

## Electrospun Polyacrylonitrile Based Carbon Nanofibers: The Role of Creep Stress towards Cyclization and Graphitization

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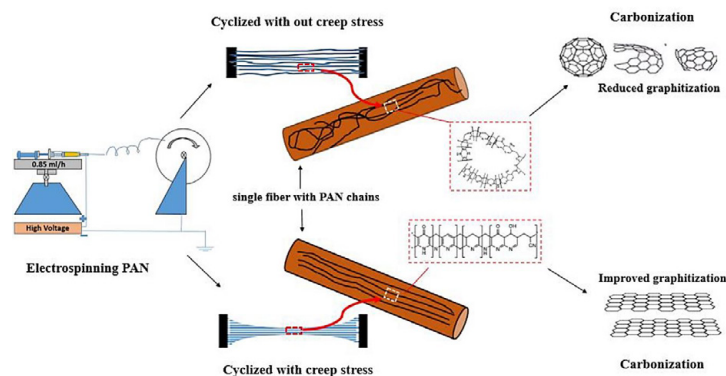
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### Abstract

The properties of these carbon nanostructures are determined by the structure and orientation of the graphitic domains during pyrolysis of carbon precursors. In this work, we investigated systematically the impact of creep stress during the stabilization process on the cyclization and molecular orientation of polyacrylonitrile as well as the graphitized structure after high temperature carbonization. Therefore, polyacrylonitrile (PAN) is electrospun and then stabilized with and without application of creep stress at different temperatures. The effect of creep stress on cyclization was monitored via Fourier transform IR spectroscopy (FTIR) and it was found that the degree of cyclization varies with the application of creep stress during the initial stages of cyclization at low temperatures (190°C and 210°C) in contrast to cyclization done at higher temperature (230°C). Herman molecular orientation factor was evaluated by polarized FTIR for PAN nanofibers cyclized with and without creep stress at 230°C-10 h. Subsequently, carbonization was performed at 1000°C and 1200°C for nanofibers cyclized at 230°C-10 h. Our results from XRD and Raman spectroscopy shows that the degree of graphitization and ordering of graphitic domains was enhanced for PAN nanofibers that were creep stressed during the cyclization process, even though both PAN nanofibers cyclized with creep stress and without creep stress showed the same amount of cyclized material. This increased degree of graphitization can be tracked to application of creep stress during the stabilization process which obviously favors the formation of  $sp^2$ -hybridized carbon planes in the carbonization process. This finding highlights the impact of mechanical stress linking the cyclization of PAN nanofibers to graphitization. Our results will pave the way for a deeper understanding of mechano-chemical processes to fabricate well-aligned graphitic domains which improves the mechanical and electrical properties of CNFs.



### Brief Summary

Effect of creep stress during the cyclization of Polyacrylonitrile (PAN) nanofibers for fabrication of carbon nanofibers has been studied and the impact of creep stress in cyclization of PAN is linked to graphitization. PAN cyclized without creep stress results in formation of curved carbon surfaces and amorphous carbon after the carbonization stage, while PAN nanofibers cyclized with application of creep stress results in improving graphitic microstructure after carbonization.

**Keywords:** Carbon nanofibers; Polyacrylonitrile; Cyclization; Graphitization

**Abbreviations:** PAN: Polyacrylonitrile; CNF: Carbon Nanofibers; FTIR: Fourier Transform Infra-red Spectroscopy; XRD: X-ray Diffraction; SEM: Scanning Electron Microscopy; RCI: Ring Cyclization Index; FWHM: Full Width at Half Maxima

### Introduction

Carbon nanostructured materials have gained a widespread attention during the recent past decades due to their extraordinary physical, mechanical and chemical properties [1,2]. Among the carbon nanostructured materials, carbon nanofibers (CNFs) with a typical dimensions of 100-300 nm have been extensively explored for different industrial applications due to their high surface area to volume ratio,

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good thermal and electrical conductivity as well as ease of fabrication [3-7]. Pitch, cellulose and polyacrylonitrile (PAN) are generally used as precursor materials for carbon fibers and carbon nanofibers (CNFs), however, PAN is the leading precursor for production of carbon fiber with a market share over 90% [8-10].

Among the traditional methods for producing CNFs such as vapor growth, spraying or catalyst supported growth; electrospinning is a comparably uncomplicated and cost effective method [11]. In a typical electrospinning process, an electrical potential is applied between the droplet of a polymer solution contained in syringe and grounded collector. When Coulombs forces acting on the droplet can overcome the surface tension of the droplet, a Taylor cone forms and the ejection of a fiber jet takes place. The collected nanofibers are then stabilized and finally carbonized to obtain CNFs [9].

Stabilization of PAN fibers in the temperature range of 200-250°C is the most critical step in the CNFs fabrication. The typical phenomena occurring in this process is the formation of ladder structures which lead to ring formation and eventually graphite like structure after high temperature carbonization [11,12]. During the stabilization process, polymeric chains relax and loose preferred orientation due to shrinkage. Hence, tension is applied to prevent physical shrinkage and increase the orientation [13,14]. Various studies have reported an increased degree of orientation and eventually improved the physical and mechanical properties by the application of stress during the stabilization step [14-16]. Gu et al. [17] found that a better molecular orientation can be achieved by optimizing the electrospinning parameters, which in turn results in an initiation of cyclization, i.e. ring formation, at lower temperatures for the PAN fibers as compared to casted PAN films. Wu et al. [18] reported that an increase of the tension during the initial stages of cyclization had a favorable effect on the degree of cyclization while in the latter stages, when cyclization proceeds in crystalline regions, the increase in tension had a depressing effect on initiation of cyclization. Another study reported, that tension affects the cyclized structure of PAN fibers and transforms the chain conformations which results in decreased energy barrier for cyclization between temperatures 175°C – 218°C [19].

Therefore, the bottom line is to have a high degree of chain orientation without reducing the amount of cyclized material, since this ring formation initiates the basis for graphite like ribbon structure after high temperature carbonization. Though some of the studies have reported on the effect of tension regarding the stabilization and degree of cyclization, almost no work was dedicated so far in investigating the effect of mechanical stress on cyclization and linking it to the graphitization process.

In this paper, we have investigated the effect of mechanical stress on the cyclization degree of PAN nanofibers at different temperatures (170°C, 190°C, 210°C, 230°C each for 2 h and at 230°C for 10 h) and related the effect creep stress during stabilization stage to the final graphitic structure. The PAN fibers cyclized with creep stress are denoted with a suffix 'T' as PAN-T indicating tension while the samples with only innate shrinkage stress are denoted suffix 'S' as PAN-S, having no application of creep stress. The findings suggest that the degree of cyclization is affected at lower temperatures and times, however at higher temperature (230°C-10 h) both samples cyclized with creep stress (PAN-T) and no creep stress (PAN-S) showed no differences in ring cyclization index (RCI). Nevertheless, the samples with creep stress showed a higher graphitization after carbonization. This implies that the molecular orientation achieved by creep stress plays an important role during graphitization.

## Materials and Methods

### Materials

Polyacrylonitrile (PAN) in powder form with molecular weight 150,000 Mw, purchased from Sigma Aldrich, was used as precursor for the fabrication of carbon nanofibers (CNFs). Dimethylformamide (DMF) was used as solvent for dissolving PAN as supplied by Carl Roth. For carbonization process, a mixture of 2% H<sub>2</sub>/98% Ar was supplied by Westfalen AG.

### Preparation of nanofibers

The complete process for fabricating of CNFs comprise three stages in total. First, PAN was dissolved in DMF by 16 wt% and then stirred over night for period of 12 h to obtain a homogenous solution. This mixture (PAN/DMF) was electrospun at 17 kV, 1 ml/h and 10 m/s collector speed while the fibers were collected on an aluminum foil.

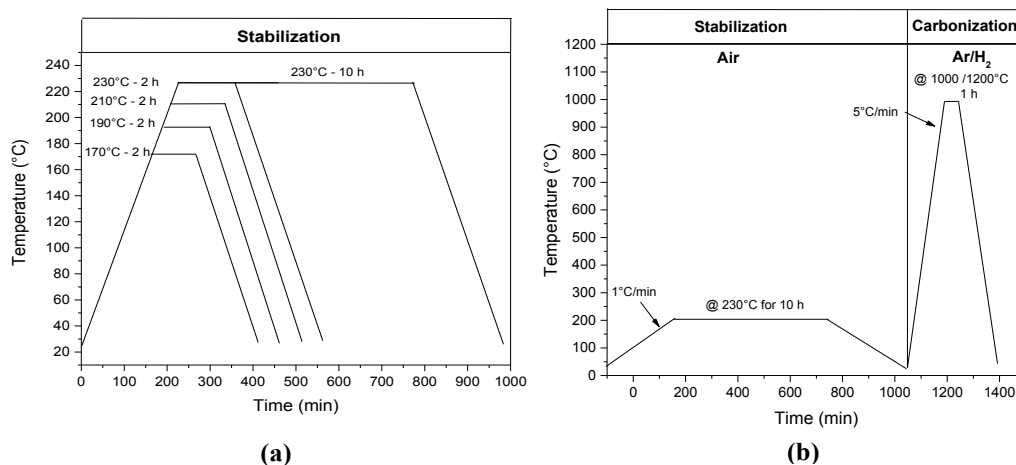
In the second stage, the as-spun fibers were dried in air before they were stabilized at different temperatures (190°C, 210°C, 230°C for 2 h and 230°C for 10 h) either with creep stress and without creep stress. Details of the temperature profiles are summarized in Figure 1a. In the present work, two different cases were considered. (PAN-T) refers to PAN cyclized with externally applied creep stress while the (PAN-S) refers to PAN cyclized without creep stress and the only strain is due to the shrinkage/retardation stress which is congenital during the stabilization stage. For the PAN-T samples, one end of the fiber mats were clamped and the creep stress was applied while for PAN-S sample the ends were just loosely clamped by fixtures but no external strain was applied. There is also a third case for stabilization, where fiber ends are neither fixed and no load is applied, which leads to loss of material after high temperature carbonization process. Finally, the stabilized nanofibers were carbonized in a reduced atmosphere of 2% H<sub>2</sub>/98% Ar at 1000°C or 1200°C. The time-temperature profile for carbonization is presented in Figure 1b.

### Characterizations

X-ray diffraction was used for the structural characterization of CNFs samples. Diffraction patterns were recorded using a Bruker D2 Phaser. Samples were scanned from 10°-80° with a step size of 0.03° using Cu-K $\alpha$  ( $\lambda=1.5406$  Å). The interlayer spacing,  $d$  (002) was calculated using Bragg law,  $d=(\lambda/2 \sin\theta)$ , where  $\lambda$  is the wavelength of the x-ray source and  $\theta$  is the Bragg angle. The crystallite sizes were estimated using the Scherrer equation,  $L_c=(K \lambda/\beta \cos\theta)$ , where  $K$  is the shape factor (0.89 for  $L_c$ ).  $\beta$  is the full width at half maximum (FWHM) expressed in radians.

Furthermore, Raman spectroscopy was used to obtain information about the structure and, in particular, disorder and defects in the CNF samples. Raman spectra were recorded using a DXR2 Thermo Fisher Scientific system with a laser wavelength of 532 nm as an excitation source. The spectra were acquired in the range of 1000-3000 cm<sup>-1</sup>. The D and G bands in the spectra were deconvoluted using Gaussian fitting after a base line subtraction via Origin lab pro software. Moreover, the crystal sizes  $L_a$  (apparent crystallite size along the basal plane) of carbon nanostructures were calculated via  $L_a$  (nm) =  $(2.4 \times 10^{-10}) \lambda^4 (ID/IG)^{-1}$  [20].  $ID$  and  $IG$  are integral ratios of respective D and G band and  $\lambda$  is the laser wavelength (532 nm). Five spectra were recorded on different samples. The incident laser power of 1 mW was used for all measurements in order to minimize heating effects.

Fourier transform infrared spectroscopy (FTIR) was used to monitor the structural changes in PAN fibers during stabilization stage



**Figure 1:** (a and b) Stabilization and carbonization time-temperature profile for PAN nanofibers.

via a Perkin Spectrum Two spectrometer operating in the wavenumber regime of 400-4000  $\text{cm}^{-1}$ . The most prominent changes occurring during the stabilization process in the PAN structure is the conversion of  $\text{C}\equiv\text{N}$  groups to  $\text{C}=\text{N}$  groups, which indicates that cyclization has taken place. Hence, the ring cyclization index (RCI) was calculated in order to estimate the amount of the crosslink ladder polymer conversion by measuring the integral intensity of absorbed IR,  $\text{C}\equiv\text{N}$  ( $2240\text{ cm}^{-1}$ ) and  $\text{C}=\text{N}$  ( $1600\text{ cm}^{-1}$ ) peaks, using the following equation:

$$\text{RCI} = \frac{I_{\text{C}=\text{N}}}{I_{\text{C}\equiv\text{N}} + I_{\text{C}=\text{N}}} \quad (1)$$

Furthermore, the molecular orientation was studied by polarized FTIR using a Tl-bromiodide (KRS-5) holographic wire grid polarizer ( $\varnothing$  25 mm). The degree of orientation is described by the Herman orientation factor ( $f$ ). Thereby, the nanofiber bundles were irradiated with polarized IR and the spectrum was obtained with the plane of polarization parallel ( $\parallel, A_0$ ) and perpendicular ( $\perp, A_{90}$ ) to the fiber axis. The orientation factor ( $f$ ) is then given by the following expression:

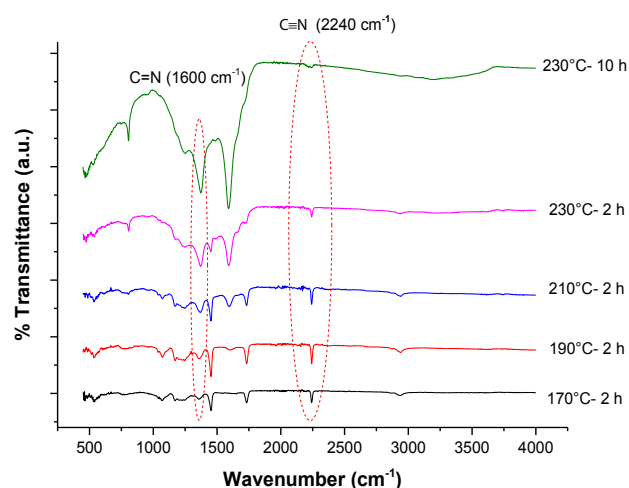
$$f = \frac{2}{32 \cos^2 \theta} \frac{D-1}{D+2} \quad \text{With } D = \frac{A_0}{A_{90}} \quad (2)$$

$D$  is the dichroic ratio of polarized absorbance intensity of the nitrile peak ( $2240\text{ cm}^{-1}$ ). The values of the Herman factor ranges from 0 to 1, where 0 indicates a random orientation of fibers while a value of 1 indicates perfectly aligned fibers.  $\theta$  is an angle between polymer chain backbone and nitrile group, which in the present case is  $70^\circ$ . This method makes use of this fixed angle ( $70^\circ$ ) between the backbone of polymer chain and the ( $\text{C}\equiv\text{N}$ ) nitrile group [21]. For polarization measurements, the potassium bromide (KBr) powder was used to prepare KBr pellets. KBr powder was placed overnight at  $50^\circ\text{C}$  to avoid moisture contaminations and the nanofiber samples were compacted in a KBr pellet. The direction of fiber axis was marked before irradiating the sample with polarized IR and spectra were recorded.

## Results and Discussions

### Effect of creep stress on cyclization

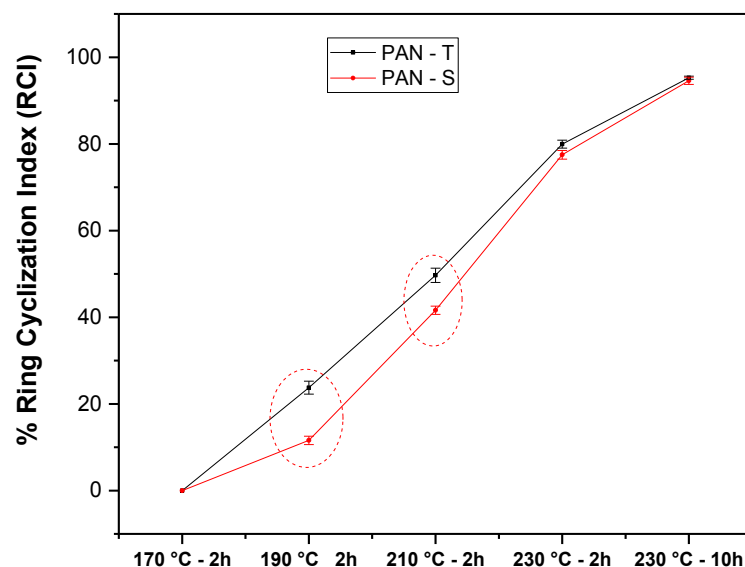
Typical IR spectra for PAN nanofibers, stabilized at different temperatures with creep stress are shown in Figure 2. As spun PAN nanofibers show IR spectra with signature peak at  $2240\text{ cm}^{-1}$  indicating nitrile group ( $\text{C}\equiv\text{N}$ ). In general, it can be observed that as the



**Figure 2:** IR spectra for PAN-T nanofibers stabilized at different temperatures.

temperature is increased the intensity for  $\text{C}\equiv\text{N}$  ( $2240\text{ cm}^{-1}$ ) gradually decreases and an evolution of a  $\text{C}=\text{N}$  ( $1600\text{ cm}^{-1}$ ) peak is detected. As mentioned earlier, cyclization is the most critical process in the stabilization process where the conjugated  $\text{C}=\text{N}$  bond formation takes place. At  $230^\circ\text{C}$ -2 h, the  $\text{C}=\text{N}$  line becomes prominent indicating that cyclization has fairly occurred and a minute amount of uncyclized PAN is present as  $\text{C}\equiv\text{N}$  with a weak intensity line [6].

The progress of the cyclization reaction is well visualized by plotting the ring cyclization index (RCI, Figure 3). Apparently, the RCI increases with increasing temperature for both PAN-T and PAN-S nanofibers. It is known that the cyclization of the nitrile group is initiated thermally by free radical mechanism and the Arrhenius equation suggests, the higher the temperature the higher the cyclization rate will be [22]. At  $170^\circ\text{C}$ , both the PAN-T and PAN-S sample showed nearly no cyclization, since no peak was observed at the position of the  $\text{C}=\text{N}$  edge (Figure 2), in agreement with previous results claiming a formation temperature of around  $\sim 180^\circ\text{C}$  [12,23]. The samples stabilized at  $190^\circ\text{C}$  show a difference in the cyclization index for PAN-T and PAN-S samples. The RCI at  $190^\circ\text{C}$  for PAN-T is around 23% whereas for PAN-S is 12%. As the temperature is increased to  $210^\circ\text{C}$  the same trend is observed, however, the difference in RCI



**Figure 3:** Ring Cyclization Index (RCI) for PAN-T (creep stress) and PAN-S (no creep stress) nanofibers cyclized at different temperatures.

for PAN-T and PAN-S sample is decreased as compared to the one observed at 190°C. Further, at 230°C-2 h the cyclization index nearly shows the same value for both samples.

The obvious difference in the RCI for PAN-T and PAN-S at 190°C and 210°C can be attributed to the fact that at lower temperatures the mobility of PAN chains is limited. The increased cyclization for the PAN-T samples at 190°C indicates that applied tension prevents a chain entanglements and helps in overcoming the dipole interactions between the adjacent nitrile groups to bring them in suitable positions for cyclization. It has been reported, that the ability to form conjugated C=N bonds depends on the isotacticity of polymers and the conformational energy changes, as the angle between the C≡N group and C-C back bone changes [24]. Hence, the likely impact of tension here is that it makes the C=N to rotate around the PAN backbone and increases the internal energy which results in overcoming the C=N repulsions and making new possible interactions to form a ladder structure (cyclization) [19]. However, at 230°C-2 h, the RCI shows nearly the same value for both samples. At 230°C, the temperature is high enough for the chain mobility to participate in cyclization reaction and the energy barrier for conformations is relatively decreased to form conjugated bonds, therefore the impact of tension is not fairly observed. Lastly, it can be observed that as the duration of cyclization is increased from 2 h to 10 h at 230°C, the RCI reaches up to ~95%. Indeed, the strong dependence on time shows, that kinetics is limiting the cyclization process.

The difference of RCI for PAN-T and PAN-S nanofibers is observed at lower temperatures, when the cyclization has just commenced. The cyclization initiates first in the amorphous regions and then extends to crystalline regions. So the impact of tension is visible in this regime, as the temperature is increased the cyclization extends to crystalline regions and mobility of chains is high enough to overcome the barrier for C=N dipole interactions [18,25]. However, it has been reported that increasing tension in the temperature regimes above 220-230°C delays the initiation of cyclization as it increases the spatial distance between the adjacent groups to get involved into the cyclization reaction [18]. The molecular orientation of the fibers was measured via polarized

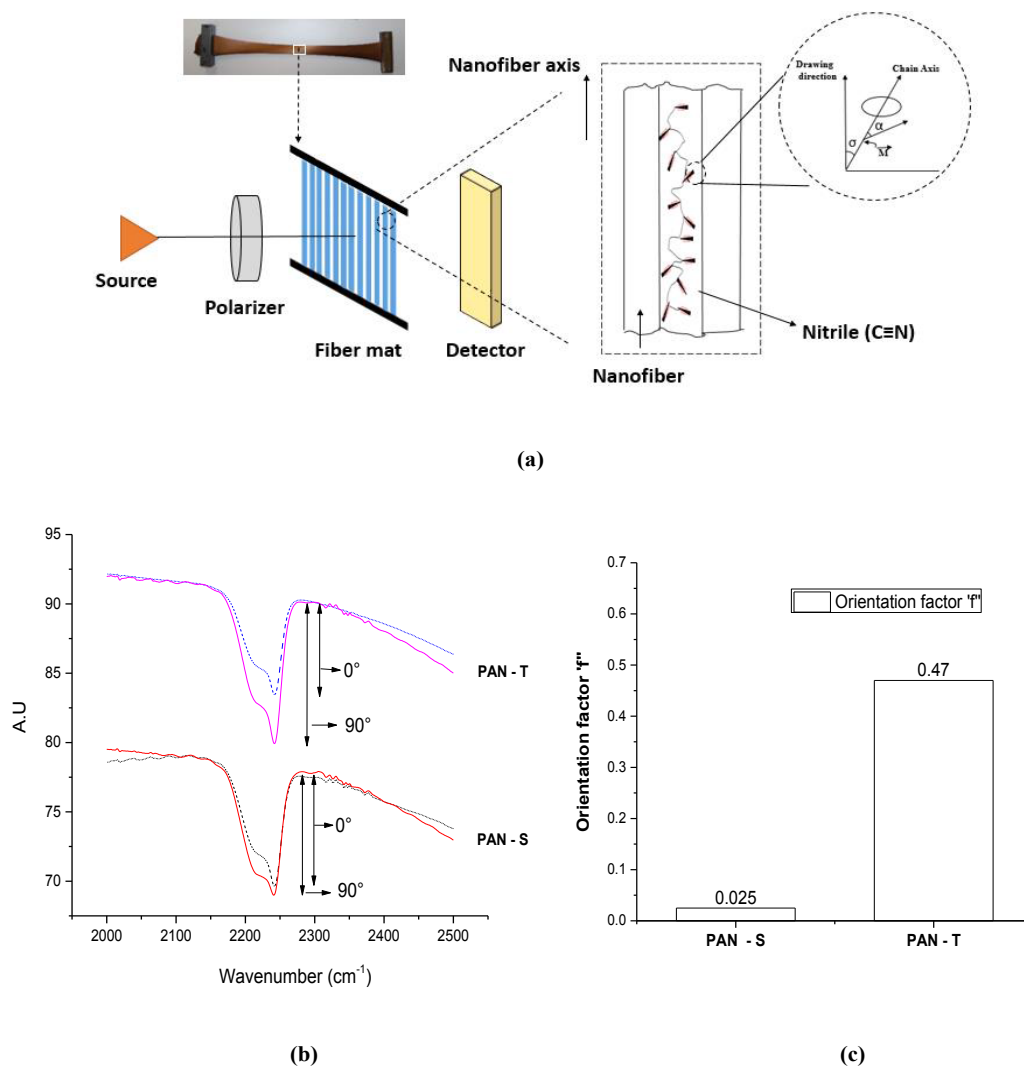
FTIR. Polarized FTIR spectra of both PAN-T and PAN-S nanofibers at 230°C-10 h are shown in Figure 4a. The dotted and solid line correspond to polarized spectra when IR incident beam is parallel and perpendicular with respect to nanofiber stretching direction. The PAN-T fiber mat revealed an elongation of nearly 150%. The relative area under the peaks of cyclization sensitive C≡N nitrile group is used to calculate the Herman orientation factor (f). Figure 4b shows the orientation factor for samples stabilized at 230°C. 5 mm<sup>2</sup> of specimen piece was cut from the very central part of the PAN-T nanofiber mat as shown by the inset in Figure 4a inset. The fibers stabilized accompanied by creep stress show orientation factor value of 0.47 while the fibers which were only clamped with fixtures (only shrinkage stress) shows lower value of 0.02. The application of creep stress, along with the macroscopic alignment of PAN fibers (as shown by the SEM image Figure 5) during the hot drawing process in fact results in the molecular orientation of PAN chains which is evidenced by crystallization sensitive C≡N band in polarized IR spectra.

### Effect of creep stress assisted stabilization on carbonization of PAN nanofibers

As observed, in presence of tension the degree of cyclization and the amount of cyclized material is increased for PAN stabilized at temperatures of 190°C and 210°C, while at higher temperatures for longer times (230°C-10 h) the amount of material is the same (RCI: 95%) for PAN-T and PAN-S nanofibers. Subsequently, to observe the influence of this creep stress during stabilization on the graphitic structure after carbonization process, both types of samples, stabilized at 230°C-10 h (PAN-T and PAN-S) were pyrolyzed at 1000°C and 1200°C. The graphitic structures and crystallite sizes were investigated afterwards by XRD and Raman spectroscopy. Thereby, more than 5 Raman spectra were collected for each sample. Typical averaged Raman spectra for samples both PAN-T and PAN-S samples pyrolyzed at 1000°C are shown in Figure 6a.

Typically, G- and D-peaks are the characteristic bands observed in carbon allotropes. The G peak is centered in the range of 1560-1600 cm<sup>-1</sup> arises from vibrations of carbon atoms in sp<sup>2</sup>-hybridized planes of





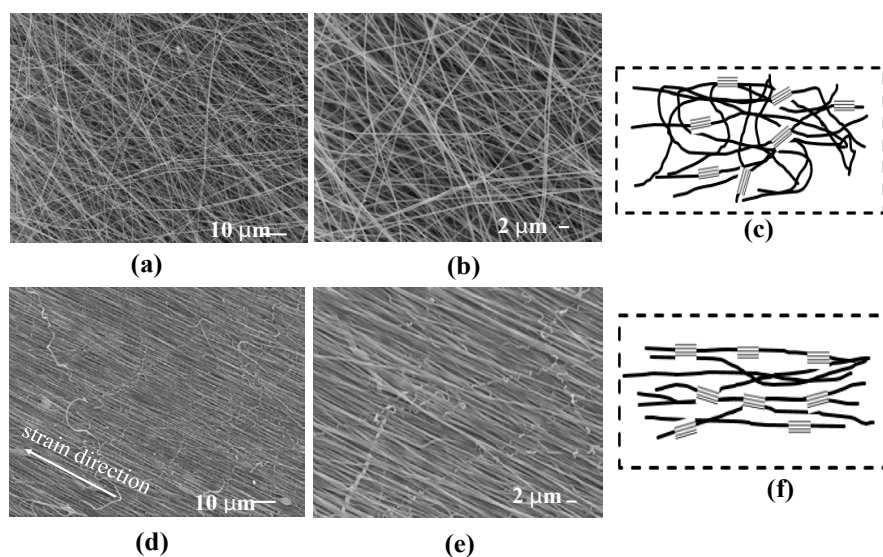
**Figure 4:** (a) Schematic of polarized IR spectroscopy process for PAN nanofiber mats, the schematic of PAN molecule in nanofiber on the right is reformed from [21], (b) Polarized IR spectrum for nanofiber mat oriented 0° and 90° with respect to detector, showing nitrile (C≡N) 2240 cm<sup>-1</sup> peak for PAN-T and PAN-S, (c) Herman orientation factor  $f'$  for PAN-T and PAN-S nanofiber mats.

carbon while D peak in the range of 1300-1400 cm<sup>-1</sup> is a defect induced band [26]. The sharpness and height of the G band peak is a qualitative representation for the presence of ordered/graphitic carbons [27]. The ratio of the integral intensity of these bands ( $ID/IG$ ) is used to probe the disorder in the graphitic carbon. This ratio decreases for the samples which were cyclized with tension (Figure 6b).  $R$  value decreased by 12% and 17% for PAN-T samples pyrolyzed at 1000°C and 1200°C. Correspondingly,  $L_a$  (crystallite size along the basal plane) as evaluated from Raman spectra increased for the samples creep stressed during the whole stabilization process. The decreased value of  $R$  hints towards the formation of large  $sp^2$ -hybridized clusters, indicating an increased graphitization [20]. Moreover, it was observed from the Raman spectrum of PAN 1000°C-T (Figure 6a) that the FWHM of the G peak decreases which is indicative for a better ordering of the domains. Furthermore, the crystallite size and graphitization was examined also by XRD. A typical XRD curve for PAN-1000°C-S and PAN-1000°C-T is shown in Figure 7a. The evolution of the (002) Bragg peak for carbon is clearly observed for PAN-1000°C-T, which is sharper and intense as compared to PAN-1000°C-S. The FWHM of the (002) peak is reduced

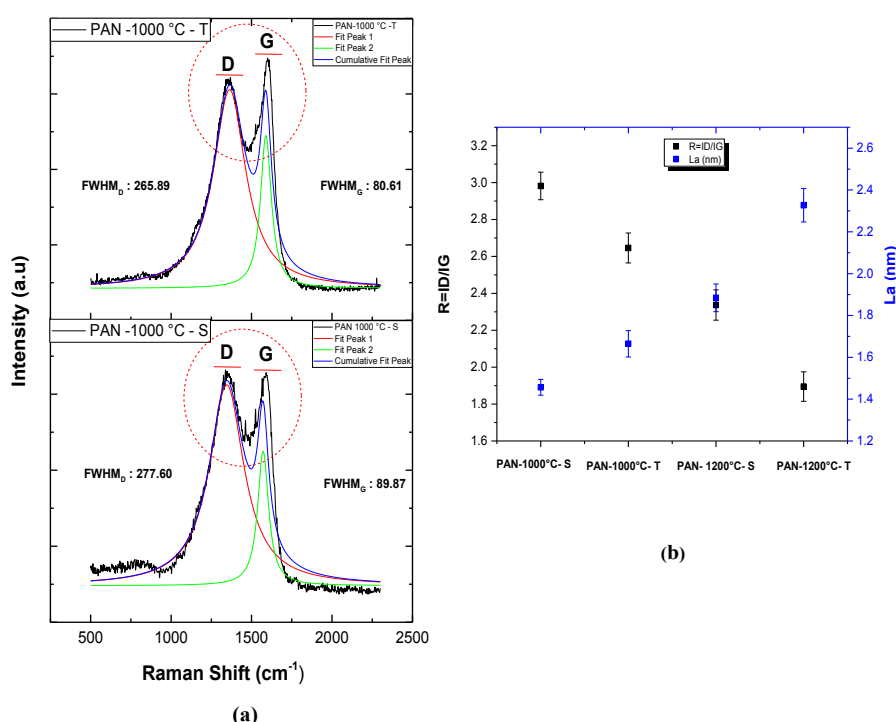
for PAN-T nanofibers (Figure 7b). The crystallite size  $L_c$  increases from 10.83 nm to 11.82 nm for samples carbonized at 1000°C samples. A similar increase in crystallite size is observed for the PAN nanofibers pyrolyzed at 1200°C.

The results from the diffraction pattern supports the Raman spectroscopy findings that the degree of graphitization increases. Both PAN-T and PAN-S samples (230°C for 10 h), before being carbonized had the same degree of cyclized material. The RCI showed a value of 95% for PAN-T and PAN-S samples, however the subsequent carbonization of these sample lead to a different degree of graphitization as observed from Raman and XRD analysis. The only difference is the degree of molecular orientation between the PAN-T and PAN-S samples as depicted in Figure 4. Hence a higher degree of molecular orientation for PAN chains is achieved during stabilization stages, assisted by the mechanical stretching has resulted in more ordered graphitic domains and relatively a higher degree of graphitization as compared the PAN stabilized without mechanical stretching.

During the oxidative stabilization process the formation of six



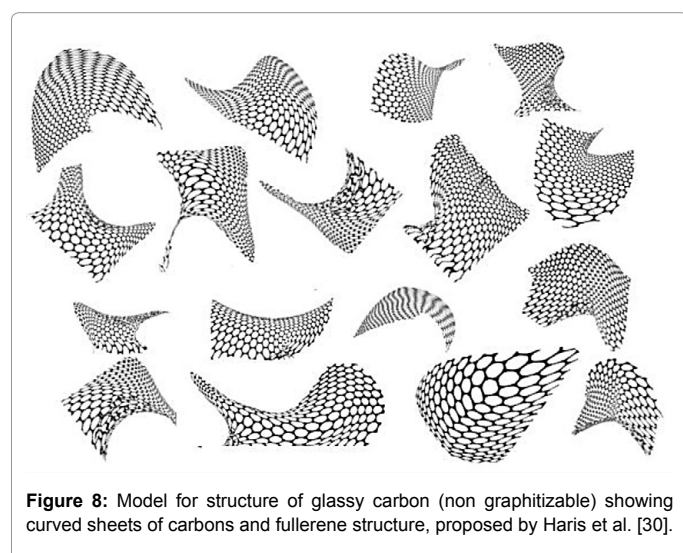
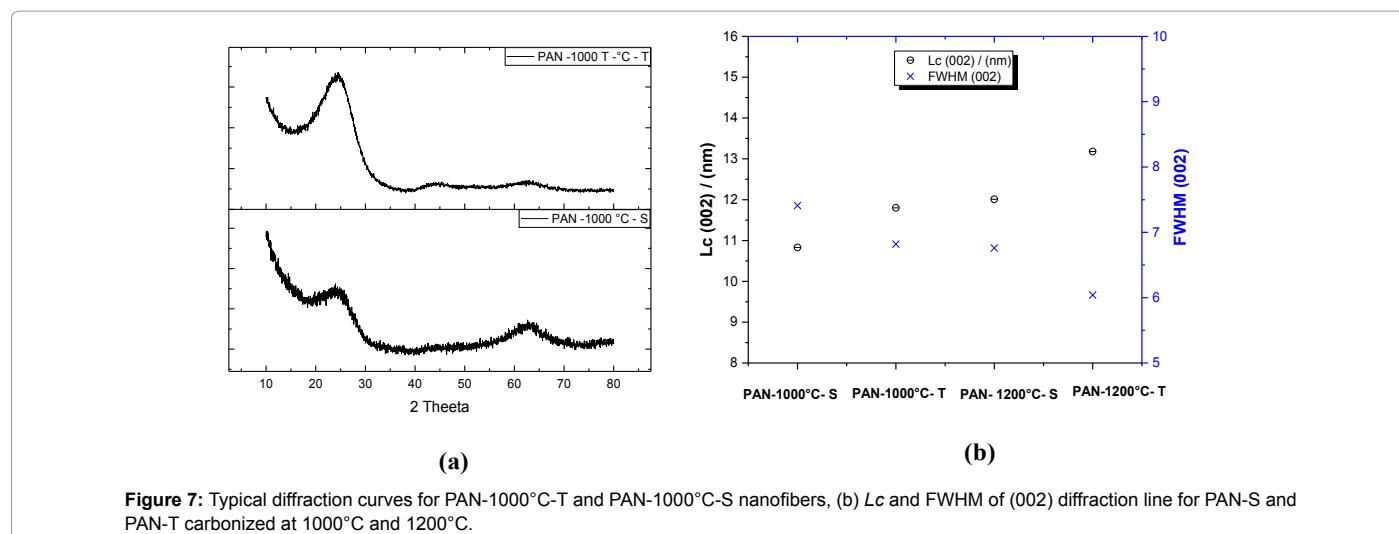
**Figure 5:** (a and b) SEM images for stabilized PAN-S nanofiber mat at 230°C-10 h and (d and e) Stabilized PAN-T nanofiber mats at 230°C-10 h. (c and f) Schematic representation of PAN-T and PAN-S nanofiber mats.



**Figure 6:** (a) Typical Raman spectra for PAN-1000°C-T and PAN-1000°C-S nanofibers, (b)  $R(I_D/I_G)$  and  $L_a$  for PAN-S and PAN-T carbonized at 1000°C and 1200°C.

membered cyclic rings takes place and PAN loses nitrogen groups to form conjugate bonds leading to the formation of  $sp^3$  hybridized bonds which later results in graphite like carbon rings [12]. It has been proposed that formation of stable fullerene structures actually prevents the process of graphitization, rendering it non graphitizable [28,29]. Hairs et al. [30] investigated the carbons produced from sucrose and polyvinylidene chloride using HRTEM, proposed a model (Figure 8) for the structure of non-graphitizing carbons stating that non graphitizing carbon actually consisted of curved carbon sheets with

randomly dispersed pentagons and heptagons (non-six membered ring). The fullerene like structures observed in such glassy carbons contained faceted structures and completely closed particles. Studies by Burket et al. [31] on graphitization of polyfurfuryl alcohol (PFA) showed that aromatic domains contained penta- and hepta-rings in addition to a six membered ring, which results in formation of curved graphene layers. This curvature in layers actually prevented the ordering of graphitic domains due to misalignment. The graphitizable carbons referred as soft carbons differs from the non-graphitizable



carbon (hard carbons) by the nanotexture of crystallites. The highly oriented nanotexture results in formation of highly graphitized carbon while the latter have lower degree of graphitization [32]. The presence of curved planes formed during the pyrolysis of polymer precursor in stabilization process eventually hinders the  $sp^3$  to  $sp^2$  conversion [33]. A higher degree of graphitization for mechanically stretched PAN fibers can be attributed to the fact that application of mechanical stress actually avoids the formation of such curved surfaces, which translates into more  $sp^2$  hybridized carbon planes. D and G band from Raman spectra also hints that the  $sp^3/sp^2$  ratio decreases for the PAN-T samples and more of  $sp^2$  clustering takes place. Hence, even though the degree of cyclization is same for the PAN nanofibers after the stabilization stage but the application of mechanically applied creep stress during the stabilization stages results in increased molecular orientation which actually plays its role in inducing increased graphitization and  $sp^2$  carbon planes, however the complete understanding of thermodynamics of this  $sp^3$  to  $sp^2$  conversion due to mechanical stress is still under research and is yet to be investigated further.

## Conclusions

In this study, the effect of creep stress during the stabilization

process for polyacrylonitrile (PAN) nanofibers has been investigated and correlated with the carbonization process where graphitized structures are obtained. Two different cases were considered for stabilization, one set of PAN nanofiber mat was clamped with fixtures and was externally strained (PAN-T) while the second set of PAN nanofibers were clamped only with no external strain applied and the only strain was the one existing due to shrinkage (PAN-S) during the stabilization. The cyclization index was evaluated at different temperatures for PAN-T and PAN-S nanofiber mats. The chain alignment and orientation due to strain was also studied. Subsequently, the carbonization was performed for both PAN-T and PAN-S nanofibers. We conclude the following:

1- Our findings showed that RCI increases with increasing temperature. RCI for PAN-T fibers and PAN-S showed different values at lower temperatures (190°C and 210°C) however at higher temperatures both PAN-T and PAN-S samples showed similar RCI values. This suggests that stretching influences the chain conformations and adjusts the chains in suitable positions to form conjugated nitrile groups which results in an enhanced rate of cyclization. However, at high temperatures (230°C), the internal energy for PAN-S fibers is high enough and dipole-dipole repulsions between the  $C\equiv N$  are reduced, therefore the difference of RCI between PAN-T and PAN-S nanofibers dissipates.

2- Moreover, the same values for RCI for PAN-T and PAN-S nanofibers (230°C-10 h) demonstrated difference in degree of graphitization. A higher degree of graphitization and less disorder was observed for PAN nanofibers stretched during stabilization stage. The difference in degree of graphitization was attributed to a potential formation of relatively more curved and fullerene structures which results in reduced degree of graphitization for the pyrolysis of PAN-S precursor, whereas PAN-T nanofibers with high molecular orientation leads to form more of the graphitic carbon planes. The application of creep stress results in higher  $sp^2$  hybridized carbon planes. Creep stress during the stabilization assists in  $sp^3$  to  $sp^2$  transformation which reflects in higher degree of graphitization.

Overall, our study emphasizes the effect of strain during the stabilization process on cyclization which lays foundation for carbonized structure. This investigation can provide further insight into inducing higher graphitization of organic precursors by modifying the mechanical stress in addition to chemical changes by the thermal energy.

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