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A comprehensive study on the oxidative stabilization of mesophase pitch-based tape-shaped thick fibers with oxygen

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Abstract

Tape-shaped pitch fibers with a transverse cross-sectional size of 400 μm width and ~30 μm thickness, melt-spun from mesophase pitch, were adopted as a model for treatment in oxygen using various temperatures and durations to investigate their stabilization behavior. Several characterization techniques were used to systematically analyze the functional group species, oxygen content and distribution, local composition, thermal pyrolysis behavior and micro-structural changes in the various stabilized tapes. After oxidative stabilization treatment, the tape-shaped fiber exhibits uniform shrinkage behavior during subsequent heat treatments thereby maintaining its

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tape shape and structural integrity. The ~30 μm thick tapes can be stabilized completely by treatment in oxygen at 220 °C for ~10 h and this indicates a high efficiency of stabilization, which is, perhaps unexpectedly, higher than that of corresponding ~30 μm diameter round-shaped fibers. Thermal decomposition pathways varied with the degree of stabilization and have obvious effects on the microstructure of the resulted tapes, which in turn strongly influences their final physical properties. Pitch tapes oxidized under mild conditions offered relatively higher mechanical performance. Tensile strength and Young’s modulus of 2500 °C graphitized tapes, previously oxidatively stabilized at 220 °C for 20 h, were measured to be about 2 and 250 GPa, respectively.

1. Introduction

Generally, carbon fibers have excellent mechanical properties including low bulk densities, high chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance. Owing to the unique and versatile properties of carbon fibers, they are increasingly being employed in the construction of next-generation composite materials for aerospace, military, electronics, construction, medical and sporting goods as well as the automotive industries etc. [1-3]. Carbon fibers are now produced from several precursors such as polyacrylonitrile (PAN), pitch, cellulose, lignin, polyethylene, and other synthetic polymers. Among these, PAN is recognized as the dominant precursor in the market for producing commercially available carbon fibers with high strength and moderate modulus [4,5]. Pitch-based carbon fibers firstly developed by Otani [6,7] are expected to be producable at lower cost than synthetic polymer-based carbon fibers, because of their relatively inexpensive source materials (coal tar pitch or petroleum pitch) and their high carbon yield, without the need for costly hot-stretching treatment to obtain the ideal physical properties (ultrahigh Young's modulus up to 960 GPa and axial thermal conductivity of ~1000 W/ m K for mesophase pitch-based carbon fibers). However, to achieve such high performance carbon fibers, the processing cost (mainly from pitch purification, mesophase formation and fiber melt-spinning) is relatively higher than that of PAN-based carbon fibers, and their annual throughput is still limited worldwide. The principal process for producing pitch-based carbon fibers typically involves pretreatment of a pitch feedstock, melt-spinning of the pitch to form pitch fibers, stabilization of the pitch fibers, carbonization of the stabilized fibers and optional graphitization at a higher temperature [8]. Of these, the stabilization treatment is the least efficient and most time-consuming process. However, it is one of the most important steps that determine the quality (physical properties) of the resultant carbon fibers. It is well known that their ultrahigh modulus and thermal conductivity is due to the inherent graphitic crystallinity in the well-ordered textures of mesophase pitch-based carbon fibers. The stabilization process changes a mesophase pitch fiber from a thermoplastic solid to a thermosetting material and thereby imparts dimensional stability to the fiber whilst “locking in” the highly aligned structure developed during the melt extrusion. That is to say, only a completely stabilized pitch fiber can be subsequently carbonized and graphitized without its structure melting, softening, relaxing or deforming. Therefore, finding promising methods and optimal conditions for stabilization is of great importance for carbon fiber technology to decrease the production cost and improve the physical properties. Nowadays, the stabilization method conventionally employed is the thermal oxidation in air or oxygen at a temperature (200~300 °C) between the glass transition temperature (T_g) and softening point (T_s) of the mesophase pitch for a few hours. (T_g and T_s gradually increase as the oxidation treatment progresses, enabling carbonization to occur subsequently without fiber softening). However, several other alternative methods (e.g., reaction with NO_2, extraction with solvents, treatment with nitric acid solution and irradiation under ultraviolet light with ozone) [9-13] have been suggested.

Many studies have been performed to investigate the stabilization reaction process, chemical structure of the oxidized fibers and the mechanism of the oxidative stabilization. For instance, Yoon et al. used thermal analyses to monitor the oxidative stabilization of mesophase pitch fibers at several heating rates in order to achieve good mechanical properties [14]. Blanco et al. employed micro-thermal analysis to study the stabilization process of pitch-based carbon fibers and to determine the softening temperature profiles across model large diameter fibers as a function of the degree of stabilization. The local oxygen content of the fiber and the depth of the stabilized region were also determined [15,16]. Mochida et al. measured the oxygen distribution in the transverse section of a mesophase pitch fiber after stabilization using electron probe X-ray microscopy and secondary ion mass spectrometry. Based on these measurements, the relationship between the oxygen profile in the pitch fiber and the stabilization conditions was discussed [17,18]. Moreover, the final tensile property of the graphitized fibers after various stabilization treatments was correlated with the oxidization conditions (oxidization temperatures and heating rates), degree of stabilization (i.e. weight gain) and oxygen content of stabilized fibers [19]. Lavin suggested that the abundance of CH_2 and CH_3 groups in pitch determines the response of the fiber to the stabilization process. It was found that evolution of CO_2 and CO was independent of H_2O production, and appeared to result from a surface reaction, contrasting with combustion reactions [20]. Nakagawa et al. proposed a plausible mechanism of stabilization by using $^{18}O_2$ to examine the gas formation, and found that only functional groups within the fibers could be expected to react with oxygen to produce H_2O [8]. Kowbel et al. designed experiments to study the reaction kinetics of the oxidation process and to identify the structural changes within the mesophase pitch fibers by several modern characterization techniques [21]. In spite of these accumulated studies reported in the past decades, the mechanism of the stabilization reaction is still not completely understood as it is very complex, and so oxidative stabilization conditions have been mainly selected from experience gleaned from examination of the structure and property of the resulting carbon fibers.

As a rule, stabilization is the process by which a pitch fiber is rendered infusible so that it may undergo further high temperature treatments necessary to produce high strength, modulus and thermal conductivity. It involves the removal of peripheral small groups from the polycyclic aromatic molecules and the insertion of bridging groups containing oxygen. That is to say, this process is realized by thermal oxidation through the formation of cross-linking sites consisting of oxygen functional groups [8,15]. Therefore, the degree of stabilization is expected to closely relate to the amount of oxygen functional groups formed during the stabilization process. The formation of such oxygen functional groups is inevitably accompanied by the evolution of lower molecular weight products such as H_2O, CO, CO_2, etc. [15,20]. Hence, a substantial change in mass, and variation in the proportions of elements present, as well as in the oxygen distribution in the resulting fibers, all simultaneously occur during the stabilization process. Furthermore, the microstructure and physical properties of the resulting carbon fibers are thought to be highly sensitive to the stabilization process conditions.

It is well-known that the diameters of round-shaped carbon fibers that can be achieved in commercial processes are restricted by the time-consuming stabilization process. Usually, as-spun mesophase pitch fibers with larger diameters (>15 μm) exhibit a serious diffusion barrier in oxidative stabilization treatment. This takes a longer time compared with those of smaller diameters and some randomization of the preferred orientation within the core of carbon fibers also occurs [22]. Therefore round-shaped carbon fibers with average diameters larger than 15 μm are rarely produced. However, tape-shaped carbon fibers can be made with a rectangular cross-section (with width up to 1~4 millimeters and thickness of 10~20 μm) that is equivalent to the total cross-sectional area of 100~200 conventional round-shaped carbon fibers. The tape-shaped fiber has a highly ordered structure, with the basal plane layers oriented predominantly parallel or perpendicular to the tape surface, which exhibits higher graphitizability and better thermophysical properties [23-25] than round-shaped fibers. Furthermore, the tape geometry does not limit the volume fraction of fibers that can be incorporated in a laminate, allowing a higher packing density, compared with the 74% v/v packing limit for round-shaped carbon fibers, in the preparation of carbon/carbon composites. The resulting unidirectional carbon tape/carbon composites can achieve ultrahigh thermal conductivity (800~900 W/ m K) in the longitudinal direction of the fibers [26,27]. In addition, tape-shaped carbon fiber does not split during subsequent heat treatment, in contrast to common round-shaped fiber due to the latter’s radial transverse texture [24,25]. Therefore, tape-shaped carbon fibers have significant advantages in potential applications.

Up to now, there have been few special studies on the oxidative stabilization of mesophase pitch-based ribbons or tapes; the previous literature on oxidative stabilization mentioned above mainly concentrates on conventional round-shaped fibers. In contrast, this work focuses on the optimization of the stabilization conditions for tape-shaped mesophase pitch thick fibers and presents the results of the application of modern characterization techniques to comprehensively study their oxidative stabilization and pyrolysis behavior. The weight gain or loss, amount, type and distribution of oxygen present and the structural changes of the tape-shaped mesophase pitch fibers during oxidation treatment are all discussed. Their thermal pyrolysis behavior and the off-gas formation rates from the stabilized fibers in subsequent carbonization processes are continuously monitored, analyzed and reported as well. Finally, the morphology, microstructure and physical properties of the resultant carbon and graphite fibers were also investigated.

2. Experimental

2.1 Preparation of tape-shaped pitch fibers

The tape-shaped pitch fibers were prepared by melt-spinning a commercial naphthalene-derived synthetic mesophase pitch (AR-MP, produced by Mitsubishi Gas Chemical Corporation) through careful control of the spinning process parameters [25]. It is well-known that naphthalene-based AR mesophase pitch has been recognized as a most promising precursor for carbon fiber with excellent properties owing to this pitch's unusual physical characteristics, such as high anisotropic content of 100 vol.%, low softening point of ~265 °C, high purity and aromaticity, narrow weight distribution, and it's linear mesogenic species. In addition, the presence of naphthenic groups and aliphatic side chains will undoubtedly favor stable melt-spinning (good flow behavior) and subsequent oxidative stabilization (high crosslinking reactivity with oxygen), compared to conventional mesophases from the thermal polymerization or heat-soaking of natural or industrial pitch [28-30].

A slot-shaped die with a length of ~3 mm and a width of ~0.1 mm was used to obtain the tape-shaped pitch fibers. The width and thickness of the transverse section of as-spun tape-shaped pitch fibers were approximately 400 and 30 μm, respectively, which shows a relatively high aspect ratio and large thickness. For comparison, some round-shaped pitch fibers with a diameter of ~32 μm were prepared from the same mesophase pitch by using a cylindrical die (Φ=300 μm).

2.2 Oxidative stabilization and high temperature treatment of the tape-shaped thick fibers

A bundle of the as-spun pitch fibers with an even length of about 18 cm were placed on a flexible graphite sheet and then inserted in the isothermal zone of a quartz tube (6 cm in diameter and 80 cm in length) furnace, which was heated at a constant rate of 2 °C/min from room temperature to a defined reaction temperature (e.g. 220, 240 and 260 °C), which was below the T_s of the mesophase pitch (265 °C). Choice of the stabilization temperature is based on the fact that the pitch fibers had a similar T_s to that of the parent pitch, although the T_s will tend to slightly increase after spinning due to some devolatilisation. Lower temperatures of stabilization below 200 °C may be time consuming and costly and were not selected in this work. Increasing the stabilization temperature above 260 °C could undoubtedly accelerate the oxidation reaction and shorten the stabilization period, but lead to softening and a consequent loss of dimensional stability in the green fibers, resulting in poorer properties of the final product. The as-spun pitch fibers were oxidatively stabilized at constant temperature for between 1~30 h in an oxygen atmosphere flowing at 200 ml/min in order to study the influence of the degree of oxidation in the stabilized fibers on the morphology, microstructure and properties of their carbon and graphite fiber derivatives. The evaluation of the efficiency of stabilization in this work is mainly based on the stabilization time required to obtain the maximum tensile strength. Of course, the speed of uptake of oxygen in the stabilized tapes or the change of oxygen content versus stabilization time, which determines whether complete stabilization (i.e. an infusible state) is achieved, are also considered as a reference. For large diameter (~30 μm) pitch fibers in certain studies, oxidative stabilization in air atmosphere was commonly carried out at high temperatures (270~350 °C) and misorientation of carbon layers or formation of "skin-core" structure in the resulting carbon fibers were unavoidable [17,22,31]. Air was not selected as the oxidative atmosphere to stabilize the tape-shaped thick fibers due to its lower oxygen content, in comparison with pure oxygen, which would result in slower oxidative reactions under the same conditions as has been verified in our previous work [25]. As a comparison, the round-shaped pitch fibers prepared with a large diameter of ~32 μm were oxidatively stabilized in both oxygen and air atmospheres for various oxidation times.

The above-stabilized taped-shaped thick fibers and round-shaped large fibers were then carbonized under argon atmosphere in an alumina tube furnace by heating at 1 °C/min to 1000 °C, held for 1 h before cooling. These 1000 °C heat-treated carbon fibers were subsequently graphitized by heating at 12~15 °C/min to 2500 °C, held for 30 min in a medium-frequency induction furnace under a controlled flow of argon, to obtain tape-shaped graphite fibers.

2.3 Characterization of the stabilized thick tapes and their carbon and graphite fibers

In order to characterize the extent and the effect of stabilization of the tape-shaped pitch fibers, various advanced characterization techniques were adopted, including Fourier transform infra-red spectrometry (FTIR), elemental analysis (EA), thermo-gravimetric–differential thermal analysis (TG-DTA), TG-FTIR, TG-mass spectrometry (TG-MS), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and mechanical testing.

A Bruker Vertex 70 FTIR was used to characterize chemical structure changes in the oxygen functional groups that may arise in the tapes as a result of the various stabilization conditions. About 1 mg of the fiber powder was mixed with 200 mg of KBr to prepare pellet-shaped samples for the analysis.

The carbon, hydrogen, nitrogen and sulfur contents (by mass) of the fibers stabilized for various temperatures and times were determined by a Vario EL III elemental analyzer. The oxygen content was obtained by subtracting the sum of carbon, hydrogen, nitrogen and sulfur.

Detailed analysis of off-gases volatilized during high temperature treatment of the various stabilized fiber samples was performed using a Netzsch STA 449C TG–DTA thermoanalyzer coupled with a Balzers Thermostar Quadrupole Mass Spectrometer (QMS). The multiple ion detector mode was used for the QMS measurements. Approximately 10 mg of sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min in an argon atmosphere flowing at 30 ml/min. The gaseous products evolved from the fiber samples were simultaneously and continuously monitored by the QMS. The QMS signals were processed by smoothing, baseline subtraction, and then normalized to the mass of the sample [32]. Special attention was paid to the most important volatile species, including H_2, CH_4, CO, CO_2 and H_2O.

The TG–FTIR system comprising a NETZSCH STA 409C thermal analysis instrument and a NICOLET NEXUS 670 Fourier transform infrared spectrometer can be used to study weight change and gas evolution. The heating rate of the TG furnace was 10 °C/min, and high purity nitrogen flowing at 100 ml/min was used as the carrier gas. About 20 mg of sample was heated from ambient temperature to 1000 °C. The FTIR spectra were collected at 8 cm^{-1} resolution, co-adding eight scans per spectrum [32].

Oxford INCA 200 EDS equipment on a NOVA 400 NANO field emission SEM, was adopted as a qualitative analysis technique to measure the oxygen distribution and content variation across the transverse sections of tape-shaped pitch fibers which had undergone stabilization at a range of times and temperatures. Tape-shaped fiber samples were vertically mounted on an aluminum stage to allow oxygen profiling across the cross-section of the investigated tape, and these samples were pre-coated with a thickness of 15~20 nm gold film to increase the electrical conduction. The morphology and microstructure of the resultant tape-shaped carbon and graphite fibers having undergone various stabilization treatments were imaged with a TESCAN VEGA 3 SEM.

The longitudinal electrical resistivities of the tape-shaped thick fibers, were obtained by averaging measurements of fifteen individual tape-shaped fibers after carbonization and graphitization treatments made using a BS407 precision millimicro ohmmeter, using a standard four-probe method at room temperature.

The tensile properties of the carbonized and graphitized tape-shaped thick fibers and large diameter round-shaped fibers after various stabilization treatments, were carefully measured using a single-filament testing machine according to ASTM standard D3822-14 at a long gauge length of 40 mm. About 30 tape-shaped fibers of each sample were tested to obtain their average value. The broken tape ends were numbered and stuck vertically around a sample platform for transverse sectional area analyses using SEM.

3. Results and discussion

3.1 Characterization of the stabilized thick tapes

3.1.1 FTIR and EA profiles of the stabilized thick tapes

The FTIR spectra of the as-spun pitch fiber and its derivatives, stabilized using various temperatures and times, as well as of the high temperature heat-treated fibers are shown in Fig. 1. The spectrum of the as-spun pitch fibers presented in Line (a) shows aromatic C-H stretching around 3040 cm^{-1}, aliphatic C-H stretching bands around 2850~3000 cm^{-1} and methylene C-H (probably naphthenic) in-plane bending around 1440 cm^{-1}. This is accompanied by aromatic C-H deformation (out of plane bending) in the range of 700~900 cm^{-1} [33,34]. The FTIR spectrum of the stabilized fibers oxidized at 200 °C for 1 h is given in Line (b), which contains different peaks in comparison to those of the as-spun fibers. The intensities of the bands around 2850~3000 and 1440 cm^{-1} are slightly weakened and an obvious band appears around 1700 cm^{-1} (attributed to carbonyl and carboxyl groups), which indicates that some oxygen-containing groups were introduced into the fibers during the oxidation procedure [35]. The band around 1600 cm^{-1} contributed by aromatic C-C stretching abruptly increases and the aromatic C-H bands (700~900 cm^{-1}) slightly increases compared with the as-spun pitch fibers, owing to a noticeable increase in aromatic contents. It is of interest that obvious differences appear between the spectra shown in Lines b and c with an increase in the stabilization temperature from 200 to 220 °C. The intensities of the bands around 2850~3000 and 700~900 cm^{-1} both sharply weaken or even disappear, and the bands around 1250 and 3450 cm^{-1} contributed by aromatic ether group (Ar-O-Ar) and phenolic hydroxyl groups (Ar-OH) markedly increase as presented in Line (c), evidencing a relatively rapid stabilization as the oxidation temperature increases to 220 °C [36]. There is little change apparent between Lines c and d, with the further increase of the stabilization temperature from 220 to 240 °C. However, the bands around 1250, 1600 and 1700 cm^{-1} become more intense in Line (e) as the oxidation temperature rises up to 260 °C, showing further progression in the stabilization. Lines (f-I) show a similar pattern and variation trend. The positions of those characteristic bands have no obvious differentia except for their intensities with increasing stabilization time from 1 to 30 h. As stabilization progresses, an increase in the functionalization of the pitch fibers is evident with a significant increase in the C-O-C and -CH_2-O- (ether or alcohol groups) asymmetric stretching bands around 1100~1300 cm^{-1}, >C=O (aldehyde, carboxyl, or ketone groups) stretching bands around 1650~1850 cm^{-1} and the development of bands between 3400~3600 cm^{-1} associated with the stretching mode of free hydroxyl groups [37]. A decrease in the hydrogen content occurs at higher temperatures (220~260 °C) which is evidenced by the disappearance of the aliphatic C-H stretching bands in the 2850~3000 cm^{-1} region assigned to the methylene hydrogen [37]. The loss of hydrogen is also confirmed by a decrease in the intensities of the bands due to the aromatic C-H out of plane vibration between 700~900 cm^{-1} with increasing stabilization temperature and time. These decreases are attributed to the formation of H_2O during the stabilization process [38]. The above-mentioned stabilization treatments at a variety of temperatures indicate that 220 °C seems to be an optimal oxidation temperature for the stabilization of the tape-shaped pitch fibers, evidenced by a moderate reaction progression and gradual chemical change having occurred during the stabilization process, which will be of benefit to the mechanical properties of the resultant carbon fibers, as will be shown subsequently.

The FTIR spectra of these fibers heat-treated at various temperatures are given in Lines J-L. For the low-temperature (400 °C) treated fibers shown in Line (J), the band around 1600 cm^{-1} significantly increases compared with the stabilized fibers, owing to the partial decomposition of hydrogen and oxygen-containing groups. With further increase of the treatment temperatures from 400 to 1000 and 2500 °C, the intensities of the bands around 1250, 1600, 1700 and 2850~3000 cm^{-1} shown in Lines K and L are markedly weakened (the band around 3450 cm^{-1} results from the adsorption of water/steam), and the intensities of the bands at wave numbers 700~9000 cm^{-1} slightly increase relative to those of the stabilized fibers. Through the high temperature heat-treatment of the stabilized tapes, the aromatic content of the resultant fibers thus significantly increases [20].

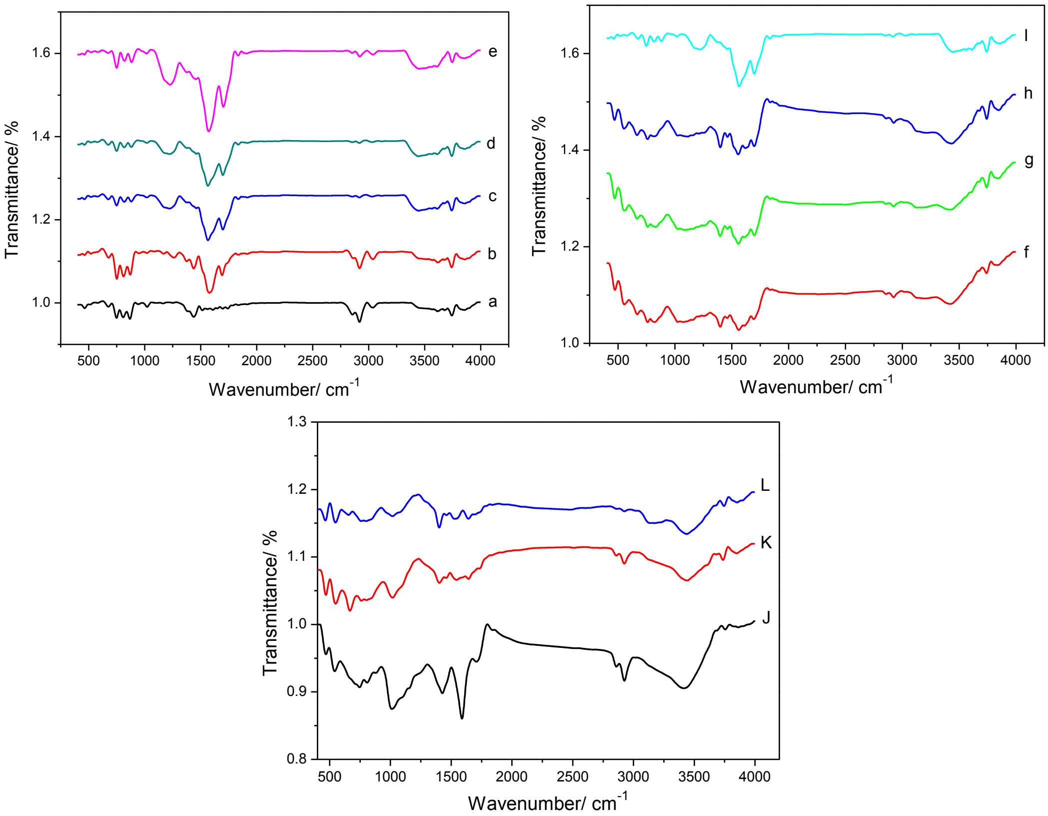


Fig. 1 FTIR spectra of the as-spun pitch fibers (Line a), their stabilized derivatives oxidized at various temperatures (Line b-200, Line c-220, Line d-240, Line e-260 °C) for 1 h and at 220 °C for different times (Line f-1, Line g-5, Line h-15, Line I-30 h), and high temperature treated samples (Line J-400, Line K-1000, Line L-2500 °C).

It is possible to track the gain in weight experienced by the fibers during the stabilization procedure by using the change in weight of the chemical components in the stabilized fibers. The EA results from various fiber samples after stabilization treatments are shown in Fig. 2. It can be clearly seen that the oxygen content of the stabilized fibers significantly increases with increasing oxidation time as shown in Fig. 2(a). The oxygen content increases quickly at the beginning of the oxidation process, and then tends to decelerate with a slow increase after 15 h oxidation treatment. As the stabilization temperature and time increase, the oxygen content appears to reach a plateau (~27 wt.%) after 30 h oxidation at 220~260 °C, which is well consistent with the previous reports [39,40]. However, the oxygen content of the tape-shaped pitch fibers after stabilization treatment is obviously higher than that of some round-shaped pitch fibers (e.g. oxygen content of heat-soaked coal tar mesophase is commonly measured to be 5~8 wt.% [17, 31] and that of naphthalene-derived mesophase is less than 14 wt.% [16,22,37]). Nevertheless, the oxygen content of the round-shaped pitch fibers with a large diameter of ~32 μm stabilized at similar conditions also shows a relatively high value of 18~20 wt.%. This is due to the fact that naphthalene-based pitch is known to be highly reactive toward oxidative stabilization causing heavy cross-linking in the tapes [22, 37], rather than because of the change in fiber shape. The higher the oxidation temperature is, the more oxygen is incorporated in the fibers. The existence of relatively high concentrations of low molecular weight components (methylene hydrogen, probably naphthenic) in pitch stock is conducive to the formation of oxygen-containing groups, which is verified by the fact that a high uptake of oxygen (~27 wt.%) has been found during the stabilization process and is consistent with the result of the FTIR spectrum analyses. Although this rapid increase in the oxygen content aids the progression of stabilization, it ultimately adversely affects the final carbon yield of the stabilized fibers and physical properties of the product due to subsequent loss of carbon, e.g. as CO_2 and CO. Consequently, the optimal oxygen content, which is closely associated with the oxidation conditions (appropriate temperature and time), seems to be the key parameter requiring control in order to dictate the quality of the resultant carbon fibers [40].

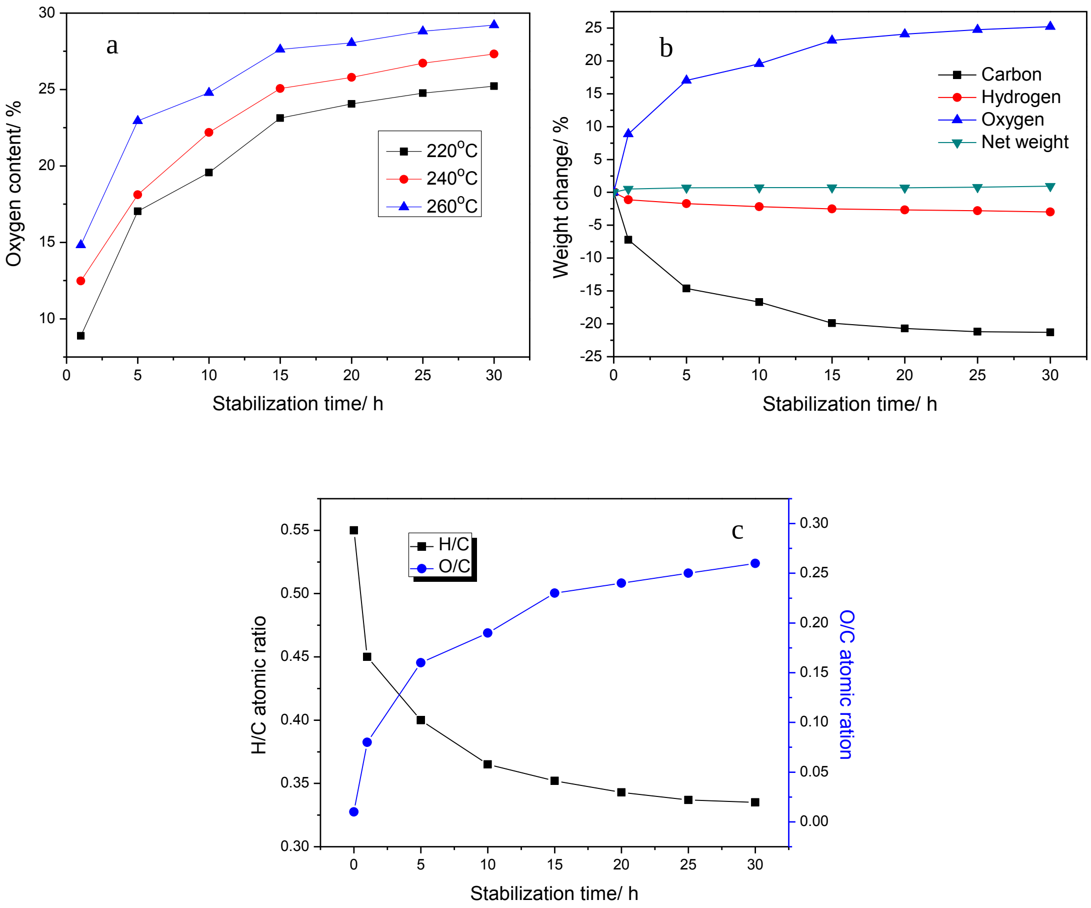


Fig. 2 (a) Change of the oxygen content of the stabilized fibers with the stabilization temperature and time, (b) C, H, O and net weight change (relative to the as-spun fibers) and (c) atomic composition ratios (H/C and O/C) of the stabilized fiber samples after oxidation at 220 °C for various times.

It can be seen in Fig. 2(b) that the weights of carbon and oxygen in the sample markedly decrease and increase, respectively, during the stabilization process, whilst the weight of hydrogen slightly decreases. A slight net weight gain (i.e. a result of a gain in oxygen content accompanied by a loss in hydrogen and carbon) results and changes only a little with increasing stabilization time due to the approximate mass balance of oxygen and carbon. Upon plotting the H/C and O/C atomic ratios shown in Fig. 2(c), it can be clearly observed that the O/C ratio gradually increases as the stabilization advances, evidencing the uptake of oxygen in the stabilized fibers. Meanwhile, the H/C ratio obviously decreases, which indicates the increase in the aromaticity of the stabilized fibers. The most noteworthy changes in the H/C and O/C atomic ratios take place over the first 5 h of stabilization. The weight change of other elements (e.g. nitrogen and sulfur) is not shown because the nitrogen and sulfur contents of all stabilized samples are as low as 0.01% and 0.1% due to the high purity of the precursor pitch, and no remarkable variation was observed for different samples.

After the subsequent carbonization treatment at 1000 °C, the H/C and O/C atomic ratios of the resultant carbon fibers sharply drop to about 0.04 and 0.02, showing a higher aromaticity, condensation and oxygen elimination for the carbon fibers, which is in agreement with the FTIR spectrum analysis results.

3.1.2 TG-DTG profiles of the stabilized thick tapes

Fig. 3 shows the TG and DTG curves of the as-spun fibers and their stabilized derivatives, previously oxidized using various temperatures and times, during their subsequent carbonization. It can be clearly seen that there are significant differences between the pyrolysis behaviors of the as-spun fibers and their stabilized fibers. The tape-shaped pitch fibers which have experienced higher temperature stabilization at 260 °C for 15 h undergo the greatest weight loss upon carbonization as shown in Fig. 3(a), while the as-spun pitch fibers exhibit the lowest weight loss. This suggests that those samples which have experienced high oxidation temperatures are going to exhibit lower final carbon yield than those samples which have undergone lower temperature stabilization. Moreover, it is important to recognize that the stabilization time (for 240 °C oxidation treatment) also has an effect on the final carbon yield. It appears that, for stabilization at high temperatures and longer times, there is a reduction in the regularity of ether link formation and an increase in the formation of non-crosslinking groups such as carbonyl, carboxyl and ester groups (as shown in the FTIR results). This non-crosslinked oxygen is then responsible for the greater weight loss from the sample; it is possible that this excess presence of oxygen is also responsible for a more significant decrease in the final carbon yield of the samples, as this non-crosslinked oxygen is likely to react with carbon within the sample to remove it in the form of CO and CO_2 upon carbonization. This again suggests that there is an optimal oxygen content in the stabilized fibers; high enough to effectively form a constructive cross-linking structure so as to achieve better performance [39,40] but not so high as to introduce excessive non-crosslinking oxygen. It is interesting to note that the fiber sample which had been stabilized at 220 °C for 20 h exhibits a weight loss which is very close to that of the as-spun pitch fibers. One possible explanation is that this is a result of the lower weight gain (i.e. oxygen uptake) during stabilization at 220 °C for 20 h, compared to that at higher temperature conditions, which is consistent with the analysis result of Fig. 2(a). This oxygen incorporated into the pitch fibers was used effectively to cross-link the carbonaceous molecules within the fibers, and then gradually eliminated in the form of limited quantities of evolved gases during the carbonization process. Fig. 3(a) corroborates that the onset temperature of weight loss for the stabilized fibers began at around 100 °C, whereas the as-spun fibers did not decompose until ~350 °C. Thus, these stabilized fibers show a complex multi-stage decomposition behavior in their TG curves, which is different to the apparent simple decomposition behavior of the as-spun pitch fibers [41]. The reason for the multi-stage decomposition is that the adsorbed H_2O on the surface of the samples and the incorporated oxygen-containing groups (hydroxyl, aldehyde, carboxyl, and ketone) within these stabilized fibers gradually volatilize at different temperatures.

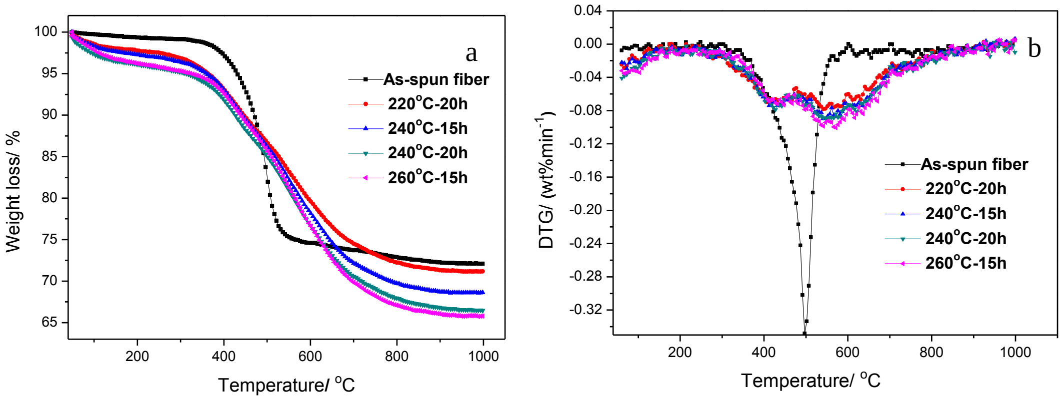


Fig. 3 (a) TG and (b) DTG curves of the as-spun pitch fibers and their stabilized fiber derivatives oxidized using various temperatures and times.

It can also be seen when examining the DTG curves as shown in Fig. 3(b) that there is a big difference between the behaviors of as-spun pitch fibers and their stabilized fiber derivatives. The as-spun pitch fibers exhibit a strong and sharp derivative weight loss peak at ~500 °C and severely decompose at 400~600 °C, however, the stabilized fibers all show a similar pyrolysis pattern (almost overlapping) reflecting gentle decomposition in this temperature range, that is quite different to that of the as-spun fibers. The two broad exothermal peaks correlating to different pyrolysis stages indicate that the decomposition of the stabilized fibers mainly takes place in two temperature zones (350~500 and 500~650 °C) and the position of the highest temperature peak increases from ~500 (for the as-spun pitch fibers) to about 580 °C. The DTG curves of the stabilized fibers also indicate that the temperature (and time) of stabilization has an influence on the thermal decomposition rate and the reactivity of the samples under a certain temperature, which results in the variety of weight losses (i.e. carbon yields) shown in Fig. 3(a). Such differential decomposition behavior of the stabilized fibers due to the various stabilization treatments can be expected to ultimately affect the microstructure and the properties of the resultant carbon fibers. That is to say, in order to obtain high performance carbon fibers, control of the stabilization degree (through appropriate choice of oxidative temperature and time) appears to be crucial.

3.1.3 TG-FTIR and TG-MS profiles of the stabilized thick tapes

Many advanced techniques can be used to study the thermal degradation of materials, for example TG and DTG, as discussed above. Owing to concurrent events, the amount of oxygen incorporated within the stabilized fibers as oxygen functional groups can be estimated neither from the measurement of the weight change alone nor from the measurement of gas formation rates alone [14]. Instead, it is important to adopt the most useful techniques such as TG-FTIR to continuously monitor the thermal decomposition behavior so as to understand the thermal degradation pathways of these fiber samples. Fig. 4 shows 3D TG-FTIR spectra of the evolved gases from the as-spun pitch fiber and its various stabilized fiber derivatives during the carbonization process. It can be seen from Fig. 4(a) that, as the carbonization of the as-spun fibers progresses, several characteristic bands appear around 1500~1600, 2200~2400, 2850~3000 and 3400~4000 cm^{-1}, which successively can be attributed to H_2O, CO_2 (CO), hydrocarbons (methane, ethane, etc.), and H_2O again. In fact, a limitation of TG-FTIR lies in detecting only non-symmetrical gas molecules which possess a permanent dipole; non-polar symmetrical molecules (e.g. H_2 and O_2) are not detected [32]. The intensities of the evolution peaks of H_2O and CO_2 can be seen to increase with heat-treatment temperature. The hydrocarbons' peaks do not appear below 300 °C and then sharply emerge at around 500~600 °C, subsequently decreasing step by step, which indicates that the majority of the weight loss experienced by the as-spun pitch fibers upon carbonization is as a result of evolution of H_2O, CO_2 and hydrocarbons in this temperature range. The obvious evolution of H_2O and CO_2 can still be seen at higher temperatures above 800 °C, which is most likely as a result of some oxidation or pyrolysis within the tape-shaped fibers. The TG-FTIR spectra of the pitch fiber samples stabilized at 220 °C for 20 h and at 240 °C for 15 h show a similar evolution pattern as shown in Fig. 4(b and c). H_2O and CO_2 obviously evolve from the stabilized fibers during the carbonization process, and in particular CO_2 evolves at around 300~600 °C, in contrast with the evolution (occurring at about 500~1000 °C) form of the stabilized fibers oxidized at 260 °C for 15 h, as shown in Fig. 4(d). In other words, the gas evolution profile is seen to be different for the stabilized samples depending upon stabilization conditions. The CO_2 evolution peak maxima for the fibers stabilized at 220 and 260 °C are at approximately 500 and 1000 °C, respectively. The functional groups responsible for the evolution of CO_2 have been attributed to the decomposition of carboxylic, ketone and anhydride groups, where one carbon is bonded with two oxygen atoms, which results in the high weight loss and low carbon yield for the excessively oxidized samples. As a result, it can be concluded that higher stabilization (i.e. oxidation) temperatures and longer times ultimately have an adverse effect on the final carbon yield of the product, which is in keeping with the above conclusions drawn from the EA and TG data. Once again, multi-stage decomposition with evolution of various gases is evident during the carbonization process. Compared with the as-spun fibers, the significant difference in the thermal degradation behavior of the stabilized fibers is the disappearance of hydrocarbon peaks (trace or no hydrocarbon evolution was detected) and the strengthening of CO_2 peaks in the spectra. It is surmised that the differences in the thermal decomposition behavior, including the various species of evolved gases and the corresponding degradation temperature as well as the concertedness of decomposition and its rate, will ultimately dictate the microstructure and properties of the resultant carbon fibers, and that, for the same batch of pitch-based fibers, this is mostly determined by choice of stabilization conditions.

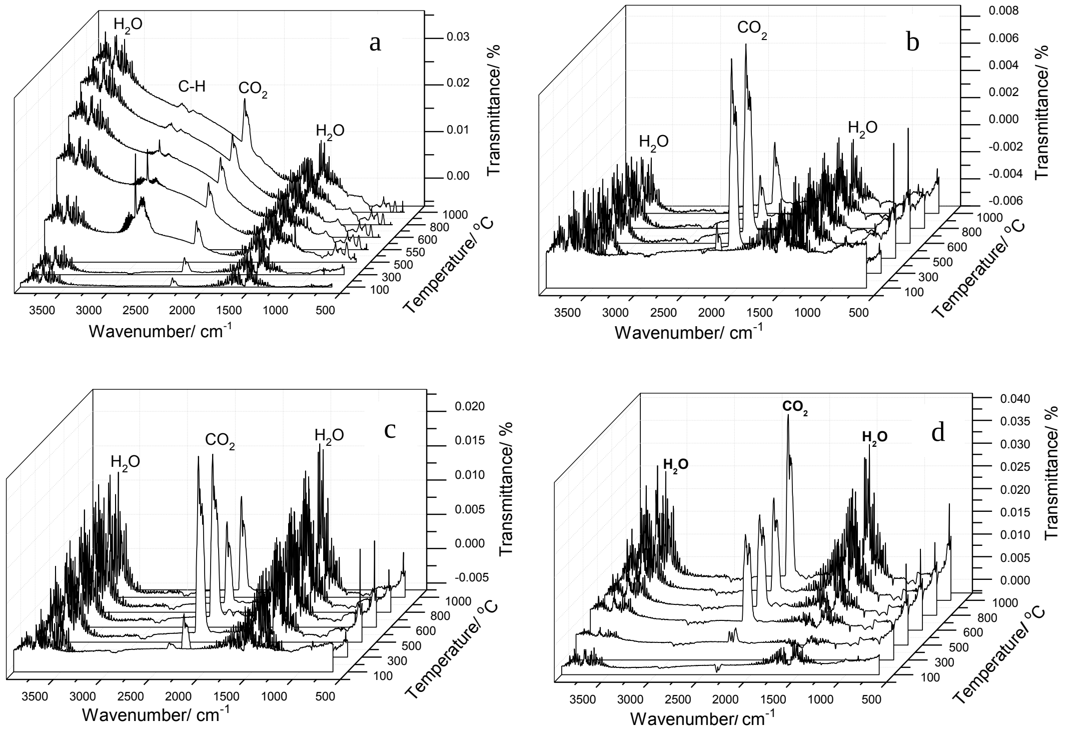


Fig. 4 3D TG-FTIR spectra of the evolution of gases from (a) the as-spun pitch fibers and their various stabilized fiber derivatives (b-220 °C-20 h, c-240 °C-15 h, d-260 °C-15 h).

TG–MS is another powerful real-time analysis technique, which can be employed to investigate the thermal decomposition behavior of the prepared tapes, and it is ideally suited to identify and quantify the molecular fragments evolved during the pyrolysis of the samples, so as to characterize the structural changes occurring in the pitch fibers during oxidative stabilization and subsequent carbonization. During TG–MS experiments, the gaseous products evolving from the fiber samples are simultaneously and continuously monitored by QMS, as recorded in Fig. 5. The major gaseous products from thermal decomposition of these samples include H_2, H_2O, CO, CO_2, CH_4, C_2H_6, etc..

In general, the H_2 evolution (as shown in Fig. 5(a)) arises initially at ~350 °C and lasts until 1000 °C. For the as-spun pitch fibers, the H_2 evolution seems to take place across all of this temperature range and the most intense release occurs at about 800 °C. However, the fibers stabilized at 220 °C for 20 h and 240 °C for 15 h exhibit their most intensive H_2 release at around 400~800 and 550~700 °C. It is interesting that the fibers stabilized at 260 °C for 15 h release H_2 at about 450 and 700 °C but show a relatively low H_2 concentration, which may imply the formation of H_2O or CH_4 instead of H_2. H_2 evolution always occurs in the high-temperature pyrolysis range (above 400 °C) and is usually considered to be a consequence of polyaromatic condensation reactions leading to the formation of an embryonic grapheme-layer structure [42].

Fig. 5(b) shows the evolution of H_2O for the various fiber samples. There is an obvious differential, in that the stabilized fibers release H_2O from a low temperature of about 100 °C to a high temperature around 900 °C whereas the as-spun pitch fibers only obviously release H_2O at high temperatures above 500 °C. This is in good agreement with the result of the TG-FTIR analyses. As a result, the rapid removal of H above 400 °C (Fig. 5(a)) from the stabilized fibers could be explained in terms of

H_2O evolution as well as H_2 evolution. It can be clearly seen that the stabilized fibers oxidized at 220 °C for 20 h intensively release H_2O at between 400~800 °C and the quantity of evolved H_2O is higher than from other samples, which may be related to the formation and subsequent partial decomposition of H_2O during the severe stabilization process at a high temperature (240~260 °C).

It is well known that the oxygen-containing gases such as H_2O, CO and CO_2, are known to be the decomposition products of the functional groups introduced during oxidation process [43]. It is interesting to note that there is only trace CO (i.e. broad low intensity peaks) detected from the stabilized fibers with TG–MS except from the as-spun pitch fibers as shown in Fig. 5(c), which markedly releases CO at about 500 °C. The inconspicuousness of CO from the stabilized samples may be due to measurement inaccuracy or other unknown reasons [32].

There is a significant difference between the as-spun pitch fibers and their stabilized fibers in the evolution of CO_2 as shown in Fig. 5(d). The as-spun pitch fibers sharply release CO_2 at a high temperature around 900 °C whereas the stabilized fibers intensively release CO_2 at around 400~700 °C. Two maxima in the CO_2 evolution profiles of the stabilized fibers are located within this temperature range, which is in agreement with the previous results [32,44]. On the other hand, there is little difference between the CO_2 evolution profiles for the various stabilized fibers. These peaks in the CO_2 evolution profiles might relate to different chemical reactions during pyrolysis which need to be further investigated. As mentioned above in relation to Fig. 4, CH_4 cannot be individually distinguished in FT-IR spectra, but it has been confirmed by TG-MS. Fig. 5(e) shows the evolution of CH_4 for the as-spun pitch fibers and their various stabilized fiber derivatives. In this regard, the pyrolysis behavior of mesophase pitch-based fibers before and after oxidative treatment shows distinct differences. The as-spun pitch fibers exhibits two CH_4 evolution peaks, i.e. intense release of CH_4 at around 400~600 °C and then again at around ~900 °C. In contrast, the stabilized fibers gradually release CH_4 over a wide temperature range from 350 to 700 °C. This indicates that oxidative stabilization treatment results in decreased CH_4 evolution, which might be beneficial for the integrity of the condensed aromatic ring structure (i.e. preserving the aromatic and naphthenic structure) [42].

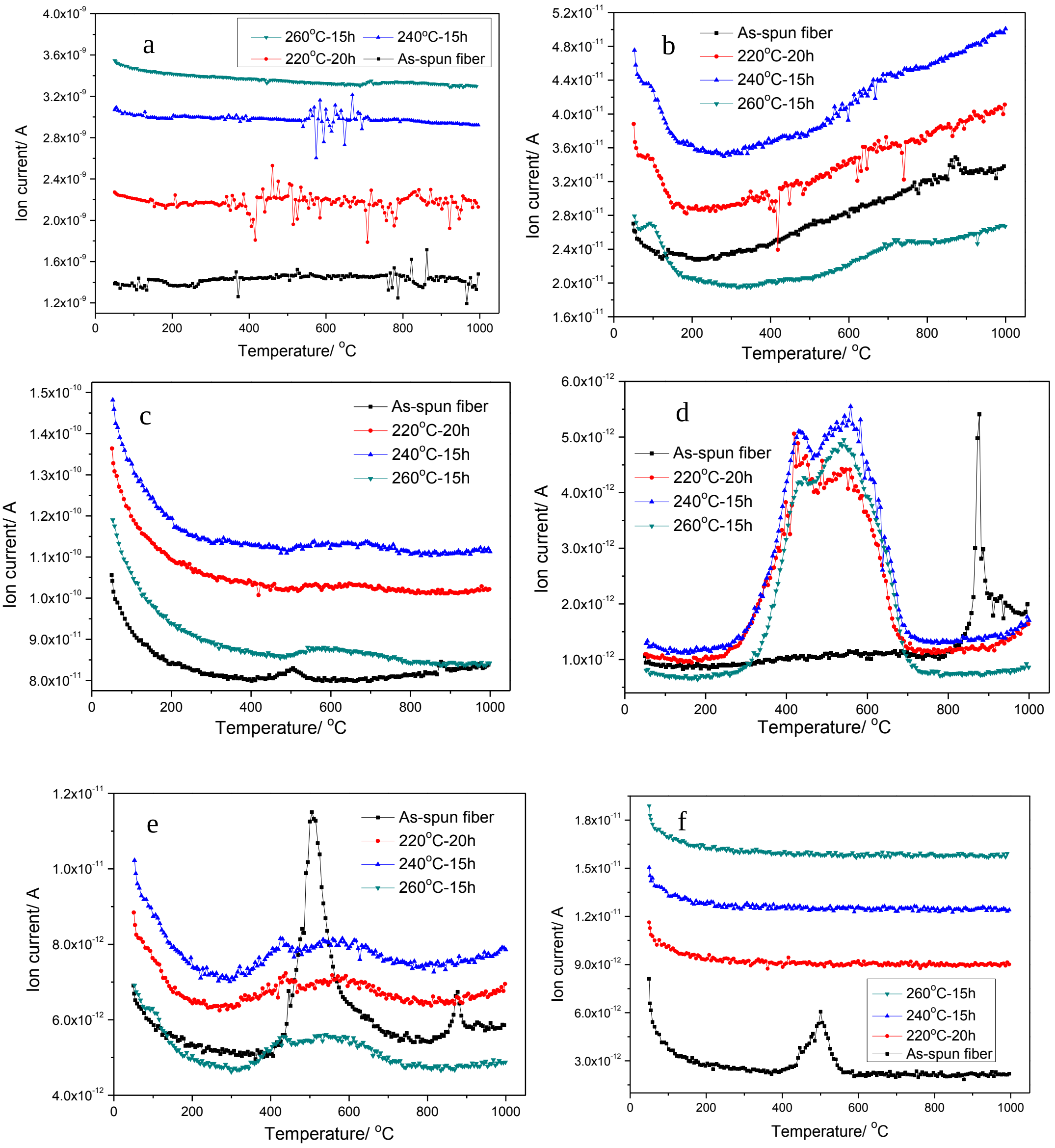


Fig. 5 TG-MS evolution profiles of various pyrolysis gases from the as-spun pitch fiber and its stabilized fiber derivatives (a-H_2, b-H_2O, c-CO, d-CO_2, e-CH_4, f-C_2H_6).

Evolution of C_2H_6 from the as-spun pitch fibers occurs at around 500 °C as shown in Fig. 5(f), and there is no or little C_2H_6 evolved from the stabilized fibers during the carbonization process. In summary, both the as-spun pitch fiber and its various stabilized fiber derivatives evolve H_2, H_2O, CO, CO_2 and CH_4 to various extents during pyrolysis, and the as-spun pitch fiber releases more low-molecular weight hydrocarbons (e.g. CH_4 and C_2H_6), the release of which can be sufficiently inhibited by the oxidative stabilization treatment at optimal temperature and time so as to improve the microstructure and physical property of the resultant carbon fibers.

3.1.4 Micro-elemental analyses of the stabilized thick tapes

Fig. 6 shows typical secondary electron images and oxygen distribution profiles of tape fibers obtained by EDS line-scanning across the transverse cross-sections of stabilized fiber samples oxidized at 220 °C for various times. As can be seen from the graphs shown in Fig. 6(a-c), the intensity and distribution of oxygen in the cross-section of stabilized fibers along the thickness direction of the tapes, clearly varies with duration of oxidative stabilization. That is to say, the oxygen distribution is obviously subjective to the stabilization conditions. At the beginning of stabilization (i.e. 1 h), the oxygen mainly concentrates near the two surfaces of the tape and only distributes discretely and lightly in the center of the tape as shown in Fig. 6(a). With the increase of oxidation time (i.e. 5 h), the intensities of oxygen both on the surface and center of the tape markedly increase as shown in Fig. 6(b), however, the distribution of oxygen along the thickness direction of the tape is still not homogeneous, which indicates a typical time-consuming process of diffusion of oxygen from the surface of tape-shaped thick fibers into the core of the tapes during the oxidative stabilization process.

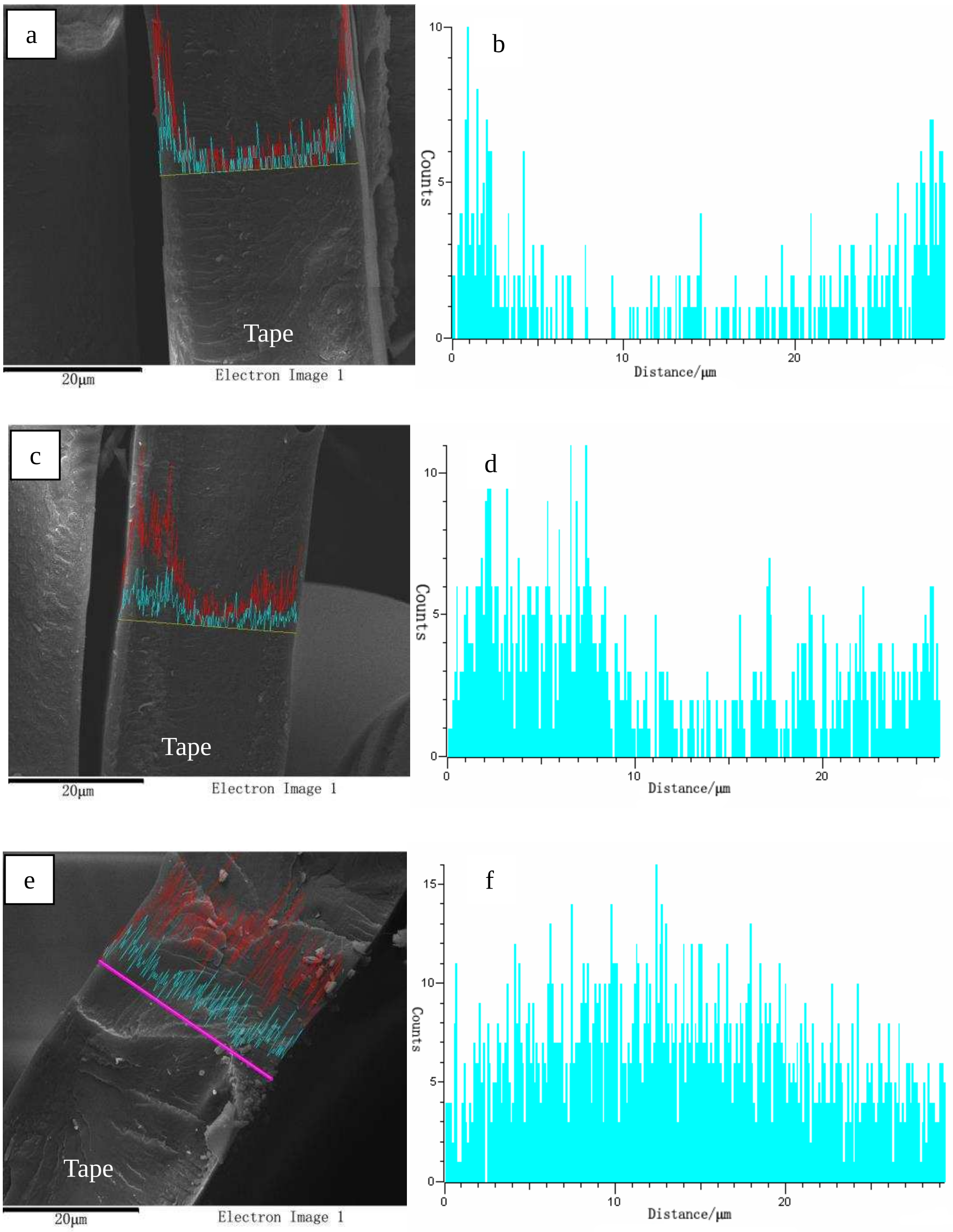


Fig. 6 (a, c, e) Typical secondary electron images and (b, d, f) oxygen distribution profiles along the thickness of tapes by EDS line-scanning on the transverse cross-sections of stabilized fiber samples oxidized at 220 °C for various times (a-1, b-5, c-10 h).

The concentrations of oxygen throughout the thickness direction of the tape are nearly equivalent as the stabilization time increases to 10 h, which indicates that complete oxidative stabilization for such tapes (ca. 30 μm in thickness) requires ca. 10 h at 220 °C. Taking into account that tapes need to be stabilized in batches for efficiency, and hence considering the pack thickness of the tapes and the homogeneity of the batch, the oxidative stabilization time may need to be further prolonged in order to improve the mechanical properties, as will be shown subsequently.

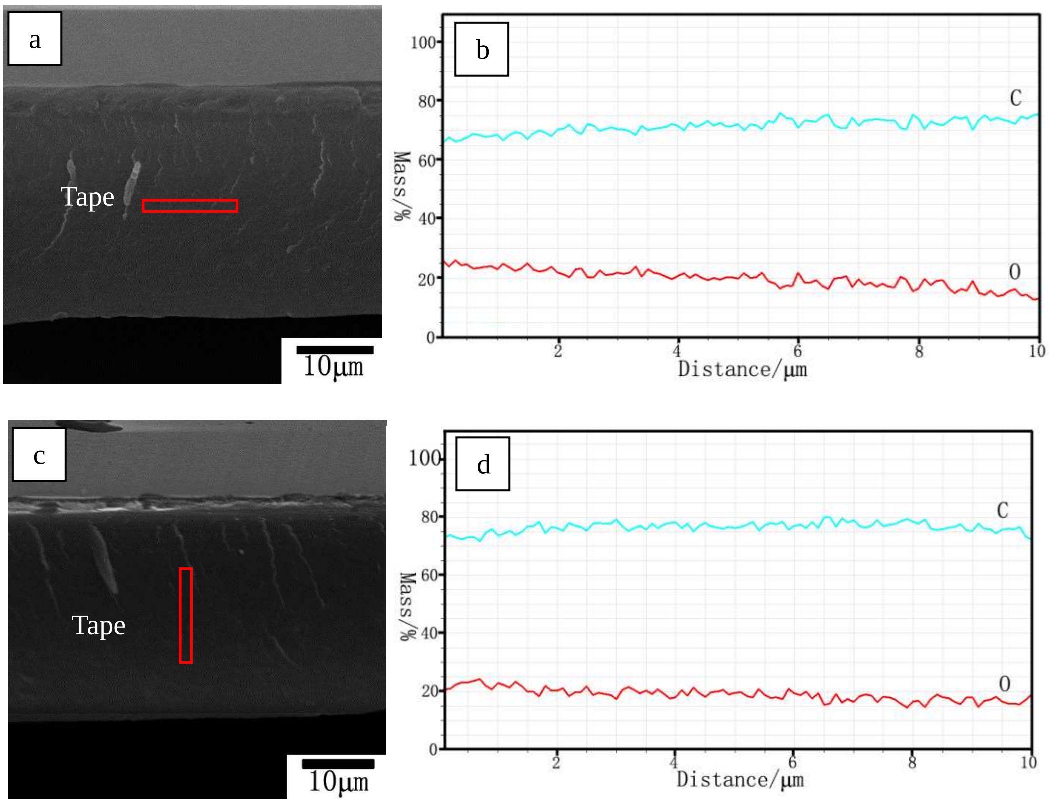
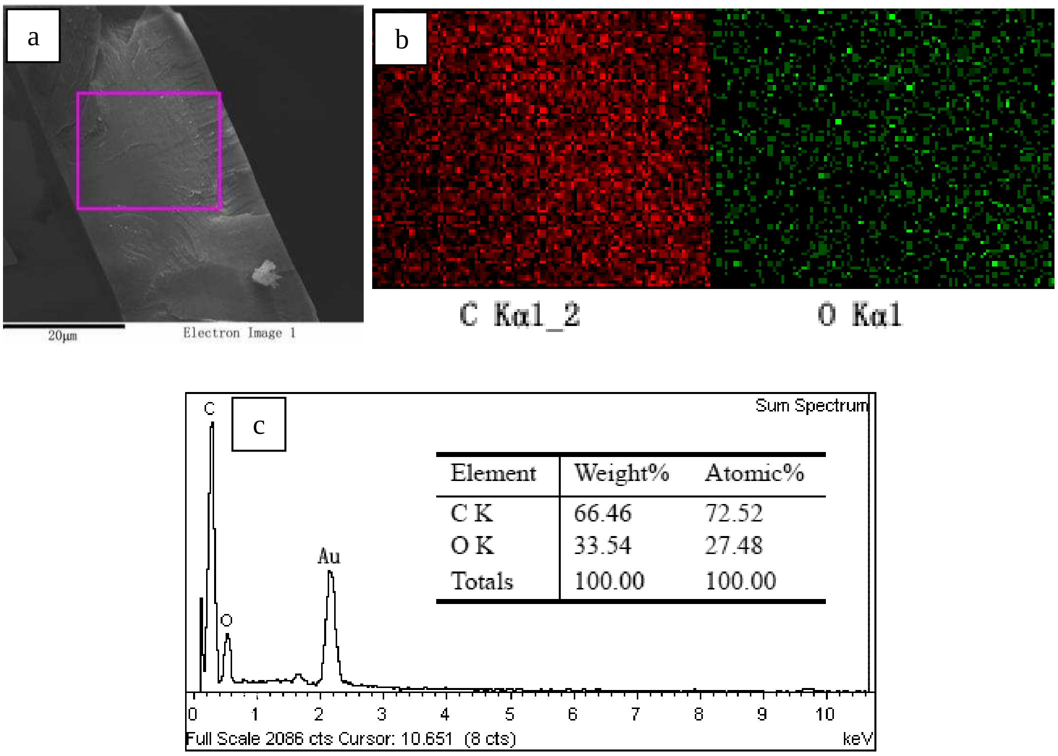


Fig. 7 (a and c) SEM images and (b and d) elemental distribution profiles for the corresponding box on the cross-section of tapes oxidized at 220 °C for 20 h obtained by electronic sector-scanning along two orthogonal directions.

Fig. 7 shows the SEM images and elemental distribution profiles obtained by electronic sector-scanning along two orthogonal directions in the transverse cross-section of the tapes oxidized at 220 °C for 20 h. The profiles show that the tape exhibits similar transversal morphology and microstructure in the two selected directions. The concentrations of oxygen and carbon across the cross-section of the tapes in the two orthogonal directions are highly equivalent. The high concentration of oxygen (about 20 wt.%) is in good agreement with the EA result, which further confirms that the oxygen content of tape-shaped fibers imparted by the stabilization process is higher than that of corresponding round-shaped fibers.



Element	Weight%	Atomic%
C K	66.46	72.52
O K	33.54	27.48
Totals	100.00	100.00

Fig. 8 (a) Secondary electron image, (b) EDS mappings of carbon and oxygen distribution and (c) EDS spectrum for the box highlighted in (a) by electronic sector-scanning on the cross-section of tape oxidized at 220 °C for 20 h.

The distribution of carbon and oxygen over the cross-section of the tape oxidized at 220 °C for 20 h is very homogeneous, as is demonstrated by the micro-field composition analyses shown in Fig. 8. This illustrates that oxidation treatment at 220 °C for ~20 h (at constant O_2 flow rate) is an appropriate stabilization condition for such batch of as-spun pitch tapes (ca. 30 μm in thickness), which indicates that the oxidative stabilization efficiency of tape-shaped pitch fibers seems to be relatively higher than that of comparable round-shaped fibers with a diameter of ~30 μm, also derived from a naphthalene-derived mesophase pitch ARA24 [16]. The very high concentration of oxygen (20~30 wt.%) incorporated in the stabilized tapes measured by micro-elemental analyses further demonstrates that the oxygen diffusion into the taped-shaped pitch fiber during the stabilization process is relatively easier than that of corresponding round-shaped fibers. As a result, the thickness of tape-shaped pitch fibers can be made up to ~30 μm [25]. Tapes of this thickness exhibit a complete stabilization in a short time (~10 h) at a low temperature (220 °C) due to relatively short oxygen diffusion pathways from their main surface to the core in all directions, as has been verified in the previous work [39,40]. However, for round-shaped fibers with an equivalent diameter (~30 μm), the rate of reaction in the pitch not only becomes slower and slower with increasing distance from the interface between the pitch and the oxidizing atmosphere but, at high stabilization temperatures, it may be further hindered as the outer surface becomes stabilized rapidly and so becomes a diffusion barrier to deeper stabilization [16,25]. The diameter of commercial round-shaped mesophase pitch-based carbon fibers is thus chosen to be less than 15 μm in order to avoid these difficulties.

3.2 Morphology and structure of the mesophase pitch-based carbon and graphite fibers

After oxidative stabilization under various conditions, the tape-shaped pitch fibers were treated at high temperatures to produce carbonized and graphitized samples for morphology and microstructure investigation. Fig. 9 shows typical SEM images of tapes carbonized at 1000 °C. It can be seen that the tape-shaped fibers maintain their shape, smooth surface, uniform thickness and continuous structural integrity without any damage (except for the obviously decreased thickness of ~20 μm), almost regardless of variation in oxidative stabilization conditions. It can be seen from Fig. 6(a) that the tape-shaped thick fiber seems to achieve an infusible state after oxidative stabilization at a low temperature (220 °C) for just a short time (5 h). However, in this short stabilization time, the oxygen distribution within the transverse section of the thick tape still does not become homogeneous as shown in Fig. 6(b). Hence, a longer stabilization time is required to improve the mechanical properties as will be discussed in the following. It is certain that oxidative stabilization plays an important role in changing the as-spun mesophase pitch-based tapes from a thermoplastic aromatic-molecule mixture to a thermosetting solid, allowing the oxidized tapes to maintain their tape geometry as shown in Fig. 9 in subsequent carbonization and graphitization processes without melting or deformation [25].

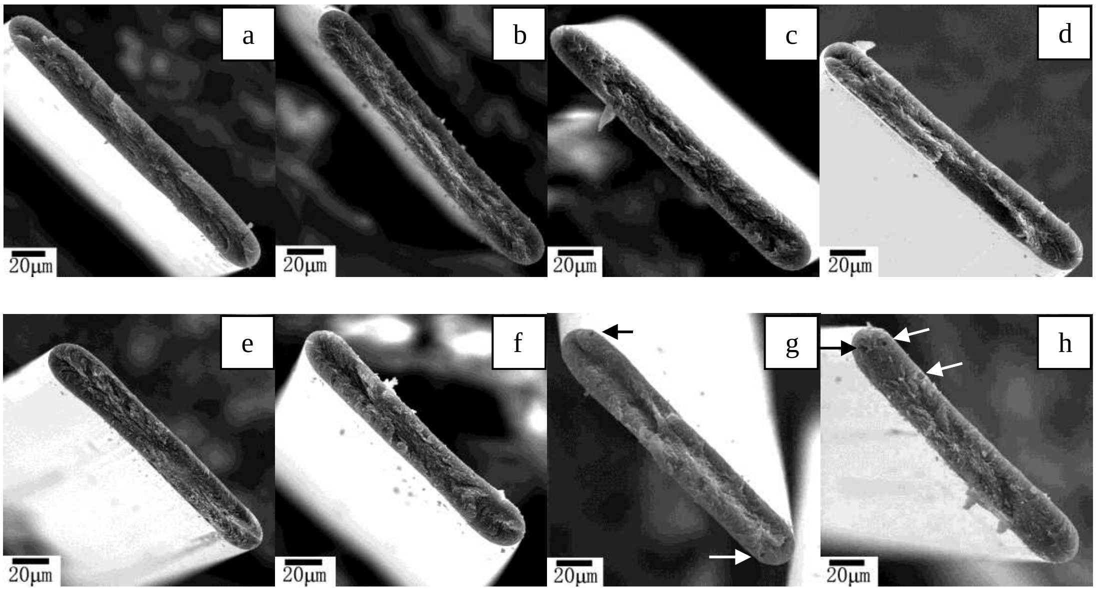


Fig. 9 Typical SEM images of the cross-section of tapes carbonized at 1000 °C following an oxidative stabilization at 220 °C (a-5, b-15, c-20, d-30 h) and 260 °C (e-5, f-15, g-20, h-30 h) for various oxidation times.

However, there are a few small holes (marked with an arrow) appearing in the cross-section of the tape-shaped fibers oxidized at 260 °C for 20 and 30 h, which may be associated with large numbers of functional groups formed during excessive stabilization and decomposed during pyrolysis and carbonization processes.

It is interesting to note that round-shaped carbon fibers with a diameter of ~28 μm (shrinkage from the pitch fiber's ~32 μm) prepared from the same mesophase pitch and stabilized with various atmospheres and oxidation times display diverse morphologies and Pac-man crack structure on their cross-sections. It is well-known that large diameter pitch fibers are prone to form "skin-core" structures in the stabilization process. After 220 °C oxidative stabilization in an air atmosphere for 5 and 15 h, the obtained carbon fibers as shown in Fig. 10(a and b) exhibit a severe melting and deformation behavior. The circular cross section of some carbon fibers changes from round shape into oval, triangle, square, etc., which is the result of incomplete oxidative stabilization. It can be found that the orientation of carbon layers, in which the mesophase pitch (incomplete stabilization) melted and deformed, significantly improves. As the stabilization time increases to 30 h, the circular cross section of the carbon fibers shown in Fig. 10(c) can be maintained. However, some hollow-cored carbon fibers unexpectedly appear due to the extensive decomposition of un-stabilized components in the center of large fibers. For the samples stabilized in oxygen atmosphere for 5-30 h, the resulting carbon fibers do not melt or deform and display a radial or radial-folded texture in their transverse sections as shown in Fig. 10(d-f). This indicates that faster oxidative crosslinking reactions take place in pure oxygen atmosphere under the same conditions in comparison with the air atmosphere. Small holes can be found in the cross-section of carbon fibers that underwent an oxidative stabilization for 5 h in oxygen atmosphere as shown in Fig. 10(d). It seems that cross linking within round-shaped pitch fibers with a large diameter of ~32 μm can be completed through oxidative stabilization for ~15 h at 220 °C in oxygen atmosphere, which is slower than for tape-shaped pitch fibers (~10 h). That is to say the taped-shaped pitch fibers show a slightly faster oxidative stabilization behavior.

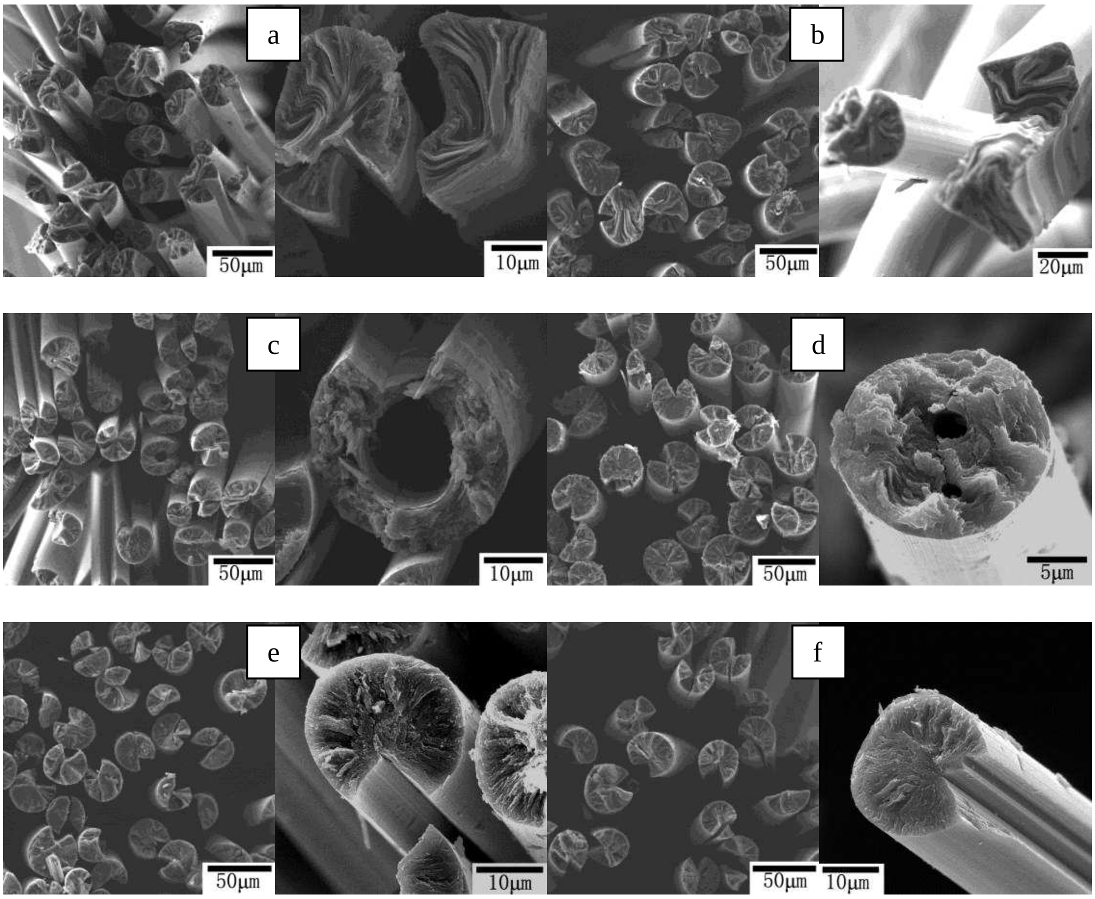


Fig. 10 Typical SEM images of the cross-section of round-shaped large fibers carbonized at 1000 °C following oxidative stabilization at 220 °C in air (a-5, b-15, c-30 h) and oxygen (d-5, e-15, f-30 h) atmospheres for various durations.

Fig. 11 shows typical SEM images of the cross-sections of tapes oxidized under various conditions and finally graphitized at 2500 °C. As following carbonization treatment, the tape-shaped fibers obtained after graphitization treatment still completely retain their morphology. (The SEM image of the tapes stabilized at 220 °C for 20 h is similar to those shown in Fig. 11(a and d) and is thus not shown). In comparison with the carbonized fibers as shown in Fig. 9, the graphitized tapes shown in Fig. 11 display more graphitic crystalline structure (i.e. high crystallinity, large microcrystallite size and high crystal orientation).

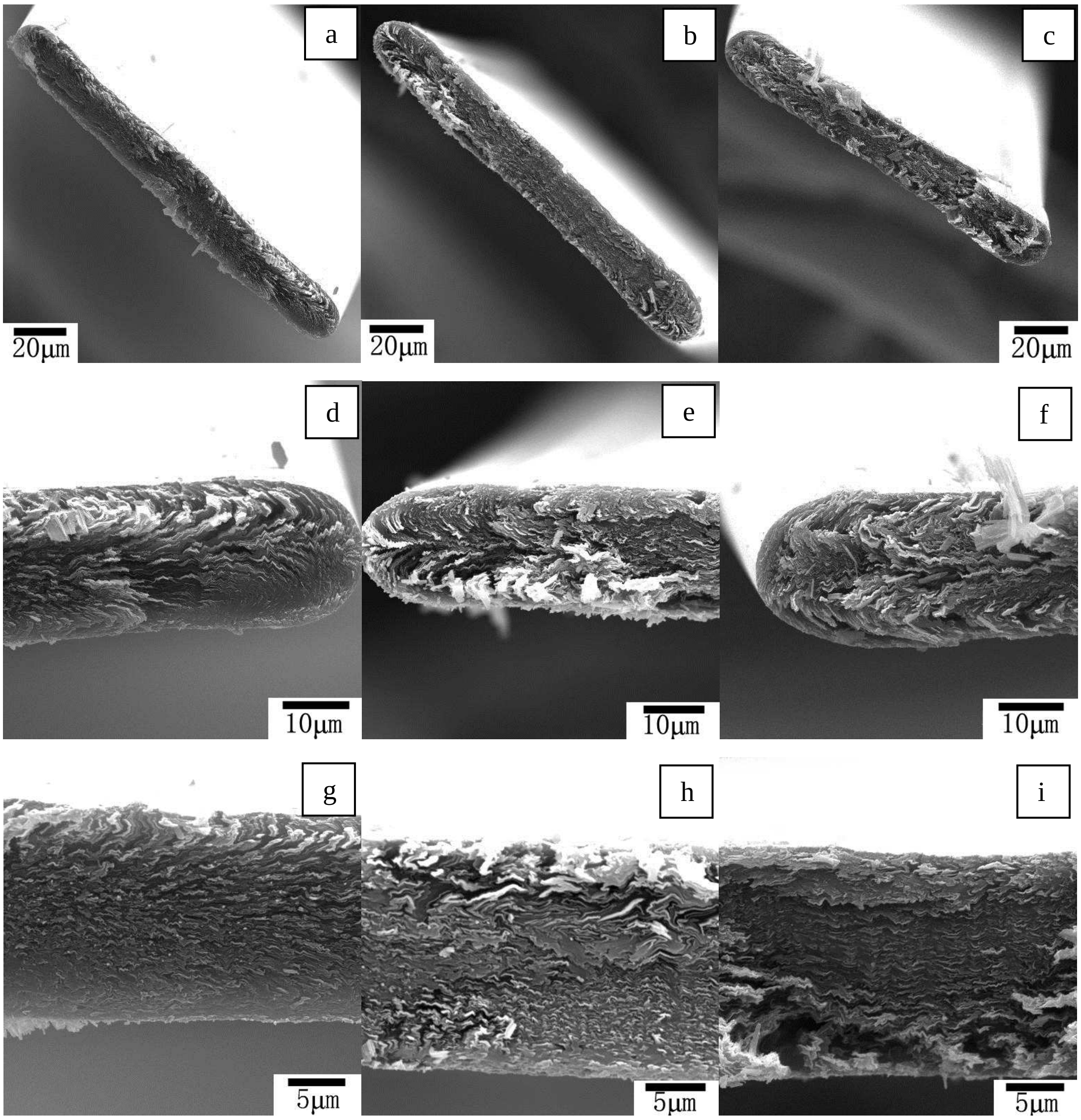


Fig. 11 Typical SEM images of the cross-section of tapes graphitized at 2500 °C following oxidation for 15 h at (a) 220 °C, (b) 240 °C and (c) 260 °C. (d and g), (e and h) and (f and i) are magnified images of the edges and centers of the corresponding tapes in (a-c).

It is worth noting that there is no obvious differentia on the edges of the tape-shaped graphite fibers after oxidation at various temperatures, which exhibits a typical radial folded or wrinkled texture (wrap around the edges) [25]. The edges of the tapes do not take place any micro-structural deformation or splitting at the stages of cross-linking reaction and high-temperature thermal pyrolysis, which markedly differs from that of conventional round-shaped fibers as shown in Fig. 10. The latter with a radial texture on the transverse cross-section usually tends to form a Pac-man wedge structure [22,45].

The carbon layers at the centers of the tape-shaped graphite fibers show significant differences in the orientation and arrangement of carbon microcrystalline domains compared with the edge sites [25], which varies with the various stabilization conditions. There is no doubt that oxidative stabilization at a relatively high temperature (i.e. 260 °C) for mesophase pitch-based pitch fibers accelerates the stabilization process and shortens the stabilization time, which will result in a heterogeneous structure. In general, the excessively stabilized fibers are prone to form a “skin-core”, relaxed or random structure [22,46] after subsequent high temperature treatments, which can also be found near the main surface regions (unhomogeneous structure) at the center of the tape-shaped graphite fibers shown in Fig. 11(h and i). This is detrimental to the improvement of mechanical properties of carbon tapes demonstrated in the following discussion.

In contrast, round-shaped carbon fibers graphitized at 2500 °C with a large diameter of ~26 μm, as shown in Fig. 12, exhibit wedge-shaped cracking behavior upon high-temperature treatment. The splitting degree (angle) of large carbon fibers is obviously aggravated as the heat treatment temperatures increase from 1000 to 2500 °C, which may be caused by internal stresses within such highly anisotropic materials due to the directional growth and preferred orientation of microcrystallines in the fiber. A few small cracks or slits appear in the cross-section of these round-shaped carbon fibers, which is the result of inhomogeneous shrinkage and orientation of carbon layers. It will undoubtedly affect their final mechanical properties. However, the tape-shaped carbon fibers can efficiently solve these problems through uniform shrinkage upon heat treatment and maintain their tape shape and structural integrity without any damage.

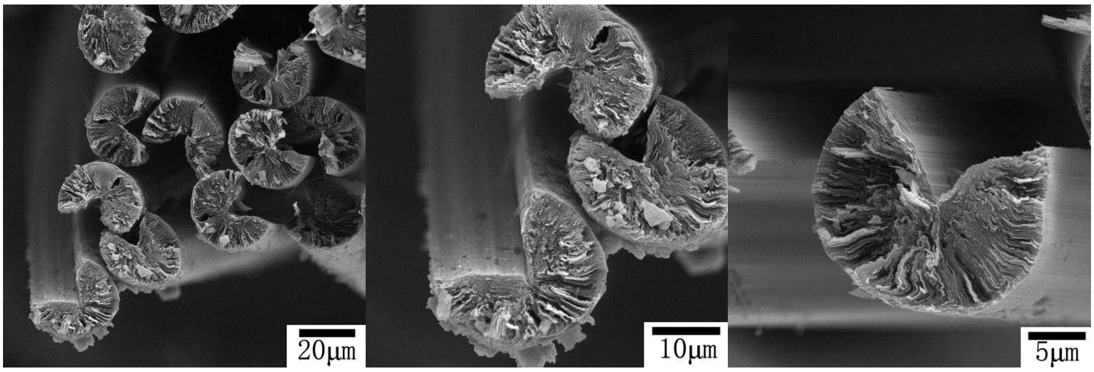


Fig. 12 Typical SEM images of the cross-section of round-shaped large fibers graphitized at 2500 °C following oxidative stabilization in oxygen atmosphere at 220 °C for 30 h.

3.3 Physical properties of the mesophase pitch-based carbon and graphite fibers

Fig. 13 plots the room-temperature axial electrical resistivities of tape-shaped carbon and graphite fibers after stabilization at various temperatures and times. Previous research [25] has demonstrated a trend of gradually decreasing axial electrical resistivities in wide tape-shaped carbon fibers with increasing heat treatment temperature. It can be seen from the graph shown in Fig. 13(a) that the axial electrical resistivities of carbonized tapes stabilized at various conditions are measured to be in the range of 11.2~12.7 μΩ m and do not show any obvious trends which may be connected with the various amounts of oxygen contained in the tapes. It was determined by EA and TG-MS analyses (not shown) that the residual oxygen content in the thick tapes carbonized at 1000 °C is about 3 wt.%. It is well known that some structural defects and most non-carbon atoms, in particular oxygen atoms, are considered to have a passive role of scattering the carrier or constraining the movement of free electrons in carbon materials [47]. The tape-shaped carbon fibers previously oxidized under various stabilization conditions have different structural defects and residual oxygen contents, which lead to the absence of clear trends in the electrical resistivities (without consideration of the acceptable errors arising from the calculation of transverse cross-sectional area). As the heat treatment temperature rises up to 2500 °C, the axial electrical resistivities of the graphitized tapes decrease into the range of 3.5~3.7 μΩ m as shown in Fig. 13(b). The trend in electrical resistivity versus the various stabilization conditions is still not obvious, but the range of the electrical resistivity values decreases from 1.5 to 0.2 μΩ m, and this may be caused by the further decomposition of oxygen in the subsequent graphitization process. It is interesting to note that the lowest value that was measured (3.5 μΩ m) for axial electrical resistivity is for the tape-shaped graphite fibers that underwent oxidation treatment at 220 °C for 20 h; and upon further heat treatment of these tape-shaped fibers up to 3000 °C, their axial electrical resistivity was measured to be as low as 1.2 μΩ m [25]. Not dissimilarly, the axial electrical resistivity of high thermal conductivity K-1100 graphite fibers (produced by Cytec Engineering) is about 1.17 μΩ m when measured in the same ohmmeter and this agrees well with the previously reported value (1.1~1.3 μΩ m) [48]. This suggests that such tape-shaped graphite fibers after 3000 °C graphitization may also have high axial thermal conductivity similar to that of K-1100 graphite fibers, which were well-verified in the previous work [25,49,50].

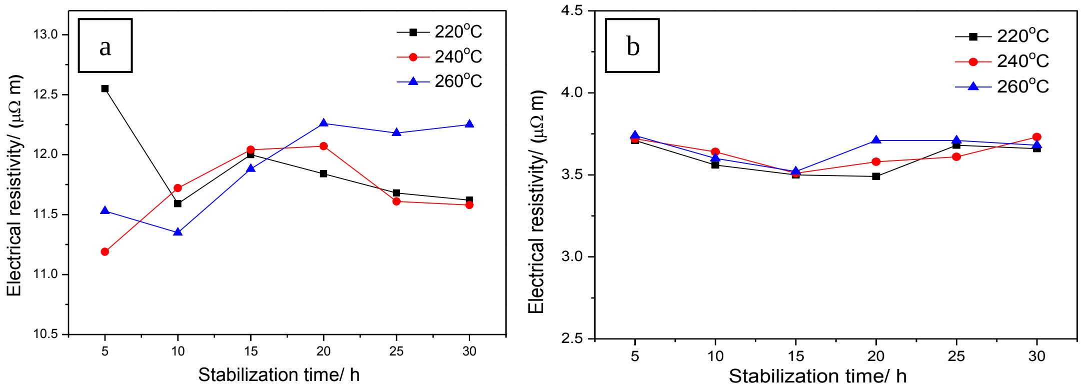


Fig. 13 Room-temperature axial electrical resistivities of tape-shaped fibers after stabilization at various temperatures and times and (a) carbonized at 1000 °C, (b) graphitized at 2500 °C.

The mechanical properties of the tape-shaped fibers carbonized at 1000 °C and graphitized at 2500 °C are shown in Fig. 14. It can be seen from the graphs shown in Fig. 14(a-d) that the tensile strength and Young's modulus of the tape-shaped carbon and graphite fibers are significantly influenced by the variety of oxidative stabilization conditions. At all of the oxidation temperatures, the mechanical properties of the tapes firstly increase and then decrease as oxidation time increases. Although an infusible state (in terms of maintaining tape geometry) for the tape-shaped thick fibers could be achieved in a short time (5 h), their average tensile strength is relatively low. The oxidation temperatures also have obvious influences on the mechanical properties of the tapes. In all cases, the tape-shaped fibers oxidized at a low temperature (i.e. 220 °C) clearly possess a relatively higher mechanical performance in comparison to those stabilized at high temperature (i.e. 260 °C). This behavior is dominated by the internal microstructure of the tapes which, in turn, is closely associated with the thermal pyrolysis behavior of the tapes during the high temperature treatment process. That is to say, the final mechanical properties are strongly influenced by the oxidative stabilization conditions. It is unexpected that different oxidative stabilization durations at 220 °C (15 and 20 h, respectively) are required to achieve the highest mechanical properties after carbonization and graphitization. This may be due to the influence of these durations on the generation and decomposition of the functional groups and the resulting intrinsic structural evolution in the tape-shaped fibers during the heat treatment process.

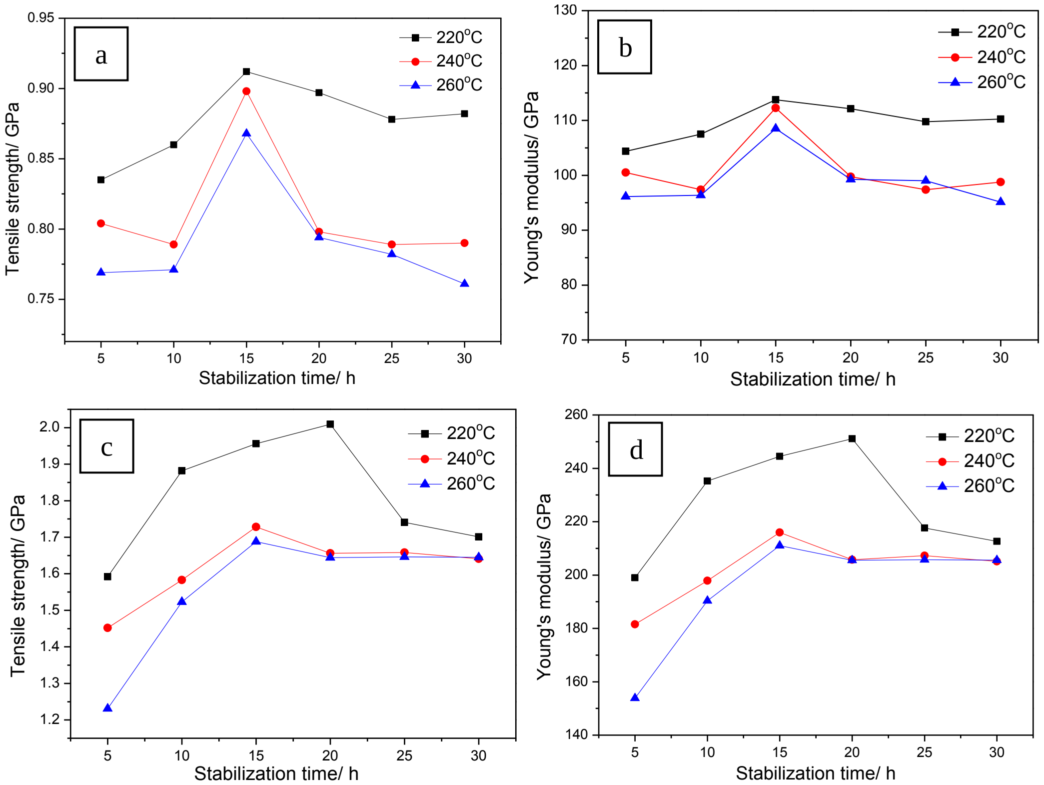


Fig. 14 (a and c) Tensile strength and (b and d) Young's modulus of tape-shaped fibers carbonized at 1000 °C (a-b) and graphitized at 2500 °C (c-d) after stabilization at various temperatures and times.

The tape-shaped pitch fibers firstly oxidized at 220 °C for 20 h, and then carbonized at 1000 °C for 1 h and finally graphitized at 2500 °C for 0.5 h possess the highest tensile performance; their tensile strength and modulus are measured to be about 2.0 and 250 GPa, respectively. These values can be favorably compared with the corresponding values (1.8~2.1 and 300~400 GPa) for previously reported graphitized narrow ribbon-shaped fibers (150~200 μm^2 in cross-sectional area) with a relatively low aspect ratio [51,52] and commercial data (1.9 and 379 GPa) of round-shaped carbon fibers (i.e. Cytec Thornel P-55S) [48].

It is interesting to point out that the oxidative stabilization treatments have a strong influence not only on the morphologies and microstructure of round-shaped carbon fibers as shown in Fig. 10 but also on their mechanical properties. The tensile strengths of round-shaped carbonized fibers with a large diameter after oxidative stabilization at 220 °C in air atmosphere for 5, 15 and 30 h are measured to be about 0.6, 0.7 and 0.8 GPa. However, in oxygen atmosphere, the corresponding tensile strength values increase to 0.9, 1.2 and 1.0 GPa, which demonstrates a similar trend to that of taped-shaped fibers. The improvement and optimization of mechanical properties of the large diameter round-shaped carbon fibers are complex and are still under study with a view to correlating them with optimal oxidative stabilization conditions (e.g. multi-step stabilization at high temperatures).

This finding is unexpectedly favourable given the larger transverse cross-sectional area of the tapes (~50 times that of the narrow ribbons reported in Refs. [51,52]), as well as the larger gauge length (40 mm) in single-filament testing experiments which could both be expected to increase the potential for internal flaws to be present in a given sample test volume. It should be noted that the measured elongation at break of the tape-shaped fibers averages about ~0.8%, which is relatively high compared with that of conventional round-shaped fibers graphitized at 2500 °C (~0.5%), thereby directly resulting in relatively lower modulus values for the graphitized tapes. However, with the further increase of graphitization temperature (i.e. to 3000 °C), the mechanical properties (e.g. modulus) of tape-shaped fibers can be expected to significantly improve [25].

4. Conclusions

A batch of melt-spun tape-shaped mesophase pitch-based fibers with a relatively high aspect ratio (ca. 400 μm in width and 30 μm in thickness) was selected as a model for detailed investigation of their oxidative stabilization. The as-spun pitch fibers underwent oxidative stabilization using various temperatures (220~260 °C) and times (1~30 h), and then carbonization and graphitization at high temperatures. The corresponding products possess a complete tape shape, a smooth surface and uniform thickness. However, round-shaped pitch fibers with a diameter (~32 μm), very similar to that of the tapes' thickness, following various oxidative stabilization treatments in air and oxygen atmospheres display a Pac-man crack wedge structure (and some even melt or deform) upon the subsequent heat treatment process. Several powerful modern characterization techniques have been used to comprehensively study the influence of oxidative stabilization of the tape-shaped pitch fibers on their final microstructure and physical properties. Through this essential oxidative stabilization treatment, the thermoplastic tape-shaped pitch fiber becomes, via cross-linking with oxygen, a thermoset tape which therefore does not melt or deform in subsequent high temperature heat treatment processes. This oxidative transformation has been tracked and verified by FTIR, EA and EDS analyses. The abundance of oxygen-containing functional groups formed during the stabilization process, within the stabilized fibers (or on their surfaces) clearly increases with the rise of oxidation temperature and time and these groups then gradually decompose in subsequent pyrolysis processes. The oxygen content and oxidative stabilization efficiency of tape-shaped pitch fibers are much higher than those of comparable round-shaped fibers. This is surprising in view of the latter’s oxygen diffusion pathways from the surface to its core which are shorter in all but a few directions. Stabilization treatment conditions have a significant influence on the thermal decomposition behavior (e.g. the rate and amount of pyrolyzed gas), local composition and micro-structural changes of the mesophase pitch-based tapes and these characteristics have been monitored effectively by TG-FTIR, TG-MS, EDS and SEM analyses.

In addition, the oxidative stabilization of the taped-shaped pitch fibers has an obvious effect on the final electrical and mechanical properties of the resultant carbon and graphite fibers, although not on their morphology. The axial electrical resistivity of the tape-shaped carbon and graphite fibers is found to be closely associated with the oxygen content, which is dominated by the various stabilization conditions and as a result of differences in fiber structure. The tape-shaped pitch fibers oxidized under mild conditions (e.g. at 220 °C) clearly offered relatively higher mechanical performance in comparison with more severely oxidized tapes. Stabilization at higher temperatures (240~260 °C) or for longer times (20~30 h) appears to be detrimental to development of mechanical performance characteristics which, in contrast, are maximized when stabilization is carried out at 220 °C for 15~20 h. The tensile strength and the Young’s modulus of tapes graphitized at 2500 °C following oxidation at 220 °C for 20 h reach maximum values, measured to be about 2 GPa (comparable to corresponding round-shaped fibers) and 250 GPa, respectively. The tensile elongation at break of the corresponding tape-shaped fibers is approximate ~0.8%, which is higher than that of round-shaped fibers (representing potentially greater damage tolerance for the tapes, albeit with slightly lower modulus).

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