

Laser Processing Technology for PAN Fiber Carbonization

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ABSTRACT

Carbon fibers (CFs) are an important engineering material due to their superior mechanical, electrical, and thermal properties. Majority of them are produced from the thermal conversion of polyacrylonitrile (PAN)-based fibers. In order to promote the CF manufacturing speed and offer the possibility to control the microstructure of the fibers, an alternative technology for carbonization of stabilized PAN fiber are explored by laser processing technology. In this work, we investigated the relationship between the laser process and the properties of fibers. Laser irradiation introduces the structural changes in the stabilized PAN fibers. The appearance of D band and G band in Raman spectrum verifies the existence of graphite structures in the laser scanned fibers. The characteristic peaks in FTIR disappear when the high laser energy condition is engaged, which indicates diminishing of non-carbon bonds. Laser treatment also introduces an obvious shrinkage in fiber diameter. The condition of laser irradiation could influence the electrical and mechanical properties of fibers. A new approach to convert stabilized PAN fiber into carbon fiber was demonstrated.

1. INTRODUCTION

Carbon fibers (CFs) are an attractive material in many realms, such as aerospace engineering, power generation (wind blade), vehicle manufacturing, and construction due to their excellent mechanical properties: tensile strength up to 6.9 GPa, Young's moduli up to 590 GPa [1], low density of about 1.8 g/cm³, and good electrical and thermal properties [2–6]. Due to the excellent properties, there is large demand of CFs each year. It's reported that 1500 tons of CFs are produced each year and the price is still as high as \$10.20 /lb [7]. Application of CFs would be even broader if their price can be further reduced. Efforts have been made in each step during CF manufacturing process in order to reduce the production cost, in which the cost for carbonization/graphitization is the 2nd largest following the cost of precursor material [8]. Among many low cost precursor materials, such as lignin, cellulose, pitch, and polyacrylonitrile (PAN) [9–15], PAN is the most used precursor for CF manufacturing currently.

The processes of PAN-based CF fabrication include stabilization and carbonization. The oxidative stabilization process takes place at temperature between 200 °C and 300 °C in air atmosphere. The carbonization process follows stabilization at temperature 500-1600 °C in nitrogen atmosphere [16]. Many complicated chemical reactions happen in stabilization process, including oxidation, dehydrogenation and cyclization [20]. The stabilization of PAN fiber is

usually done in oxidizing atmosphere, which is typically air. The oxygen is an initiator for the formation of activated center for cyclization because of the increase in the activation energy [21]. Dehydrogenation of the formation of double bond that stabilizes carbon chain and cyclization is the reaction of the nitrile groups in the precursor polymer with adjacent groups to form a stable ladder structure [22]. The stabilization process changes the chemical structure of fibers and prepares them to sustain high temperature without melting [21]. In carbonization process, the stabilized PAN is converted into a graphite-like structure. Carbonization is an aromatic growth and polymerization in which fiber would be treated in high temperatures to remove non-carbon elements as volatile gas [17]. Generally, the CFs' modulus depends on the process temperature. Carbonization at 1000 °C or lower would produce CFs with low modulus, while the intermediate modulus CFs needs temperature higher than 1000 °C and up to 1500 °C [17,18]. The CFs with high Young's modulus are obtained by an additional heat treatment process at a temperature up to 3000 °C in argon atmosphere. Conventional heat treatments of the PAN fibers are performed in furnaces, which demands significant amount of energy and requires extensive furnace maintenance resulting in a high processing cost. Besides, the exothermal chemical reaction during heat treatment might lead to non-uniform energy distribution along the fiber and deterioration of mechanical properties [23]. Therefore, a more efficient and low energy consuming method is highly recommended for alternative of the current furnace-based heat treatment.

Lasers are used widely in manufacturing processes [24–27] due to their ability to deliver a large amount of energy on a local area in a short time. Based on its high energy density output capability and noncontact treatment possibility, laser heating is an attractive substitute of furnace heat treatment in carbonization process. Moreover, the crystallization and restructuring of the micro-fiber structures are likely achieved along the laser scan direction. Shieh *et al* used a pulsed near-infrared laser to achieve the crystallization of amorphous silicon [28]. The work shed light on the possibility that the carbon atom could reorganize under pulsed laser and the carbonization process can be achieved by laser scan. Chyan et al [29] proposed probable mechanism of graphite formation from polymer. They suggested the carbon precursor first is first photo-thermally converted into amorphous carbon, then subsequent exposures of amorphous carbon under laser transform the amorphous carbon into graphite. The inducing of laser treatment could simplify the pyrolysis system largely, which makes it possible to achieve large-scale manufacturing. The fast rate of generating highly concentrated and precise amounts of energy is able to increase the efficiency meanwhile minimize the energy lost to the environment and reduce the total energy cost.

In this work, we explore the laser processing for CF fabrication. The stabilized PAN fibers were treated by CO₂ laser under argon atmosphere. Different laser conditions were used to scan the fibers. Structural changes have been verified via Raman spectroscopy and Fourier-transform infrared spectroscopy. The morphology of stabilized PAN fiber before and after laser irradiation was also observed by scanning electron microscope. Commercial carbon fiber T300 was introduced to make structural comparison with the stabilized PAN fiber scanned by laser. This study provides insights on the feasibility of laser-induced heat treatment in converting stabilized PAN fiber into carbon fiber.

2. EXPERIMENTATION

The stabilized PAN fibers were used as starting material in this study. The diameter of stabilized PAN fiber was $\sim 13\text{ }\mu\text{m}$. The experimental setup is shown in Figure 1a. A single stabilized PAN fiber filament was fixed on a sample holder using double-sided tape on both ends. The samples were placed in a chamber filled with argon gas. The laser (VLS2.30, Universal Laser Systems Inc.) with an infrared (IR) wavelength of $10.6\text{ }\mu\text{m}$ was utilized to raster-scan the suspended fibers. The laser beam was carefully aligned with the fiber and the laser scanned along the fiber in the fiber axes direction. The laser beam diameter on focal plane was $100\text{ }\mu\text{m}$. The number of pulses per inch (PPI) was set as 500 for all experiments. The samples were placed on the plane where was 1.4 cm lower than the laser focal plane for all experiments in order to achieve larger beam size and uniform laser beam energy (Figure 1b). The beam size was then increased to $1000\text{ }\mu\text{m}$. It is known that the laser radiation energy fluence was proportional to the laser output power and inversely proportional to the scan speed [30]. The laser powers and speeds were changed in order to investigate their effects on carbonization process.

In order to verify the laser induced carbonization process on the stabilized PAN fiber, the Raman spectroscopy (Renishaw, Inc., InVia Raman) with the laser wavelength of 785 nm was utilized to characterize the crystallinity change of fibers before and after laser irradiation. Several points of a single fiber filament were tested by Raman to ensure the credibility and uniformity. All samples were well-focused in the center of the cross-line indicator of the microscope and tested under the same Raman conditions: 10 s of exposure time, 5% of Raman laser power, and one-time accumulation. These setups ensured the comparability of the Raman signal intensity.

Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet NEXUS 470) was used to obtain the spectra of pristine stabilized PAN fibers and laser-treated fibers. The analyses were performed by ATR mode in $4000\text{--}850\text{ cm}^{-1}$ range at 4 cm^{-1} resolution. Moreover, the morphology of the fibers including pristine PAN fibers and laser-treated fibers was observed under scanning electron microscope (SEM, FE 7407F, JEOL Ltd.).

The tensile tests of single fiber filaments were performed using dynamic mechanical analysis (DMA2980, TA Instrument). The tensile specimen was prepared by transferring the suspended fiber onto a paper frame and fixed with an instant cyanoacrylate adhesive [31]. After the specimen was mounted to the mechanical testing machine, the paper holder was cut into two parts before running the test program. The gauge length was 5 mm and the crosshead speed was 2% per minute. All tensile tests were conducted under laboratory temperature. In electrical property investigation, a single fiber filament was carefully placed on two copper-based electrodes separated in 5 mm and the resistance of the fiber was measured by two-probe method using multimeter (Multimeter 403, Extech). To enhance the electrical contact between fiber and copper electrodes, silver paste was used to fix the fiber onto the electrodes. The electrical conductivity of the fiber was calculated based on fiber resistance and size.

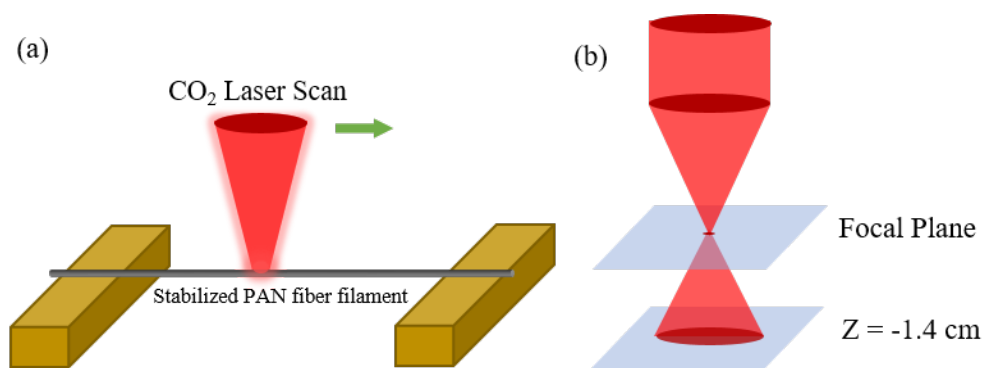


Figure 1. (a) The schematic illustration of the laser-treatment system for carbonization process. (b) Diagram of defocusing on the substrate to increase the laser beam size.

3. RESULT AND DISCUSSION

Raman spectroscopy is one of powerful tools for characterizing carbonaceous materials. Figure 2 shows the first-order Raman spectra of pristine stabilized PAN fiber and the stabilized PAN fibers treated under different laser conditions. A broad Raman spectrum is observed for pristine stabilized PAN fibers (Figure 2a). Lacking ordered molecular arrangement leads to the broadness of Raman spectrum [32]. Figure 2b shows the Raman spectrum of stabilized PAN fiber scanned by laser with power 0.8 W with speed 2.5 cm/s. Though D-peak and G-peak start to show up, these characteristic peaks are still weak to verify the existence of carbon structure. When the speed lowers to 2.0 cm/s, while keeping the same scanning power, the two main bands at 1360 cm^{-1} and 1575 cm^{-1} become obvious (Figure 2c). The former corresponds to D band which is related with turbostratic and/or disordered carbonaceous structures, whereas the latter corresponds to G band which is attributed to the vibration mode E_{2g} of graphitic cells [33]. As the speed decreasing, D peak and G peak become sharper and well separated, indicating the increase of crystallinity of carbon structure induced by laser scan (Figure 2b-d). It is notable that Raman signal intensity of pristine PAN fiber is remarkably high (up to 150,000 counts) while T300 carbon fiber show the low Raman intensity around 600 counts under same test condition, as shown in Figures 2a and 2h. The overall high Raman intensity of stabilized PAN fiber irradiated by low energy laser is likely to indicate the existence of polymer structure. Though the peaks of D band and G band are well-separated in Figure 2d, the intensity of overall Raman signal is high (around 1,000 counts) compared with T300 fiber (around 600 counts).

It seems the higher laser power or lower scanning speed should be applied to further enhance the carbonization level in the fibers. However, when the power reached 1 W and the scanning speed kept 1.5 cm/s, most fibers were broken during laser treatment. Similarly, scanning speed 1.0 cm/s with power 0.8 W also breaks the fiber. The breakage mostly happened at the position where the laser beam first touched the fiber sample. It is speculated that the instant high laser energy falling on the fiber leads to sudden chemical structure change and diameter shrinkage [21]. The junction between pristine stabilized PAN fiber and the part that scanned by laser become unstable, finally leading to breakage. To further accomplish carbonization, twice scans are employed. In the first scan, the laser power of 0.8 W and scanning speed of 1.5 cm/s are for all fibers. In the 2nd scan, the scan speed of 2.5 cm/s is kept the same while the laser power is

set at 1.0 W, 1.2 W, and 1.4 W. The first scan would endow the fiber more stable structure and preparing it to sustain under higher laser power energy without breaking.

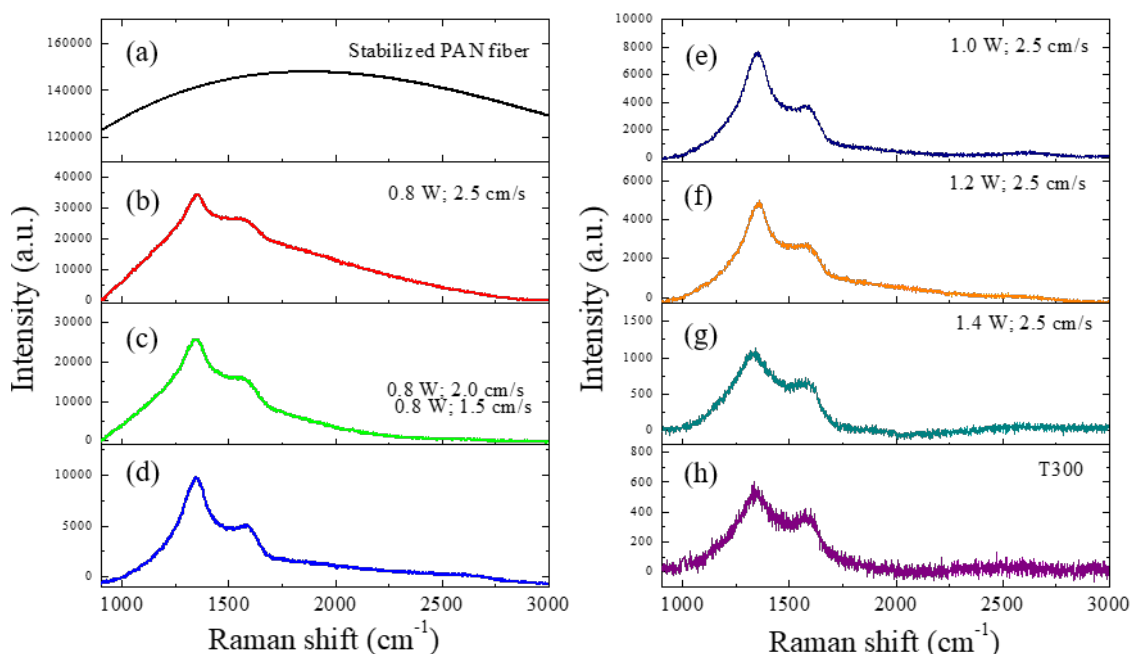


Figure 2. Raman spectra of (a) stabilized PAN fiber; (b-d) the stabilized PAN fibers treated by one laser scan under the same laser power of 0.8 W but different scanning speed of 2.5 cm/s, 2.0 cm/s, and 1.5 cm/s, respectively; (e-g) the stabilized PAN fiber treated by two laser scans. In the first scan, laser power of 0.8 W and speed of 1.5 cm/s are used for all fibers. In the second scan, scan speed of 2.5 cm/s is kept the same, but laser power is 1.0 W, 1.2 W, and 1.4 W, respectively; (h) T300 carbon fiber.

The Raman spectrum of the fibers laser scanned twice is shown in Figure 2e-g. The D peak and G peak can be well observed at 1345 cm^{-1} and 1585 cm^{-1} . Similar results regarding to the peak position were reported [33][34]. The intensity of single laser scan with power 0.8 W and speed 1.5 cm/s (Figure 2d) is reduced to half after the second scan with power 1.2 W and 2.54 cm/s is involved (Figure 2f). After further increasing the laser power in second scan to 1.4 W, the Raman intensity drops down to 1,000 counts, which is closer to Raman intensity of T300 carbon fiber. The low Raman intensity indicates that the polymer structure in the fiber has been almost eliminated and the increased crystallinity of carbon structures has been developed.

The surface chemistry and relevant function groups of the stabilized PAN fibers before and after laser treatment were investigated by FTIR spectroscopy. Figure 3 shows the FTIR spectra of the fibers treated by laser at different stages. The FTIR spectrum of the stabilized PAN fiber is shown in Figure 3a. A sharp peak can be seen at 1580 cm^{-1} from Figure 3a, which represents a mix of C=N, C=C and N-H could exist in the stabilized PAN fibers. The shoulder peak at 1680 cm^{-1} shows the existence of C=O. Beside, a broad peak centered at 1250 cm^{-1} indicates the presence of C-N [35]. An obvious decrease of transmittance at 1580 cm^{-1} after the fibers are scanned once by laser condition of power 0.8 W and speed 1.5 cm/s indicates the reducing of C=N, N-H structures. The declining of the broad peak positioning from 1000 cm^{-1} to 2000 cm^{-1} represents

that the content of N, H, O are reduced and also testifies that the cross-linking condensation reactions between two monomer units of the adjacent ladder polymeric chains happened during the laser treatment. When the fibers were scanned twice (Figure 3d-f), the FTIR spectra become flatter, the characteristic peaks further diminish. Remarkably, the characteristic peak around 1580 cm^{-1} disappears completely when the second laser scan engages power 1.4 W. The FTIR spectrum is very similar as that of T300. This indicates high carbon content has been achieved.

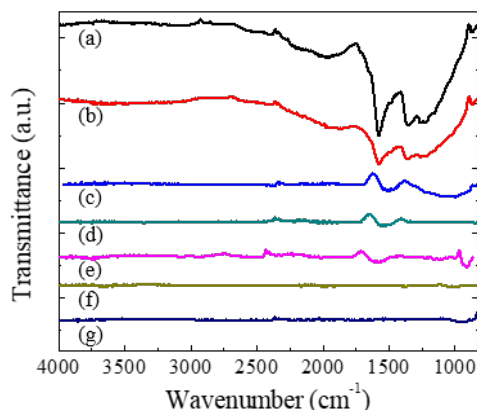


Figure 3. FTIR spectra of (a) the pristine stabilized PAN fiber; (b) the stabilized PAN fiber scanned by the laser with 0.8 W power and 2.0 cm/s scan speed; (c) the stabilized PAN fiber scanned once by the laser with 0.8 W power and 1.5 cm/s speed; (d-f) the fiber scanned twice by laser, the first scanning condition is same: power 0.8 W, speed 1.5 cm/s, and the second scanning conditions are speed 2.5 cm/s and power 1.0 W, 1.2 W, and 1.4 W, respectively; (g) T300 carbon fiber.

Large diameter is one of the limitations of fiber strength [21]. Many groups have reported that during the carbonization process, the shrinkage of fiber diameter would happen [33][36]. In our study, the morphology of fibers in different stages were observed in same scale by using SEM. Figure 4a shows the surface of pristine stabilized PAN fiber. The fiber had diameter 11-13 μm . The fiber begins to shrink and diameter reduced to 8-10 μm when the fiber is scanned by the laser with power 0.8 W and speed 1.5 cm/s (Figure 4b). After the second scan with power 1.4 W and speed 2.5 cm/s is employed, the fiber further shrinks. The diameter decreases to $\sim 7\text{ }\mu\text{m}$ (Figure 4c). The junction of the stabilized PAN fiber first hit by laser with power 0.8 W and speed 1.5 cm/s is shown in Figure 4d. The fiber diameter largely decreases due to first laser irradiation. The fiber scanned once keeps its diameter until the second scan happens. The second scan further diminish the diameter of the fiber to about 7 μm (Figure 4e). The significant shrinkage in diameter after twice scan is another indicator of successful carbonization by laser irradiation.

Figure 5a shows the electrical conductivity of stabilized PAN fiber scanned by different laser conditions. Fiber A is the stabilized PAN fiber. Fiber B represents the stabilized PAN fiber scanned by laser with power of 0.8 W and speed of 1.5 cm/s. Fiber C, D, and E are laser irradiated twice, the first irradiation is the same as Fiber B, while the second scan is at speed of 2.5 cm/s and laser power of 1.0 W, 1.2 W, and 1.4 W, respectively. The stabilized PAN fiber is not electrical conductive (Fiber A). Fiber B possess low electrical conductivity, which indicates the amorphous carbon structure formed after stabilized PAN fiber was scanned once. The

conductivity increases largely when the second scan power increases from 1.0 W to 1.4 W. The conductivity of fiber E reaches 544 S/m implying the higher second laser irradiation helps to further realize carbonization and establish ordered carbon structure.

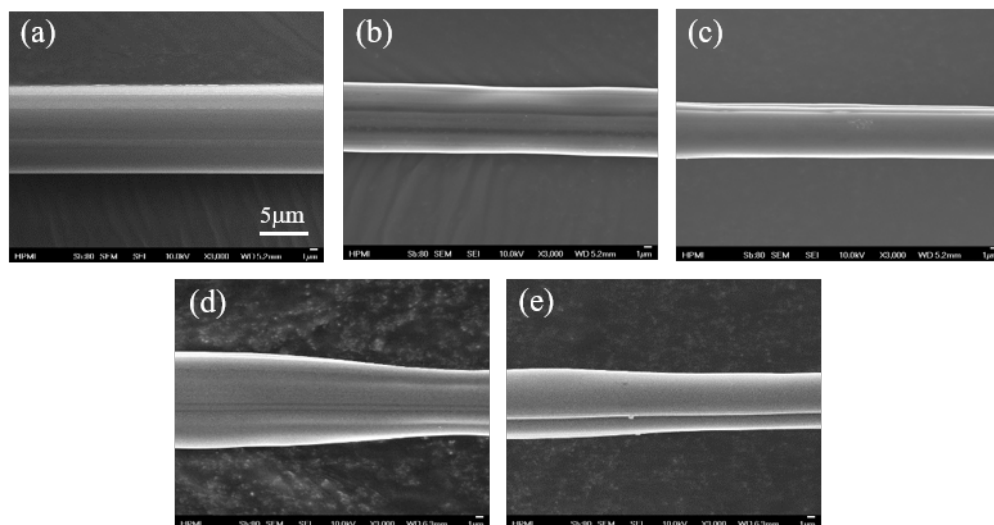


Figure 4. SEM images of (a) stabilized PAN fiber; (b) the stabilized PAN fiber scanned once by laser power 0.8 W and speed 1.5 cm/s; (c) the stabilized PAN fiber scanned second time with power 1.4 W and speed 2.5 cm/s based on the first scan condition of (b); (d) the stabilized PAN fiber and the part scanned by laser condition of power 0.8 W and speed 1.5 cm/s; (e) the joint of stabilized PAN fiber scanned once by laser condition of power 0.8 W and speed 1.5 cm/s and second scan by laser power 1.4 W and speed 2.5 cm/s. All the SEM images are in the same magnification.

Tensile tests were performed for stabilized PAN fibers and laser treated fibers to investigate the effect of laser treatment on mechanical properties (Figure 5b). The stress-strain curve of stabilized PAN fiber (Fiber A) is depicted in black line. Tensile strength of as-received stabilized PAN fiber is 240 MPa and the strain-to-failure is 6.6 %. The non-linear stress-strain relationship starts at 0.8 % strain. When the fiber is scanned with laser condition of power 0.8 W and speed 1.5 cm/s (Fiber B), the strain decreases to 2.5 % and the stress increases to 612 MPa. The stress-strain curve still shows slightly non-linear. When second laser scan is involved with power 1.2 W with speed 2.5 cm/s, the strain decreases to 1.6 % while the stress rises to 855 MPa (Fiber D). However, further increasing the power to 1.4 W does not increase the tensile stress, but reduces the strain to 1.45 % (Fiber E). The stress of the sample was almost linearly proportional to the strain until failure. The modulus rises from 9.4 GPa (pristine PAN fiber) to 59 GPa (fiber E) after laser treatment. The enhance of the modulus and ultimate stress indicates the graphite structure is formed.

The Raman and FTIR spectra verify the carbonization can be achieved via laser irradiation. However, the mechanical and electrical properties of the fibers irradiated by laser are still lower than the commercial carbon fibers T300 [31]. One of the reasons could be that the high laser scanning speed induces the fast heating and fast cooling in the fiber, which might cause quench effect, so that the carbon atoms are not able to rearrange and form large crystalline domain. Another possibility is that intrinsic discontinuous laser energy output contributes to the discontinuous carbonization and structural change along the axis of carbon fiber, thus the

mechanical properties are impacted. The laser process for carbonization can be further improved to achieve high quality carbon fibers. The laser process has potential to achieve high production rate of carbon fiber and lower the production cost in carbonization process.

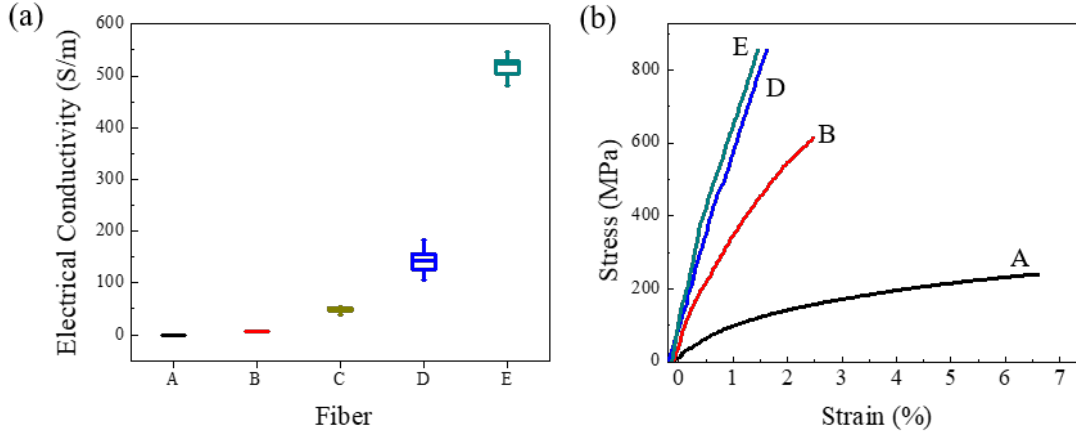


Figure 5. (a) the electrical conductivities of different sample specimen: Fiber A: stabilized PAN fibers; Fiber B: stabilized PAN fiber scanned once by laser power 0.8 W and speed 1.5 cm/s; Fiber C-E: first scans have the same laser-treatment condition with Fiber B, the second scan shares the same scanning speed 2.5 cm/s, but with different power 1.0 W, 1.2 W, 1.4 W respectively. (b) Typical tensile stress-strain curves for Fiber A, B, D, E. The color is corresponding to (a).

4. CONCLUSIONS

A laser-scanning based treatment as an alternative method to carbonize the stabilized PAN fibers was proposed. Raman spectroscopy, Fourier transform infrared spectroscopy, and scanning electron microscopy were used to characterize the pristine stabilized PAN fibers and the fiber scanned by laser at different stage of evolution. Raman spectra indicate that twice laser scan can achieve better crystalline structure. FTIR spectra imply that the functional groups decrease after laser-treatment, especially second scan engaged with power 1.4 W. SEM images approve that the shrinkage happens after the stabilized PAN fibers are scanned by laser with power 0.8 W and speed 1.5 cm/s and further shrink after twice scan. The laser scan converts the insulate stabilized PAN fiber into conductive one. The strength and modulus become much higher than pristine stabilized PAN fibers while the strain decreased. This study gives an insight into the time and energy-saving approach to achieve high quality carbon fibers in the future.

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