Characterization of Structural Changes in Thermally Enhanced Kevlar-29 Fiber

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Received 11 November 2002; accepted 28 March 2003

ABSTRACT: This exploratory investigation examined the structural mechanism accounting for the enhanced compressive properties of heat-treated Kevlar-29 fibers. A novel theory was set forth that hydrogen-bond disruption and concurrent misorientation of crystallites may account for the observed augmentation of compressive properties. To examine the said theory, as-received Kevlar-29 fibers were characterized by thermogravimetric analysis and differential scanning calorimetry in an effort to determine if crosslinking and/or hydrogen-bond disruption was responsible for the improved behavior in compression. Additionally, Kevlar-29 fibers that had been exposed to treatment temperatures of 400, 440, and 470°C were profiled by Fourier transform infrared spectrophotometry to determine if crosslinking and/or hydrogen-bond obfuscation had been promoted. The results indicate that both mechanistic changes occurred within the Kevlar-29, albeit in different regions of the rigid-rod polymer. In particular, heat treatment of poly-*p*-phenylene terephthalamide appears to have resulted in crosslinking of its skin region and hydrogen-bond disruption within the core realm. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 417–424, 2004

Key words: high performance polymers; fibers; Fourier transform infrared; compression; differential scanning calorimetry

INTRODUCTION

Kevlar, poly-*p*-paraphenylene terephthalamide (PPTA), is an organic fiber with a distinct chemical composition of wholly aromatic polyamides (aramids). Kevlar possesses a unique combination of high tensile strength and modulus, toughness, and thermal stability.[1] In air, PPTA demonstrates seven times the tensile strength of steel on an equal weight basis. In seawater, this advantage in tension increases by a factor of twenty.[2]

The exceptional strength of Kevlar fiber in tension is a direct result of its primary, secondary, and tertiary chemical structure. The primary, or molecular structure, of the Kevlar extended chain can be classified as monoclinic with the following lattice parameters: $a = 7.87$ Å, $b = 5.18$ Å, and $c = 12.9$ Åwith a 90° unit cell angle.[3] Its "rigid-rod" characteristic is a function of the *para*-substitution of the benzene ring, as well as the covalent bond strength in the c direction, which allows an axial stress to be distributed evenly throughout the highly linear macromolecular chain. The primary structure of Kevlar is illustrated in Figure 1.

The secondary structure of Kevlar, depicted in Figure 2, can be characterized as a pleated sheet configuration that is oriented perpendicular or transverse to the fiber axis. Pleats form within the core region when PPTA enters the coagulation bath, in response to the relaxation of the local stress field at the onset of coagulation.[4] This pleated conformation of the polymer chains is primarily governed by a consortium of intra- and intermolecular interactions between the conjugated groups within the PPTA primary structure. These interactions include (1) the resonance effect attempting to stabilize coplanarity of the amide groups and the phenylene groups, (2) the counteracting steric hindrance found between the oxygen and an *ortho*-hydrogen of the *p*-phenylene moieties, as well as between the amide hydrogen and an *ortho*-hydrogen of the terephthalic segment, and (3) the centrosymmetric pairs of hydrogen bonds between the amide and carbonyl groups.[5]

In a PPTA crystal, intermolecular hydrogen bonding between the C═O and the N—H acts along the b direction.[6] The pleating of the fibrils is superimposed on the fibrillar structure of PPTA, with a variation from linearity of approximately 5° and a periodicity of 500 nm as determined by optical microscopy.[7]A schematic of the pleated nature of the PPTA microstructure is illustrated in Figure 3. Other analytical methods, including x-ray diffraction and electron microscopy, have corroborated the existence of the pleated sheet secondary structure of Kevlar fibers.[5,8] It is this secondary structure that establishes the nearly perfect uniaxial linearity that defines Kevlar. However, Kevlar's microstructure cannot be described as perfectly linear due to the existence of microvoids and other crystalline defects located mainly around the periphery of the fibers.[9]

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Journal of Applied Polymer Science, Vol. 91, 417–424 (2004)

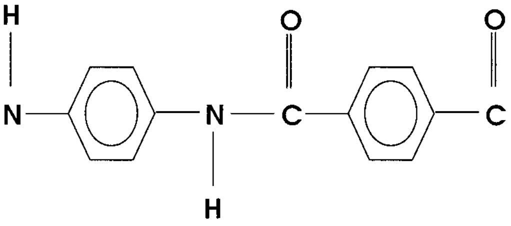

Figure 1 The primary structure of Kevlar.

Additionally, Kevlar possesses a clearly discernible tertiary structure. During the course of the spinning and postreatment stages of Kevlar processing, a skin–core morphology develops. The major distinction between skin and core regions is the higher degree of order and intermolecular bonding in the core region as compared to the skin. Consequently, the core region possesses an elastic modulus of 60.8 GPa. In contrast, the skin region of Kevlar's tertiary structure is virtually noncrystalline, and thus possesses a significantly lower elastic modulus of approximately 13.4 Gpa.[10] However, the skin may be critical in the prevention of crack propagation within the crystalline core region.

The tremendous behavior of Kevlar in tension can be attributed to structural characteristics including its stiff, extended chain conformation and nearly perfect uniaxial orientation. Despite the superlative tensile strength and modulus of PPTA in its fiber form, it possesses a comparatively low compressive strength due to its highly linear and regular microstructure. The compressive strength of Kevlar is 1/10 of its ultimate tensile strength.[11] Additionally, Kevlar exhibits a compressive-to-tensile strength ratio of between 0.13 and 0.25, while that of carbon fiber often exceeds 1.0.[12] This imbalance of the high tensile and low compressive properties has proved to be a limiting factor in its widespread incorporation into many structural composites. Compressive weakness relative to behavior in tension is not unique to Kevlar, but is quite pervasive within high performance fibers as illustrated in Table I.

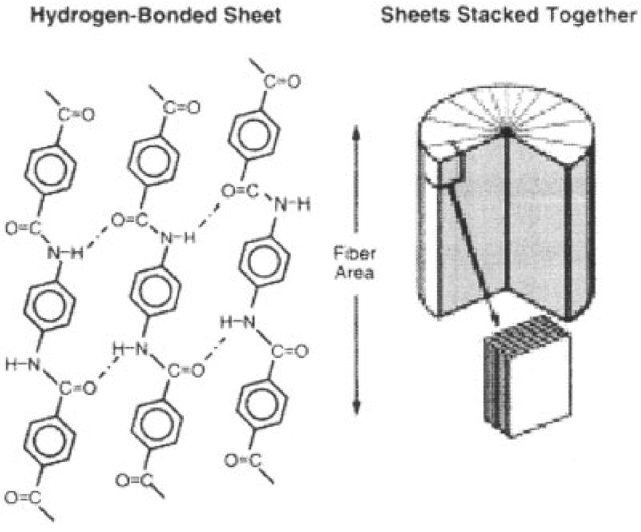

Figure 2 Thesecondary structure of Kevlar.

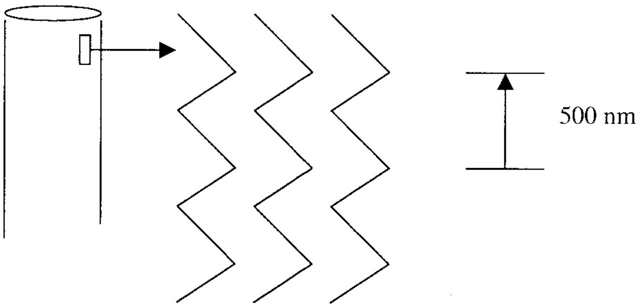

Figure 3 The pleated sheet microstructure of Kevlar.

Efforts to improve the compressive strength of Kevlar fibers have been conducted by many groups. Approaches to enhance the axial compressive strength of Kevlar may be classified into two main techniques. The first entails the incorporation of an additive or modifier into the Kevlar microstructure during the wet spinning or polymerization process, with the proposed goal of facilitating the formation of intermolecular covalent crosslinkages. The second involves achieving the same goal by subjecting the PPTA fibers to a postspinning treatment, such as elevated temperature or electron bombardment.

Sweeny et al.[13] attempted to improve the compressive modulus of Kevlar-29 by incorporating an activated aryl halogen into the molecular sequence of PPTA. The activated aryl halogen functioned as a copolymer and thus was introduced during the polymerization of the aromatic polyamides. Sweeny recognized that a high degree of crosslinking could not be accommodated without affecting the interchain hydrogen bonding. Moreover, it was concluded that the crystal structure of Kevlar would not accommodate a high level of crosslinking. Jiang et al.[11] also developed an activated form of PPTA by incorporating XTA, a benzocyclobutene-modified derivative of terepthalic

TABLE I
Tensile and Compressive Strengths of Several Rigid Rod Fibers[3,12]

High performance fiber	Tensile strength (GPa)	Compressive strength (GPa)
Polybenzoxazole (PBO)	5.7	0.20
Polybenzothiazole (PBZT)	4.1	0.28
Kevlar 29	2.8	0.35
Kevlar 49	2.9	0.37
Carbon Fiber (AS-4)	3.6	1.44

TABLE II
Tensile and Recoil Compressive Strengths of E-Beam Treated Kevlar-29 Fiber[14]

Radiation level (kGy)	Mean tensile strength (MPa)	Mean recoil compressive strength (MPa)
0	2160 ± 60	365 ± 6
100	2043 ± 120	368 ± 8
200	1996 ± 86	381 ± 9
500	1891 ± 71	404 ± 8
1000	1786 ± 93	472 ± 7
1100	1723 ± 87	487 ± 7

acid, into the polymer backbone during prefiber production. The XTA was triggered into reactive status via heat treatment at temperatures within the range of 325 and 425°C. Summarily, the XTA-rich PPTA fibers appeared to exhibit crosslinking as verified by swelling assays. Accordingly, recoil tests showed a slight improvement in the compressive strength of these modified Kevlar fibers, accompanied by a decrease in tenacity.

An investigation by Newell et al.[14] provided an example of enhancement of as-spun, unmodified Kevlar fiber. Unlike more common methods including thermal treatment or the addition of a crosslinking agent during spinning, this article describes the use of electron beam bombardment to induce what is purported to be crosslinking in Kevlar-29. The recoil compressive strength of the fiber increased significantly with increasing radiation exposure, reaching 487 MPa at a dose of 1100 KGy. Other key findings are depicted in Table II. The augmentation of axial compressive strength adversely affected the tensile strength of the poly-*p*-phenylene terephthalamide by approximately 20%.

Sweeney et al.[15] achieved similar results through thermal treatment of an unmodified form of Kevlar-29 fiber. Three levels of maximum treatment temperature, soak rate, and soak time (dwell) were examined within the scope of this study. It was concluded that maximum treatment temperature had a marked effect on the compressive strength of Kevlar fiber, with the higher treatment temperature resulting in a significant enhancement of compressive strength. Moreover, as seen in the aforementioned studies, this improvement in compressive behavior was accompanied by a compromise in strength in tension.

Clearly the enhancement of compressive properties can be realized in both modified and unmodified Kevlar-29 fibers by employing a postspinning stimulus such as thermal or ionization treatment. However, the structural mechanism accounting for the observed increase in compressive properties and accompanying decrease in tenacity has largely been a source of debate. In particular, unresolved is whether this compressive enhancement was due to a crosslinking phenomenon or hydrogen-bond obfuscation and concurrent crystallite misorientation.

THEORETICAL

There is strong empirical reason to support the theory that intermolecular crosslinking within the PPTA could provide an explanation accounting for the enhanced compressive strength. Such crosslinking would provide a covalent bond lattice in the a direction, thereby improving compressive behavior. However many of these studies relied upon an activated, or modified, form of poly-*p*-phenylene terephthalamide that would readily form a chemically labile moiety in order to promote free radicals upon heat treatment.[11,13]

The Kevlar-29 studied in the study by Sweeney et al.[15] was devoid of such activated species, yet if transaxial intermolecular covalent crosslinks within the core region were not responsible, another structural phenomenon must account for the markedly improved compressive properties of the Kevlar fibers that had been treated at 400, 440, and 470°C.

Sweeny[13] claimed that a high degree of crosslinking could not be accommodated within the current crystal structure and without disruption of intermolecular hydrogen bonding. It is likely that the secondary, or radially oriented pleated sheet, structure of Kevlar poses a steric limitation to the development of crosslinks within the core region of the PPTA. Moreover, in a study that characterized the pyrolytic behavior of aramid fibers, Mosquera et al.[16] concluded that below 500°C, only minor changes associated with loss of hydrogen bonds is prevalent, and that no noticeable framework changes take place until 545°C—the temperature at which notable chain scission begins.

As mentioned previously, Jiang et al.[11] concluded that lateral covalent crosslinks had been established via thermal treatment based upon swelling trials. This group concluded that the enhancement of compressive properties was a direct result of crosslinking, exclusively. This swelling study involved placing a small section of a Kevlar fiber on a glass slide and introducing the polymer to a few drops of sulfuric acid. Solubility of the PPTA fiber was then evaluated. Fibers treated above 330°C were characterized as insoluble and this finding was attributed to bulk crosslinking within the fiber. However, this conclusion does not take into consideration the tertiary structure of the Kevlar fiber. It is quite possible that the skin region, devoid of a highly crystalline packing order, was crosslinked while the core region was not. A crosslinked skin region could possibly render the fiber insoluble by creating an impermeable sheath around a highly linear and uncrosslinked core region.

The correlation between crystallite perfection and tensile behavior of Kevlar is well documented. Barton[17] studied x-ray peak shape parameters for PPTA fibers variously treated to produce a range of tensile moduli. He demonstrated an excellent correlation between the axial paracrystalline distortion parameter and the tensile modulus. From this work, he concluded that overall crystal perfection is the controlling feature for the tensile modulus. Additionally, Hindeleh[18] reported a correlation between tensile modulus and transverse crystallinity, which is highly dependent upon hydrogen bonding. These studies illustrate the strong relationship between the tensile behavior of the PPTA fibers and its transverse and axial crystalline perfection. Accordingly, the relationship between crystallite perfection and behavior in compression must not be overlooked.

Lee et al.[4] showed that when Kevlar fibers are subjected to a temperature of 400°C under an applied low tensile force (0.1 g/d), misalignment of the crystallites ensues. Secondly, the author asserted that misalignment of the crystallites increases with temperature and time of heat treatment, accompanied by a decrement in tensile modulus. Logically, misalignment would be even more pronounced when such a tensile force is absent. Lee also discovered that upon heat treatment under tension, the pleating conformation begins to vanish, the depleated region working inward from the skin, or boundary region. Thus, the decrease in tensile strength and improvement in compressive behavior observed by Sweeney[15]could be attributed to the aforementioned spatial distortion of the crystallites resulting from the destruction of interchain hydrogen bonding and concurrent destruction of pleated sheets within the core. While the theory that covalent crosslinks between crystallites would limit structural maneuverability, and therefore reduce creep abounds, the role of hydrogen bonding has been largely ignored in articles addressing induced thermal crosslinking of Kevlar microfibrils. Microfibril/fibril buckling within high-performance fibers is directly related to compressive strength (σ_c) according to the following equation:

$$\sigma_c = C\pi E(R/L)^2 \tag{1}$$

where C is an empirical constant, E the axial rigidity of the test specimen, R the radius of the fiber; and L the length of the fiber.[12]

Any compromise of Kevlar's nearly perfect uniaxial orientation, in particular the misalignment of crystallites, would correlate with an increase in axial rigidity (E), and ultimately, an increase in compressive strength. Since transaxial and axial alignment of crystallites is contingent upon interchain hydrogen bonding, the destruction of these bonds would likely yield an improvement in compressive strength. Without the existence of transaxial bonds, the polymer chains are unlikely to orient uniformly into pleated sheets, and would consequently develop a chiasmatic or crossing orientation. The resulting chiasmas, or plexuses, formed at the treatment temperatures studied may very well account for the observed increase in structural rigidity and compressive strength. Moreover, misorientation of the crystal structure comprising the pleated sheet configuration within the core structure would result in an increase in the radius of the fiber, thereby decreasing compressive deformation by increasing the diametric area upon which to distribute a compressive load.

Clearly, the theory that hydrogen-bond disruption may account for measurable crystal misalignment, and consequently, enhanced compressive strength and lower tensile strength, warrants legitimate consideration. The objective of this work was to determine which structural change, crosslinking and/or hydrogen-bond disruption, was responsible for the enhancement in compressive strength of the Kevlar fibers heat treated by Sweeney.[15]

EXPERIMENTAL

Thermally treated and untreated Kevlar-29 fibers were subjected to a variety of analyses in order to elucidate the structural mechanism by which the compressive strength of the Kevlar-29 studied by Sweeney[15] had been enhanced. The treated Kevlar-29 fibers were those prepared by Sweeney in a Thermodyne oven under nitrogen purge at temperatures of 400, 440, and 470°C. These PPTA fibers were characterized by thermogravimetric analyzer (TGA), differential scanning calorimeter (DSC), and Fourier transform infrared spectrophotometer (FTIR).

Thermogravimetric experiments were conducted using a Mettler-Toledo TG-50 TGA under an inert nitrogen purge in an effort to quantify mass loss associated with crosslinking at elevated temperatures. Differential Scanning Calorimetry assays were performed using a Mettler-Toledo DSC25 with a TC15 TA controller in order to observe thermal transitions (endo- or exotherms) within the polymer. An FTIR spectrophotometer was used to investigate specific peak locations and intensities of the heat-treated Kevlar-29 fibers. The FTIR was a Perkin-Elmer Spectrum One spectrophotometer with HATR assembly. All requisite calibrations were performed prior to characterization of the heat-treated Kevlar-29.

As-received Kevlar-29 fibers were subjected to TGA isotherms at select temperatures in order to quantify mass loss and gain insight into the initiation temperature necessary to promote significant levels of crosslinking within the PPTA fibers. The ramping rate used in these TGA experiments was 100°C/min. During the ramp, an empty crucible was situated upon the

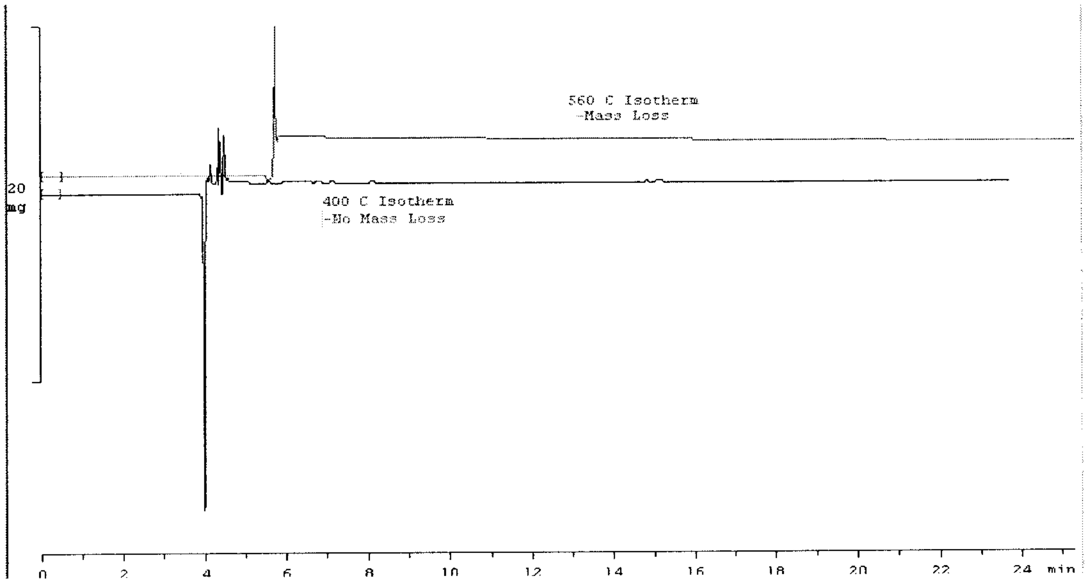

Figure 4 Thermogravimetric isotherms of Kevlar-29 fiber.

microbalance. When the target temperature was reached, the balance was zeroed and a 2–5 mg sample of Kevlar-29 was then placed within the crucible. The time at temperature for isothermal experiments was invariably 23 min. All isotherms were performed in an inert nitrogenous environment to preclude side reactions such as oxidation.

In order to discover what structural change (crosslinking and/or hydrogen-bond disruption) was occurring within the PPTA fibers at elevated temperatures, a DSC scan was performed on 5 mg of untreated Kevlar-29 fibers. The temperature sweep began at 25°C and ended at 600°C, and entailed a slow heating rate of 5°C/min in order to capture the structural change. Both the reference and sample DSC pans were heated under an inert nitrogen purge of 1 L/min.

FTIR spectrophotometry analysis was also performed in an effort to elucidate the structural mechanism accounting for the compressive improvements of Kevlar-29 fibers treated at 400, 440, and 470°C. According to the chemical formula and structure of PPTA, the IR band assignments of 1018 cm^{-1} for an in-plane, C—H vibration (characteristic of *para*-substituted aromatic compounds, particularly polyaramids) can be made. The band assignment for out-of-plane C—H vibrations of two adjacent hydrogens in an aromatic ring (*para*-substitution of the aromatic) would be 827 cm^{-1}. The loss of hydrogen-bonded amide functionality (3432 cm^{-1}) was also assessed to estimate the degree of interchain hydrogen bond destruction.[11] FTIR scans were performed in reflectance mode, applying a wavenumber range of 650–3600 cm^{-1}. Sixty-four total scans were performed for each of the three assays, corresponding to the three different maximum treatment temperatures employed by Sweeney.

RESULTS AND DISCUSSION

In order to establish a single covalent crosslink between the Kevlar macromolecules, dehydrogenation must occur. This would involve the loss of two hydrogen atoms from an aryl ring component. In order to achieve the level of lateral enhancement witnessed in the unmodified, heat-treated Kevlar study, dehydrogenation would need to occur on a widespread scale within the fiber. Quantification of this statement is difficult. However, at least one crosslink per nine repeat units could account for a crosslink density capable of achieving improved compressive strengths.[13] Hydrogen losses at these crosslink densities should result in a detectable mass loss that may be captured via TGA measurements. Detection is likely given the sensitivity of the microgram TGA balance, which is capable of detecting a mass loss as miniscule as one-millionth of a gram.

The isotherm at 400°C indicated that no detectable decrement in mass had occurred during the 23-min interval within the untreated, as-spun Kevlar-29 fibers. This result is illustrated in Figure 4. Accordingly, an isotherm temperature was then selected beyond 470°C, the highest temperature level enacted by Sweeney. An isotherm at 480°C demonstrated that no mass loss of as-received Kevlar-29 fiber had occurred within the 23-min interval. Thus neither the isotherm at 400 or at 480°C, each with an aggressive holding time of 23 min, resulted in substantive mass losses according to the TGA analyses performed at these conditions.

Mosquera[16] had purported that Kevlar is thermally stable up to about 545°C; below this temperature only minor change associated with the loss of hydrogen

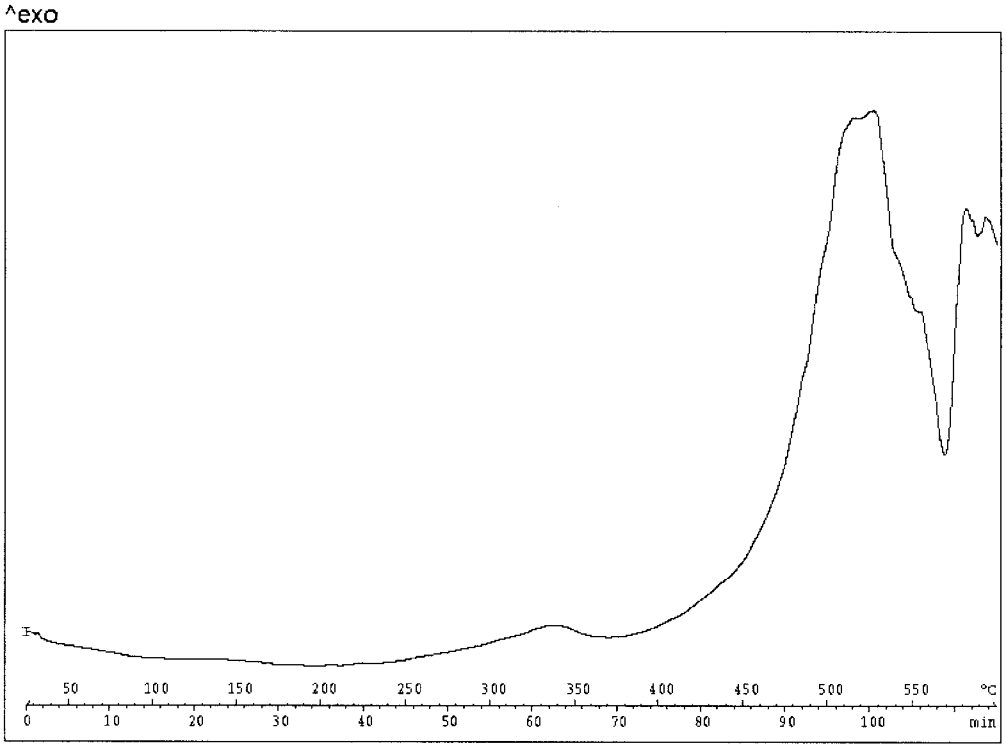

Figure 5 DSC scan of Kevlar-29 fiber.

bonds occur. In order to test the validity of this claim, an isotherm at 540°C was first performed. The results demonstrated that no significant mass loss had occurred within the PPTA fibers during the 23-min hold time. Secondly, a temperature beyond the critical 545°C mark was selected, utilizing the same treatment interval. Remarkably, an isotherm at 560°C did indicate a mass loss of 0.1 mg, or 4.5%. The scan depicting this higher-temperature isotherm is also included in Figure 4.

These thermogravimetric findings support the claim by Mosquera [16] that no significant mass loss occurs within Kevlar fibers below 545°C. If crosslinking is initiated at treatment temperatures of 400, 440, and 470°C, this structural change is not accompanied by appreciable or detectable mass loss, according to the previous results obtained on the Mettler-Toledo TG-50 TGA. This raises doubt as to whether the structural mechanism accounting for enhanced compressive strength within heat-treated Kevlar fibers is exclusively, or even primarily, crosslinking.

If crosslinking was the predominant mechanistic change accounting for the enhancement of compressive properties within thermally treated Kevlar-29, the formation of crosslinks should result in a detectable exotherm within the DSC profile. Crosslink formation is exothermic due to the thermodynamically favorable conformation that such interchain covalent bonds would promote. Conversely, the destruction of interchain hydrogen bonding and thus the pleated sheet structure would be captured as a DSC endotherm. As a result, the DSC serves as an excellent tool for determining which structural change, crosslinking, or hydrogen-bond destruction is accounting for improved compressive properties and compromised behavior in tension.

The DSC scan, shown in Figure 5, depicts a gradual exotherm that begins at approximately 380°C and continues until a temperature of 530°C is achieved. It is likely that this exotherm corresponds to a crosslinking event within the Kevlar-29 fibers. According to the DSC scan generated within this study, the maximum crosslinking rate commences at approximately 470°C. At 560°C, a large endotherm was observed in the DSC scan, most likely corresponding to degradation of the PPTA and the formation of pyrolytic products such as hydrogen cyanide, benzene, toluene, and benzonitrile.[4] However, the TGA result indicated that no measurable mass loss occurred below 560°C.

Crosslinking in polymers is an exothermic phenomenon due to the thermodynamically favorable conformation achieved by the formation of an interchain lattice structure. When order within the polymer structure is decreased as a result of thermal treatment, as is the case during polymer melting, an endothermic event ensues. Therefore, the destruction of interchain hydrogen bonds can be characterized as an endothermic event within the DSC spectra. No such endothermic event was detected in the DSC spectra of untreated Kevlar-29 fiber. Hydrogen-bond destruction

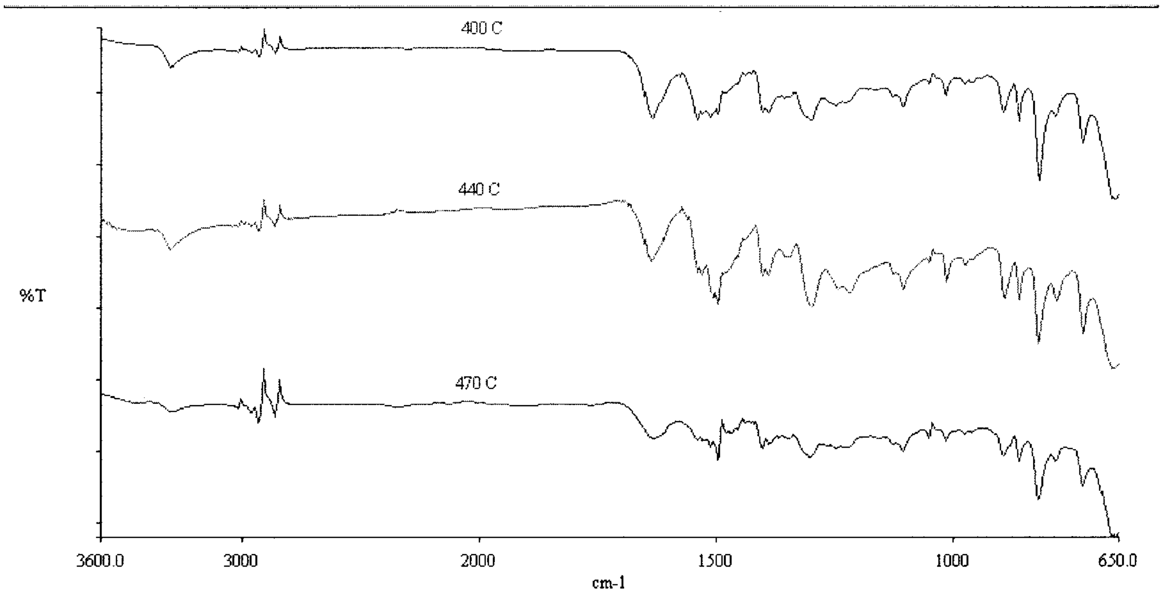

Figure 6 FTIR spectra of heat-treated Kevlar-29 fibers.

may have been below the level of detection of the calorimeter, or simply not prevalent to such a degree as to elicit a distinct endotherm. Conversely, a clear exotherm was identified and supports the theory that crosslinking is occurring within the polymer chain. It is possible that an endo- and exothermic event is occurring simultaneously, with the dominant thermodynamic change being detected by the DSC.

The TGA and DSC results indicate different, although perhaps not mutually exclusive, information as to the structural mechanism accounting for improved compressive properties in heat-treated Kevlar-29 fibers. The FTIR, however, is arguably the most sensitive technique for discerning if crosslinking and/or the entropic effect of hydrogen-bond obfuscation are taking place within the polymeric fibers.

The peak intensity of Kevlar-29 fibers at approximately 824 cm^{-1}, corresponding to the out-of-plane C—H vibration, decreased with increasing treatment temperatures. Similarly, the peak intensity at 1018 cm^{-1}, reflecting the in-plane aryl C—H vibration, decreased within increasing treatment temperatures. This indicates that the loss of hydrogen atoms from the benzene ring increases with increasing treatment temperature. This finding may be explained by the formation of free radicals in the initiation stage of crosslink formation.

A clear decrease in peak intensity and area was observed with increasing treatment temperatures at an approximate wavenumber of 3432 cm^{-1}, corresponding to the loss of hydrogen-bonded amide functionality. This result indicates that interchain hydrogen-bond destruction is occurring within the Kevlar-29 fibers that had been treated at 400, 440, and 470°C. The FTIR scan illustrates that both hydrogen-bond destruction and crosslinking is taking place simultaneously at the treatment temperatures utilized by Sweeney. A split view of the FTIR spectra is depicted in Figure 6.

Summarily, the results of the TGA scan indicate that no significant mass loss corresponding to dehydrogenation of aryl hydrogens is realizable at temperatures below 560°C, supporting the theory that hydrogen-bond destruction is accounting for the observed increased compressive and decreased tensile properties within heat-treated PPTA fibers. Conversely, the results of the DSC thermal profile indicate that crosslinking is the mechanism accounting for the observed changes in mechanical properties. The FTIR scans indicate that both structural changes arise when Kevlar-29 is heat treated at thermal treatments of 400, 440, and 470°C.

Initial impressions may lead one to conclude that these results are irreconcilable. However, an understanding and appreciation of the tertiary structure of poly-*p*-phenylene terephthalamide may provide a plausible interpretation for the findings detailed within this work.

It is likely that both structural changes are promoted within different regions of the polymer when exposed to elevated temperatures. The microstructure comprising the skin region may be crosslinking, while the inner core region experiences an entropic effect of hydrogen bond destruction and misorientation of the crystallites within the pleats.

It is feasible that crosslinking is not detected through TGA analysis because the bulk of the fiber is experiencing hydrogen-bond destruction rather than a crosslinking phenomenon. Thus, dehydrogenation of the aryl hydrogen is below the level of detection of the TGA. The FTIR analysis, when performed in reflectance mode, would detect the crosslinking within the skin region as the beam must penetrate the skin. Additionally, the infrared beam would partially penetrate the core region as well before experiencing full reflection, thus capturing the structural change within the core region as well. During thermal profiling via DSC analysis, heat would penetrate the fiber from the boundary inward, and therefore crosslinking within the skin region is the dominant thermodynamic change captured by this instrument. These analyses have demonstrated that thermal enhancement of Kevlar-29 is achieved through both structural changes, crosslinkin, and hydrogen-bond destruction, working in concert to promote the augmentation of compressive strength.

CONCLUSIONS

The thermal enhancement of compressive properties in Kevlar-29 fibers likely is achieved through two mechanisms: (1) free-radical formation within the external skin region of PPTA, resulting in the formation of interchain crosslinks; and (2) hydrogen-bond disruption resulting in the destruction of the highly ordered, pleated sheet configuration within the core region of PPTA. Interchain covalent crosslinks improve the compressive strength of the aramid fiber by limiting the structural maneuverability of the fiber skin, thus augmenting its rigidity. Hydrogen-bond disruption within the core region results in misorientation of crystallites within the core region, thus enhancing the compressive properties of Kevlar by compromising its nearly perfect linearity.

Several high-temperature thermogravimetric isotherms were performed in order to characterize the degree of dehydrogenation within the PPTA fibers, corresponding to the formation of covalent, interchain crosslinking between the aryl moieties. No significant mass loss was detected at a temperature of 540°C or below. The TGA results indicate that no detectable mass loss related to the bulk development of crosslinking throughout the fiber occurs at elevated temperatures as high as 540°C.

The DSC profile did not indicate the presence of a distinct endotherm at elevated temperatures below 540°C. Therefore, a specific event relating to hydrogen bond disruption within Kevlar-29 fiber was not captured by the DSC. In contrast, DSC indicates that a crosslinking event is occurring within heat-treated Kevlar-29 fiber. This is evidenced by a gradual exothermic event that develops at a treatment temperature of approximately 380°C and continues until a temperature of 530°C is achieved. At a temperature of 560°C, a clear endothermic peak is observable, most likely corresponding to degradation of the polymer into volatiles such as hydrogen cyanide, benzene, toluene, or benzonitrile.

FTIR spectrophotometric assays of heat-treated Kevlar-29 fiber arguably provide the greatest insight into what structural changes account for the improved behavior of the polymer in compression. The FTIR indicates that both structural mechanisms, crosslinking and hydrogen-bond destruction, account for the improved compressive properties of the polymer.

It is likely that both the entropic effect of hydrogen-bond disruption and interchain crosslinking are promoted within heat-treated poly-*p*-phenylene terephthalamide, albeit in distinct regions of the polymer matrix. The anisotropic microstructure comprising the skin is crosslinked, while the core region characterized by a pleated sheet configuration experiences the entropic effect of hydrogen-bond disruption and a concurrent misorientation of the crystallites. Crosslinking of the skin region and misorientation of core crystallites appear to serve together as the structural mechanisms that promote the enhancement of compressive strength of heat-treated Kevlar-29 fiber.

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