

FACTORS CONTRIBUTING TO THE DEGRADATION OF POLY(P-PHENYLENE BENZOBISOXAZOLE) (PBO) FIBERS UNDER ELEVATED TEMPERATURE AND HUMIDITY CONDITIONS

A Thesis

by

IQUGRJ 'O OQøPGKN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

August 2006

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,
Committee Members,

Head of Department,

Roger Morgan
Jaime Grunlan
Michael Bevan
F gppku'QøP gcn

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ABSTRACT

Factors Contributing to the Degradation of Poly(p-phenylene benzobisoxazole) (PBO)

Fibers under Elevated Temperature and Humidity Conditions. (August 2006)

Liquan O O O P g n B.S., Texas A&M University

Chair of Advisory Committee: Dr. Roger J. Morgan

The moisture absorption behavior of Zylon fibers was characterized in various high temperature and high humidity conditions in a controlled environment. The results of these thermal cycling tests show that PBO fibers not only absorb, but also retain moisture (approximately 0.5-3%) when exposed to elevated temperature and humidity cycles. Also, the impurities of Zylon fibers were characterized through the use of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and solid state Nuclear Magnetic Resonance (NMR). These tests demonstrated that, in addition to other impurities, PBO fibers may contain up to 0.55 weight percent phosphorus, and that this phosphorus is present in the form of phosphoric acid. It was also shown through accelerated hydrolytic degradation tests that production procedures used to neutralize the acid present in the fibers have a beneficial effect on the hydrolytic performance of the fiber. The data collected in this study was then compared and contrasted to known Kevlar studies, identifying similarities, differences, and potential trends. The results of these tests seem to indicate that there is accelerated acid catalyzed hydrolysis occurring in the fiber which is causing these fibers to degrade at an increased rate. This condition is further accelerated by heat and humidity induced permanent fiber swelling.

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CHAPTER I

INTRODUCTION

Body Armor in History

Throughout recorded history, humans have been in a race to create ever more and more effective weapons to use against each other. As a consequence of this, a concurrent race has been taking place to create increasingly effective protection against these weapons in the form of body armor. Some of the earliest forms of body armor were animal skins which were worn over the body. These were then supplemented or replaced by shields made out of animal hide, wood, or metal. Prior to the middle ages, humans began to wear metal armor such as plate mail or chain mail which could help protect against a blow from a sword or similar weapon. With the advent of the widespread use of firearms in the late 16th century, the push for personal ballistics protection began. While the medieval Japanese were apparently the first to use fabric (silk) as personal protection against firearms, it was not until the late 19th century that the use of fabric for protection against firearms was recorded in the United States. During the early 20th century body armor made from metals such as steel was being invented concurrently with the use of lighter but less effective soft body armor made from material such as cotton padding. World War II saw the development of soft body armor made from material such as cotton padding to protect against shrapnel. With the marketing of the high strength fabric Kevlar in 1971, a material was finally available which was much more suitable for use as lightweight

This thesis follows the style of *Journal of Composite Materials*.

ballistics protection for both law enforcement as well as military use. This material has been highly effective in this use and remains one of the dominant materials to this day in the field of lightweight ballistics protection.

Brief History of Zylon

One of the most recent developments in the field of soft body armor was the marketing of the high strength fiber Zylon (PBO) in 1998. PBO is currently the highest tensile modulus, highest tensile strength, and most thermally stable commercial polymeric fiber [1]. While the marketing rights to Zylon originally belonged to Dow Chemical, Dow sold these rights to the Japanese Toyobo Company, Ltd. It was not long after production began in 1998 that potential problems began to be seen with this material. Finally, in 2003 a police officer in the city of Forrest Hills, Pennsylvania was killed when a .40-caliber bullet penetrated the Zylon based body armor that he was wearing at the time.

This incident as well as several other failures of such vests precipitated an investigation by the United States National Institute of Justice (NIJ) beginning in the summer of 2003. Preliminary investigations by the NIJ indicate that there may be degradation occurring in the ballistic performance of Zylon based body armor. Tests performed on the armor in Forest Hills Incident showed that the tensile strength of single yarns were up to 30% lower than new fibers. Thus, it is evident that Zylon, when used in a body armor application, does not perform in the expected manner. This behavior may be due to detrimental affects resulting from moisture and heat in the environment. In fact, Toyobo

has admitted that the strength of Zylon will gradually decrease in high humidity conditions, even in temperatures of less than 100°C [2].

The objective of this thesis is to characterize the behavior of Zylon fibers in high temperature and high humidity conditions thereby allowing us to determine if temperature/relative humidity induced permanent fiber swelling takes place. This swelling might facilitate faster diffusion for acid impurities present in the fiber, which might in turn act as catalysts for hydrolytic degradation of the fibers. An additional goal was to perform tests to characterize the impurities present in the PBO fiber. The data produced by these tests will then be compared to known data collected for Kevlar fibers, to determine if similar degradation mechanisms are present in both fibers.

CHAPTER II

THEORY AND REVIEW OF LITERATURE

Zylon

Zylon is a trademark name for the high strength polymer PBO fiber (Poly-p-phenylene benzobisoxazole). The chemical structure of PBO can be seen in Figure 1.

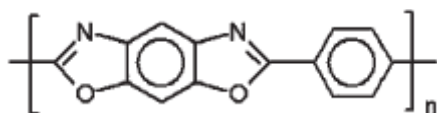


Figure 1. Chemical structure of PBO

The PBO molecule is generally synthesized by condensing 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid (TA) or a derivative of TA such as terephthaloyl chloride in a poly-phosphoric acid (PPA) solution [1] as shown in Figure 2.

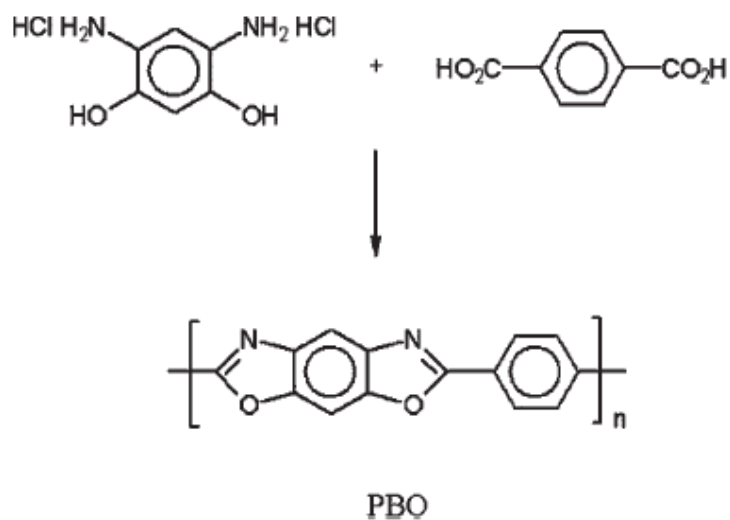


Figure 2. Synthesis of PBO

In this synthesis, poly-phosphoric acid serves three different functions, acting as solvent, catalyst, and dehydrating agent. This allows the formation of polybenzobisazoles in situ without the need for a separation process. In other words, the dopes which are to be spun into the fibers are available directly from the polymer synthesis mixtures.

Like most polymer solutions, the intrinsic viscosity of the PBO solution is dependent on the solvents used. For the solution of PBO in methanesulfonic acid (MSA) the equation relating viscosity to molecular weight is given by the following Mark-Houwink equation [3].

$$\eta \approx 2.27 \times 10^{-7} \overline{M}_w^{1.8}$$

The Mark-Houwink exponent for this solution of 1.8 indicates the relatively high rigidity of the PBO polymer molecule.

It is possible that during the polymerization process of PBO not all of the oxazole rings close. This would result in an amide linkage present in the PBO macromolecule, thus making the molecule more susceptible to acid catalysed hydrolytic degradation.

In order for this molecule to achieve the form of a fiber, it must first be dissolved into a solution. As stated above, this solution is directly available from the polymer synthesis solution. In the case of PBO this is accomplished through the use of a strong acid. Most commonly used are poly-phosphoric acid (PPA) and methanesulfonic acid (MSA).

Once the polymer molecules are in solution a critical concentration of the rigid rod molecules must be achieved. When this value is achieved, the solution will become anisotropic, that is, the molecules in the solution will align, and take on a liquid crystal phase. In the case of PBO this value is usually between 14 and 20 weight percent [4].

Such a solution of PBO will be in the nematic phase. In the nematic liquid crystal phase the molecules do not have positional order, but they tend to be aligned in the same direction. During this stage of the process, the polymer dope is kept at a temperature between 140 and 200°C [4]. The fiber is then formed in a process where the polymer is spun from a spinneret into a quenching bath. The fiber is then spun from a spinneret into a quenching bath. The fiber is then spun from a spinneret into a quenching bath.

pressure through a single- or multihole spinneret out to a narrow air gap, and then quickly enters a non-solvent coagulating bath such as water or dilute phosphoric acid, subsequently followed by str gwejkpi .y cujkpi ."cpf "f{ki ö"ß]. The purpose of the coagulation and washing process is to remove as much of the solvent remaining in the fibers as possible. Ideally, the solvent remaining in the fiber has a value of less than 0.1 percent [4]. In addition to this, the washing process is used to neutralize any of the acid not removed from the fibers by washing. High modulus fibers are achieved by adding a final step of heat drawing. The air gap described above is used to cool the fibers before they enter the coagulating bath. This air gap must be at a temperature between 60 and 90°C in order for spin stability to be maintained [4]. It is during the coagulation process that the material changes from a liquid crystal solution to a polymer fiber. The product of this process is an interconnected network of oriented microfibrils [5].

It is widely accepted that the generally excellent mechanical properties of high strength polymer fibers is a result of the fact that the rigid nature of the polymer molecules in solution causes the molecules to align in the form of a nematic liquid crystal phase as described above. During the spinning of the fiber, the molecules are further aligned parallel to the fiber axis, and coagulation ensures that this high degree of orientation is maintained in the polymer fiber. This orientation is generally thought to be the main source of the strength of high strength polymer fibers such as Zylon.

In the case of PBO, the result of this process is a fiber with one of the highest strengths and modulus available today. Indeed the strength and modulus of Zylon is almost double that of a p-Aramid fiber such as Kevlar with values of 270 GPa compared with the 109 GPa modulus of a p-Aramid fiber [2].

Because the commercial availability of Zylon fibers is a relatively recent occurrence, the understanding of the relationship between fiber degradation and various factors such as service environment conditions is nascent at best. For this reason, the degradation of Zylon fibers is an area of great interest to many scientists today.

The crystal structure and morphology of PBO fibers has been extensively studied and characterized in previous works. The morphology of PBO fibers was characterized using wide angle X-ray scattering (WAXS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [6]. A similar effort was performed using wide angle X-ray scattering (WAXS), selected area electron diffraction (SAED), dark-field transmission electron microscopy (DF) and high-resolution electron microscopy (HREM) [7]. An attempt to survey all of this knowledge was performed in which crystal size, orientation of the crystal, fibrils, microvoids, and fine structure were discussed [8]. Finally, the X-ray data acquired was compared to values using a computer simulation technique. This structural model found through the use of the computer simulation was shown to fit well with the observed and calculated crystal structures [9]. More recently,

solid state NMR was used to study the chemical composition and structure of PBO fibers [10].

This work has been important in establishing a structural model characterizing PBO fibers. As stated before a single PBO fiber consists of an interconnected network of microfibrils. Between these microfibrils are many microvoids which are connected to each other through cracks or imperfections in the microfibrils.

Kevlar

Kevlar is a trademark name for the high strength polymer fiber poly(*p*-phenylene terephthalate). The chemical structure of Kevlar can be seen in the Figure 3.

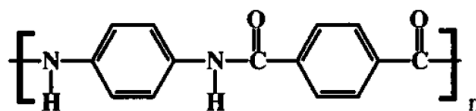


Figure 3. Chemical structure of Kevlar

Kevlar is considered a p-Aramid fiber, that is, a polyaromatic amide because it contains aromatic and amide groups. Figure 4 shows the aromatic and amide groups.

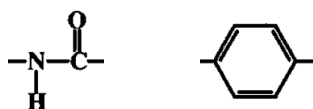


Figure 4. Amide group (left) and aromatic group (right)

Kevlar was invented by Dupont in 1966 and first marketed in 1971. It is the most commonly commercially used high strength polymer fiber on the market today. These uses include naval and aerospace applications as well as run-flat tires, protective gloves, and high performance sporting equipment.

Kevlar fibers are produced in a manner similar to the production of Zylon fibers as described in the **Zylon** section. The acid used to put the poly(*p*-phenylene terephthalamide) (PPTA) molecules in solution is sulfuric acid H_2SO_4 . The fibers are extruded from the spinneret at $\sim 80^\circ\text{C}$ and pulled through a water bath and washed. A schematic of this process can be seen in Figure 5 [11].

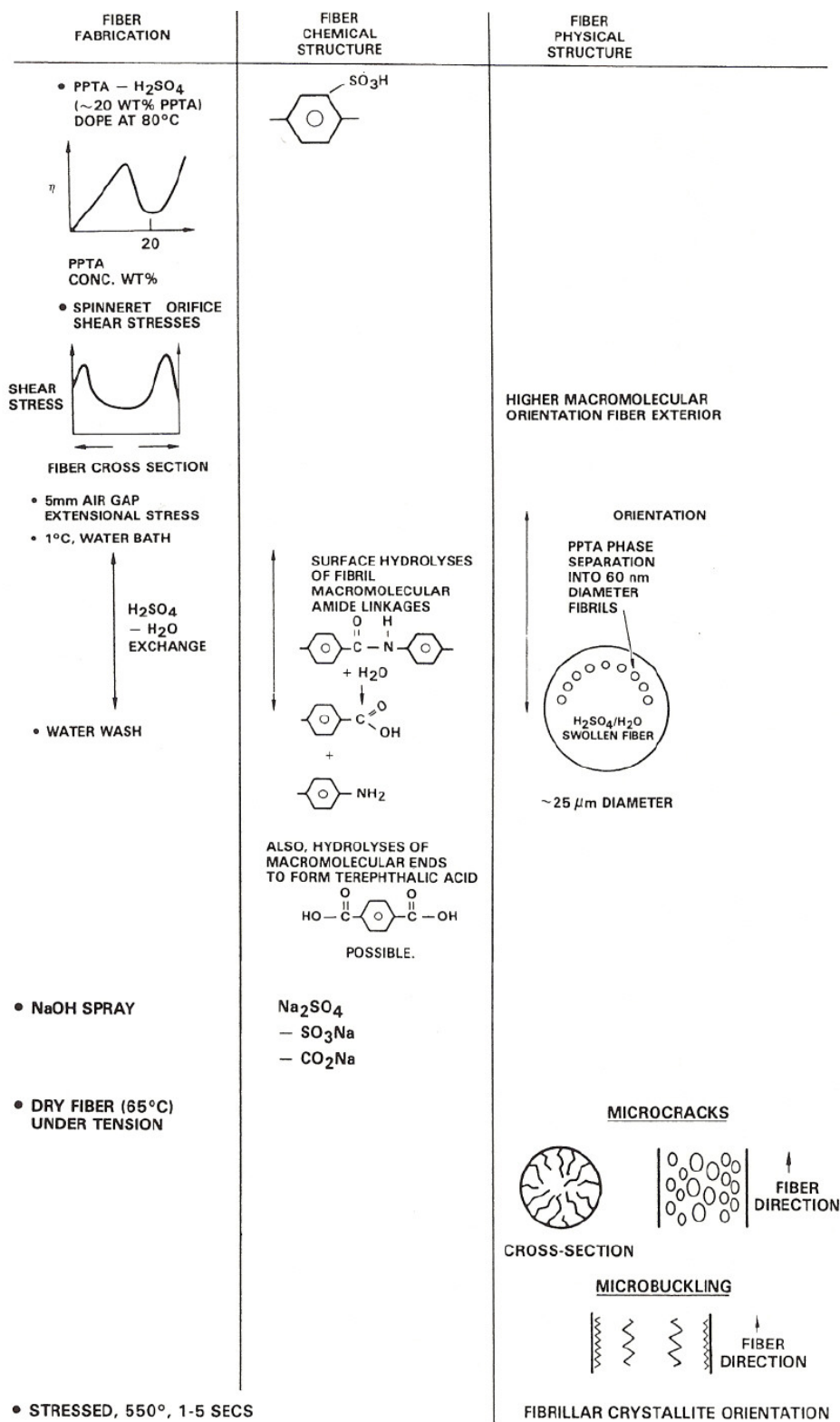


Figure 5. Schematic of Kevlar fiber production process [11]

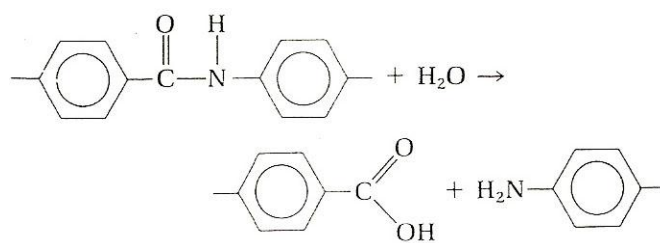


Figure 6. Hydrolytically induced chain scission of PPTA molecule

The reason for the high strength of Kevlar fibers is also similar to the reason given for the high strength of Zylon fibers. Like Zylon, Kevlar molecules contain benzene rings on the main parent chain. Also, both fibers achieve a high degree of molecular orientation parallel to the fiber axis due to the properties of the liquid crystal solution and the spinning process.

One of the most important chemical aging mechanisms of Kevlar is hydrolytic degradation. In this type of degradation, the amide linkage in the PPTA macromolecule undergoes hydrolytically induced chain scission as seen in Figure 6.

It has been shown that only 4% of the amide linkages must hydrolyze to result in zero strength, and that 1 scission of the amide linkage per PPTA macromolecule decreases the strength of the Kevlar fibers by fifty percent [12-14]. It has also been shown that the rate of this hydrolysis reaction is directly proportional to the relative humidity of the environment at room temperature, and that this reaction may be accelerated by the presence of H_2SO_4 or NaOH impurities that originate from the fiber spinning process and are present in the fiber acting as catalysts for the hydrolytic reaction [15,16].

Hydrolytic degradation of bare Kevlar 49 yarns as a function of time and temperature for one hundred percent relative humidity can be seen in Table 1 [17].

Table 1. Rates of hydrolytically induced strength degradation of Kevlar 49 fiber as a function of temperature at 100% RH [17]

| Exposure Conditions at 100% RH | | Strength Degradation (% / year) |
|--|-------------|------------------------------------|
| Temperature (°C) | Time (days) | |
| 200 | 2 | 12,426 |
| 175 | 4 | 5,585 |
| 175 | 4 | 5,466 |
| 150 | 14 | 1,563 |
| 125 | 32 | 199 |
| 125 | 40 | 264 |
| 100 | 162 | 64 |
| Each Test Performed on a Different Spool | | |
| 100 | 281 | 77 |
| 100 | 281 | 77 |
| 100 | 281 | 76 |
| 100 | 281 | 78 |
| 100 | 281 | 86 |
| 100 | 281 | 83 |
| 65 | 440 | 3 ^a |
| 65 | 440 | 1.5 ^a |
| 65 | 440 | 5 ^a |
| 65 | 440 | 4 ^a |

^a Statistically meaningful data.

Figure 7 [17] shows a plot of $\ln(dg/dt)$ versus $1/T$ for various hydrolytic aging data available in literature. From this figure we see that Kevlar 49 fibers degrade approximately 200 times faster in a 100% relative humidity environment than in a 0% relative humidity environment.

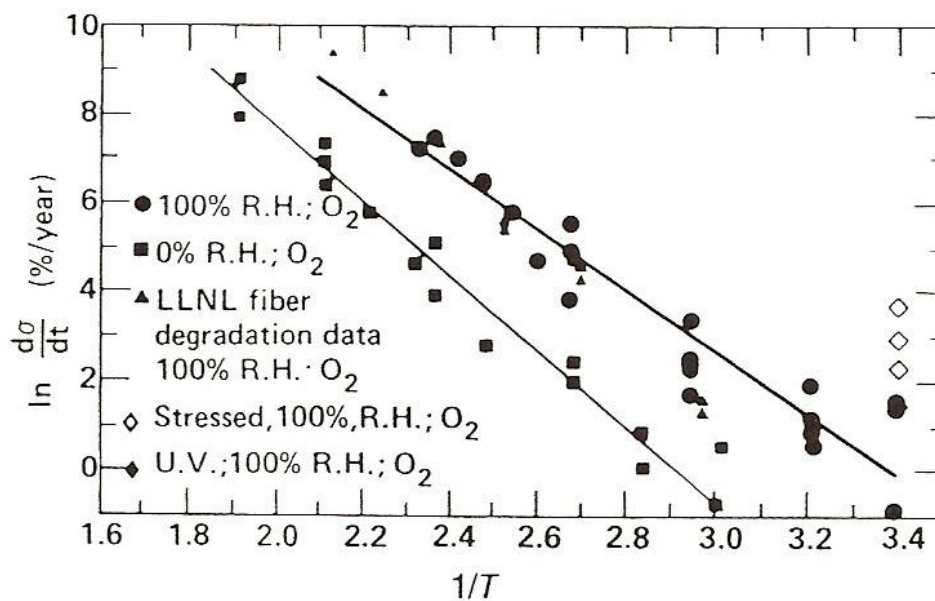


Figure 7. Plot of $\ln(dg/dt)$ versus $1/T$ for degradation of Kevlar fibers [17]

In order to determine estimated rates of fiber degradation for conditions which more accurately reflect possible service environments, the $\ln(dg/dt)$ versus $1/T$ plot seen in

Figure 1 has been extrapolated along with degradation models available in literature to produce the data in Table 2 [17].

We can see from this table that in typical service environment conditions and in the nonstressed state, fibers may experience rates of degradation of up to 3% a year.

Table 2. *Estimated Kevlar 49 strength degradation from hydrolysis [17]*

| Exposure Temperature (°C) | Imposed Stress Level (%) | <i>Strength Degradation</i> (%/year) |
|---------------------------|--------------------------|--------------------------------------|
| 65 | 0 | 3.0 |
| | 20 | 4.6 |
| | 75 | 16.3 |
| 38 | 0 | 0.5 |
| | 20 | 0.8 |
| | 75 | 2.8 |
| 23 | 0 | 0.2 |
| | 20 | 0.3 |
| | 75 | 1.1 |

Typical fracture topographies of Kevlar 49 fibers which have failed in tension show that the fibers split axially 20 to 50 times their diameter [18-23]. This typical behavior is different, however, from the behavior seen in fibers which have experienced chemically induced degradation in the form of PPTA macromolecular chain scission. These defects decrease the transverse crack resistance of the Kevlar fibers, thereby decreasing the tensile strength. Thus, in degraded Kevlar, the fibers tend to fail in a transverse manner before sufficient shear stresses can develop which may result in typical axial failure. This transverse failure of the Kevlar fibers has been shown to indicate a loss of tensile strength in the fibers of at least thirty percent [13]. Because the manner in which degraded Kevlar fails is significantly different from the way in which non-degraded Kevlar fails, it is possible to determine from microscopy if fiber failure is a result of decreased strength due to chemical aging [13]. An example of the characteristic transverse failure fracture topography of hydrolytically degraded Kevlar fiber can be seen in Figure 8 [11].

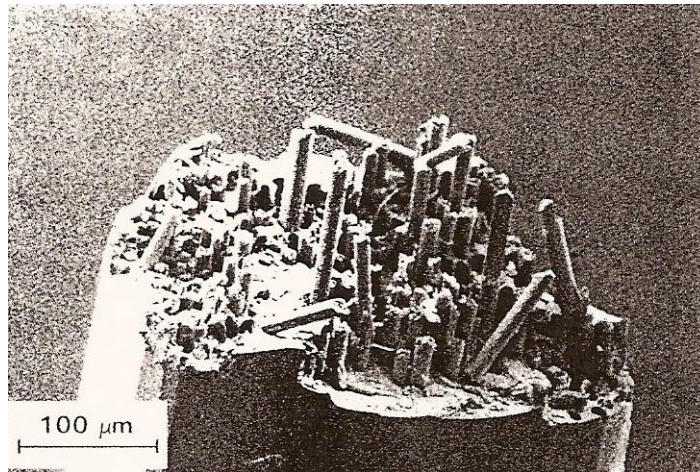


Figure 8. Scanning electron micrograph of the fracture topography of a Kevlar 49-epoxy composite strand with hydrolytically degraded fibers [11]

We can see in Table 3 the results of chemical analyses which show the concentrations of various impurities in parts per million by weight (ppm) and the range of these values observed in 25 Kevlar 49 spools [11, 24-25].

Table 3. *Ash, Na, SO₄²⁻, and S in Kevlar 49 fibers [11]*

| Impurity | Average (ppm) | Range (ppm) |
|-------------------------------|---------------|--------------------|
| Ash | 10,950 | 6,200 – 615,700 |
| Na | 3,750 | 2,000 – 65,100 |
| SO ₄ ²⁻ | 5,050 | 800 – 68,650 |
| S | 4,050 | 3,600 – 64,600 |

Morgan and Pruneda have proposed a model of characteristics of the impurities in Kevlar 49 fibers [11]. Based upon the assumptions of this model and the average values for impurities shown in Table 2, the chemical nature of the impurities in Kevlar 49 can be seen in Table 4 [11].

Table 4. Chemical impurities in Kevlar 49 fibers [11]

| Chemical | Concentration (ppm) |
|---|---------------------|
| Na ₂ SO ₄ | 7,450 |
| δ SO ₃ ⁻ Na ⁺ | 4,550 |
| δ SO ₃ H | 2,400 |
| δ Na ⁺ (COO ⁻ Na ⁺ end groups) | 350 |
| Metallic oxides | 350 |
| <i>Total</i> | <i>15,100</i> |

According to this model, approximately fifty percent of the impurities present in Kevlar 49 exist in the form of Na₂SO₄ situated between the Kevlar microfibrillar crystallites and are most likely concentrated in small clusters along preferential diffusion paths that form during drying. These clusters may later contribute to the formation of microvoids in the fiber.

It is also possible that not all of the H₂SO₄ used in the production of Kevlar is completely neutralized or washed from the fibers. If any of this sulfuric acid remains in the fiber, it may result in accelerated hydrolytic and oxidative degradation of the PPTA macromolecules. Traces of H₂SO₄ have been detected in Kevlar 49 fibers by mass spectrometry [25].

It has been proposed [11] that the H_2SO_4 that may remain in the fibers may be present in the form of $\text{NH}_3^+\text{HSO}_4^-$ macromolecular end groups. Since the ends of the PPTA macromolecules are aligned due to the properties of the liquid crystal polymer solution, this will result in a cluster of ionic ends in transverse planes of the fiber. This may result in a concentration of sulfuric acid residing in the regions in between the microfibrils of the Kevlar fibers in a state of equilibrium as seen below where R represents the PPTA macromolecule:



This mobile residual H_2SO_4 will accelerate hydrolytic degradation of the PPTA molecule, and thus of the fiber as a whole.

CHAPTER III

EXPERIMENTAL DETAILS

Materials

Industry Name: Zylon[®] (PBO Fiber)

Chemical Name: Poly(p-phenylene benzobisoxazole)

Structure: As shown in Figure 1

Manufacturer: Toyobo Co., Ltd.

In all of the tests described below, two different types of Zylon were used. The first was gold in coloration which indicates that water, and possibly calcium hydroxide were used as coagulating and neutralizing agents and for the neutralization of the production acids. The second was blue in coloration. This indicates that in addition to water and possible calcium hydroxide, and additional bath of copper hydroxide was used to neutralize the acid used in production.

Humidity Moisture Absorption Test Details

The oven used for this experiment was a VWR Model # 1321P. The experiments were performed by Cyndi Young and Jose r j 'QøP gñ'cv'vj g"i tcfwcg'b ge j cplecn'gp i kpggtlp i" polymer lab, Texas A&M University. The samples were pieces of woven Zylon fabric measure approximately 3 inches square and weighing approximately 2g. The experimental procedure is as follows:

- 1) Samples were dried in a vacuum desiccator at room temperature ($\sim 25^{\circ}\text{C}$) using anhydrous calcium sulfate desiccant, and weights of the samples were recorded
- 2) Samples were then placed in a desiccator partially filled with distilled water, but not in direct contact with the water. Samples were left at room temperature for 24 hour period and then weights were recorded
- 3) Samples were then heated in oven while in moist environment described above for 24 hour period and then weights of the samples were recorded. The temperature was varied between 40°C and 90°C for each separate test run.
- 4) While still in the moist environment described above, the samples were then placed at room temperature for 24 hour period after which the weight of the samples was recorded
- 5) The samples were then placed in desiccator with the anhydrous calcium sulfate desiccant and vacuum pressure for 24 hour period and final weight was then recorded.

The purpose of this procedure was to detect permanent fiber swelling which would allow enhanced moisture absorption due to increased hydrogen bonding sites accessible in the swollen fiber.

Chemical Analysis Details

The instrument used for this experiment was an inductively coupled plasma-emission spectrometry (ICP) device. The experiments were performed by Robertson Microlit Labs, Madison New Jersey. The weight of the samples tested was approximately 2 g.

An inductively coupled plasma-emission spectrometry (ICP) device contains a source which generates and emits high energy plasma. This high energy source is used to excite the atoms in the sample to levels above their ground states. When the energy source is removed, the atoms will return to their ground states, releasing characteristic wavelengths of radiation. These wavelengths are measured, and when analyzed can give information as to the elemental composition of the sample. When the intensities of these wavelengths are compared to known standards, the concentrations of the elements in a sample can be determined.

The purpose of this experiment was to determine the levels of phosphorus impurities present in the PBO fibers.

Solid-State NMR Details

The instrument used for this experiment was a Bruker Avance-400 spectrometer. The experiments were conducted by Vladimir Bakhmoutov, Department of Chemistry Texas

A&M University, College Station, Texas. The weight of the samples tested was approximately 0.02g.

Solid-state Nuclear Magnetic Resonance (SSNMR) spectroscopy is a form of NMR spectroscopy in which the sample being analyzed is in the form of a solid rather than the more common solution state NMR. Nuclear Magnetic Resonance exploits the fact that, like electrons, protons and neutrons have a spin angular momentum. This spin may lead to a magnetic moment in the nucleus of some atoms whose nucleus has protons and neutrons with unpaired spins. This magnetic moment is what makes NMR possible. These magnetic nuclei are aligned with a powerful external magnetic field, and this alignment is then perturbed. The response to this perturbation gives information as to the structure of the sample being studied.

Solid-state NMR is similar in procedure and results to solution state NMR with some important exceptions. Unlike solution state NMR, in solids Brownian motion is not present to allow an averaging of anisotropic interactions. Thus Solid-state NMR is chiefly characterized by this anisotropy and procedures must be used to overcome this limitation. This is accomplished in some cases by carefully orienting the sample on a macroscopic level, or more commonly, by using magic angle spinning (MAS). In MAS the sample is spun using an air turbine mechanism about a particular angle with respect to the magnetic field at a frequency usually between 1 and 40 kHz. This allows anisotropic effects to be averaged and thus eliminated.

As stated above, not all atoms have a magnetic moment in their nucleus. Thus, only certain atoms in a material can be affected by NMR.

The purpose of this experiment was to determine the chemical form in which the phosphorus was present in the fiber.

Boiling Fiber Details

Vj gug"vguu'y gtg"rgthq to gf"d{ 'Lqugr j 'QØP gkmt the graduate mechanical engineering polymer lab, Texas A&M University. In this experiment small samples on the Zylon fabric were boiled continuously in water for extended period of time (up to three months). The samples were removed on a weekly basis and tested to determine if the samples had degraded sufficiently to allow them to be broken by hand. We know from previous studies that breaking the Zylon fibers by hand would indicate a loss in the tensile strength of the fibers of at least sixty percent [26].

CHAPTER IV

DATA ANALYSIS AND DISCUSSION

Humidity Moisture Absorption

The purpose of this test was to determine and quantify the behavior of Zylon fibers in an environment similar to that which might be seen by a body armor vest being used in the field. This test would allow detection of permanent fiber swelling which would allow enhanced moisture absorption due to increased hydrogen bonding sites accessible in the swollen fiber. This in turn may lead to enhanced mobility of any residual acid present in the fiber. Thus, the variables which were controlled in this experiment were the level of humidity, the temperature, and the time of exposure. A full description of this experiment can be found in Chapter III of this thesis. Through this test it was possible to determine and quantify the moisture pickup of the fibers as well as their moisture retention. Hydraulic incremental analysis was used to analyze the data acquired from this experiment. The principal equation used can be seen below.

$$X = 1 + \frac{X_{moist_weight} - X_{initial_dry_weight}}{X_{initial_dry_weight}} * 100 \quad (1)$$

where:

X is the ratio of the weight of the absorbed water to the original weight of the fiber given as a percent

X_{moist_weight} is the weight of the fiber after it has been exposed to the moist heated environment for a 24 hour period

$X_{initial_dry_weight}$ is the initial weight of the fiber sample after it has remained in the desiccator with the desiccant for an extended period of time and before it has been exposed to the moist and hot environment

Figure 9 is a graph showing the typical behavior of a fiber sample when subjected to the test described above. The graph shows the change in weight of the fiber sample over time. The y-axis represents the weight of the fiber sample, and the x-axis represents time. The graph is divided into five sections, corresponding to the steps in the experiment. The first section shows the fiber sample in a desiccator at room temperature. The second section shows the fiber sample in a moist environment at room temperature. The third section shows the fiber sample in a moist environment at 40°C. The fourth section shows the fiber sample in a desiccator at room temperature. The fifth section shows the fiber sample in a desiccator at room temperature. The graph shows that the fiber sample absorbs moisture in the moist environment, and that the majority of the moisture is absorbed when the sample is subjected to elevated temperatures, in this case 40°C (step 3). It is also important to note that the sample retains a significant amount of moisture even when the sample is returned to room temperature. In addition to this, the sample also retains some of the absorbed moisture even after being dried in the desiccator for a 24 hour period.

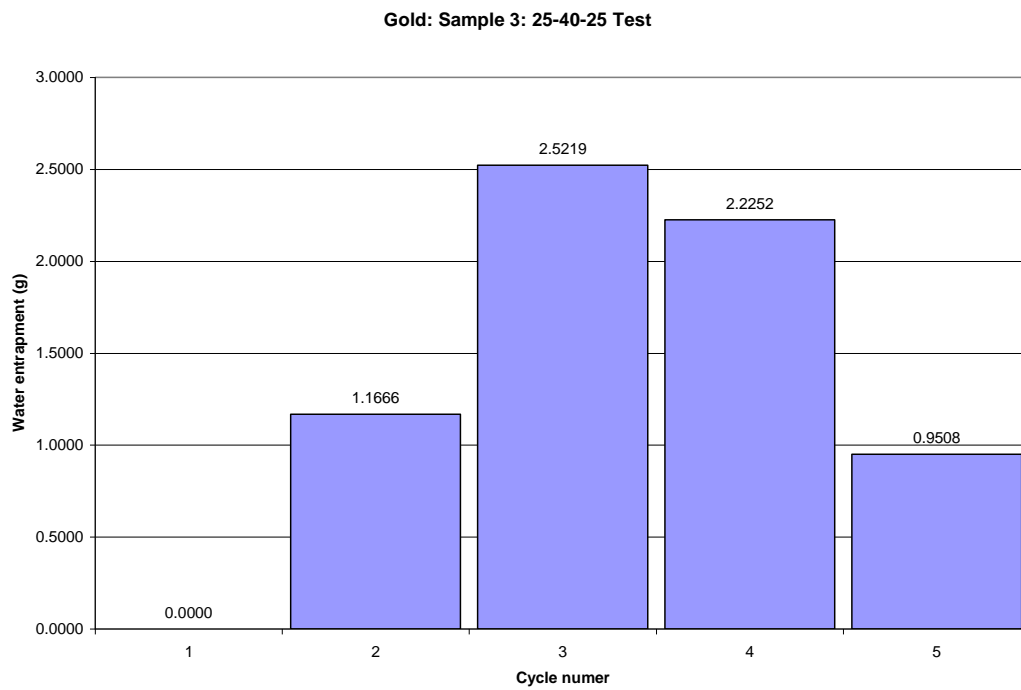


Figure 9. Typical behavior of Zylon sample during moisture absorption test

Figure 10 shows a plot of the results of experiments performed on four different samples for the same temperature-moisture cycle.

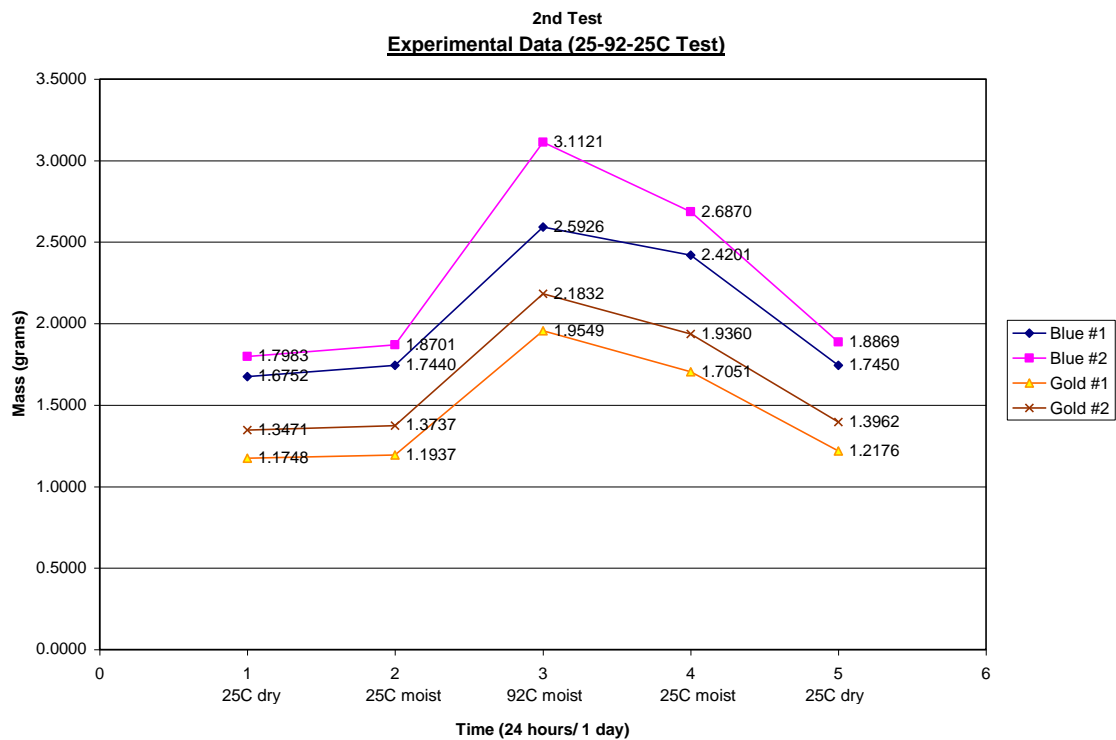


Figure 10. Four samples subjected to the same temperature-moisture cycle

We can see in Figure 10 typical behavior for a given humidity moisture absorption test.

In this case the independent axis shows the total weight of the sample. The following

figure shows the same set of experiments, but the results are given in the form of percentages of the original dry weight of the fiber.

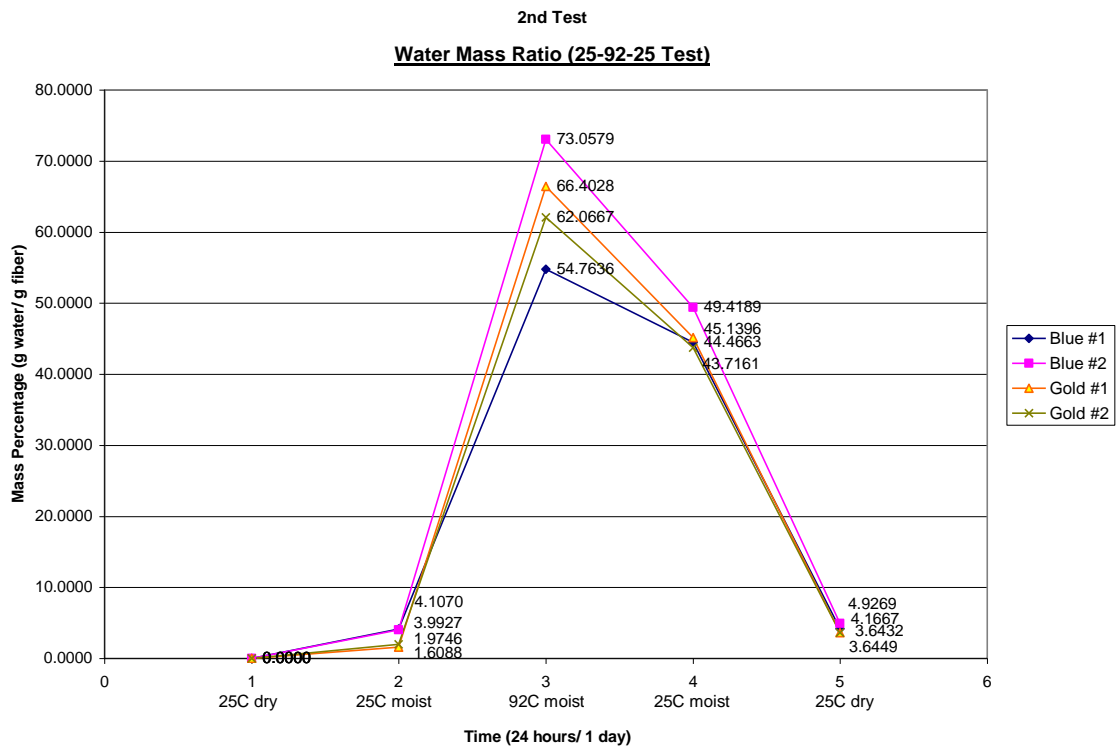


Figure 11. Moisture pickup given as percentage of original dry fiber weight

We can see in Figure 11 that at the height of the temperature-moisture cycle the Zylon fiber samples can absorb up to 73 percent of its own weight in moisture. Also, even

after drying, the fiber will tend to retain between 3 to 5 percent of its weight in absorbed moisture.

Finally, we can examine the effects of the different temperatures on moisture absorption.

These effects can be seen in Figures 12 and 13.

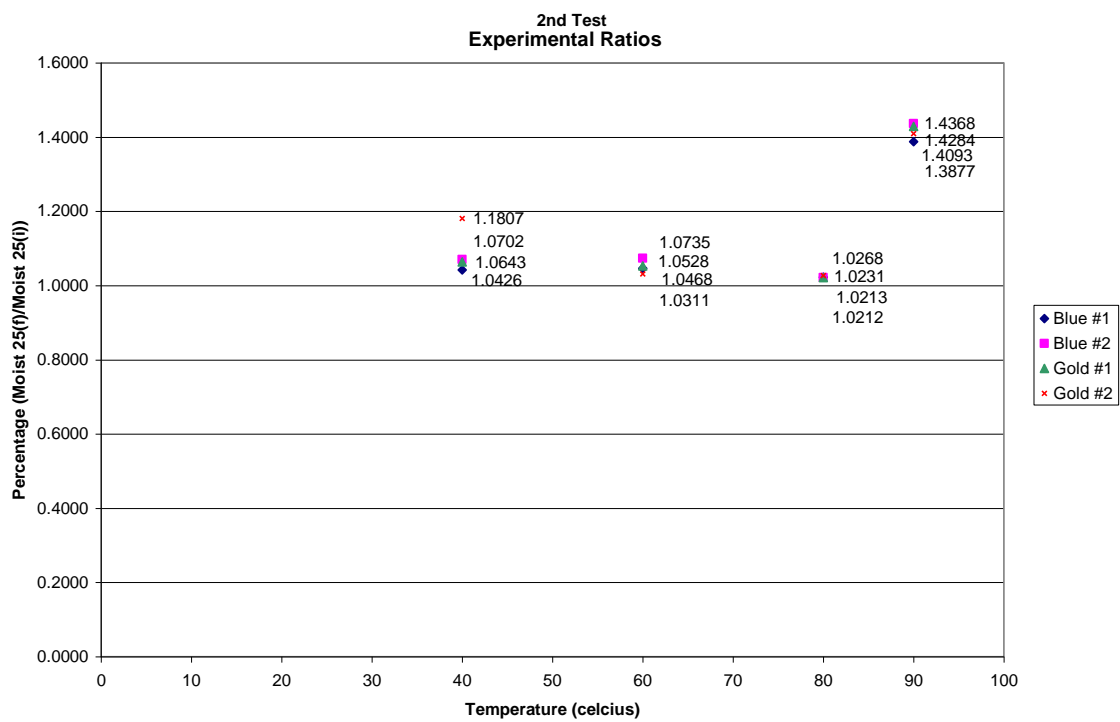


Figure 12. Experimental ratios of percentage of moisture pickup

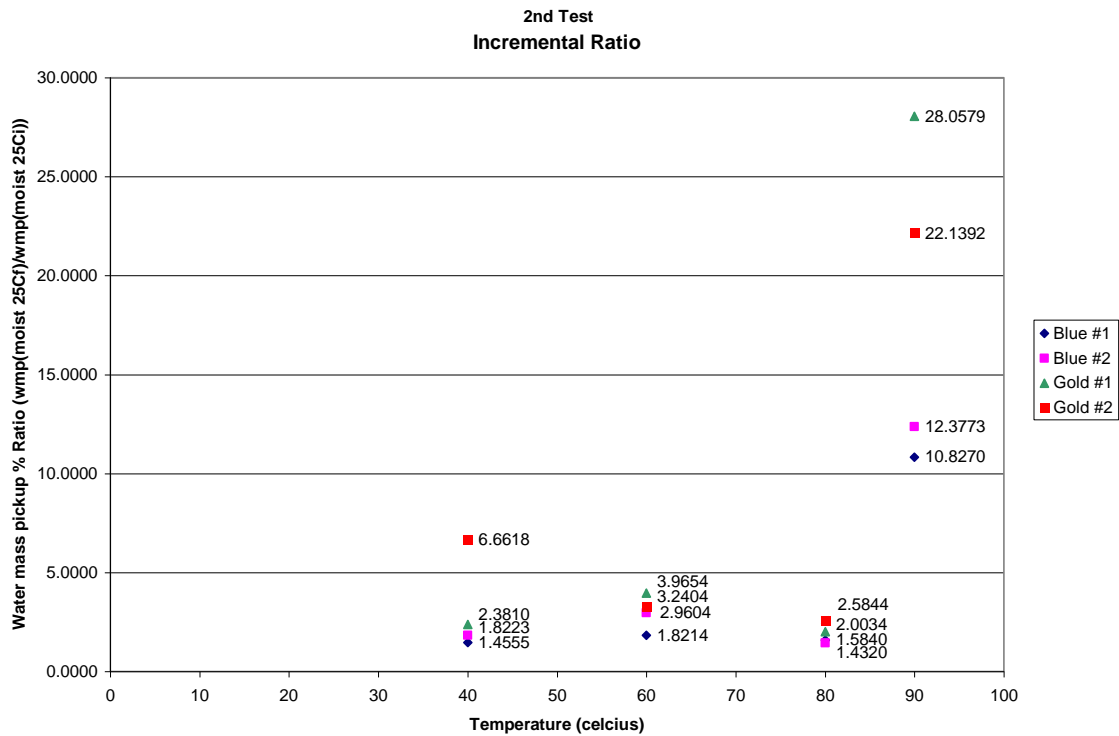


Figure 13. Incremental ratios of percentage of moisture pickup

Figure 12 shows the results for a test of four different samples at 40, 60, 80, and 90°C.

The values on the independent axis are simply the ratio of initial moist weight (after step 2) to final moist weight (after step 4). We can see from Figure 12 that the moisture absorption behavior of the fibers remains relatively constant at a value between 0.02 and 0.18 weight percent for the 40 to 80°C range. However, there does appear to be a significant difference appearing at the 90°C temperature mark. Here we see a significant

increase of around 20% in the moisture absorbed in the fiber during the heating process. This plot allows us to see the degree of permanent swelling in the fiber due to moisture absorption. It is this permanent swelling that would allow enhanced mobility for any residual acid impurities in the fiber, which in turn would increase the rate of hydrolytic degradation of the PBO fibers.

Figure 13 shows the results when this same data is compared using percentages. Once again, in general we see an increase in the moisture absorbed in the fiber during the heating process at the 90°C mark.

In addition to this, when the data for the gold samples was compared with the data for the blue samples as a whole for this test, little significant difference was found between the moisture absorption behavior of the two types of Zylon. It was seen, however, that the gold samples tended to retain more moisture subsequent to drying that was retained by the blue fibers.

Chemical Analysis

The purpose of this test was to determine and quantify the impurities present in the Zylon sample. Since it is known that polyphosphoric acid is used in the synthesis and processing of PBO, the samples were tested to determine the amount of residual phosphorus present in the sample. The results of these four tests can be seen in Table 5.

Table 5. Results of ICP chemical analysis showing weight percent of phosphorus

| | TEST 1 | TEST 2 | TEST 3 | TEST 4 |
|-----------------|--------|--------|--------|--------|
| P Content (wt%) | 0.46 | 0.557 | 0.42 | 0.37 |

The results of the inductively coupled plasma emission spectroscopy tests demonstrate that not only is there residual phosphorus present in the fiber, but it may be present in levels greater than 0.5 weight percent.

In addition to this, it was found that there was no significant difference between the phosphorus contents of the blue fiber and gold fiber samples.

Solid-State NMR

It was known from the chemical analysis tests described above that there was residual phosphorus present in the Zylon fibers. Therefore, in order to determine the chemical form in which this phosphorus is present in the fibers, it was necessary to perform Phosphorus-31 NMR. The results of this test can be seen in Figure 14.

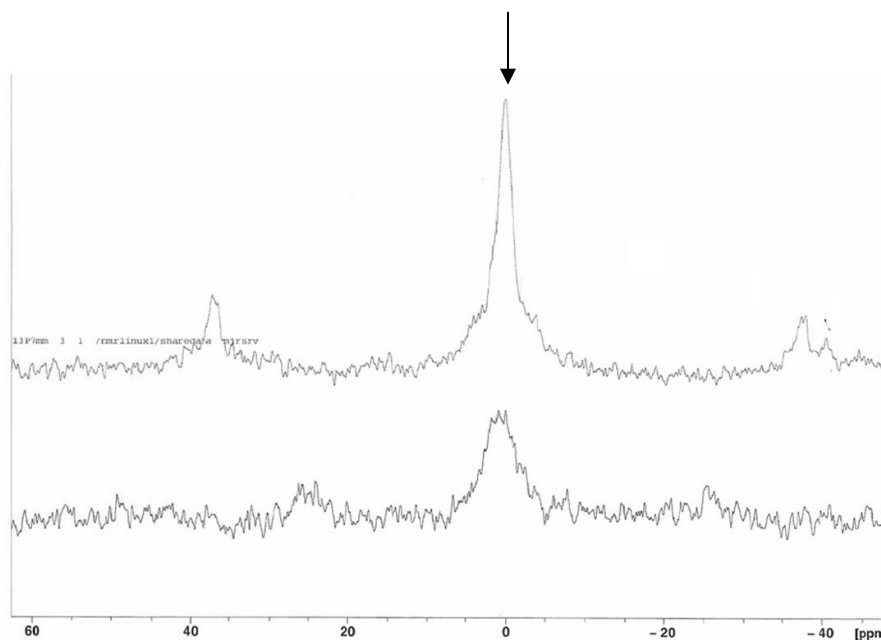


Figure 14. Phosphorus-31 NMR spectra

We can clearly see from the figure above that there is a significant peak at 0ppm. This indicates the presence of H_3PO_4 in the fiber. Thus, the phosphorus that is still present in the fiber after coagulation and washing is in the form of phosphoric acid.

Boiling Fiber Test

The results of this test showed that the gold Zylon fibers were able to be broken by hand after a period of boiling of approximately 76 days. The blue Zylon fibers failed after a period of approximately 103 days. This is a difference of approximately 25%. Since the

purpose of the boiling fiber test is to characterize the hydrolytic performance of the fiber at an accelerated rate, this test indicates that there is a slight difference between the hydrolytic degradation behavior of the gold and blue Zylon samples. The test indicates that the hydrolytic degradation performance of the blue Zylon fibers is slightly better than that of the gold fibers.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

From the experimental results of the chemical analysis tests, it is evident that a significant amount of phosphorus remains present in the Zylon fiber subsequent to processing. This element may be present in the fibers in levels greater than 0.5 weight percent. It was also shown by the experimental results of the P-31 NMR tests that these phosphorus impurities in the fiber are in the form of phosphoric acid.

It was also shown from the experimental results of the humidity moisture absorption tests that when subjected to a moist environment the fibers will absorb and retain moisture. This effect is also increased when the fibers are subjected to elevated temperatures, however the effects of elevated temperature are essentially the same between 40 and 80°C. The fibers can absorb greater than seventy percent of their own weight in water and even after drying may retain up to five percent of their weight in water. This residual moisture present in the fiber leads to permanent swelling of the fiber and increased space between the microfibrils. This will increase the mobility of the acid molecules present in the fiber.

It is known that the Zylon fibers are composed of an interconnected network of microfibrils and that a network of microvoids exists between these microfibrils which are in turn connected to each other by cracks and imperfections in the microfibrils [5].

These microvoids present a good environment for the retention of acid subsequent to processing, as well as a location for the absorption and retention of moisture from the environment.

Given the experimental evidence above, a model may be proposed which attempts to explain the unexpectedly poor hydrolytic performance of Zylon fibers. Unlike Kevlar which has an amide linkage that has been shown to be highly susceptible to hydrolytic degradation, the chemical structure of the PBO molecule is highly stable. In order for hydrolytic degradation of the PBO molecule to take place, and in order for this reaction to be accelerated by the presence of impurities such as phosphoric acid, this structure must be less stable in some way. It is possible that during production, not all of the oxazole rings in the PBO molecule fully close. This may lead to residual amide linkages in the macromolecules which would be more susceptible to acid catalyzed accelerated hydrolysis.

While the result of the two different fiber samples tested in the boiling fiber test were very similar, this test did demonstrate a slightly better performance of the blue fibers. This tends to support the conclusion that the copper hydroxide used to neutralize the acids present in the fiber subsequent to production does indeed improve the hydrolytic degradation performance of the fibers, if only slightly. This again seems to show that the presence of unneutralized acid in the fibers accelerate hydrolytic degradation. In addition to this, it is possible that the copper phosphate salt that is formed in the

neutralization process is more stable in the presence of moisture than the calcium phosphate salt. This would result in less phosphoric acid formed, or at least decrease the rate at which it is formed.

In the future it may be possible to expose soft body armor vests to humidity-temperature-time tests similar to those performed on the fibers described in this paper. The ballistic performance of these vests may then be evaluated. In addition to this, these tests will yield fiber failure modes under ballistic impact. In particular, these tests may yield fiber split lengths, which may be characterized by various microscopy methods. Because a decrease in fiber split length is indicative of hydrolytic degradation, this information will be very useful in characterizing the hydrolytic degradation characteristics of the vests under ballistic conditions.

Finally, all of the data characterizing the degradation of Zylon fibers may be used to form a ballistic lifetime probability model. This model may be used as a practical guide to determine the acceptability of a particular vest under real conditions.

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VITA

Joseph M. QøP gkny cu'dq tp'kp"J qwuxqp.Vgzcu'kp1980. He received his B.S. in mechanical engineering from Texas A&M University in College Station, Texas in 2004. He graduated with an M.S. in mechanical engineering from Texas A&M University in 2006.

His permanent address is:

Department of Mechanical Engineering

C/O Dr. Roger Morgan

3123 TAMU

College Station, TX 77843-3123