

Thermal Aging of a Blend of High-Performance Fibers

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ABSTRACT: The focus of this work is the study of the thermal aging of high-performance fibers used in the making of fire protective garments. Accelerated thermal aging tests were carried out on fabric samples made up of a blend of Kevlar® (poly *p*-phenylene terephthalamide) and PBI (poly benzimidazole) staple fibers, as well as on yarns pulled from this fabric, by means of exposure to elevated temperatures, comprised between 190°C and 320°C. All samples underwent loss of breaking force retention. The material thermal life, defined as the time required for the fibers to attain a 50% reduction of the original breaking force, ranged between a dozen of days at the lowest exposure temperature, to less than an hour at the highest. Breaking force data were fitted using the Arrhenius model following two different approaches, namely the extrapolated thermal life value and the shift factors yielded by the time-temperature superposition

(TTS). The Arrhenius model seemed to describe appropriately the overall aging process, as inferred from the excellent fit obtained when using both approaches, although activation energies provided from both approaches are different. To follow the chemical evolution of the material with thermal aging, Fourier-transform infrared (FTIR) analyses were conducted. The qualitative analysis of the FTIR spectra showed little evidence of chemical changes between the aged and the nonaged samples, indicating either that the aging process carries on without significant modification of the chemical structure of the fibers, or that FTIR is not an appropriate method to spot such a modification. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3031–3039, 2010

Key words: thermal aging; Kevlar; PBI; breaking force; Arrhenius; master curve; FTIR

INTRODUCTION

The market for high-performance synthetic fibers has experienced an incredible growth in recent years.¹ Such growth is driven to a large extent by the need of the automotive and aerospace industries to find materials both light and resistant (thermally and mechanically) to be used as replacement for metals. Transportation is not the sole niche for these materials, as they are extensively used in sport equipments and protective garments as well. The increasing use of these fibers has spurred some concern over their long term behavior. However, while there is plenty of literature concerning the chemical aging of thermoplastics and elastomers,^{2–7} in the case of high-performance synthetic fibers, the number of papers is very limited. A comprehensive study of the chemical aging process of high-performance polymer fibers is therefore compulsory if some insight is to be gained about the suitability of this type of materials in applications where a long service life in extreme harsh conditions is required. Such a study is the matter of this work, as we evaluate

the thermal aging of a fabric commonly used in the fabrication of fire protective garments.

The performance of protective gear used by fire fighters has been the object of very few studies, due to the fact that the level of protection offered by the garments after a certain time of service is very difficult to assess. Some authors have studied the effects of environmental and operating variables on fire protective garments; among these, Day et al.⁸ followed the evolution of the mechanical properties of various types of fabrics used in fire fighters' garments after being exposed to high levels of light radiation and heat; Rossi et al.^{9,10} estimated the variation in mechanical properties such as tensile and tear strength for different fabrics after exposure to high thermal fluxes, and concluded that the loss of mechanical properties may occur without any visual indication, making any estimation of protective performance based on the appearance of the garments not advisable; On the other hand, Makinen¹¹ compared the results of flammability and heat transfer tests carried out on several types of fire protective garments assembled from different fabrics and retired from service, to find that the variation of color is a good indicator of the residual protection level of the garments. Some other studies have focused on evaluating different methods used for the assessment of fire protective garments, such as

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the work of Thorpe and Torvi¹² in which the authors evaluated the potential of different nondestructive methods to determine the condition of fire protective garments in active service. The conclusion that can be drawn from these studies is that a robust predictive method for the performance of fire protective gear is yet to be found.

In this study, we evaluate the suitability of using the Arrhenius model, applied to the mechanical property measurements, to predict the thermal aging behavior of a fabric made from Kevlar[®] and PBI fibers. Complementary infrared spectroscopy analyses were undertaken to monitor the chemical composition of the materials during aging. In the past, infrared (IR) spectroscopy has been used to estimate the number of chain scissions in fibrous structures (particularly polyamide 6) through the concentration of newly formed end groups.^{13,14}

Kevlar[®] (poly *p*-phenylene terephthalamide) is a lyotropic liquid crystalline polymer that possesses extended domains of highly oriented chains which account for the ultrahigh strength and modulus of this fiber. PBI (poly benzimidazole) is a thermoplastic polymer with a remarkable thermal stability that enables a continuous operating temperature of up to 250°C in air. The glass transition for PBI is reported to be 450°C.¹

While the quantity of publications dealing with the thermal aging of Kevlar[®]-reinforced composites is impressive, the works focusing on the aging of the Kevlar[®] fiber itself are scant. Downing and Newell¹⁵ and Sweeney et al.¹⁶ investigated the enhancement of the compressive mechanical properties of Kevlar[®] following thermal treatment. According to the authors, the observed enhancement is due to a dual phenomenon of chain scission at the core and cross linking at the skin of the Kevlar[®] fibers. Parimala and Vijayan¹⁷ and Jain and Kalyani¹⁸ studied the loss of tensile strength after exposure to elevated temperatures of Kevlar[®] fibers. They found experimental evidence suggesting that the decrease in tensile strength is caused by the diminished crystallinity brought about by elevated temperatures. In the case of the aging of PBI fibers, nothing can be found in the literature. Musto et al.¹⁹ monitored the thermo-oxidative degradation of PBI films at high temperatures using FTIR analyses. FTIR spectra revealed the apparition of several new oxidized groups, as well as the cleavage of imidazole rings. From the scarce literature on the subject, it is clear that a much in-depth analysis is required to fully understand the aging process of these two fibers.

Thermal aging

Aging is defined as the change in a certain property of a material which often leads to detrimental effects

in terms of performance or appearance. Aging of polymers can be classified in two categories: physical aging, which relates to property changes caused by processes linked to the inherent thermodynamic instability of the amorphous phase such as recrystallization, and chemical aging, in which property changes are caused by a modification of the original chemical structure of the material. The three main reactions that take place during chemical aging of polymers are random chain scission, cross-linking, and depolymerization, and though any of them may occur at some point during aging, in most of the cases chain scission is the reaction that largely dominates the process. The likelihood for a given polymer to experience chain scission depends on the nature of its constitutive chemical bonds and their particular dissociation energy. Chain scission is often coupled with oxidation, which leads to a self-sustained chain scission process that involves the highly reactive free radicals produced during the oxidation. The decrease in molecular weight associated with chain scission is expected to have an effect on the ultimate mechanical properties of the polymer (breaking strength, ultimate elongation, etc.), whereas the properties at small deformations (elastic modulus, yield strength, etc.) are frequently left unchanged.²⁰

Thermal aging models

The Arrhenius model is one of the most commonly used methods to predict the service life of thermally aged polymer materials.^{21,22} The Arrhenius model assumes that the aging of a material is caused by a single chemical reaction whose kinetics follows the following relationship:

$$\frac{dC}{dt} = KC^\alpha \quad (1)$$

where C is the concentration of a chemical species, K is the rate constant of the reaction, and α is the reaction order. The basic assumption of the Arrhenius equation is that K varies with temperature according to the equation as follows:

$$K = K_0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where E is the activation energy of the reaction, R is the universal gas constant, and T is the absolute temperature. Neglecting the fact that in the case of polymers, there are generally multiple reactions involved in the aging process and despite the unclear link between chemical and physical properties, the Arrhenius model is extensively used for the prediction of thermal life L of polymers, which, according to the model, is given by the following:

$$L = L_0 \exp\left(\frac{E}{RT}\right) \quad (3)$$

A common approach when using the Arrhenius model is to set a given mechanical property as the response variable of the aging process, and then run several accelerated aging tests to establish the relationship between this variable and the aging time for various temperatures. A predetermined value of the response variable is then arbitrarily selected as the material thermal life. In practice, L is calculated by extrapolation of the data collected in the accelerated aging tests. The values of L are plotted in logarithmic scale against the reciprocal of the absolute aging temperature. A linear fit enables the extrapolation of the thermal lives at temperatures different than those used in the accelerated aging tests. This plot is known as the Arrhenius plot and may be used to determine the activation energy for the aging process.

As an alternative to the use of the predetermined thermal life to construct the Arrhenius plot, many authors prefer a different approach using shift factors obtained when constructing the time-temperature superposition (TTS) master curve, based on the fact that this method uses the entire data set instead of just a single point to build the Arrhenius plot.^{23,24} In this approach, all property-loss vs. time curves for each aging temperature are horizontally shifted by an empirically calculated constant factor taking one temperature as reference, to obtain a smooth curve covering the whole property-loss spectrum.

To assess the convenience of using the Arrhenius model to describe the aging process of the Kevlar®/PBI blend studied in this work, the results obtained by the two aforementioned approaches will be compared.

In addition to the Arrhenius model, the Eyring model is also extensively used to characterize the thermal aging of polymers. According to this model, all activated processes are controlled by an energy barrier, the Gibbs activation energy (ΔG), which includes an entropic term in addition to the enthalpy of the Arrhenius model.²⁵ The Gibbs activation energy is thus defined by the following:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

where ΔH and ΔS correspond to the activation enthalpy and entropy, respectively. The entropy term is frequently non-negligible in the case of polymers. The thermal life in Eyring's model is given therefore by the following:

$$L = (kT/h) \exp(\Delta G/kT) \quad (5)$$

where k and h are Boltzmann and Planck constants, respectively. It is often found that data that deviate

from linearity using the Arrhenius model in a $\log t$ vs. $1/T$ graph may be straightened up using the Eyring model.²⁶

EXPERIMENTAL

Materials

The material used in this study is a fabric made up of a blend 60/40 wt % of Kevlar® and PBI staple fibers, that was provided to us by Innotex and distributed commercially under the tradename Gemini®. Individual yarns pulled from this fabric as well as pieces of fabric were tested. For comparison purposes, 4 ply Kevlar® threads with a linear density of 70 tex were also measured.

Accelerated aging tests

Two aspects were considered when choosing the temperatures for the accelerated aging tests. First, the fabric and yarns should exhibit the required decrease in breaking force retention (i.e., a 50% reduction) when exposed at the chosen temperatures in a relatively short amount of time. This excluded temperatures below the thermal index of either material (the thermal index is the temperature for which after a long exposure time, usually 20,000 h, the material is deemed to still be in operating condition). It is worth noticing that the reported thermal indexes of Kevlar® and PBI are 190 and 250°C, respectively.¹ Second, the temperature domain for the accelerated aging tests should reflect the real temperatures encountered by fire fighters while in service. The exposure conditions faced by fire fighters have been classified in three categories depending on temperatures and heat flux: routine (up to 60°C and/or 2.1 W/m²), hazardous (up to 300°C and/or 10 W/m²), and emergency (above 300°C and/or 10 W/m²).²⁷ At the same time, measurements taken during controlled burns in a room showed that temperatures can reach 750°C at human chest height⁹ and that the average gas temperature in a post flashover fire can be as high as 1000°C.²⁸ While most of the time the situations met by fire fighters can be included in the routine category, they can potentially be much harsher. Therefore, temperatures of 190, 220, 275, 300, and 320°C were selected for the aging program. The accelerated aging tests were run in an electrical convection oven where the samples were introduced and then removed following a programmed schedule.

Mechanical tests

Tensile breaking force was selected as the parameter to quantify the advance of the aging process. This

property was measured for all samples in a MTS Alliance tester coupled with an automatic data acquisition program. Fabric was tested according to ASTM D 5034 standard²⁹ at a constant moving head speed of 500 mm/min. For each aging condition, four fabric samples were tested to determine the mean and standard deviation. Individual yarns pulled from the fabric and Kevlar® threads with a 10 cm length between the clamps were tested at a moving head speed of 100 mm/min. To prevent damage from the grips, the sections of the yarns and threads clamped between the grips of the tester were “sandwiched” with duct tape. In the case of yarns and Kevlar® threads, eight tests were required for each aging condition to calculate the mean and standard deviation. Care was taken to ensure that the testing for the fabric and yarns was performed using the same weaving direction for all samples.

The thermal life at a given temperature was defined as the exposure time after which the tensile breaking force had decreased by an amount of 50%.

FTIR analyses

Infrared spectra were collected via two different reflection techniques: Diffuse Reflectance (DR) and Attenuated Total Reflectance (ATR). ATR analyses were carried out using a Thermal Continuum FTIR microscope. Individual fibers pulled from the fabric were crushed and flattened with a little roller and then taped onto an aluminum-coated slide. A Germanium crystal was used for the analyses and a total of 120 scans with a resolution of 8 cm^{-1} were required to produce each spectrum.

DR analyses were undertaken with the help of Dr. Kenneth Cole at the Industrial Materials Institute (IMI) facilities at Boucherville, Canada. Potassium bromide powder and an “intragold” gold disk were used as background materials for the collection of DR spectra.

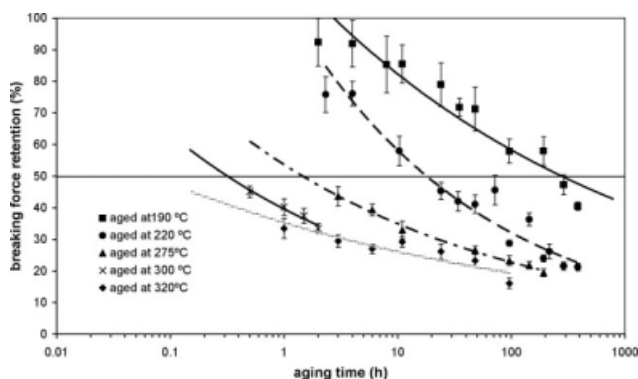


Figure 1 Breaking force retention curves and their corresponding power-law interpolation for aged samples of Kevlar®/PBI yarn.

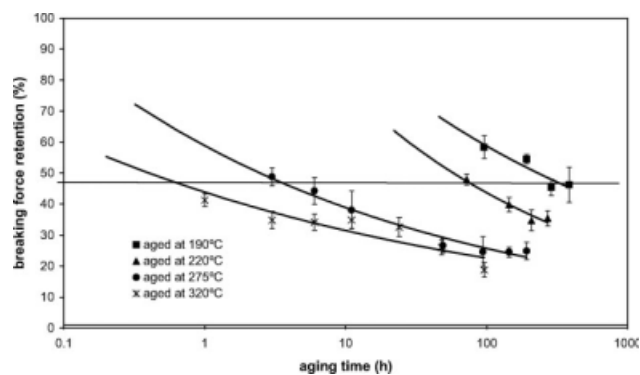


Figure 2 Breaking force retention curves and their corresponding power-law interpolation for aged samples of Kevlar®/PBI fabric.

RESULTS

The value of the tensile breaking force for the as-received fabric was measured to be $1214 \pm 202\text{ N}$ whereas for the nonaged yarns, the value is $34 \pm 2.8\text{ N}$. In the case of the Kevlar® threads, the breaking force was found to be $60.3 \pm 3.1\text{ N}$. To be able to compare the aging behavior of all samples, the results were converted into breaking force retention percentage. The results for the Kevlar®/PBI yarns, the fabric and the Kevlar threads are shown in Figures 1–3, respectively. A comparison of the curves at the lowest and highest aging temperature is displayed in Figure 4, which shows that all three materials tested exhibit a fairly similar decrease in breaking force retention at all aging temperatures, although the breaking force of Kevlar® threads at the highest aging temperature was lower than the other two materials. This suggests that the response of the fabric when confronted to aging is controlled by the behavior of the constitutive yarns and not by the assembly factors, like the weaving method, which seem to have a rather limited effect. As expected, thermal life decreased with increasing

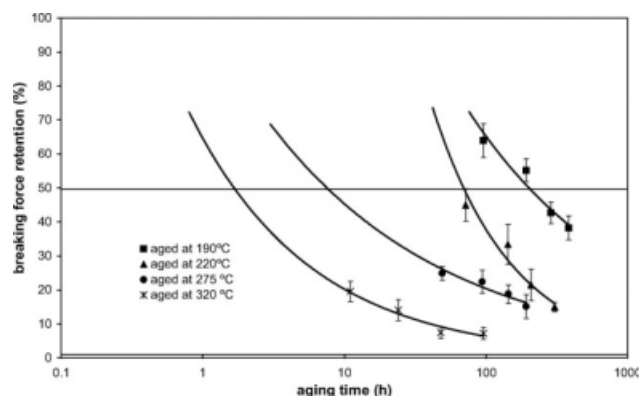


Figure 3 Breaking force retention curves and their corresponding power-law interpolation for aged samples of Kevlar® threads.

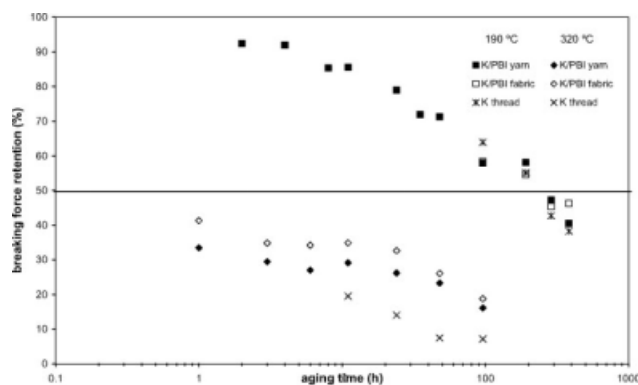


Figure 4 Comparison between the breaking force retention curves for the Kevlar[®]/PBI fabric and yarns and Kevlar threads at the lowest and highest aging temperatures.

aging temperature, resulting in thermal lives spanning from about 2 weeks at 190°C to less than an hour at 320°C. It is worth pointing out the fact that a 50% loss in breaking force retention was obtained at 190°C after 2 weeks, even though this temperature is reported as the thermal index of Kevlar and therefore the material is not supposed to meet the end of service life (i.e., the 50% reduction in breaking force retention) after such a short time.

The predetermined thermal life approach

The data set corresponding to the Kevlar/PBI yarns was used to construct the Arrhenius model for the aging process. The thermal life corresponding to a 50% loss of breaking force was calculated at each aging temperature using an empirical power-law regression given by the following:

$$F_b = At_a^B \quad (6)$$

where F_b is the breaking force retention, t_a is the aging time, and A , B two constants depending on temperature. The values of A and B and the calculated thermal life (L_f) for each temperature are listed in Table I.

The logarithm of the thermal lives calculated from the regressions was plotted against the reciprocal of

TABLE I
Empirical Constants and Thermal Lives Obtained from the Power Law Interpolations of the Breaking Force Retention Curves

Aging temperature (°C)	A	B	L_f (h)
190	116	-0.15	278.00
220	105	-0.26	18.00
275	54	-0.19	1.45
300	40	-0.20	0.32
320	35	-0.13	0.07

the absolute aging temperature to provide the Arrhenius plot shown in Figure 5.

The good agreement between the thermal aging data for Kevlar[®]/PBI yarns and the Arrhenius model is outlined by the excellent correlation coefficient, R^2 , shown on the plot. According to these results, the Arrhenius model can conveniently predict the thermal life of the Kevlar[®]/PBI fabric and yarns based on the temperatures met while in service. The value of the activation energy E calculated from the Arrhenius plot is equal to 137 kJ/mol.

Time-temperature superposition (TTS) approach

To further corroborate the convenience of the Arrhenius model as a valid way to describe and predict the thermal aging behavior of the Kevlar[®]/PBI blend studied, the time-temperature superposition (TTS) was used as an alternative approach. As previously done with the thermal life approach, the data set corresponding to Kevlar[®]/PBI yarns (Fig. 1) was used as the basis for the construction of the time-temperature superposition (TTS) master curve. Using the curve at 190°C as pivot, the TTS master curve for the aging process was put together by multiplying the remaining breaking force curves by a constant empirical shift factor a_T (different for each aging temperature), until a smooth curve was achieved. The TTS master curve is shown in Figure 6 and the corresponding shift factors are listed in Table II.

Here again, an Arrhenius plot was created using the shift factors from the TTS technique. This plot is shown in Figure 7. As with the previous approach, the Arrhenius model seems to fit data correctly, a fact reflected by the excellent correlation coefficient that once again is obtained. The activation energy calculated using this approach is 107 kJ/mol. From the excellent agreement obtained when using either approach, as illustrated in Figures 5 and 7, it is evident that the thermal aging of the Kevlar[®]/PBI blend complies with the Arrhenius model, and

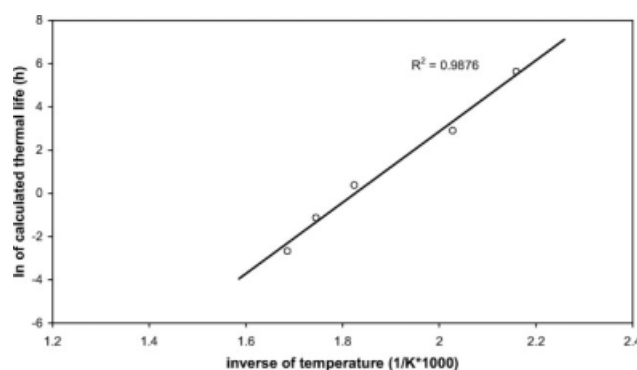


Figure 5 Arrhenius plot of the calculated thermal lives of aged Kevlar[®]/PBI yarns.

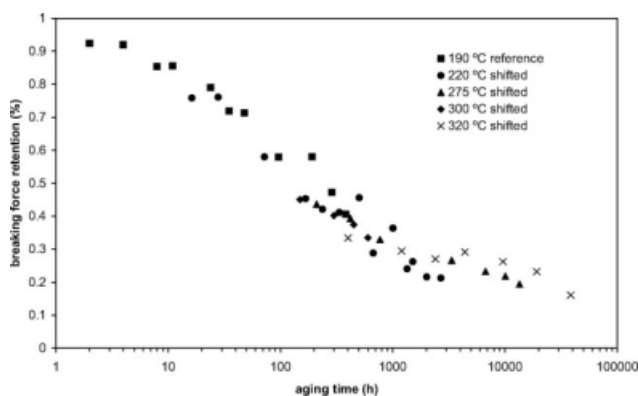


Figure 6 TTS master curve for the aging of Kevlar/PBI yarns.

therefore, we do not require to use any other thermal aging model (like Eyring's) to further improve the fitting in the Arrhenius plot.

FTIR analyses

To evaluate the effect of thermal aging on the chemical composition of the materials, Attenuated Total Reflectance (ATR) FTIR analyses were performed for both Kevlar®/PBI yarns and Kevlar threads. The spectra, in arbitrary absorption units, are shown in Figure 8.

The spectrum of the Kevlar®/PBI blend is almost identical to the one of Kevlar®, with no peaks characteristic of PBI showing up. This may be attributed to the higher weight percentage of Kevlar® within the blend yarns. The band assignment for the Kevlar®/PBI blend is shown in Table III. It agrees with previous works found in the literature on the subject.^{30–32}

A comparison of the spectra of Kevlar®/PBI yarn samples non-aged and aged at 275°C for different periods is provided in Figure 9. Qualitative end group analysis, carried out to reveal the eventual presence of new end groups linked to polymer chain scissions, shows that the variation of the absorption peaks as aging time increases is minimal, even for samples that have already shown a significant drop in breaking force retention. This was a rather surprising finding. Indeed, new absorbing bands of

TABLE II
Empirical Shift Factors Used in the TTS Master Curve

Aging temperature (°C)	Empirical shift factor (h)
190	1
220	7
275	70
300	300
320	400

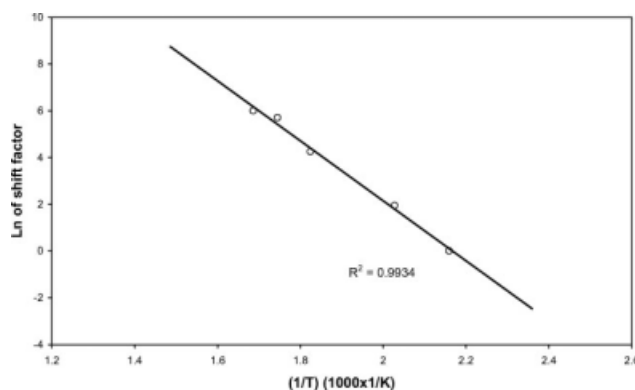


Figure 7 Arrhenius plot of the shift factors used in the TTS model for Kevlar/PBI yarns.

oxidized groups created during thermal aging were expected to appear, especially in the carbonyl (1700–1800 cm^{-1}) region due to the fact that traces of H_2SO_4 , introduced during spinning, make Kevlar® fibers prone to oxidation.³³ This result suggests that chain scissions, if present, do not lead to the creation of any FTIR detectable end-functions for this particular material. Similar results have been observed for all aging temperatures.

However, no quantitative analyses of the ATR spectra could be done due to irregular contact surface between the ATR crystal and the fiber. It is worth pointing out that ATR is a surface technique that does not provide any information about the bulk of the fiber.

With the aim of solving the quantitative analysis problems associated with ATR, diffuse reflectance (DR) analyses were undertaken. The DR spectra for aged and non-aged Kevlar samples are shown in Figure 10 in Kubelka-Monk units. While most of the absorption peaks of ATR spectra are maintained in DR, the overall shape of the spectrum is somewhat different, especially in the region between 1200 and

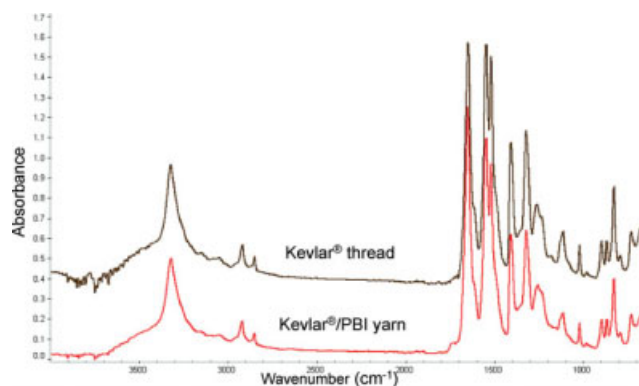


Figure 8 Comparison of ATR spectra of nonaged samples of Kevlar®/PBI yarns and Kevlar® thread. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Band Assignment for Absorption Peaks of Nonaged Kevlar/PBI Yarn Spectrum

Frequency (wavenumber, cm^{-1})	Band assignment
3320	N—H stretching of amides groups hydrogen bonded
1646	Stretching of C=O bonds in hydrogen linked amide
1608 and 1515	C=C stretching in aromatic groups
1543	N—H deformation and C—N stretching coupled modes
1305	C—N stretching in aromatic groups
1240	C—N stretching, in-plane N—H bending and C—C stretching coupled modes in amides
1018	In-plane C—H bending in para-substituted aromatic compounds
827	Vibration of 2 adjacent hydrogens in aromatic groups
865, 729 and 526	Out of plane deformation of N—H bonds

1800 cm^{-1} , where the strongest peaks are located. It is readily seen that DR displays a poorer peak resolution compared with ATR. In addition to this, the front-surface reflection (that tends to give the spectrum a more derivative-type shape) adds to the reflection of the bulk of the fiber (that presents itself in the usual transmission-type shape) making DR results unsuitable for any further analysis.

DISCUSSION

A large reduction in breaking force has been observed after exposing the Kevlar®/PBI blend to elevated temperatures. In addition to bulk fiber aging, there are other parameters which may contribute to this outcome, including yarn conformation

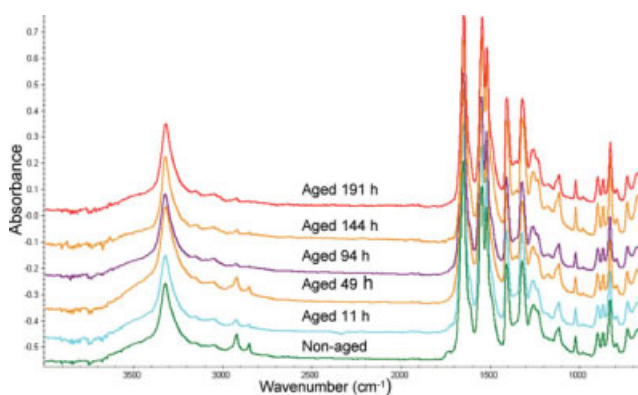


Figure 9 Comparison of the ATR spectra of Kevlar®/PBI yarns aged at 275°C for different periods. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

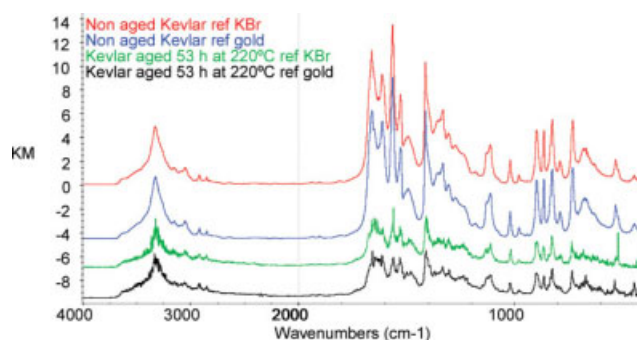


Figure 10 DR spectra of nonaged and aged samples of Kevlar®/PBI yarns. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

parameters such as the number of turns per unit length, interfilament slippage and staple fiber length. However, as suggested by the similar behavior exhibited by Kevlar®/PBI yarns and the Kevlar threads (which have different configuration), all these parameters do not appear to undergo significant modifications after thermal exposure. The extensive loss of mechanical strength is suspected to be the result of a generalized chain scission process sustained by polymer macromolecules within the aged samples. However, the qualitative end group analysis carried out on the FTIR spectra of aged samples did not show any indication of newly formed end groups associated to the cleavages of polymer molecules.

The Arrhenius model seems to describe correctly the thermal aging process of the Kevlar/PBI blend as illustrated by the excellent fit obtained using both the predetermined thermal life and TTS approaches. While the initial assumptions of the model, namely a unique aging mechanism with a rate constant that varies exponentially with the reciprocal of the temperature, may appear overly simplistic, the fact remains that the model offers an excellent depiction of the whole aging process, and it could eventually be used as a thermal life prediction model, provided that a satisfying explanation of the chemical reactions involved in the aging process is supplied. On the other hand, the activation energies yielded by the two approaches (137 kJ/mol for the calculated thermal life approach and 107 kJ/mol for the TTS approach) were found to be quite different. This may be the consequence of the large uncertainty introduced when extrapolating the thermal life value at high temperatures (for instance at 320°C). Thus, the real behavior may deviate from the predicted power-law regression used to determine the thermal life. The inherent nature of each approach may also play a role in the important gap found between the two activation energies since, as previously stated, the TTS approach uses the whole set of data to

produce the shift factor at each aging temperature, whereas the calculated thermal life approach relies on the information provided by a single point to predict the value of the thermal life. Therefore, the activation energy yielded by the TTS approach is arguably more meaningful and adjusts better to the actual aging process than the activation energy obtained when using the predetermined calculated life approach. The FTIR analyses seem to support the idea of no oxidation reaction taking place during thermal aging, since no significant alteration of the FTIR spectrum was observed for the aged samples of Kevlar/PBI yarns and Kevlar threads. However, oxidation reactions cannot be ruled out from the aging process based solely on FTIR results since it has been previously reported in the literature that the concentration of the oxidation products during thermal aging may be too low to be measurable by ATR.^{6,34}

CONCLUSIONS

The results of the mechanical tests for the Kevlar/PBI fabric and yarns indicate that this material, composed of staple fibers known for their outstanding thermal stability, is readily affected by thermal aging, as reflected by the sensible loss in terms of mechanical performance after exposure to high temperatures. These results came as a surprise given that degradation of the material took place even at the lowest aging temperature, which coincides with the continuous operating temperature reported in literature.

The progression of the thermal aging was evaluated in terms of breaking force retention, and the material thermal life was defined as the time needed to reach a 50% loss of the original value of this parameter. Continuous exposure at elevated temperatures, ranging from 190 to 320°C, resulted in thermal lives spanning from 12 days at 190°C to less than 1 h at 320°C.

The suitability of the Arrhenius model for describing the aging process of the Kevlar/PBI blend was assessed by using two different techniques to fit the breaking force tests results, namely the calculated thermal life and the time-temperature superposition (TTS). In both cases, the Arrhenius plot showed an excellent fit of the mechanical tests results, suggesting that the Arrhenius model offers an adequate depiction of the actual thermal aging process. However, the activation energies calculated from each technique showed a significant difference between them which is believed to be caused by extrapolation errors in the thermal life approach.

The evolution of the chemical structure of the Kevlar/PBI blend with thermal aging was followed by means of FTIR analyses. Two different reflection techniques, Diffuse Reflectance (DR) and Attenuated Total Reflectance (ATR), were evaluated, the latter yielding

better results. The comparison of the FTIR spectra of aged and nonaged samples revealed little modification of the chemical structure as no noticeable changes in the absorption peaks were observed between them. The results from the FTIR end group analysis suggest that FTIR may not be a convenient technique to spot polymer chain scissions for this material.

To ensure the validity of using the Arrhenius model to predict the service life of the studied fibers, a further investigation of the aging mechanisms is needed to identify the chemical reactions or physical phenomena linked to the observed loss in mechanical strength.

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