elapsed since the glass transition temperature of the material was last exceeded. Looking at the glass transition as the upper temperature limit, the next lowest transition,  $T_b$ , may be viewed as the lower temperature limit for physical aging. Thus, physical aging is a function of the glassy state only and is not a direct function of chemical structure. Physical aging is characterized as a slowly occurring process, where an attempt is made to establish thermodynamic equilibrium through a decrease in free volume and molecular mobility of the amorphous polymer chains. This free volume concept states that transport mobility of particles in a closely packed system primarily depends on the degree of packing, or in other terms, on the free volume.

Physical aging is thought to result in the formation of domains possessing greater order and more effective cross-links within the amorphous matrix and a higher degree of packing. A continual change in the structure and properties of materials results with increasing aging times and, consequently mechanical properties may be used as a gauge for the measurement of physical aging. Physical aging like most physical phenomena is temperature dependent, leading to varying aging rates at different temperatures.

While numerous mechanical properties are altered during aging and could be used as a measure of

physical aging, we choose to employ tensile creep, defined as "delayed elasticity", as the basis for measurement in this research. Differences in creep measurements taken before and after erasure of physical aging of the sample, form the basis for computing the age of our samples

In considering creep measurements as a measure of aging, one finds that it is not a simple process and it is affected by many factors. A rather complex interrelationship exists between the strain rate, strain temperature along with its relation to  $T_g$ , the applied stress field with effects of hydrostatic pressure such as from humidity, thermal history, loading history as described by Boltzmann's Superposition Principle and molecular features of the fiber samples. For reasons of simplicity, many of the above factors have been assumed to be constant through the course of experimentation.

The purpose of this study was to develop a micro-technique applicable to creep measurements of short lengths of single fibers and to use this technique to study physical aging of fibers in the cellulosic generic class. This involved constructing a suitable apparatus and measuring the aging rate of six types of cellulosic fibers at three temperatures believed to be within their aging temperature limits. In addition, measurements of density and birefringence of these fibers allowed the effects of crystallinity and orientation of the fiber samples to be estimated. This data



was used to evaluate the possibility of estimating the physical age of textile fibers of unknown origin having chronological ages spanning from a few days to a few thousand years.

Polymeric materials whose tensile creep has been studied as a function of aging are mostly unoriented and amorphous. Most textile materials, on the other hand are oriented and semicrystalline. Struik (1) hypothesizes that orientation and crystals cause a local decrease in the segmental mobility of the non-crystalline matrix and have the effect of broadening the glass transition temperature range. This leads to the conclusion that the presence of crystallites will modify the temperature range but not the rate of aging. However, the influence of crystallinity on physical aging of textile fibers has not been studied enough to test the above hypothesis. This study provides an opportunity to examine this more closely.

The immediate practical application of this study is in dating textiles fiber of unknown chronological age. A single fiber aging technique would be applicable to most textiles and may offer the most practical way to estimate the chronological age of textiles of limited sample size such as many historic textiles, especially when they have been subjected to relatively constant conditions of temperature and humidity over long periods of time. These conditions may be found in tombs, burials or sunken ships. Since the glass transition temperature of cellulosic fibers

are estimated to be well above room temperature and secondary transitions near room temperature (2), the use of our technique to estimate the date of cellulosic textiles in many applications would seem to be reasonable. Even though previous research (1) lead to the expectation of linear aging rates over long aging times, a non-linear, although useful function was found in this study.

#### Assumptions and Limitations

In determining the physical age of fibers and claiming their chronological age to be the same, it must be assumed that the fibers have been subjected to a fairly constant temperature between  $T_g$  and  $T_b$  and no other conditions have erased their physical aging. Small molecules are known to change thermal transition temperatures by plasticization and the fiber mechanical properties are changed accordingly. Consequently, one would expect small molecules to affect physical aging. For example, water in the atmosphere may act as a plasticizer for hydrophilic polymers, lower the  $T_g$  and thus change their aging behavior. These effects may occur in a variety of places, including during laundering, weathering, storage, or use. Since the presence of plasticizers effectively lowers the glass transition temperature of polymers, humidity variations during aging of cellulosic materials constitute a possible error. In this study, we have not considered humidity as a variable as all tests conducted at the various reference temperatures were subjected to approximately the same humidity level.

Temperature variations during the period of aging occurs in almost all practical circumstances and this would be expected to affect the rate of aging. Such variations were bound to occur in this study when working with samples between their aging and testing periods. However, the magnitude of this effect may be estimated from theoretical considerations along with a few measurements of the temperature dependence of aging.

Amorphous polymers are known to exhibit damping transitions that occur even at temperatures above their  $T_g$ . By subjecting the fiber samples to their glass transition temperature, we assume that the transitions occurring above the  $T_g$  do not affect physical aging. In reality, the effect of these transitions on aging is not known.

It is assumed there is no change in the cross-section of the fiber samples during creep measurements and creep erasure. By assuming the fiber cross-sectional area remains constant, the need to account for creep compliance was averted and creep was measured simply as a function of strain adjusted for initial length. This was thought to be a reasonable procedure since the magnitudes of fiber strain used in this study were low and a constant load was used for a complete set of fiber samples at all temperatures.

In addition, shrinkage was eliminated by fixing the ends of each fiber specimen during creep erasure. This was done to minimize unwanted structural changes accompanying shrinkage.

The existence of mechanically enhanced aging also serves as a limitation to this study. Mechanical enhancement of aging occurs when the application of tension on the fiber serves to accelerate the rate of aging (3). This phenomenon is a potential source of experimental error in age determinations. In this study, however, stress levels and creep time are relatively negligible with respect to the aging times and this problem is assumed not to introduce a significant error.

Another limitation arises since each fiber sample varies structurally in innumerable ways. This restricts the interpretation of creep data in terms of the fiber structure. Variability in fiber structure has been minimized to practical limits by using the same sample at any reference temperature in most cases while testing for various aging times.

## REVIEW OF LITERATURE

Physical aging in glassy polymers has long been a subject of research interest. Physical aging refers to the the process occurring when quenched polymeric glasses gradually approach an equilibrium state from a non-equilibrium state with concurrent loss of volume and enthalpy. The aging process is presumed to occur by an ordering of disordered domains (4,5). Physical aging has been studied in terms of a decrease in free volume, heat content, molecular mobility as well as with azochromophoric labels (1,6).

Various views of physical aging on the molecular level have been proposed. With increasing aging times, alpha processes (fast kinetic process) decreases in the glassy state with approximately the same time scale as enthalpy relaxation (6). This phenomenon is related to the fraction of high segmental mobility in regions of high free volume produced by thermal fluctuations. In his molecular theory of aging based on rotation around short segments of the polymer main chain, Robertson (7) suggested that the initial fast volume relaxation is due to molecular rearrangements in regions of particularly high free volume produced by these thermal fluctuations. It also has been hypothesized that the lower temperature limit of aging,  $T_b$ , is associated with the motions within the polymer chains and the upper limit,  $T_g$ , is associated with relaxation of the whole polymer network (8). Struik (9) has explained the glassy state

as a non-equilibrium state engaged in many dynamic processes. He claims the thermodynamic and kinetic transformations associated with physical aging occur because disorder in the non-crystalline matrix of a polymer is being reduced. These changes are presumed not to result from the crystalline section of the polymer and it has been experimentally demonstrated that the crystalline section remains unchanged during physical aging (10).

Struik (1) has clearly defined  $T_g$  and  $T_b$  as the practical temperature limits through which aging occurs. These two transition temperatures have been carefully determined for many polymeric samples. Chapman (11) has demonstrated the occurrence of physical aging below  $T_g$ , persistence of aging over long periods of time and aging temperature dependence. In the case of textile fibers, the  $T_g$  and  $T_b$  transitions span a wide range of temperatures. For cellulose in particular,  $T_g$  is thought to occur around  $230^\circ\text{C}$  whereas  $T_b$  is thought to occur around  $25^\circ\text{C}$  (2).

Changes in properties of a material during aging form the crux of many studies. Changes in thermal and mechanical properties are the most commonly used parameters in studying aging, since they are easily detectable. Changes in creep behavior with increasing aging times of polypropylene and sulfonated poly-styrene samples have been studied (10,12). Struik has studied the effect of physical aging on torsional and tensile creep compliance of totally amorphous materials (1). Chapman (11) accounts for the shifting of stress

relaxation curves of keratin fibers aged for different times in a way analogous to shifting of creep curves observed by other researchers (1,10,12).

Thermal analysis has been used to study physical aging (13) and thermal properties have been found to be affected by aging.

Any kind of mechanical treatment has been found to accelerate the rate of physical aging (3). It has been concluded that aging is accelerated in both tension and compression, enhanced aging varies with the square of the stress in a creep test and the square of strain in relaxation tests, and enhanced aging persists all the way to zero stress or strain. The effect on aging of stress level during creep measurements have been specifically studied (1). A shift in the logarithmic creep times have been shown to result from stress differences. By keeping the stress level low and nearly constant for all fiber samples, variations due to this change may be reduced to an insignificant level.

In creep tests identified as short time tests, creep times are negligible compared to their corresponding aging times and properties determined by such studies are called momentary properties. These tests have an advantage over long-term tests in that the behavior of the material is not affected by treatment.

## AGING IS REVERSIBLE

Struik (1) has done extensive research with regard to physical aging of totally amorphous polymers. He clearly demonstrated that thermoreversibility of aging occurs simply by heating the sample to above  $T_g$  where thermal equilibrium is reached and the sample has "forgotten" its history and any previous aging it may have undergone below its  $T_g$ . In other words, the upper temperature limit of aging is realized at the  $T_g$  and erasure of previous aging occurs at temperatures above  $T_g$ . In demonstrating physical aging in keratin fibers (14), researchers have reversed aging by simply immersing the sample in water at room temperature for a few minutes since keratin becomes heavily plasticized by water and the  $T_g$  drops to below room temperature. We adopted a similar methodology in this study. However, the temperature to which our wetted samples was to be subjected to erase aging was determined from calculations of plasticizer based glass transition temperature depression using the theories of Wortmann and Fuzek (15,16).

## AGING OCCURS IN SIMILAR WAYS

Aging has been defined as a phenomenon universally occurring in the glassy state irrespective of the chemical nature of polymers. Struik has demonstrated aging to occur in a similar way in a large variety of amorphous polymers, with aging rates approximately the same for all samples at temperatures between  $T_g$  and  $T_b$ .



Based on short time tests of samples with aging times of three years, Struik has established the persistence of aging through shifts in creep curves for samples aged for different periods. Also, he has found the rate of aging to be constant for many polymers over long periods of aging times at any one aging temperature. This finding, however, was contradicted by the results of this study.

#### TEMPERATURE DEPENDENCE OF AGING

The general temperature dependence of physical aging is illustrated in Figure 1 and may be summarized as follows: At 0°K, aging does not occur since molecular motion does not exist. With increasing temperature, the rate of aging presumably slowly increases as molecular motions slowly increase. When  $T_b$  is reached, molecular motions that are effective in reducing free volume are induced so the rate of aging increases substantially. Since molecular mobility remains approximately constant from  $T_b$  to  $T_g$ , the rate of aging remains approximately constant. Major segmental motions allowing thermal equilibrium to be reached are induced at  $T_g$  so the rate of aging quickly decreases to zero as  $T_g$  is attained.

Struik (1) performed a limited number of creep measurements on semicrystalline polymers. The physical aging behavior observed was identical to that of totally amorphous polymers, in that a linear relationship between  $\log(\text{aging time})$  and  $\log(\text{shift})$  was found. This work was viewed as experimental verification of his hypothetical expectation

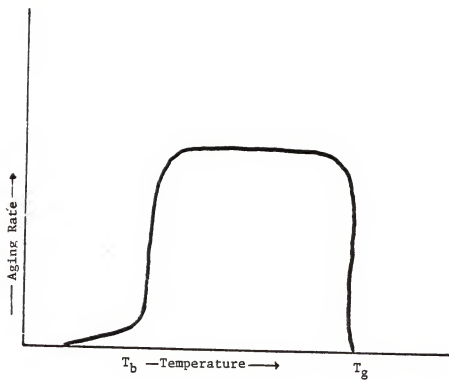


Figure 1. Temperature Dependence of Aging

that the presence of crystallinity will not modify the rate of aging. Consequently, results obtained from studying totally amorphous polymers were generalized to include all polymer materials regardless of their morphology.

Some evidence indicating this generalization may not be completely valid is available. For example, many studies found that semicrystalline polymers age at temperatures above their  $T_g$  (17-19). Consequently, physical aging seems to be affected by morphology of the sample. In addition, there is reason to believe that crystallinity has a long-term effect on the free volume and mobility of amorphous domains since crystallites restrict amorphous chain movement somewhat and crystalline regions themselves do not undergo any change during aging as indicated by X-ray diffraction IR spectroscopy.

Researchers have examined the creep and creep recovery of textile fibers (20-22). For example, Hunt and Darlington (23,24) studied the effects of temperature, humidity and previous thermal history on the creep properties of nylon 6,6. They were able to explain the shift in creep curves with changes in temperature and humidity. Similar findings have been reported by researchers studying other fibers (25). Leaderman (26) has studied the time dependence of creep and the creep qualities of filamentous materials at different temperatures. Shifts in creep curves due to changes in temperature and humidity are explained with simple equations and convenient shift factors. Meredith (27)

has studied many mechanical properties including creep of several generic fiber types. Morton and Hearle (28) have examined the dependence of fiber creep on temperature and humidity. Phenomenological theory of linear viscoelasticity on semicrystalline polymers has been tested by creep measurements performed on textile fibers (25). From these works one can readily appreciate that creep behavior is affected by many factors.

This study has been restricted to studying creep behavior of cellulosic fibers in relation to their physical aging. Studies show that creep behavior of cellulosic fibers is dependent on their structural features. Leaderman (26) examined the creep and creep recovery of textile fibers including viscose rayon and acetate and observed that these filaments have instantaneous moduli much lower than that corresponding to cotton. Together with the fact that these materials have large primary creep, this suggests that a relatively large amount of amorphous material is present. The acetate filament gave the lowest of instantaneous modulus, presumably due to large amounts of amorphous material present as a result of the acetate side-chains. In examining the temperature effect on creep properties of acetate, Leaderman has examined temperature effects ranging from room temperature to 90° C. With an identical shape otherwise, clear shifts in the  $\log(\text{shift})$  was observed for creep at different temperatures. This shifting procedure enables one

to construct a "master curve" leading to the time-temperature correspondence (26).

Meredith (27) has theoretically justified some of the above results. He also has considered the effects of humidity on the creep of rayon reported in studies by Steinberger (29-31). At relative humidities less than 40%, the amount of creep was not found to vary considerably for cellulosic fibers.

The application of a simple Boltzmann's law to predict creep behavior does not suffice without considering the previous complex thermal and loading histories of samples examined. Previous thermal and loading histories have strong implications on the mechanical behavior of samples.

However, the basic nature of creep curves is explained at the molecular level as a distortion of intramolecular distances for short times and as a reorientation of chain segments at longer times. The distortion in intramolecular distances in highly oriented polymer samples such as typically found in textile fibers results from the straightening of the skeletal bonds. A continuous deformation under constant load resulting from chain orientation then may be reasoned to increase with time, following the discussion above (26).

The literature encompassing physical aging concentrates mainly on large amorphous polymers that can be subjected to large loads and produce large displacements in creep (1,14,25,32). Electronic sensing of minute displacements

with sensitive oscillators and amplifiers have been employed in measuring displacements when loads of the order of 1 to 50 Kg. were applied.

Analogous to a study by Wilding and Ward (33), strain was calculated in this study by measuring grip displacements. Initial length determination was done by extrapolating creep curve for short times to zero time to circumvent problems arising from instantaneous creep.

Possible problems associated with this study have been pointed out by earlier researchers. The presence of thermal transitions occurring above  $T_g$  (17,19), may account for not entirely erasing former aging when samples are subjected to  $T_g$ . If this problem was to be overcome by erasing former aging at a temperature well above  $T_g$ , melting of small crystals and reformation of new ones may result. These transformations are bound to alter the mechanical properties. Hence, aging was conveniently erased at lower temperatures using water as a plasticizer in this study.

Often, mechanical properties of polymers in the glassy state are measured and presented as functions of time. This is valid only if the polymer is in volume equilibrium. On waiting long enough, this equilibrium may be reached. However, the waiting time is a function of temperature and ranges from a few seconds to several months; the lower the temperature, the longer the waiting time. As this waiting time is impractical, measurements of mechanical properties

for the most part are done in a nonequilibrium state which may yield to variations in results (9).

The equation to be used in this experiment to determine the aging rate is empirical in nature and has been defined by Struik (1). The equation requires plotting strain vs.  $\log(\text{creep time})$  creep curves for different aging times, estimating their  $\log(\text{creep time})$  shifts from these plots, plotting values of their  $\log(\text{shift})$  versus  $\log(\text{aging time})$  and calculating their aging rates. Mathematically the aging rate is defined as ; (vide. Figure 2)

$$m = - (d \log a) / (d \log t_e)$$

where  $m$  = aging rate

$a$  = horizontal shift in time scale for creep curves, and

$t_e$  = aging time.

This equation forms the basis for computing aging rates. Thus it becomes obvious that physical aging affects mechanical properties of the polymer. The direction in which the properties are affected assumes a negative value for shifts to the right implying that longer aging times subsequently result in further changes in mechanical properties.

Changes in mechanical properties are proportional to aging time. The proportionality constant is denoted by "m", and can be calculated when the aging time and creep time are known using the above equation if their linear relationship is linear. This study demonstrated a nonlinear relationship between  $\log(\text{shift})$  and  $\log(\text{aging time})$  in contradiction to the generally expected behavior of polymeric materials.

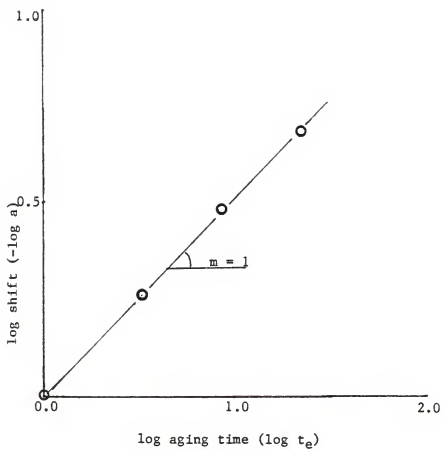


Figure 2. Linear Aging Behavior for Short Aging Times



## METHODOLOGY

The source and dates of origin of fiber specimens tested in this study are listed in Appendix I. The methodology in this research would consist of four parts:

1. construction of apparatus,
2. determination of temperature dependence of aging,
3. fitting an equation to describe plots of  $\log(\text{shift})$  versus  $\log(\text{aging time})$ , and
4. measurements of optical birefringence and density.

The apparatus that was constructed and used is illustrated in figures 3-4. The chamber is workable under operating conditions ranging from room temperature to 150°C. An electrically heated resistor located in the chamber was used to obtain temperatures above 20°C.

Fiber lengths tested ranged from 2 to 5 cms. All lengths were measured microscopically, using a macroscopic objective and an eyepiece micrometer. Thus, length changes of the order of 10 microns were detected. During testing, one end of the fiber was secured by a pair of hinged magnetic clamps fixed at one end of the sample platform. Another magnetic piece formed an union between the other fiber end and a glass fiber that did not elongate under the loads used. The glass fiber passed over a pulley and supported loads ranging from 0.1 to 0.7 gms.

The loads resulted in tensile creep in the fiber samples but caused no creep in the other components of the

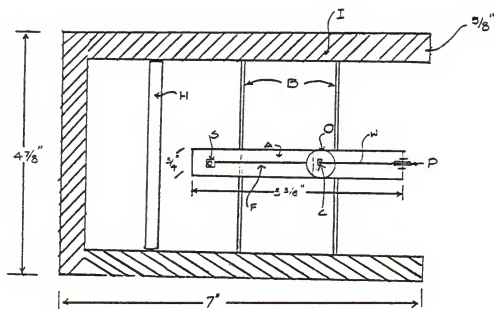


Figure 3. Top View of Apparatus

KEY

A	Platform	O	Microscope Objective
B	Bar Supports	S	Hinged Magnetic Clamp
C	Magnetic Coupling	P	Pulley
F	Fiber Being Tested	W	Glass Fiber Coupling
H	Heater		
I	Insulation		

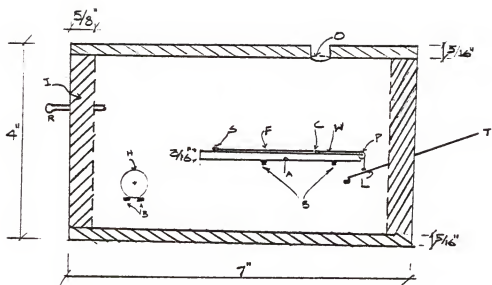


Figure 4. Elevation of Apparatus

KEY

A	Platform	O	Microscopic Objective
B	Bar Supports	P	Pulley
C	Magnetic Coupling	R	Optical Fiber
F	Fiber Being Tested	S	Hinged Magnetic Clamp
H	Heater	T	Mechanical Lever
I	Insulation	W	Glass Fiber Coupling
L	Load		

apparatus. The amount of load that was used for each of the fiber types was predetermined from the stress-strain characteristics of the fiber types.

The chamber was built with walls made of 5/8" thick R-Max insulation board and sealed on the edges with aluminium adhesive tapes. The dimensions of the box were 7" x 4 7/8" x 4". The chamber contained horizontal aluminium bar supports running across the sides that helped support a heater and the fiber mounting platform. The heater, a 50 ohms resistor, was placed at the bottom of the fiber platform so that hot air would effectively heat the fiber sample. A thermometer was introduced from the top to monitor the temperature. Except for creep measurements at room temperature, the temperatures inside the chamber was controlled with a 120 V transformer correct to  $\pm 2^{\circ}\text{C}$ .

The platform dimensions were 3 3/8" x 3/4" x 3/16" and made of aluminium. 1/4" from one of its edges, the platform had a 0.0625" dia' steel pin that hinged a pair of 0.6" square magnets. At the other edge of the platform is a fixed pulley with its groove having a 1/16" clearance from the surface of the platform. Between the pulley and pin and 2" from the latter, a line was etched on the surface of the platform to serve as a reference point for length measurements. The platform was milled to a smooth and low friction surface.

The pulley originally was tested for frictional drag by introducing weights on both sides. Results from this

test indicated the minimum load required to rotate the pulley was 0.010 gms. The combined frictional drag of the pulley and magnet was measured similarly and found to be 0.110 gms.

Creep in the samples were viewed through a Projectina microscope with a 7x macro objective and no ocular. The top of the insulation box was bored to fit the objective. After determining the focal length of the objective, supports were made in the box to position the fiber platform in the focal plane of the objective. An optical fiber was inserted through the box to illuminate the fiber for length measurements.

A mechanical lever was incorporated so the load could be applied and removed from the fiber without opening the sample chamber. A metal plate attached to one end of a metal rod held the load until it was ready to be released by lowering the other end of the rod which protruded outside the box.

A fly-back stop-watch with precision to 0.01 seconds was used in timing the experiments.

The steps followed in determining the aging rate at different temperatures are as follows:

1. Four specimens of each fiber category were teased from yarns of textiles of known physical and chronological ages.
2. Three of the specimens were erased of previous aging by being immersed in warm water at their predetermined

temperatures. Table 1 lists the temperatures used for different fiber types.

3. Each of the treated specimens was conditioned (aged), at predetermined temperatures of 25°C, 50°C and 75°C and roughly 65% relative humidity for an aging period of approximately 48 hours.

4. Each of the conditioned specimens was subjected to a creep test at the same temperature it was aged. Time intervals for every 0.0014 cms. creep were recorded. Table 2 lists the loads for each of the different fiber categories. A maximum creep time of  $10^4$  seconds was used.

5. The specimens were relaxed overnight and again erased of their prior aging by repeating step 2.

6. Each of the specimens was subsequently aged again but for approximately 72 hours at the same aging temperatures used for the 48 hour aging.

7. Creep data obtained for 72 hours of aging was recorded by repeating step 4 for identical amounts of strain.

8. Specimens were relaxed overnight, and again erased of their previous aging by repeating step 2.

9. Each of the specimens again was aged again but for an aging time of approximately 96 hours at the same temperatures used previously.

10. Creep Measurements were recorded by repeating step 4 for identical amounts of strain.

This procedure was repeated for each of the six fiber types. These are cotton, flax, viscose rayon, acetate,

cuprammonium rayon and high wet modulus rayon.

Figures 5 - 19 show shifts in the logarithmic creep times for different aging times for each fiber type aged at 25°C. The temperature dependence of aging is illustrated in figures 20-25.

TABLE 1. Temperatures of Wetting to Erase Previous Aging

Fiber Type	Water Bath Temperature (°C)
Cotton	60
Flax	60
Viscose Rayon	50
Cuprammonium Rayon	50
Acetate	40
High Wet Modulus Rayon	50

TABLE 2. Load Levels Applied in Creep Measurements

Fiber Type	Load (g)
Cotton	1.483
Flax	1.635
Viscose Rayon	1.483
Cuprammonium Rayon	1.483
Acetate	1.483
High Wet Modulus Rayon	1.483
Viscose Rayon	1.635

The fourth specimen from each of the fiber types remaining from the previous procedure was subjected to a creep test at 25° C without erasure of its age to a strain level identical to that done previously. The fiber then was erased of its aging and subsequently aged for 48 hours and subjected to another creep test. The dates of origin of the textile samples ranged from from 1500 A.D. to 1960. Figures 26-30 contain data points of  $\log(\text{physical aging time})$  vs.  $\log(\text{shift})$ , for each of the fiber types aged at 25°C. Also included are data points of  $\log(\text{chronological age})$  vs.  $\log(\text{shift})$  for various textiles of the same fiber type. In addition, the figures contain plots of exponential functions fitting the data points of each of these fibers.

Birefringence measurements provide a measure of the average orientation of the molecular chains, while density measurements provide a measure of fiber crystallinity. Birefringence measurements were obtained by the Becke Line Method (34,35). Density measurements were obtained by the sink-float method(2,36).



## RESULTS AND DISCUSSION

In using tensile creep as a measure of aging, a noticeable shift in the creep times of differently aged samples was observed. Figure 5 shows creep curves for cotton fibers aged and tested at 25 °C for aging times of nearly two, three and four days. Figures 6 to 11 show analogous creep curves for other fiber types. The creep curves were found to shift to the right for longer aging times as expected. This shift is denoted by "a". Shifts to the right are conventionally considered negative and so a  $(-\log a)$  value would mean a logarithmic shift of "a" units to the right. Shifts were determined by measuring the horizontal shifts at five different places on the curves and then calculating an average value. A greater load was required for flax and viscose rayon to obtain amounts of strain roughly equal to that of other fiber types. In the case of viscose rayon, the larger diameter of the sample apparently accounted for the greater load level required whereas the high modulus typical of flax resulted in the need for a greater load.

The general temperature effect on aging is illustrated in Figure 1. Results from this study are consistent with the expected temperature dependence. Each of the fiber types exhibited varying aging behaviors at different temperatures. The absolute values of creep at the three reference temperatures for each fiber type increased for the same stress at increased temperatures. The temperature dependence of aging

for different fibers are shown in Figures 19-24. Table 3 summarizes the "m" values for each fiber types at 25°C, 50°C and 75°C.

Table 3. Temperature Dependence of Aging

Fiber Type	m Values		
	25° C	50° C	75° C
Cotton	1.04	1.03	0.82
Flax	0.66	0.41	-
Viscose Rayon	0.87	0.64	0.58
Cuprammonium Rayon	1.11	0.56	-
Acetate	1.06	0.48	0.21
High Wet Modulus Rayon	0.82	0.70	0.68

As illustrated in Figure 1, the aging rate was expected to be approximately constant at temperatures between  $T_b$  and  $T_g$ . In addition, m values previously measured for a wide variety of polymers (1) indicated the general nature of aging and predicted m values to be approximately equal to unity.

Cotton exhibited a consistency in aging rates at 25°C and 50°C, with m nearly equal to unity. At 75°C, m dropped to 0.82. This indicates cotton is well between  $T_b$  and  $T_g$  at 25°C and 50°C but is approaching  $T_g$  at 75°C.

The aging rate of flax decreases from an m value of

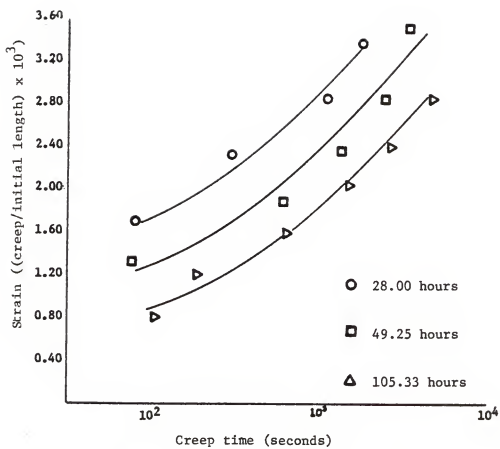


Figure 5. Creep Curves for Cotton Exposed to Short Aging Times

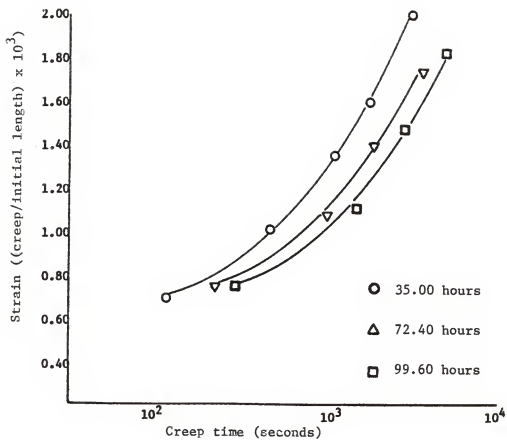


Figure 5. Creep Curves for Flax Exposed to Short Aging Times

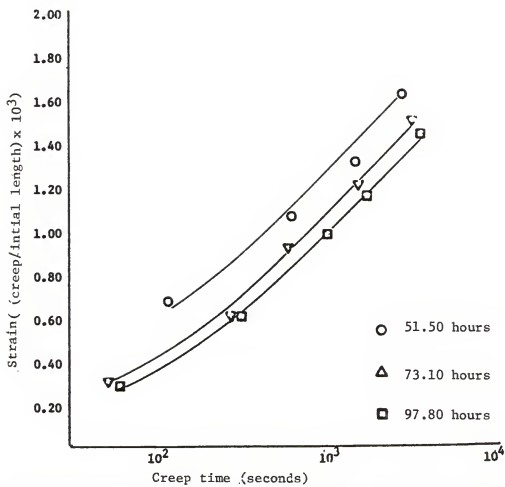


Figure 7. Creep Curves for Viscose Rayon Exposed to Short Aging Times.

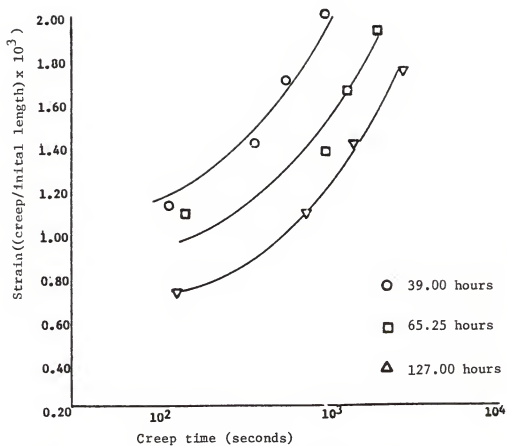


Figure 8. Creep Curves for Cuprammonium Rayon Exposed to Short Aging Times

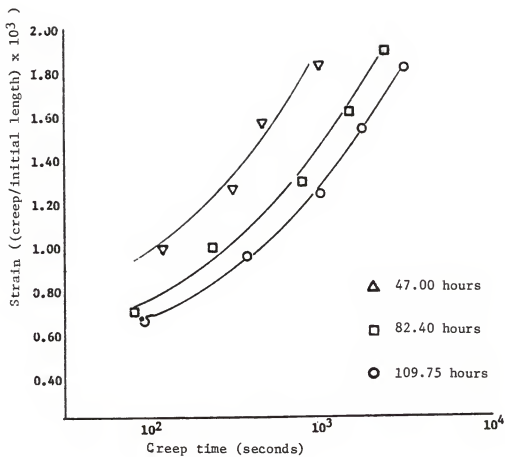


Figure 9. Creep Curves for Acetate Exposed to Short Aging Times

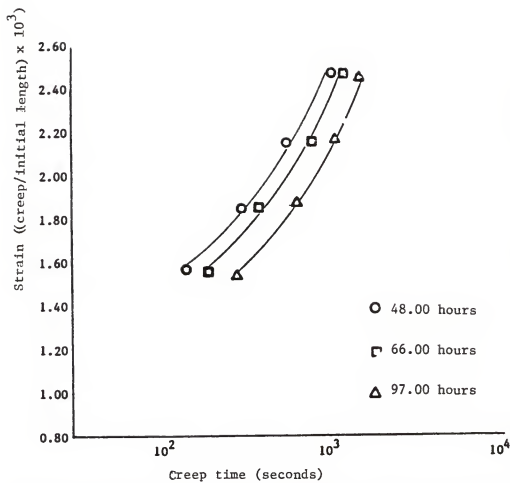


Figure 10. Creep Curves for High Wet Modulus Rayon Exposed to Short Aging Times



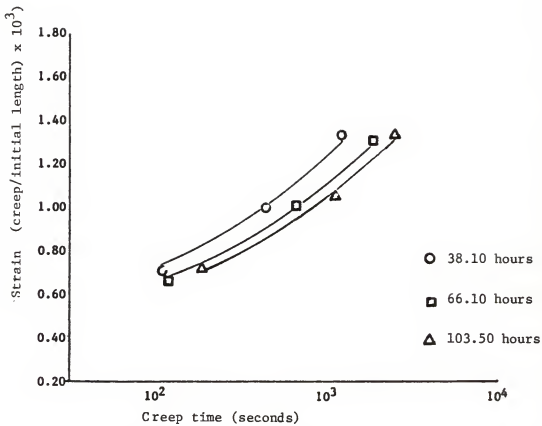


Figure 11. Creep Curves for Viscose Rayon Exposed to Short Aging Times.

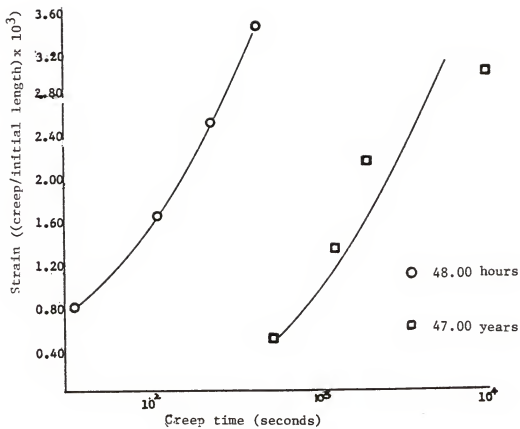


Figure 12. Creep Curves for Cotton (47 years) Exposed to Longer Aging Times

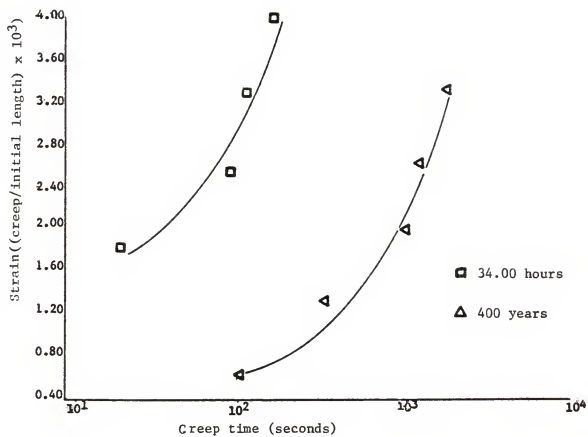


Figure 13. Creep Curves for Cotton (400 years) Exposed to Longer Aging Times

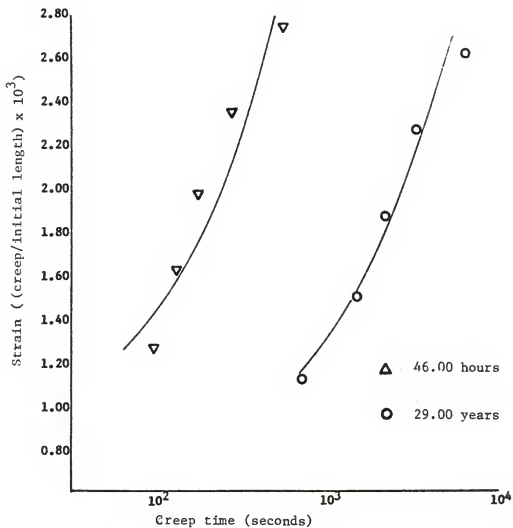


Figure 14. Creep Curves for Flax (29 years) Exposed to Longer Aging Times.

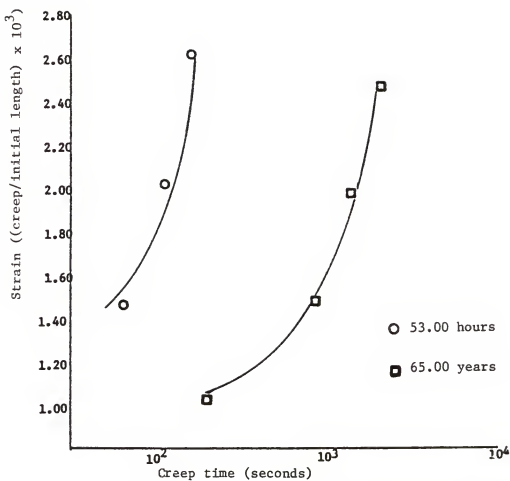


Figure 15. Creep Curves for Flax (65 years) Exposed to Longer Aging Times

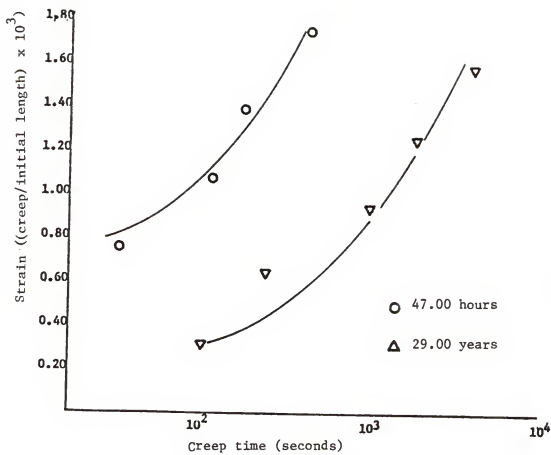


Figure 16. Creep Curves for Viscose Rayon (29 years), Exposed to Longer Aging Times

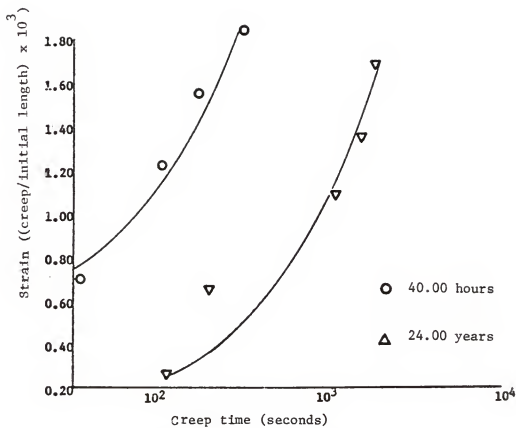


Figure 17. Creep Curves for Cuprammonium Rayon (24 years) Exposed to Longer Aging Times

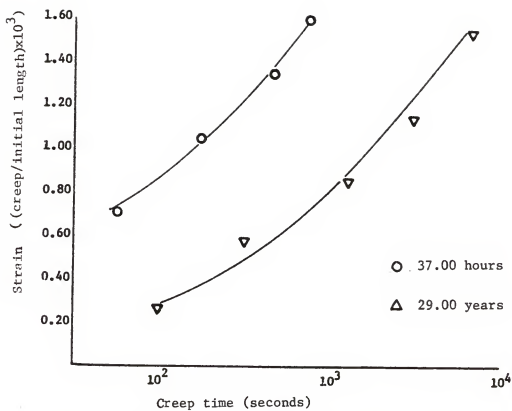


Figure 18. Creep Curves for Acetate (29 years) Exposed to Longer Aging Times



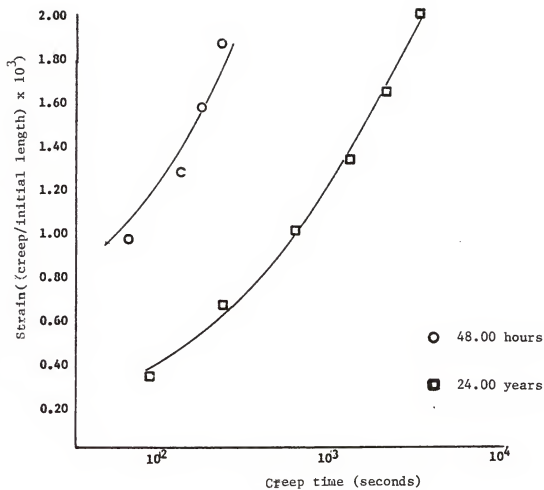


Figure 19. Creep Curves for High Wet Modulus Rayon (24 years) Exposed to Longer Aging Times.

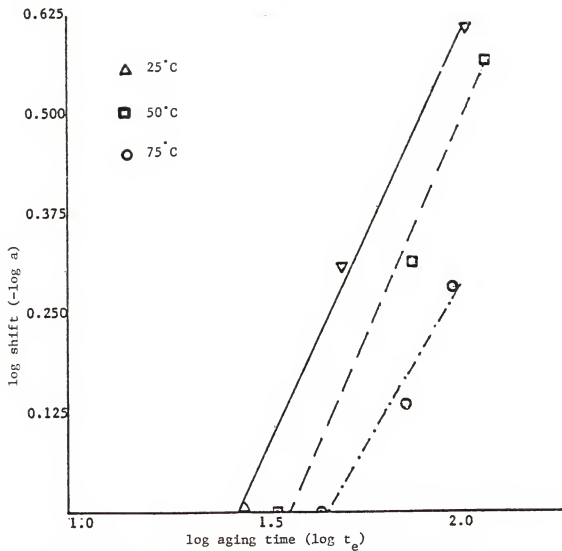


Figure 20. Temperature Dependence of Aging for Cotton

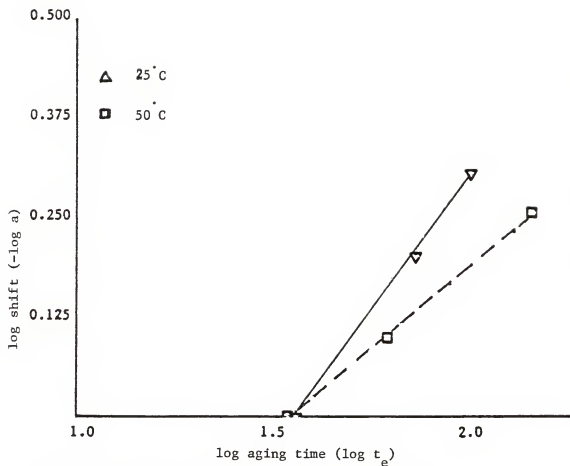


Figure 21. Temperature Dependence of Aging for Flax

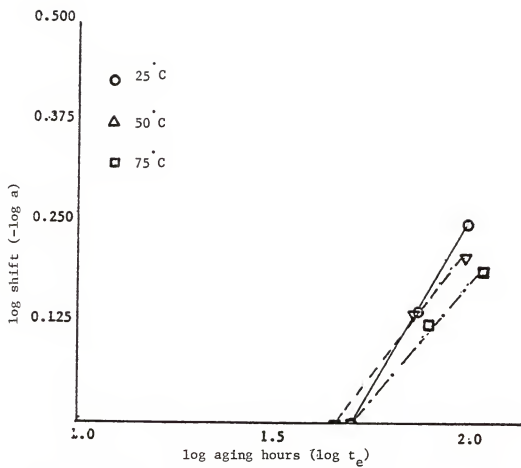


Figure 22. Temperature Dependence of Aging for Viscoze Rayon

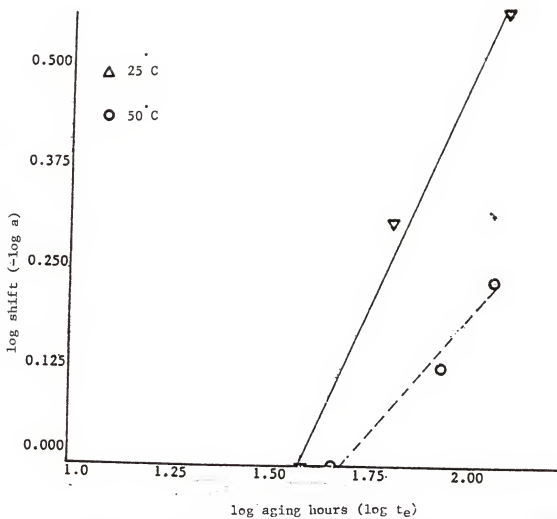


Figure 23. Temperature Dependence of Aging for Cuprammonium Rayon

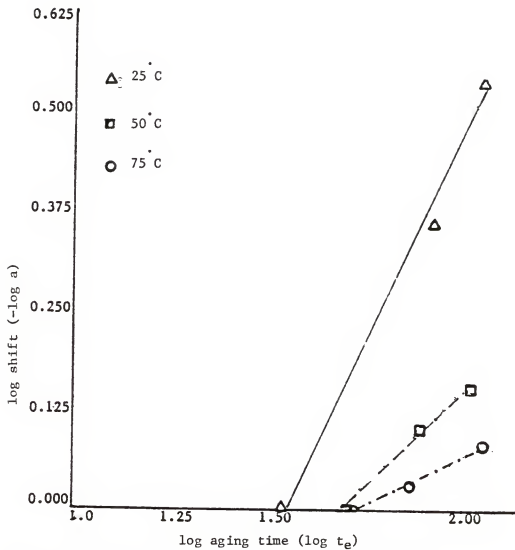


Figure 24. Temperature Dependence of Aging for Acetate

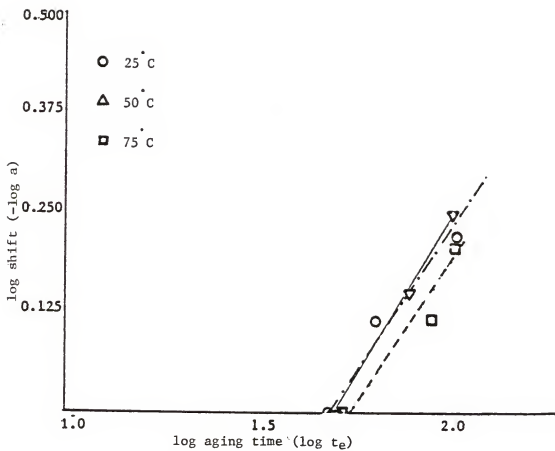


Figure 25. Temperature Dependence of Aging for High Wet Modulus Rayon

0.66 at 25°C to an  $m$  value of 0.41 at 50°C. Flax could not be tested at 75°C because fiber slippage between the clamps could not be eliminated. However, decreasing aging rates at 25°C and 50°C indicate that  $T_g$  is being approached.

Viscose rayon exhibits an aging rate of 0.87 at 25°C that slowly decreased to 0.64 at 50 °C and at 75 °C was 0.58. Although this may indicate an approach to  $T_g$ , this slow decrease in aging rates ( $m$  values) is less abrupt than expected from reviewing Figure 1.

High wet modulus rayon had fairly constant aging rate at all three testing temperatures. This behavior indicates the testing temperatures lie in the plateau region of aging illustrated in Figure 1 where the aging rate is constant and suggests that  $T_g$  is not near the testing temperatures.

The aging rate of cuprammonium rayon, dropped remarkably from 1.11 at 25°C to 0.56 at 50°. At 75 °C the fiber exhibited irregular creep behavior which was suspected to arise from structural changes accompanying shrinkage during creep erasure. Hence, a proper  $m$  value at 75°C could not be determined. The rapid increase in aging rate indicates that cuprammonium rayon is approaching its  $T_g$ . Since the lower temperature limit of shrinkage is  $T_g$ , the presence of shrinkage at 75°C also supports this conclusion.

Acetate showed a decline in aging rate from 25°C through 75°C. At 25°C, the aging rate nearly equal to unity at 1.06 and at 75°C it dropped to 0.21. The literature value (16) for glass transition temperature of acetate is



around 85°C. Consequently, the "m" value found are consistent with the literature Tg value, although the decline in aging rate observed from 25°C to 75°C is more gradual than expected from a consideration of Figure 1.

In summary, the temperature dependence of aging for these six cellulose fiber samples between 25°C and 75°C show a constantly decreasing aging rate for flax, acetate and cuprammonium rayon that suggests testing temperatures lie in the high temperature portion of Figure 1 and a fairly constant aging rate for cotton, viscose rayon and high wet modulus rayon that suggests testing temperatures are in the plateau of Figure 1. The gradual declining nature of the aging rate of these samples compared to those found for totally amorphous samples (1), suggests that morphology is influencing the aging mechanism in some way.

The glass transition temperature of unplasticized cellulose is reported to be approximately 230°C. The Tg of cellulose at 65% R.H. would be expected to be substantially lower because of plasticization and may be consistent with the results of this study just mentioned. It is difficult to confirm this, however, since the temperature of the glass transition of cellulose is in much dispute.

Figures 5 through 19 show the creep curves obtained from testing fiber specimens at 25°C. The general form of these plots was as expected with increasing horizontal shift found for all samples of increasing age. However, results atypical of the predicted behavior were observed in another

respect. A nonlinear relationship between  $\log(\text{aging time})$  vs.  $\log(\text{shift})$  was observed for all samples for long aging times. That is, the aging rates increased linearly with increasing aging times to several days but then changed at an increasingly slower rate. The general form of this behavior is one of an exponentially decaying function.

A function of the following form was fitted to the aging rate data to describe this behavior :

$$y_i = A (1 - \text{EXP} [-(x_i - D)/C])$$

where  $y_i = \log(\text{aging time})$ ,

$x_i = \log(\text{shift})$ ,

$D = \log(\text{aging time})$  corresponding to zero shift,

$A =$  a constant corresponding to the asymptotic value of  $\log(\text{shift})$ , and

$C =$  a constant.

The constants  $A$  and  $C$  were computed for each of the fiber types by solving simultaneous equations. These values are presented in Table 4. By substituting values for  $x_i$ ,  $y_i$ , and the constants  $A$  and  $C$ , computer generated plots describing aging rates over a few thousand years can be obtained for each fiber type. Figures 26-31 contain these plots along with data points actually measured.

In summary, a nonlinear relationship between  $\log(\text{shift})$  and  $\log(\text{age})$  was found for all fiber types examined, although previous studies (1), found linear behavior and nonlinear behavior was not predicted under any circumstances.

An earlier research (6) indicates a function such as the one above as being applicable to the change in heat content and mobility in the polymers with increasing aging time. It has been pointed out that physical aging occurs with a decrease in heat content and molecular mobility in the polymer. Apparently, the nonlinear behavior observed results from the effects of sample morphology. These effects have not been thoroughly investigated in previous studies.

Table 4. Values of Constants A and C

Fiber Type	A	C
Cotton	1.21	0.82
Flax	1.22	1.66
Viscose rayon	1.14	0.99
Cuprammonium rayon	1.10	0.69
Acetate	1.08	0.54
High Wet Modulus Rayon	1.06	1.05

Measurements of optical birefringence and density were obtained in an attempt to correlate total polymer orientation and the amount of fiber crystallinity with aging behavior observed for the fibers. These values are presented in Table 5. The birefringence value tabulated for cotton is not the measured value but rather is a value for the fiber core measured by interference microscopy (34). Since the

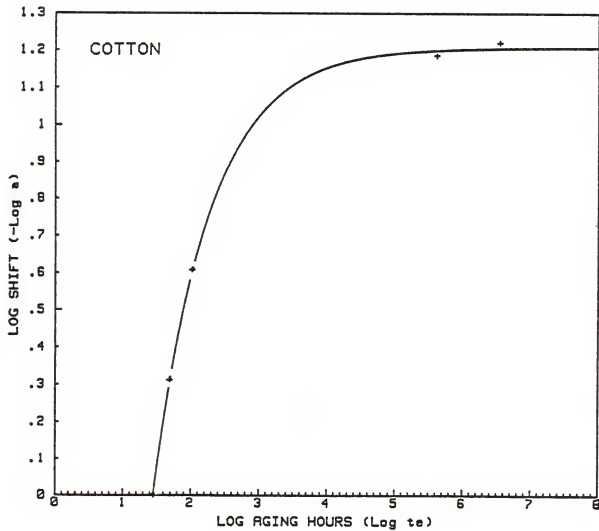


Figure 26. General Aging Behavior of Cotton

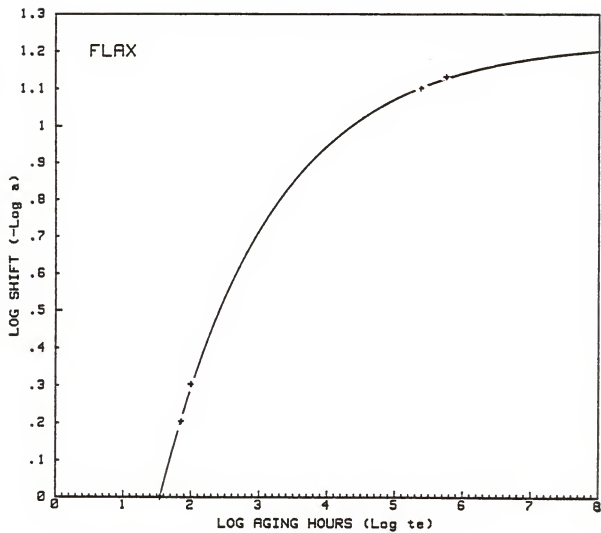


Figure 27. General Aging Behavior of Flax

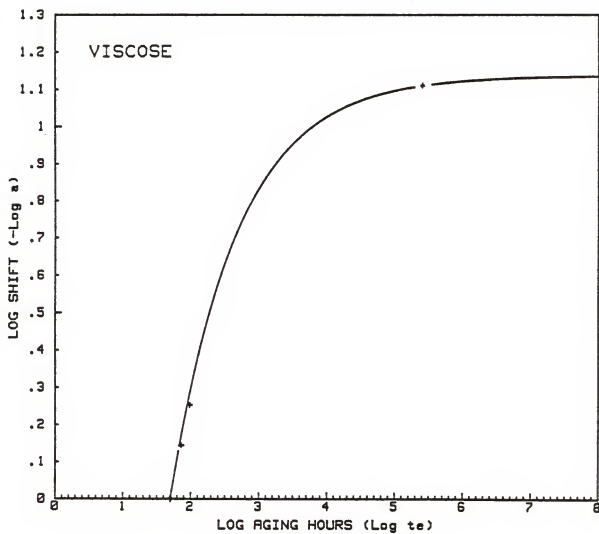


Figure 28. General Aging Behavior of Viscose Rayon

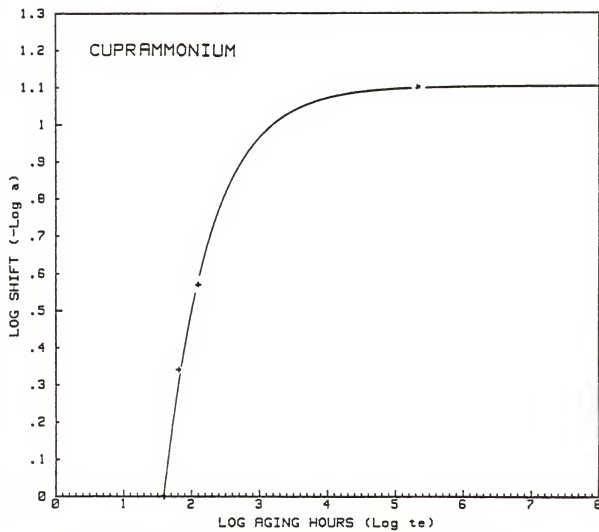


Figure 29. General Aging Behavior of Cuprammonium Rayon

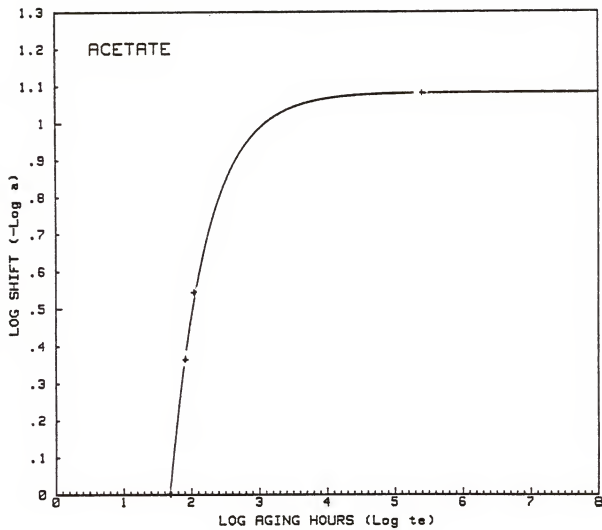


Figure30 . General Aging Behavior of Acetate



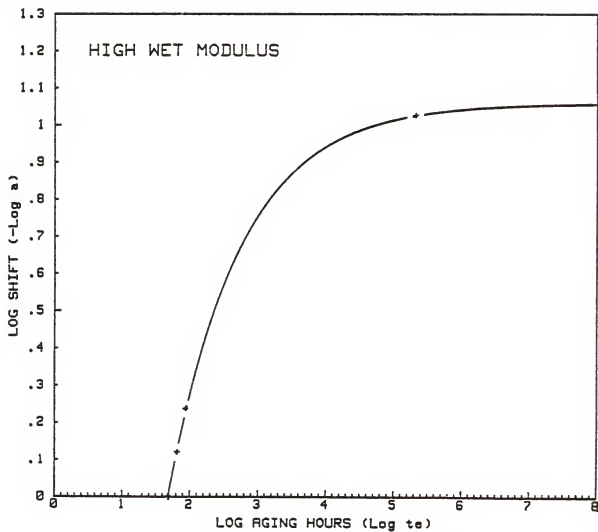


Figure 31. General Aging Behavior of High Wet Modulus Rayon

core of cotton comprise the majority of the fiber volume and the Becke line method used in this study provides a measure of the fiber skin, it was thought more reasonable to use the core birefringence value from interference microscopy measurements. Table 6 shows correlation coefficients between density and birefringence, and the constants A and C. The density of acetate is omitted from this correlation since its density would not reflect fiber crystallinity in the same way as the other fiber types.

Table 5. Birefringence and Density Measurements

Fiber Type	Birefringence	Density (gms/cm <sup>3</sup> )
Cotton	.028 *	1.485
Flax	.060	1.500
Viscose Rayon	.028	1.471
Cuprammonium Rayon	.029	1.481
Acetate	.003	-
High Wet Modulus Rayon	.030	1.473

\* Literature value (34), 0.48 measured.

Table 6. Correlation Between Fiber Structure and Constants A and C

Structural Variable	Correlation Coefficients	
	A	C
Birefringence	0.03	0.86
Density	0.64	0.12

It was hoped that a little better understanding of the effects of morphological features on the aging behavior of the fiber types would be obtained with these correlations. A strong correlation ( $r = 0.86$ ) exists between birefringence and constant C. This correlation indicates the aging rate is dependent on polymer orientation. There is no correlation between birefringence and A. A moderate correlation ( $r = 0.64$ ) appears to be present between density and the value of A, the asymptotic value of  $\log(\text{shift})$ . This suggests that aging is dependent on the amount of crystallinity present in a fiber. There is no correlation between density and constant C.

In summary, physical aging was found to be dependent on sample morphology. This was an unexpected result since previous work (1) indicated aging was independent of morphology.

The results from this study suggest that the physical age of a textile of unknown age can be estimated from a minimum of two creep measurements from a short length of a single fiber. However, the error associated with the estimated age found by this method must be known to properly interpret the findings. Since this study only comprised a general inquiry into physical aging of cellulosic textile fibers, a thorough error determination was not performed. However, a rough estimate of error was made so the applicability of the results of this study can be determined. Of

course, additional measurements would decrease error but a rough estimate of error associated with the minimum of two creep measurements would be useful.

A blind test using a cotton fiber laundered 814 days before testing was conducted to evaluate the applicability of the equation describing cotton aging and provide a rough estimation of the error associated with the technique. The specimen was subjected to a tensile creep test using the methodology developed in the study. A value of 214 days was obtained for the age of the sample. The discrepancy between 214 and 814 days indicates an error of several hundred percent is associated with the technique when the minimum of two creep measurements from one fiber is performed. One would naturally expect this error to be decreased if more than the minimum number of measurements were performed. On the other hand, longer aging periods would carry more error than shorter aging periods since the curves start to flatten out to an appreciable degree and decrease sensitivity to minute shifts in the y-axis.

A more comprehensive assessment also was done. In this case, a procedure known as sensitivity analysis was employed. This procedure can be used to estimate error only if the aging rate is linear, such as, during the initial aging periods. The fundamental equation used in determining the age of unknowns is

$$m = (-d \log a / d \log t_e)$$

This may be written as

$$m = (\log t_2 - \log t_1) / (\log t_{e_2} - \log t_{e_1})$$

Solving for  $t_{e_2}$ , the unknown age,

$$\log t_{e_2} = \{(\log t_2 - \log t_1) / m\} + \log t_{e_1}$$

Partially differentiating, one obtains

$$dte_2/te_2 = -(dm/m^2) \log t_2 + (1/m) (dt_2/t_2) + (dm/m^2) \log t_1 \\ - (1/m) (dt_1/t_1) + (dte_1/te_1).$$

This expression provides a measure of the error associated with the unknown age,  $dte_2$ , in terms of the values and associated errors of the shift factor,  $m$ , the creep time  $t_1$  corresponding to  $te_1$  hours of aging, creep time  $t_2$  corresponding to  $te_2$  hours of aging and aging time  $te_1$ .

This expression was applied to the high wet modulus textile for short aging time. Values for the variables in the expression were obtained from the data available in the original measurements and from measurement uncertainties inherent in the analytical techniques; one variable,  $dm$ , was roughly estimated by equating  $dm$  with the range in  $m$  found by determining  $m$  for two fiber samples aged to nearly identical amounts. The resulting error in age,  $dte_2$ , was calculated to be approximately 5%. The error obtained here was substantially smaller than the several hundred percent error associated with the 814 day old sample. One reason

for this may be that the high wet modulus fiber tested was only 87 hours old and one would expect less error with samples of smaller age. Also, there is a possibility for greater variations with fiber specimens that differ considerably in their aging behavior. In addition, humidity was not controlled during storage of the 814 day old sample, so the value of its physical age is not known with certainty.

## CONCLUSIONS

This study involved examining physical aging behavior of six cellulosic textile fibers and examining the possibility of using a single fiber creep technique to estimate the physical age of textile fibers. A simple apparatus was constructed to allow microscopic observations of short lengths of single fibers to be performed.

Results from testing specimens at 25°C, 50°C and 75°C indicated a strong temperature dependency of aging as expected. Temperature dependency generally was as expected, except for a substantially more broad change in aging rate with temperature changes observed for some fibers than predicted from some studies of totally amorphous materials. Apparently, this anomaly results from the influence of sample morphology.

Creep was examined most extensively at 25°C. The general form of all the creep curves was as expected. However, results atypical of predicted behavior were observed in another respect. Plots of  $\log(\text{shift})$  vs.  $\log(\text{aging time})$  were not linear as expected, but rather assumed the form of an exponentially decaying function. Apparently, this unexpected behavior results from sample morphology.

Measurements of optical birefringence and density were obtained to test for a correlation between polymer orientation and the amount of fiber crystallinity, and aging behavior as modeled by the exponential functions of each fiber

type. A strong correlation was found with birefringence and a moderate correlation was found with density. These results indicate that sample morphology may indeed be responsible for the nonlinear behavior observed with these samples.

The application of single fiber creep measurements to estimate the physical and, in favorable cases, chronological age of textiles seems quite promising. With an improved apparatus design, error should be substantially reduced so applicability of this technique may be extended to a large number of samples.

Suggestions for future studies in this area include:

1. A quicker means of determining aging effects by considering a mechanical property that is more sensitive than creep.
2. Construct a more sophisticated apparatus if creep is to be used as a measure of aging, including incorporating electronic sensing of fiber displacements, the capacity to monitor changes in length to one micron, and less frictional drag in the apparatus.
3. Age determination at more broad temperature and humidity ranges.

The potential for further research in this area is large. This includes determining the aging rates of other generic fiber types. A ready made table to read out the aging rates for different fiber types at different temperatures would be useful for those concerned with physical



properties and might constitute a standard physical characterization. Research in this field may apply to a broad range of people, including industrial workers, fiber forensic scientists, textile conservators, archaeologists and historians.

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APPENDIX I

## DEFINITIONS

1. Tensile Strain : The relative length deformation exhibited by a specimen subjected to a tensile force (37).

Strain = (change in length/initial length)

2. Creep : Deformation under constant load gradually increasing with time (37)

a. Primary Creep : The recoverable part of creep.

b. Secondary Creep : The nonrecoverable part of creep.

3. log (a) : Acceleration factor or horizontal shift factor, where shift is the difference in log (creep time) for equal amounts of strain of differently aged samples.(1)

4. Aging Rate "m": Change in logarithmic shift with respect to change in the corresponding logarithmic aging times.

$$m = -(d \log a / d \log t_e)$$

where "a" = horizontal shift factor.

$$t_e = \text{aging time in hours.}(1)$$

5. Birefringence , fiber : The algebraic difference of the index of refraction of the fiber for plane polarized light vibrating parallel to the longitudinal axis of the fiber and the index of refraction for light vibrating perpendicular to the long axis.(37)

## APPENDIX 2

## SAMPLE PARTICULARS

Fiber type	Source	Age
Cotton	USDA raw cotton	47 years
Cotton	Peruvian dig	400 years
Flax	Collection of Historic Costumes, Dept. of Clothing, Textiles and Interior Design, Kansas State University.	68 years
Flax	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	29 years
Viscose Rayon	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	29 years
Viscose Rayon	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	-
Cuprammonium Rayon	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	24 years
Acetate	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	29 years
High Wet Modulus Rayon	Fabric Samples, Dept. of Clothing, Textiles and Interior Design, Kansas State University	24 years

AGE DETERMINATION OF CELLULOSIC FIBERS  
FROM CREEP MEASUREMENTS

by

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AN ABSTRACT OF A MASTER'S THESIS

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REQUIREMENTS FOR THE DEGREE

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## ABSTRACT

A simple microscopic apparatus operable from room temperature to 150°C was constructed to measure the tensile creep of single textile fibers when viewed on a microscope. Changes in creep behavior resulting from physical aging of six cellulosic fiber types was studied at aging temperatures of 25°C, 50°C and 75°C. In addition more extensive measurements of creep at 25°C were done for cellulosic fibers ranging in chronological age from nearly 500 years to 25 years.

Results of this study indicated that the rates of aging for cellulosic fibers are influenced by fiber morphology. Previous studies on totally amorphous polymer materials suggested aging occurs independently of sample morphology, but aging rates observed in this study correlated with optical birefringence and density measurements of the fibers. The creep behavior for each fiber was described with a mathematical model. With a minimum of two creep measurements from a short length of a single fiber, these equations may be used estimate the physical age of textiles. In favorable cases, the physical age of a textile may be equated with its chronological age and this technique may be used to provide an estimate of the chronological age of textiles. This information is expected to be useful for a variety of people, including textile historians, industrial workers and forensic scientists.