Fabrication and Characterization of Carbon Nanofibers from Polyacrylonitrile/Pitch Blends

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ABSTRACT

Continuous carbon nanofibers had been widely studied based on different processing methods and precursors. Especially, electrospinning was introduced as a versatile method for fabricating ultrathin fibers. However, as the limitation of precursor, pitch had not been well studied due to its viscosity and miscibility problem. A comprehensive study on the electrospinning of the blends (pitch and polyacrylonitrile (PAN)) was explored. Thermodynamic miscibility was studied by using Differential Scanning Calorimeter (DSC). Fourier Transfer Infrared Spectroscopy (FTIR) was used to show interaction and potential reaction between pitch and PAN molecules. Finally, smooth, continuous and cylindrical carbon nanofibers were successfully fabricated by electrospinning technique. Based Raman analysis result, the addition of pitch enhanced the carbon crystallite which improved the overall electrical conductivity and modulus of nanofibers.

INTRODUCTION

Pitch and PAN are the most common precursors for the fabrication of high performance carbon fibers. However, reducing the cost of carbon fibers remains very challenging. Few attempts were made to increase carbon yield and reducing cost by using polymer blends or additives\(^1\)-\(^4\). Use of carbon nanotubes \(^4\)-\(^7\), graphene ribbon\(^8\), lignin\(^1\)-\(^4\) and other polymers\(^2\) were studied. As a result, multiple benefits were demonstrated and properties were improved. However, some challenges were unsolved such as, how to increase the carbon yield, reducing cost and keep the mechanical properties unchanged\(^1\). Another approach of obtaining carbon fibers with less defects is to reduce the fiber diameter less than 2\(\mu\)m. By reducing the diameter, the defects concentration could be minimized and the fiber orientation could significantly enhance the physical properties of carbon fibers, such as thermal, electrical and mechanical properties. Commercially, the carbon
fiber’s diameter is in the range of 6-8µm. Using traditional wet and melt spinning process does not guarantee yet any reduction in fiber diameter. However, electrospinning is a promising method to fabricate nano sized fibers with tailored diameter length and orientation\textsuperscript{9,10}. All these features and dimensions can be controlled using high voltage, spinning distance and the appropriate syringe orifice\textsuperscript{11}. Long and Bittner studied electrospinning of various small molecules\textsuperscript{12,13}. These small molecules have strong intermolecular interaction and behave like entangled polymer chains\textsuperscript{12-14}. In contrast, the disk shaped pitch molecules do not have such an intermolecular interaction, pitch solution could only be electro-sprayed into beads\textsuperscript{14-16} or whiskers\textsuperscript{17}. A binder for pitch molecules is needed to create the entanglement between molecules. An addition of polymer in pitch solution could solve this problem by increasing system viscosity. Yang et al. studied PAN and pitch blends via electrospinning process\textsuperscript{17-19}. His study showed spinning-ability was sensitive to the concentration of PAN and obtained microfibers with a diameter of 2 µm. Murugesan\textsuperscript{20} and Yan\textsuperscript{21} studied thermal properties of carbon nanofiber produced by electrospinning of polyimide/pitch blends. The presents of pitch helped in the formation of carbon crystallite, and enhanced thermal conductivity, electrical conductivity and modulus significantly\textsuperscript{18-22}.

The property of as-spun fiber will be highly affected by the degree of molecular alignment\textsuperscript{10,23,24}. The key parameters that affect the alignment of polymer chain during the spinning process are macromolecular chemistry, viscosity, surface tension of solution and spinning condition\textsuperscript{9-11}. Among these factors, the chemistry and viscosity of precursor are the critical parameters for the formation of thin and high performance carbon fiber. The rheological behavior of the precursor will dictate the feasibility of the spinning process. The rheology behavior of the blend solution
will change drastically from polymer blends\textsuperscript{25}, nanofiber/polymer\textsuperscript{26} and nanoparticle/polymer\textsuperscript{27,28}. Rheology property of the blend solution is sensitive to the physical properties of the materials and also depends on the surface tension and miscibility of two materials. Elisa et al. studied the effect of modified silica nano-spheres on an immiscible polymer blend system\textsuperscript{29}. In their study, the polymer viscosity changed dramatically with the silica concentration. Many similar studies confirmed a change on miscibility would lead to a great difference on their rheology behavior\textsuperscript{30,31}.

In this paper, miscibility of Pitch and PAN will be studied, especially the interaction at molecular level. In order to have a better understanding of rheology behavior of the blends, miscibility property will be investigated using Differential Scanning Calorimeter (DSC) and Fourier Transform Infrared Spectroscope (FTIR). Miscibility behavior of pitch and polymer blends is a delicate issue because of the complex chemistry of pitch material\textsuperscript{32,33}. Pitch such as A240 is a reactive and isotropic pitch material with partial solubility in N,N-Dimethylformamide (DMF). Dickinson provided an average structure for A240 petroleum pitch: an aromatic multi-ring structure with short aliphatic side groups (Figure 1)\textsuperscript{34}. Solubility is also an interesting parameter for electrospinning process\textsuperscript{35}, DMF soluble pitch content will be used in this study to form a homogenous viscous solution. After proper stabilization and carbonization process, clean carbon nanofibers were successfully fabricated. Structural, mechanical and conductive properties were studied respectively.

**EXPERIMENTAL**

**Materials & sample preparation**
Polyacrylonitrile (6% methyl acrylate copolymer, Mn=100,000 g mol$^{-1}$) was purchased from Scientific Polymer Inc. and used as received. Pitch material (A240, Coppers) was refluxed in DMF by Soxhlet and filtrated before use. For the miscibility study, all mixtures were stirred at 60°C for 2 days. The total concentration of PAN and pitch in DMF solvent was controlled to be 1wt%. The fraction ratios for pitch and PAN were labeled as pitchXPANY respectively. For example, pitch3PAN7 means a blend of 30wt% of pitch with 70wt% of PAN. Then the obtained mixtures were dried in oven (60°C) for 2 days. For the rheology study and fiber electrospinning, the concentration of PAN was kept at 7wt%. The parts of pitch on PAN was changed from 0 to 1. For example, a pitch0.5PAN1 sample means 0.5 part of pitch against 1 part of PAN.

**Electrospinning set up**

Electrospinning process was carried out with a syringe pump (New Era Pump Systems, Inc. NE-300), voltage controller (Stanford Research Systems, Inc. Model PS375), and #17 needle. Voltage between needle and collector was 15kV, distance between needle and collector was about 30cm, feeding rate was about 3µL min$^{-1}$. Fibers were collected on a cylindrical rotator (linear velocity, ~7.5m s$^{-1}$).

**Stabilization and carbonization**

The prepared precursor fibers were thermally stabilized in air with a tube furnace (Thermal Scientific, Blue) by a multistep procedure. The fibers were heated up to 250°C then 280°C at a rate of 2°C min$^{-1}$, and the holding time is 2hr for each temperature stage. After cooling to ambient temperature, the stabilized fibers were carbonized in argon atmosphere at 1000°C for 30min, the heating rate was 2°C min$^{-1}$.
Characterization

DSC (Q2000, Thermal Analysis) was used to show the thermodynamic property of blends, glass transition temperature (T_g) was determined with a heating rate of 10°C min⁻¹ in the range of -40°C to 150°C. Interaction and reaction of PAN and pitch was studied by a FTIR spectroscope (Nicolet is50-FTIR, Thermal Scientific), it was set to scan 128 times and a resolution of 4cm⁻¹ under ATR (Attenuated Total Reflectance) mode. Rheology study was processed on an Anton Paar MCR-302 Modular Compact Rheometer at 25°C with cone fixture. A valid torque data range for rheometer used in this experiment was between 0.01 mN·m and 200 mN·m. Carbon yield of the precursors were measured using a TGA (Thermal Gravity Analysis, Q500, Thermal Analysis) in N₂ atmosphere, the heating program was set to be ramping to 800°C at 10°C. Scanning Electron Microscope (SEM, ProX, Phenom) was used to see the morphology of as-spun, stabilized and carbonized fibers. Raman spectrum of stabilized and carbonized fiber mats was recorded with a Renishaw in-Via Raman Microscope (633nm laser). The thickness of carbonized fiber mats was measured by TMA (Thermal Mechanical Analysis, Q400, TA instruments) in expansion mode, and mechanical properties were tested in Film/Fiber Tension mode at room temperature. Conductivity of carbonized fiber mat thin strips were tested with Multimeter/Data acquisition system (Keithley 2700) under optical microscope/probe station (Signatone 1160 Series Probe Station) at room temperature.

RESULTS AND DISCUSSION

Thermodynamic Study on Glass Transition

The glass transition temperature of PAN was measured by using DSC and it is 102°C. However, the glass transition temperature of the pitch will be affected greatly by its chemical composition."
A240 was examined and it is obvious that $T_g$ for pitch7PAN3 sample could not be determined easily (figure 2a). By differentiating the heat flow as function of temperature, a peak could be identified (figure 2b) at 55°C. Using the same analytical method, $T_g$ of PAN was found at 106°C. As shown in figure 2a, DSC heat flow curves of each sample had a gradual changing as function of temperature. Base on normal $T_g$ determination method, it was hard to determine the exact $T_g$ values for pitch3PAN7 and pitch5PAN5 blends. The interceptions of tangent lines are highly depending on the choice of onset and offset point. This $T_g$ determination method is not precise and rigorous against the definition of glass transition temperature, but it’s indeed useful on determination $T_g$ in such a complex situation. Again, it is much easier to use the derivative analytical method as shown in figure 2b. Derivative heat flow curve of PAN showed two peaks, this may due to the effect of 6% methylacrylic content in PAN or different amorphous states of PAN. Methylacrylate group could affect the surrounding acrylonitrile segments and increase amorphous form percentage. Methylacrylate group could also form hydrogen bonding with cyano group, it could act as an obstacle for the movement of segments and result a higher peak at 111°C. The gradual change of peaks in figure 2b indicates PAN and pitch are thermodynamically miscible.

The gradual change of $T_g$ indicates that the interaction or reaction between pitch and PAN caused their miscibility. As introduced, the A240 petroleum pitch is more reactive than any other mesophase pitch. The various effects of pitch analyzed above showed probably some interaction and/or chemical reaction occurred between PAN and pitch during the blending process. Even the blending process was under moderate temperature, the possibility of chemical reaction had to be considered.
FTIR Study of PAN/Pitch Blends

In order to have a better understanding of the effect of mixing for these blends, FTIR was used to characterize functional groups’ differences in blends. Figure 3a shows C-H stretch region for PAN and pitch, peaks were normalized. For PAN and pitch raw materials: peaks at 3030cm\(^{-1}\) (unsaturated C-H), 2960cm\(^{-1}\) and 2850cm\(^{-1}\) (-CH3), 2930cm\(^{-1}\) (-CH2-) are relate to C-H stretch on PAN backbone, methacrylate units and edged of pitch molecules. The gradually change shown in figure 3a indicates the blends were well prepared. Figure 3b shows smaller wavenumber region differences. 1730cm\(^{-1}\) is attributed to C=O stretch from methacrylate units\(^{38}\). 1600cm\(^{-1}\) peak indicates the aromatic system in pitch and the blends. 1450cm\(^{-1}\) is C-H bend or methyl group of methacrylate. The peak around 1375cm\(^{-1}\) indicates the short aliphatic groups or aldehydes groups of pitch and its blends, also the weak peak at 2735cm\(^{-1}\) lead to the same assumption (aldehydes groups exists). 1170cm\(^{-1}\) peak clearly shows the existence of acrylate in PAN and the blend. Figure3c shows 2240cm\(^{-1}\) peak, which is the fingerprint peak for -CN group.

However, beside the peaks relate to PAN and pitch, new peaks are found for the blends. The strong peaks at 1667cm\(^{-1}\), 1266cm\(^{-1}\), 1252cm\(^{-1}\) and 1100cm\(^{-1}\) clearly showed that new bonds were formed during blending process. 1660cm\(^{-1}\) peak could be a response from C=C or C=N group, and there are two possibilities: 1. the heteroatom on pitch molecules reacted with the cyano group of PAN; 2. the reaction between pitch and PAN side groups changed the structure of pitch, and result the 1667cm-1 sharp peak. Both explanations are possible because of the appearance of 1266cm\(^{-1}\), 1252cm\(^{-1}\) and 1100cm\(^{-1}\) peaks. These peaks may come from acrylates or aromatic esters\(^{39}\). As a conclusion, these peaks come from newly formed aromatic esters.
On the other hand, -CN group fingerprint peak (cyano stretching) does not change much (about 1cm⁻¹) with the addition of pitch to PAN. As shown in figure 3c, the 2243cm⁻¹ normalized peak of PAN has a slight red shift and became broader after blending with pitch. Such a small shift was also observed by Goh, et al.⁴⁰ and Yeo, et al.⁴¹ in the study of miscibility of PAN with other polymers. The red shift of cyano bond is possibly contributed by π-orbital cyano band⁴². In this case, the red shift probably came from the interaction between conjugated system on pitch and cyano bonds.

The formation and interaction of new bond and the interaction on cyano bond are supposed to be the cause of change of glass transition temperature. The new aromatic ester could create a larger free space than it used to. The larger free space would require less energy for PAN amorphous region to reach a higher energy state, in the other word, a lower glass transition temperature. In summary, the reaction (aromatic ester) and/or interaction (cyano group and aromatic rings) contribute to the miscibility of PAN and pitch.

**Rheology Study**

The rheological characterization was carried out to control further the electrospinning process. Adam et al. used lignin and PAN to prepare carbon nanofiber via electrospinning⁴³. In their study, the total concentration was set at 18wt%, however, the blend of 18wt% of lignin was less viscous which causes difficulties in making nanofibers. After spinning, they could only prepare lignin material in the form of beads rather than continuous fiber.

After several trials, the concentration of PAN was set to be 7wt% in order to reduce the formation of beads in electrospinning process. The ratio of pitch to PAN was controlled as 0.5/1, 1/1.
Results were shown in figure 4a. The viscosity of these blends decreased with the increase in shear rate. As the concentration of pitch increase from 0 to 50wt% ratio (sample: PAN, Pitch0.5PAN1, Pitch1PAN1), viscosity has not changed a lot. Especially, while shear rate becomes higher, less difference on viscosity could be recognized. As the limitation of instrument, the highest shear rate measured was 2000 s\(^{-1}\). however, for a real spinning process, the shear speed could be as high as 10m s\(^{-1}\) (shear rate: 10,000 s\(^{-1}\))\(^{11}\). As a consequence, there should be no significant difference on viscosity for different samples during electrospinning process. Based on the result of rheology test, the electrospinning of PAN and pitch hybrid fibers were fabricated from PAN solution, Pitch0.5PAN1 sample solution and Pitch1PAN1 sample solution.

**TGA Analysis**

The as-spun fibers were used for TGA test and results are shown in figure 4b. The carbon yield for PAN, Pitch0.5PAN1 and Pitch1PAN1 samples were calculated to be 0.46, 0.51 and 0.55. Same as prediction, the addition of pitch content results in a higher carbon yield of the CNF. Different from bulk sample, in order to prepare the testing sample, the as-spun fibers were folded after peeled off from the electrospinning substrate. Air would be trapped in the sample, and cause the weight increase during the test. It is very interesting to see that the PAN sample is oxidized more than the pitch added samples. This phenomenon indicates that the degradation behavior of PAN was changed by adding pitch, and which might be caused by the interaction/reaction between pitch and PAN. The initial weight loss of Pitch1PAN1 sample compare to Pitch0.5PAN1 sample may due to the vaporization of small molecules in pitch.

PAN/pitch as-spun, stabilized, and carbonized fibers
Cylindrical fibers were successfully prepared via electrospinning process. Optical microscope images (figure 5a-c) and SEM images (figure 5d-f) show the morphology of as-spun fibers. Diameters of all as-spun fibers are generally ranged from 500-700nm (table 1). In figure 5a, b, c, the color of as-spun fibers become darker with an increase of pitch concentration, from white to red or brown. Most of the fibers had smooth surface. However, due to the difficulties of fully eliminate tiny insoluble pitch particles (less than 1μm), some particles were embedded inside as-spun fiber (figure 5e, f). The insoluble pitch particles were smaller than fiber diameter, but observable in some regions on the nanofiber surface under microscopes. Processing procedures are essential for fabricating of carbon nanofibers, such as stabilization and carbonization. In order to avoid potential fusion of fibers, a 2-steps stabilization process was chosen. The stabilization process at 250°C was for PAN and 280°C was for pitch. Heating rate is also important in avoiding fusion of fibers, here we chose it to be 2°C min⁻¹. Stabilized and carbonized fiber morphology were shown in figure 6 and smooth, clean nanofibers were obtained. In figure 6, carbon nanofibers surfaces are all quite smooth and the diameters are uniform (table 1).

Raman analysis

Shown in figure 8a, Raman results show the clearly difference between different carbon nanofibers. The two broad peaks at about 1350cm⁻¹ and 1580cm⁻¹ are the D band and G band. Normally, D band and G band are referred to the disordered structure (sp3) and graphene-like ordered structure (sp2). Thus, the sp3 hybrid bonds could contribute to the inter-planar connection and interlock and which could contribute to a higher strength. On the other hand, With the increase of pitch content, the normalized D band become smaller and G band become narrower. It is easier to compare the valley between D band and G band, by increase pitch
content, the valley becomes deeper. Which means the sub-peak at around 1490 cm\(^{-1}\) become smaller and 1580 cm\(^{-1}\) peak (G band) become sharper. According to previous study, the sub-peak at 1490 cm\(^{-1}\) attribute to amorphous graphitic structure\(^{44}\). Decrease of 1490 cm\(^{-1}\) peak indicates less amorphous content appears in pitch added carbon nanofiber.

Figure 7b shows sharpness of G band and ratio of G band to D band. In order to have a better illustration of shaper of the G peak, here we define the sharpness of a peak to be the ratio of its normalized height to FWHM. No obvious change in \(I_D/I_G\) could be found on G band, on contrary, sharpness of G band increased with the addition of pitch content obviously. The sharpness of G band suggests the graphite structure becomes larger, thicker and more uniform. And which generally means higher modulus and conductivity.

**Mechanical and conductivity properties**

A test for single fiber segment is truly useful for fundamental study of the nature of carbon nanofiber\(^{45}\). However, thus studies cannot present the role of defects and the property in a larger scale. In this study, Mechanical tests were performed for fiber mats by using TMA in film/fiber tension mode. As shown in figure 8, modulus of Pitch1PAN1 carbon nanofiber mat was higher than that of PAN, increased by 20%. Same trend showed on the conductivity result, Pitch1PAN1 carbon nanofiber had a higher than PAN based carbon nanofiber. And it’s also should be noted that, with an additional increasing of pitch content (Pitch1PAN1), the physical properties did not follow a linear increasing. The higher modulus and conductivity suggest better graphite structure (larger) and this agree with the conclusion which made by mechanical test and Raman spectrum.

**CONCLUSIONS**
Based on DSC results, the addition of pitch lowers the overall $T_g$ of PAN. The sample blends exhibit two $T_g$ values. At this level of study, we can only assume that thermodynamically pitch and PAN are partially miscible. This assumption was confirmed by FTIR results. The interacting on cyano band and the new band at 1660 cm$^{-1}$ showed the $\pi$ (cyano) - $\pi$ (pitch conjugate) interaction and reactions relate to transesterification. Rheology study was helpful to have a better understanding of electrospinning process. The viscosity of the blends did not change significantly as the amount of pitch increased which provides a stable condition during electrospinning process.

In this study, homogenous carbon nanofibers were produced using all various mixtures between PAN and pitch. The final product, the carbon fibers from pitch added precursor showed an enhancement on mechanical property and electrical conductivity. Raman spectrum confirmed the increase of ordered structure in PAN/pitch based carbon nanofibers by analyzing the sharpness of G band. As a result, the addition of pitch increases the degree of alignment because of the high amount of liquid crystal present in the pitch and eventually it enhances the physical properties of the carbon nanofibers.

REFERENCES AND NOTES

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FIGURE 1 Average Structure of A240 pitch.

R: -CH₃ or -CH₂CH₃ or H

FIGURE 2 DSC result of PAN, pitch and their blends. (a) Glass transition of the blends; (b) Derivate curves of (a).

FIGURE 3 FTIR results of PAN, pitch and their blends. (a) 3000 cm⁻¹ region for C-H. (b) 900-1800 cm⁻¹ region for C-O bonds and C-C bonds; (c) 2250 cm⁻¹ region for cyano bond of PAN.
FIGURE 4 (a) Rheology result of PAN and the blends. (b) TGA result of PAN and the blends.

FIGURE 5 Optical(a-c) and SEM(d-f) images of PAN(a),(d), Pitch0.5PAN1 (b),(e), Pitch1PAN1(c),(f) as-spun fibers.
TABLE 1 Diameter ranges of as-spun, stabilized and carbonized fibers.

<table>
<thead>
<tr>
<th></th>
<th>As-spun fibers (nm)</th>
<th>Stabilized fibers (nm)</th>
<th>Carbonized fibers (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>843±116</td>
<td>747±77</td>
<td>427±70</td>
</tr>
<tr>
<td>Pitch0.5PAN1</td>
<td>863±187</td>
<td>534±69</td>
<td>389±39</td>
</tr>
<tr>
<td>Pitch1PAN1</td>
<td>795±103</td>
<td>584±70</td>
<td>453±62</td>
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FIGURE 6 SEM images of Stabilized(a-c) and Carbonized(d-f) PAN(a),(d), Pitch0.5PAN1(b),(e), Pitch1PAN1(c),(f) fibers.

FIGURE 7 Raman spectroscopy results. (a) Difference on D band and G Band; (b) sharpness of G band and D-G ratio.
FIGURE 8 Conductivity and Modulus of the carbon nanofibers.