

Oxidative Stabilization of PAN/VGCF Composite

Dan Zhu,¹ Ai Koganemaru,¹ Chunye Xu,² Qundong Shen,³ Suolong Li,³ Masaru Matsuo²

¹Graduate School of Human Culture, Nara Women's University, Nara 630-8506, Japan

²Department of Clothes and Apparel Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8506, Japan

³Institute of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

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ABSTRACT: An oxidative stabilization process to prepare carbon films was carried out for a new kind of precursor using the composite of polyacrylonitrile (PAN) and vapor-grown carbon fiber (VGCF) by a process of gelation/crystallization from dilute solutions. It was found that the new precursor has special features in the stabilization process different from those of the homopolymer in regard to thermal and morphological aspects. In the stabilization process under heat treatment at 180–350°C in an oxidative atmosphere, it was inferred that, although the introduction of VGCF hinders the initiation and propagation step of the cyclization and dehydrogenation reactions, the precursor

helps the oxidation and the additional aromatization and intermolecular crosslinking reactions in the stabilization process, thus promoting the formation of the later carbon product in film's shape with good performance. From characteristic works by wide-angle X-ray diffraction (WAXD), FTIR, Raman, and DSC, the changes of the precursors in structure, morphology, and mechanical property in terms of different heat-treat temperatures and tensions were studied. Through a series of experimental results, the effect of the VGCF's introduction on those changes was discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2063–2073, 2003

INTRODUCTION

PAN-based carbon fiber has been commercially available for over 20 years and now dominates nearly 90% of all the carbon consumption all over the world because of its high tensile strength, high strain to break, and low volume fraction of voids.^{1–4} It is also well known that, for developing carbon fiber from polyacrylonitrile (PAN) precursors, oxidative stabilization is considered to be the most decisive step, and it is also of the utmost importance in industrial fabrications, since it largely governs the final structure of the fiber and, hence, its ultimate mechanical properties. Accordingly, a large number of excellent reviews for oxidative stabilization have been reported.^{5–9} The stabilization process involves heat treatment at lower temperatures (200–300°C) under tension in an oxidative atmosphere, usually air, and produces changes in the chemical structure of the precursor so that it becomes thermally stable to the subsequent high-temperature treatment.

Until now, stabilization has always carried out by a controlled heating range, seldom above 280°C, and a severe heating rate of 1–2°C/min.¹ As to the precursor itself, a copolymer of PAN is required,¹⁰ since the

homopolymer will result in a poor quality of carbon fiber. It was also confined to a fine denier (less than 5–10 denier or 10–12 μm in diameter/filament), since that is helpful for the dissipation of heat which is evolved during conversion of the precursor to the carbon fiber.⁵

In our former research, instead of the copolymer of PAN, a new kind of precursor, a composite of the homopolymer of PAN of a high molecular weight and vapor-grown carbon fiber (VGCF), which is from the thermal decomposition of benzene with a fiber length shorter than 20 μm ,^{11–13} was attempted, and by a stabilization and carbonization process, a thick carbon film with a cross section 6000 times more than that of the commercial carbon fiber was obtained with satisfactory electrical and mechanical properties,¹⁴ but many puzzles remained unsettled. To explain such puzzles and because of the importance of the stabilization process to the later carbonization, we continued our work and concentrated on the stabilization process. We found in this process that the new precursor showed unusual features in the thermal and mechanical properties compared with those of the traditional PAN precursor. So, we discuss concretely in this article the differences in the structural changes and reaction mechanisms for the new precursor in the morphological aspect. In this new precursor, the PAN homopolymer of a high molecular weight and the production method of gelation/crystallization^{15,16} were adopted, so that a higher stretch ratio of 20–30 times could be obtained, while in the normal wet

Correspondence to: M. Matsuo (m-matsuo@cc.nara-wu.ac.jp).

TABLE I
Differences Between Our Research and the Commercial Carbon Fibers

Parameter	Commercial carbon fiber	Present research
Precursor used	Copolymer of PAN	Composite of PAN and VGCF
Precursor preparation	Wet spinning	Gelation/crystallization and stretching
Stretch ratio	<800%	20–30 folds
Stabilization rate	1–2°C/min	2–5°C/min
Final temperature	<280°C	300–330°C
Form of carbon product	Fiber	Thick film
Cross-section area	10^{-6} cm ²	10^{-3} cm ²
Thickness	<10 μm	300 μm

spinning, it only reached as much as 800%.¹ Generally, the stretch improves the orientation of the molecular chains in the direction of the fiber axis, which will effectively reduce the dipole–dipole interactions among the nitrile groups, so that the temperature for the initiation of the cyclization reaction and the energy of activation will decrease. During the research, special features of the new precursor were found in the stabilization process. The differences between the new precursor and the traditional one are listed in Table I. The heating range and rate are not so severely confined as before, and a thick fiber or film could be obtained with good performance by the new precursor and the new method. Incidentally, we repeated the data of the specimen heat-treated under 270°C which were used in our former article¹⁴ to describe our viewpoint systematically.

EXPERIMENTAL

The PAN homopolymer powder of average molecular weight ($M_w = 500,000$) was furnished by the Mitsubishi Rayon Co., and the VGCF, which is from the thermal decomposition of benzene at 1100°C in the presence of fluid ultrafine catalytic particles of metals, was furnished by Prof. Endo, Shinshuu University.^{12,13} The mixture of PAN and VGCF powder in the solvent of DMSO was heated to 110°C for 20–30 min under nitrogen. The concentration of PAN against DMSO was fixed at 6 g/100 mL and the weight proportion of PAN and VGCF was 1/0 (only PAN), 9/1, and 3/1. The obtained slurry was removed from a Petri dis immediately, quenched in ice water, then settled quietly for generating a gel. After the gel was formed and then further dried for about 1–2 months, the filmlike composite could be cut into strips and be stretched.

The elongation was carried out manually by a stretching device in the oven at about 160°C. The draw ratio was marked as λ . For developing a carbon product of high grade, after being dried in a vacuum oven under 60°C to remove the residual solvent and before the final carbonization beyond 1000°C, the stretched films must undergo a process of preheating, which is always termed as stabilization, in an oxidizing atmo-

sphere of air at 250–350°C under the application of tension of about 1 MPa. Chemical reactions that occurred in this period are listed in Figure 1(a).¹

X-ray measurement was carried out by a 12-kW rotating-anode X-ray generator (Rigaku RAD-rA) with point focusing, and monochromatic $\text{CuK}\alpha$ radiation (wavelength of 0.154 nm) was used. In this condition, an incident beam was collimated by a collimator of 2 mm in diameter and the diffraction beam was detected by a slit of 0.9×0.9 mm. Wide-angle X-ray diffraction (WAXD) patterns were taken with a flat camera. Corrections of the X-ray diffraction intensity were made for air scattering, background noise, polarization, and absorption.

The thermal behavior was analyzed on the basis of differential scanning calorimeter (DSC) curves. A specimen of 5 mg was placed in a standard aluminum sample pan with a mesh-formed cover and the heating rate was 10°C/min. The IR spectra were taken by a Fourier transform infrared spectrophotometer of FTIR-8300 from Shimadzu with a standard laser spectrum of 632.8 nm. The Raman counts were taken by a Raman scope of the JRS-System 1000 from Renishaw with a He–Ne gas laser as a light source and the standard spectrum was 520 cm^{-1} (silicon). Before the measurement, all specimens were polished by sandpaper. The temperature dependence of the dynamic tensile modulus was estimated by a viscoelastic spectrometer (VES-F) from Iwamoto Machine Co., Ltd., at a fixed frequency of 10 Hz over a temperature range of -150 – 300°C .

RESULTS

Figure 2 shows WAXD photographs of the stabilized specimens ($\lambda = 20$) treated for 1 h at different temperatures of 250, 270, and 330°C for the three kinds of composites with PAN/VGCF proportions of 1/0, 9/1, and 3/1. As can be seen in the column of 250°C, two well-defined equatorial reflections around $2\theta = 17.0^\circ$ and 29.5° were observed. The former is intense and the latter is faint, corresponding to the lattice spacing of approximately 0.52 and 0.3 nm, respectively.^{5,10} The

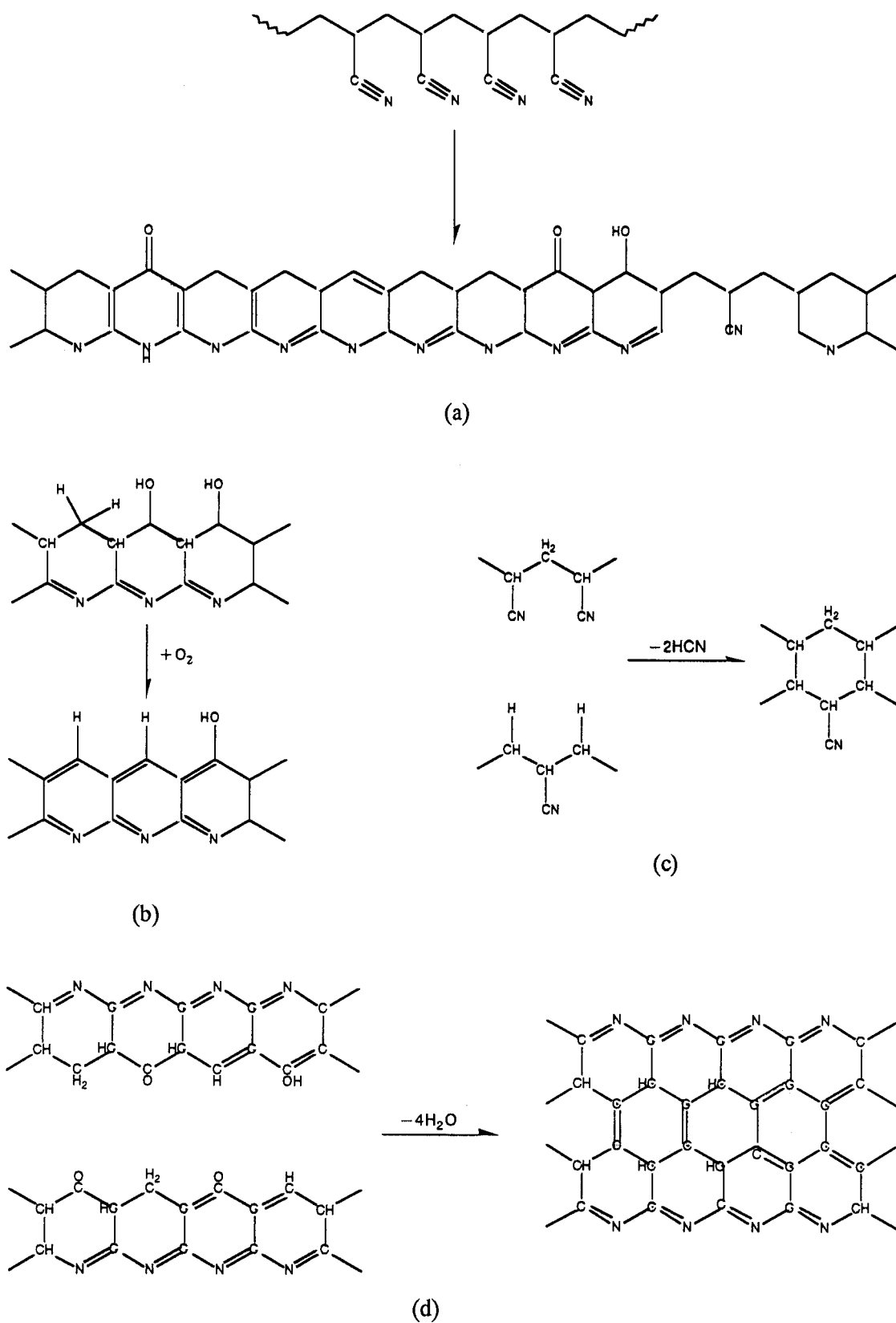


Figure 1 Reactions that occurred during the oxidative stabilization process: (a) sequence of reactions during thermooxidative stabilization of PAN precursor; (b) aromatization reaction in stabilization in the presence of oxygen; (c,d) intermolecular crosslinking reaction during stabilization between 300 and 400°C.

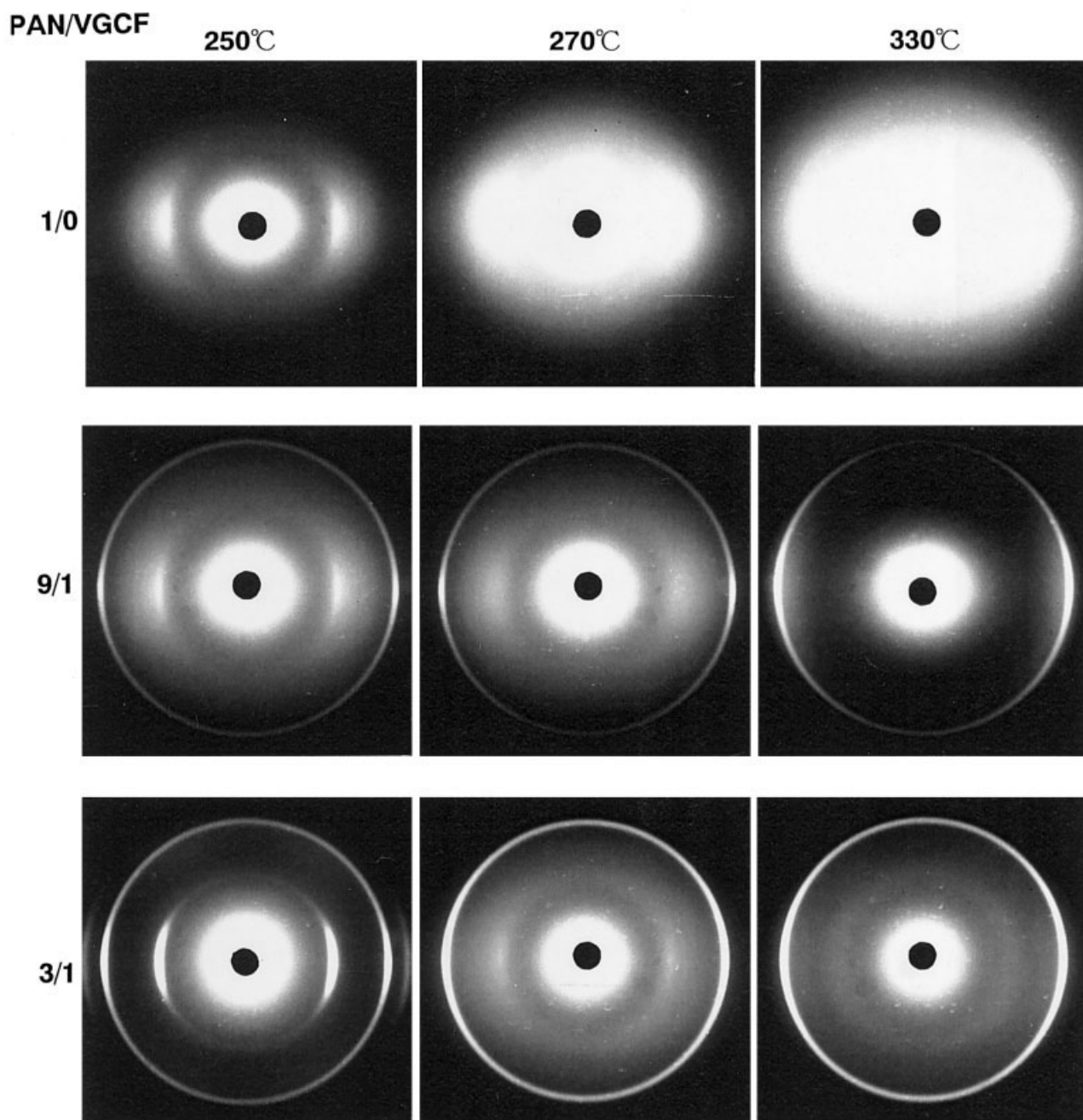


Figure 2 WAXD patterns from the stabilized specimens treated at (a) 250°C, (b) 270°C, and (c) 330°C with the PAN/VGCF compositions of (1) 1/0, (2) 9/1, and (3) 3/1.

azimuthal intensity distribution of the equatorial reflection is predominantly determined by the orientation distribution of the chain axis. For the 3/1 composite film in this column, the equatorial reflection is broader perpendicular to the equator compared with the other two, indicating that the introduction of a large amount of VGCF leads to a small crystal size and a significant crystal disorder exists along the chain axis. The diffraction are appeared at $2\theta = 26.5^\circ$ in this column for the 9/1 and 3/1 composite films, corresponding to the (002) reflection from the layer planes

of about 0.34 nm, which are the typical patterns observed usually for the carbon or graphite structure. It is obvious that they are due mostly to the contribution from the VGCF initially introduced. When the stabilization temperatures were increased to 270 and 330°C, the intensity of patterns for PAN became indistinct, indicating the disruption of the PAN crystalline morphology due to the chemical reaction associated with oxidation, dehydrogenation, and cyclization. For the 9/1 and 3/1 PAN/VGCF composite films, the intensity of the (002) reflection became higher under higher

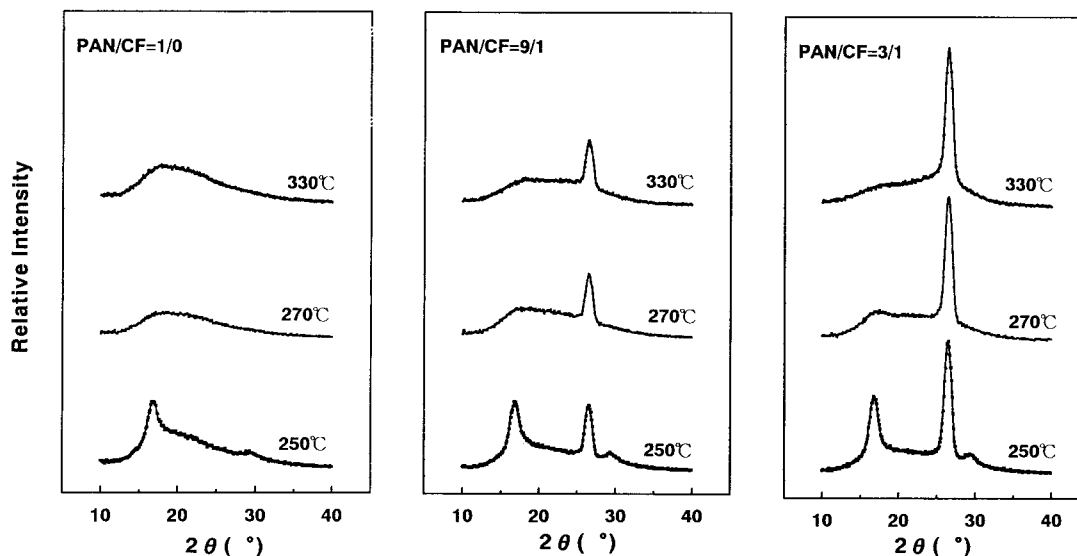


Figure 3 X-ray diffraction intensity distributions for the stabilized specimens treated at (a) 250°C, (b) 270°C, and (c) 330°C with the indicated PAN/VGCF compositions.

stabilization temperatures, which can be seen more clearly from the X-ray diffraction intensity distributions for the same proportions and stabilization stages in Figure 3. The increase was considered as the transition from PAN to a nongraphitizing turbostratic (irregular) organization of the carbon layer planes.¹¹ In the $\text{CuK}\alpha$ X-ray diffraction, no difference could be established between the turbostratic carbon and the graphite. On the other hand, no such increase could be observed for the PAN film in the stabilization, and, from general knowledge, such a transition from PAN to the stacked carbon layer could be realized only under the carbonization process at least above 1000°C. This reveals the fact that the carbonization process took place for the PAN/VGCF composite material even at a stabilization stage with the benefit of VGCF.

Figure 4 presents DSC curves of the stretched PAN/VGCF films ($\lambda = 20$) with 1/0, 9/1, and 3/1 compositions. The curve of the PAN homopolymer film shows an sharp exothermic peak at 265°C associated with the main reactions such as cyclization, dehydrogenation, and oxidation of PAN when it is heated above 180°C. However, another small and relatively broad exothermic peak is observed around 330°C, which was found to be related to additional aromatization and intermolecular crosslinking reactions taking place during heating to the temperature range of 300–400°C (refs. 7,17,18) [see Fig. 1(b–d)¹⁷]. The raw material of VGCF was heat-steady to temperature change. For the PAN/VGCF films with 9/1 and 3/1 compositions, two predominant exothermic peaks could be observed around 285 and 330°C. The first one was estimated to be the shift of the peak about 265°C observed in PAN film.

We know that, in the case of the PAN homopolymer, cyclization is achieved through a radical mecha-

nism. So, the production of the free radical on the nitrogen atom of the nitrile group due to the homolytic bond fission in some defective structures at a

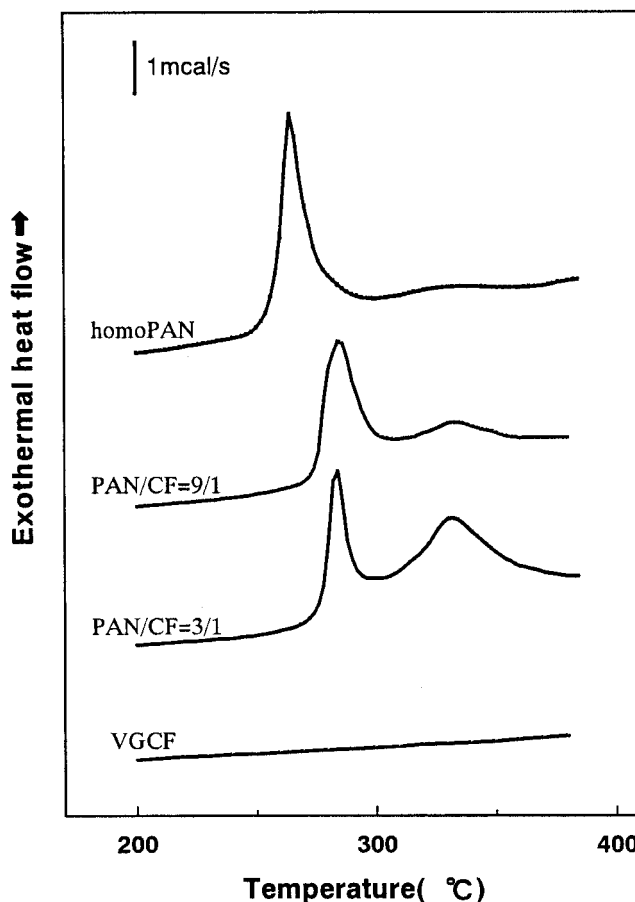


Figure 4 DSC curves measured for the VGCF powder and untreated films with a draw ratio of 20 folds in the indicated PAN/VGCF compositions.

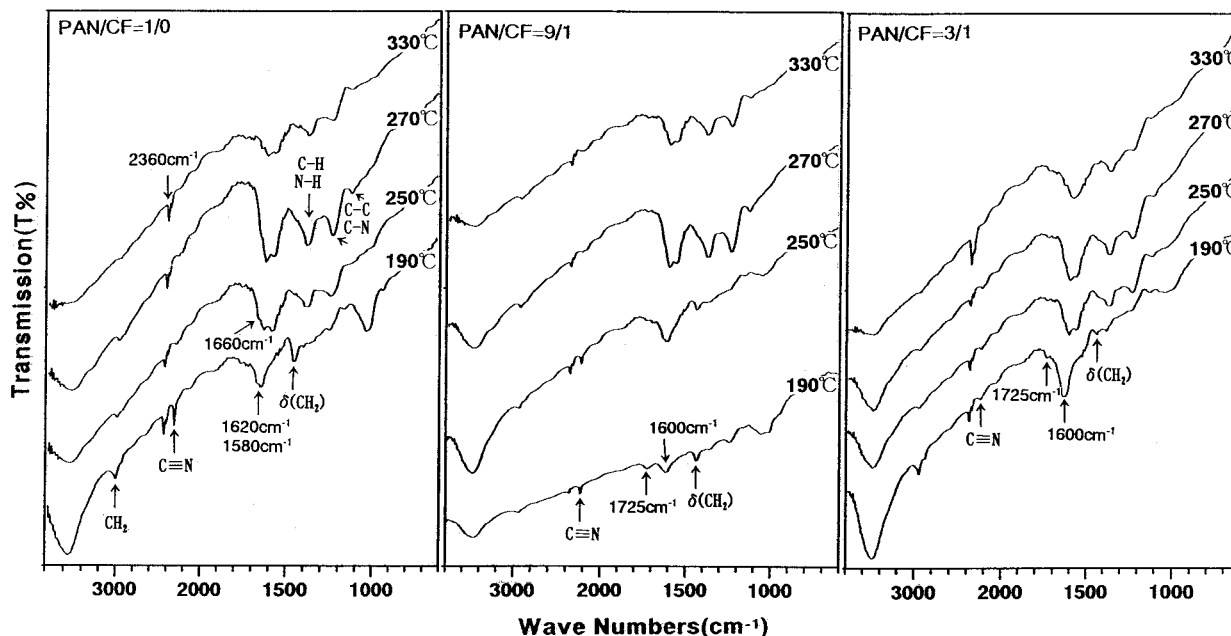


Figure 5 IR spectra measured for the stabilized specimens treated at (a) 190°C, (b) 250°C, (c) 270°C, and (d) 330°C with the indicated PAN/VGCF compositions.

higher temperature decides the initiation of the oligomerization, and the bond formation between the carbons of the adjacent nitrile groups is a fast propagation. The IR spectrum of the VGCF also presents two faint peaks around 2341 and 2360 cm^{-1} . In considering such a region, only the vibration of the triple bond and continuous double bond could reasonably appear. It is speculated as being a continuous double bond such as $\text{C}=\text{C}=\text{O}$ and $\text{C}=\text{C}=\text{N}$, and as these functional groups are of higher electronegativity, the nitrile group may be restrained to a more stable state. So, the initiation and propagation steps in PAN were hindered or slowed down, in that we see in the DSC curves a peak shifting to higher temperature for the PAN/VGCF composite. As stated in many studies,^{1,3,4,10} heat is evolved at a rapid rate with cyclization in the case of PAN film and the dissipation of this heat is of importance, as excessive heating may cause chain scission and result in a poor-quality carbon product. Here, the peaks' area decreased from the homopolymer of PAN to the blends due to the lessening of the specific heat capacity, on the one hand, and, on the other, as the VGCF is a rather fine heat conductor, it transfers the heat generated in the reactions to the surrounding areas, so the exothermal peaks are not as sharp as those of the homopolymer. The peak that appeared around 330°C shows that VGCF's existence promoted the reactions of aromatization and intermolecular crosslinking and helped the molecular chain undergo realignment, reorientation, and reinforcement to a formation of a highly ordered and compact structure which had been found to be helpful for the later carbonization in many studies.^{17,18}

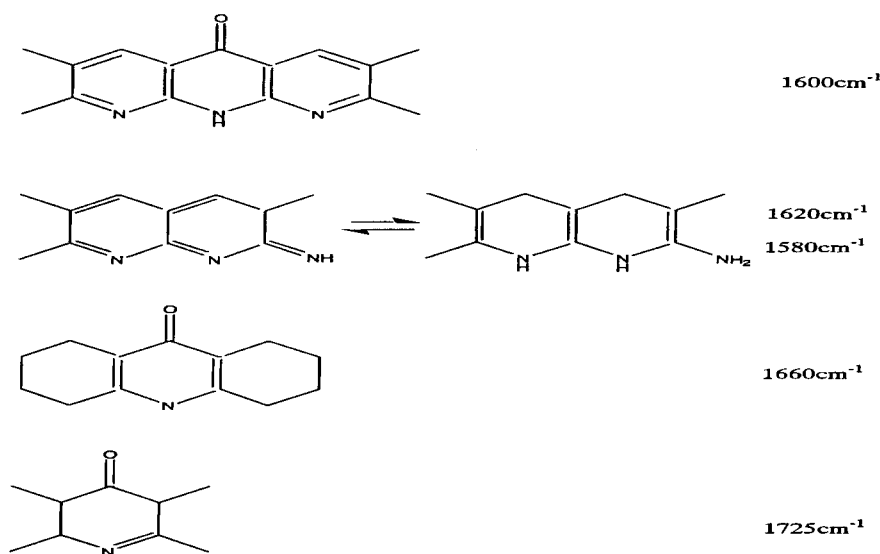
The evidence for these explanations could be found in the IR and Raman spectra as follows:

Figure 5 shows the changes of the IR spectra measured for the 1/0, 9/1, and 3/1 composites with the indicated heat-treatment stages. The main changes are similar, indicating the change of PAN's structure. As reported in the literature,¹⁹ the major absorption bands in PAN are the carbon-nitrogen triple dangling bond stretching at 2240 cm^{-1} , C—H stretching in the $-\text{CH}_2$ group at 2940 cm^{-1} , and C—H bending at 1450 cm^{-1} . These peaks start to decrease with the initial cyclization reaction beyond 180°C [see Fig. 1(a)] and decrease considerably when the samples are heated to 270°C. Simultaneously, new overlapped peaks appear around 1660 cm^{-1} . The shoulder peak is assigned to the conjugated β -diketone group in the acridon ring,²⁰ and it has also been reported to belong to the conjugated ring ladder frame structure.

Peaks around 1580 and 1620 cm^{-1} could also be observed. They have been reported to belong to the conjugated pyridone structure of $\text{C}=\text{C}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{N}-\text{H}$ bands,²¹ from the ladder structure as shown in Figure 1(a). These two peaks appeared for the PAN film stabilized at 190°C, while for the composite, the two peaks could not be seen until being stabilized above 250°C. This means that the cyclization and dehydrogenation appeared earlier for the PAN film than for the PAN/VGCF composite and this is consistent with the DSC analysis. On the other hand, at this stabilization stage of 190°C, the composite film showed two different peaks at 1725 and 1600 cm^{-1} . The former is reported as due to the $\text{C}=\text{O}$

stretch vibrations of an aliphatic ketone, and the latter, to the combination vibrations of C—N, C—C stretching, and N—H in-plane bending of the ladder frame.²⁰ This demonstrates the fact that for the PAN/VGCF composite the oxidation occurred before it did for the PAN film, for the same reason that we described in the DSC analysis, that such continuous double bonds as C=C=O and C=C=N exist in the initial VGCF and its fission at higher temperature introduced the oxidant. In the spectra for the specimens stabilized at

270°C, new peaks also appeared around 1380 cm⁻¹, which are from C—H, N—H, and around 1260 and 1105 cm⁻¹, which are from C—C, C—N.²¹ The latter may correspond to a side reaction taking place in the process. With the progression of the reaction, the magnitudes of 1660 and 810 cm⁻¹ from ν (=C—H) increased, while that of methylene δ (CH₂) at 1450 cm⁻¹ decreased. The conjugated structures concerning 1580, 1600, 1620, 1660, and 1725 cm⁻¹ are illustrated as follows:



Also, near the peak of 2240 cm⁻¹, there is an unreported one appearing around 2340 and 2360 cm⁻¹, the same as that of the VGCF. It could be detected from all the stabilized samples as well as from the untreated film. It is speculated as being from the continuous double bonds such as O=C=O or C=C=O from the initial VGCF for the PAN/VGCF composite or from production in the heat treatment even during stretching from the precursor for the PAN homopolymer.

Figure 6 shows the Raman counts measured for the stabilized PAN/VGCF composite with the 3/1 composition under the indicated heat-treatment temperatures (HTTs) of 250, 270, 330, and 350°C. The spectrum of the PAN homopolymer shows a typical peak at 2248 cm⁻¹, which is accounted for by the carbon-nitrogen triple dangling bond. For the samples treated under 250°C, there are no peaks that could be observed; the carbon-nitrogen triple bond also disappeared after heat treatment. When the specimen was heat-treated above 270°C, new peaks around 1600 and 1370 cm⁻¹ appeared,^{22,23} and the higher the treating temperature, the larger and more evident were the peaks. For graphite, the first-order spectrum shows only a sharp peak at 1580 cm⁻¹ (the E_{2g} carbon-carbon vibration in the aromatic plane), but for less organized carbons, the 1580-cm⁻¹ band is displaced to 1610 cm⁻¹

and an additional peak is added at 1350–1380 cm⁻¹. It is clear that, in the stabilization process for the PAN/VGCF composite film with a 3/1 composition, reactions occur, leading to the structures of aromatic rings and even to the stacking of aromatic layers. Here, we must emphasize that the two peaks that appeared for the specimens stabilized beyond 270°C become more intense through the carbonization, and such clear peaks could not be observed for the stabilized films produced from the PAN homopolymer film as a starting material. It is interesting that, in industry, only when heat-treated above 1000°C for more than 24 h could a carbon product be obtained from the PAN precursor, but in the case of the PAN/VGCF precursor, only in the lower temperature of 200–300°C has the partly transition from PAN to turbostratic carbon layers been achieved.

Figure 7 shows the temperature dependence of the storage modulus E' and the loss modulus E'' at a frequency of 10 Hz measured for the composite films ($\lambda = 20$) with the 1/0, 9/1, and 3/1 compositions. The measurements were done for stabilized specimens heat-treated at 250, 270, and 330°C, respectively. It is seen that E' decreases with increasing temperatures for all the samples, but E' for the stabilized ones treated at higher temperatures showed somewhat less

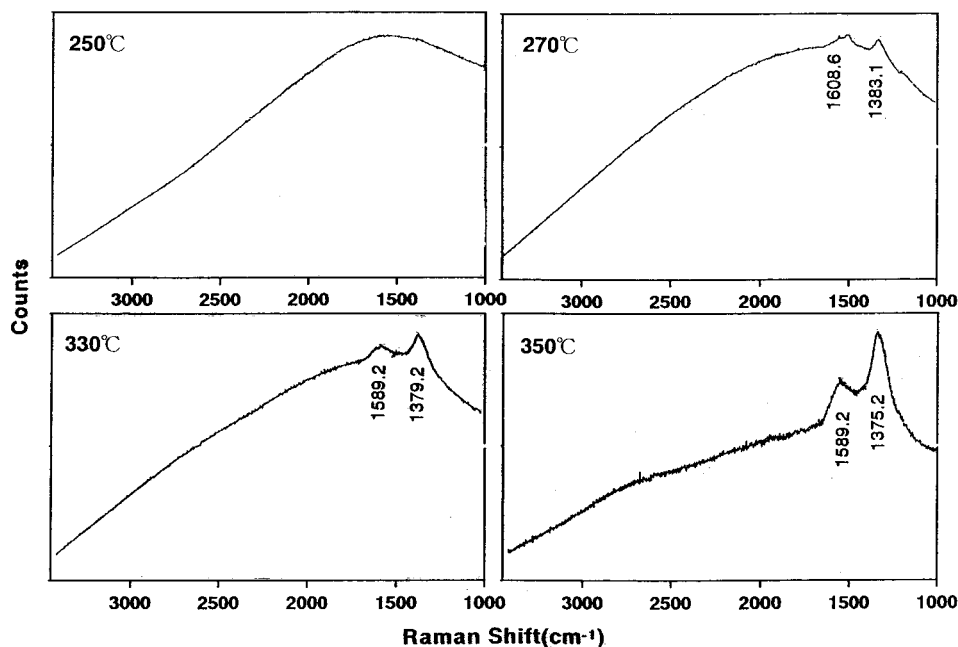


Figure 6 Raman spectra measured for the stabilized specimens of PAN/VGCF composition of 3/1 under the HTTs at (a) 250°C, (b) 270°C, (c) 330°C, and (d) 350°C.

temperature dependence in comparison with that of the one treated at lower temperatures, and the magnitude of E' measured at room temperature increased

when the samples were heat-treated at higher temperatures. The specimens of the composites of VGCF showed a higher E' than that of the homopolymer. The

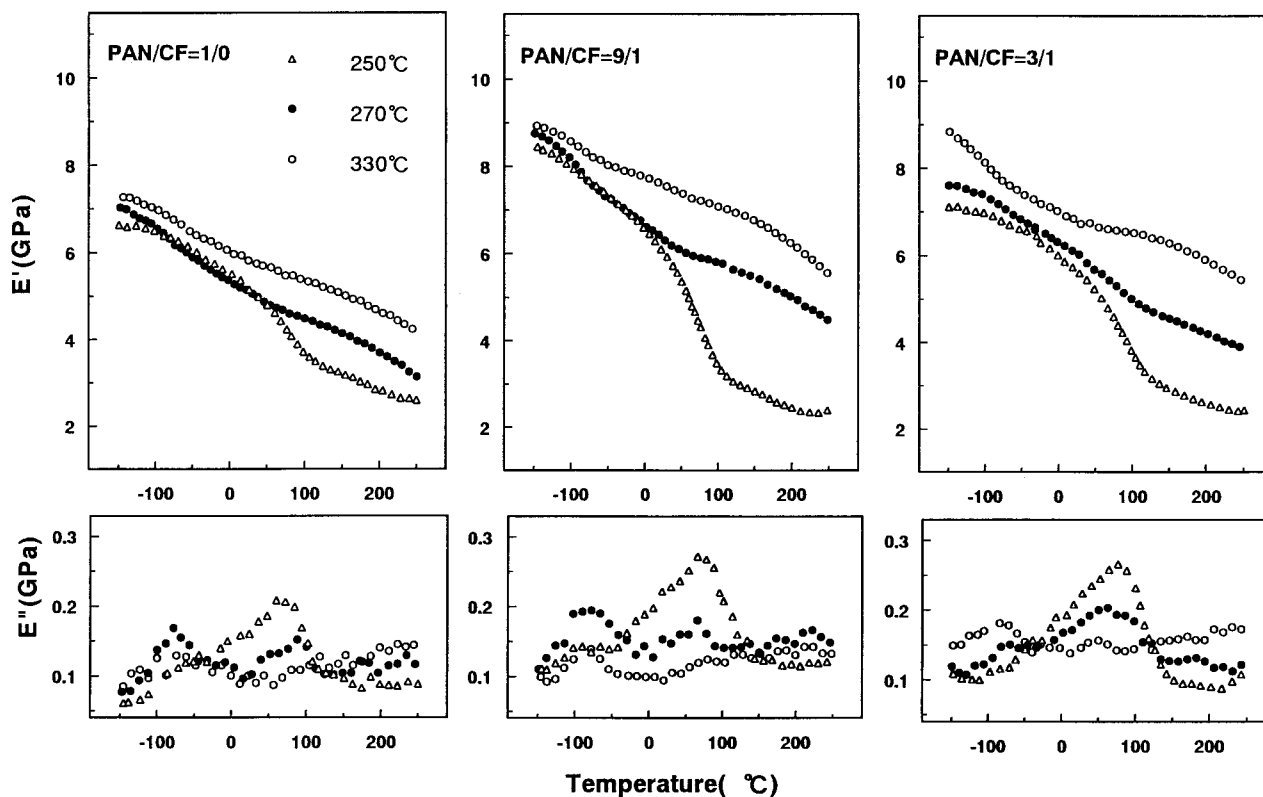


Figure 7 Temperature dependence of the storage and loss moduli measured for the stabilized specimens treated at 250, 270, and 330°C, respectively, with the indicated PAN/VGCF compositions.

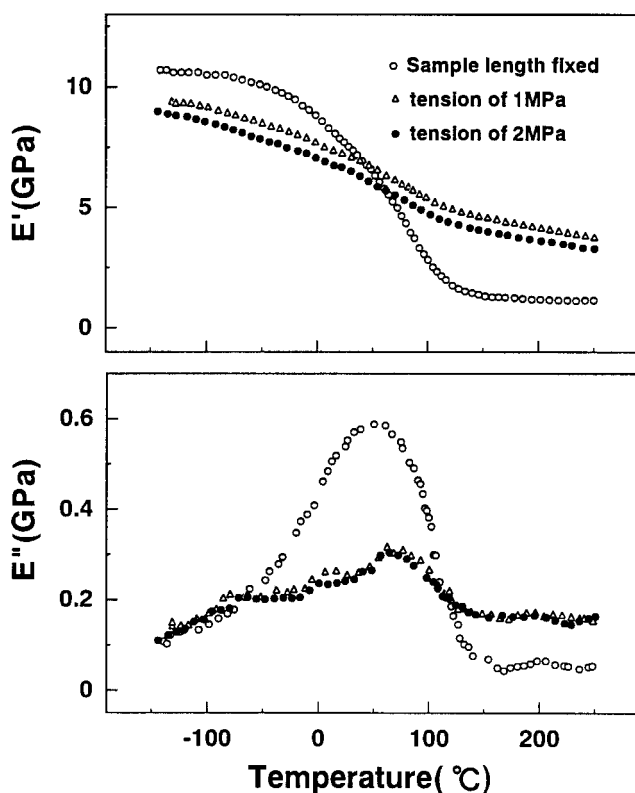


Figure 8 Storage and loss moduli measured for the stabilized 9/1 composite film ($\lambda = 20$) under different tensions against the temperature change.

temperature dependence of E'' for three kinds of stabilized specimens (1/0, 9/1, and 3/1) showed the α -transition around 40–100°C, and the higher the treating temperatures, the more indistinct are the peaks. Judging from there being no dispersion peak for the 9/1 and 3/1 blends, the dispersion of the PAN homopolymer film is thought to be due to grain boundary phenomena associated with reorientation and/or slippage of PAN crystal or quasi-crystal grains between oriented grains.²⁴ In the 9/1 and 3/1 composite films, there exist PAN crystallites and carbon planes from VGCF, and the carbon layers formed should invoke no dispersion in spite of unstable structures with a large fluctuation for the lattice spacing.

Figure 8 shows the storage and loss moduli measured for the stabilized 9/1 composite film ($\lambda = 20$) under different tensions against the temperature change. The film which was stabilized with a fixed length, or with infinite tension, demonstrated a relaxation as significant as those untreated films, and the other two, with definite tension, showed the typical dispersion of the stabilized ones, that is, less temperature dependence for the storage modulus and an indistinct relaxation for the loss modulus. In the fiber or film for the PAN series precursors, shrink always occurs due to both the physical and chemical reasons. The physical shrinkage is attrib-

uted to the entropy recovery of a drawn and quenched material; the strains developed during stretching will relax in the heat treatment, while chemical shrinkage occurs as a result of chemical reactions during the stabilization process, which leads to the formation of a cyclized ladder polymer. As a result, the precursor with proper tension would show less significant relaxation after shrinking in the stabilization treatment, and while the infinite tension prevented the shrinkage, it also prevented the process of stabilization.

We may draw the following conclusions from a morphology aspect according to the WAXD, IR, Raman, and DSC analyses for the PAN and PAN/VGCF composite precursors: (1) When PAN film is heated in air above 180°C, a reaction such as dehydrogenation, cyclization, and oxidation takes place, leading to the condensed ring structure containing the carbon–nitrogen double bond, which is often known as the ladder structure [Fig. 9(1)] and which was confirmed by the IR spectra. (2) As the heat-treatment temperature increases (300–400°C), the ladders become closer to each other and additional aromatization and certain intermolecular crosslinking reactions occur, so ordered and compact structural units appear, which are usually called the elemental units of carbon or the basic structural units (BSU), (3) As these nitrogenated BSU are mobile, under about 600°C in carbonization, they graft upon edges and align themselves parallel to a plane and polyaromatic BSU components are formed. (4) With subsequent coalescence under 1300°C by dehydrogenation, a continuous aromatic layer appears. (5) Under later local molecular orientation (LMO) at about 1500°C, aromatic layer stacks form, although they are now still disordered and in a turbostratic structure. (6) *But* after being heat-treated at even higher HTT (more than 2000°C and even more than 2700°C), the carbon layer with increased crystallites size and alignment and even graphite will be obtained. (1) and (2) are concerned just with chemical reactions such as cyclization and aromatization; (3) and (4), with condensation in the solid state, which leads to the growth of an aromatic plane; and (5) and (6) with, increase of three-dimension regularity, until the growth of graphite crystals.

In the case of the PAN/VGCF composite precursor, the introduction of VGCF showed an advantage to develop many aromatic BSU at an early stage, so it promoted the reactions of (3)–(5) at much lower HTTs for stabilization. The WAXD pattern, WAXD intensity distribution, and Raman spectra have indicated that such aromatic layer stacks even formed below 400°C, while for the PAN homopolymer precursor, an HTT as high as 1500°C was needed.

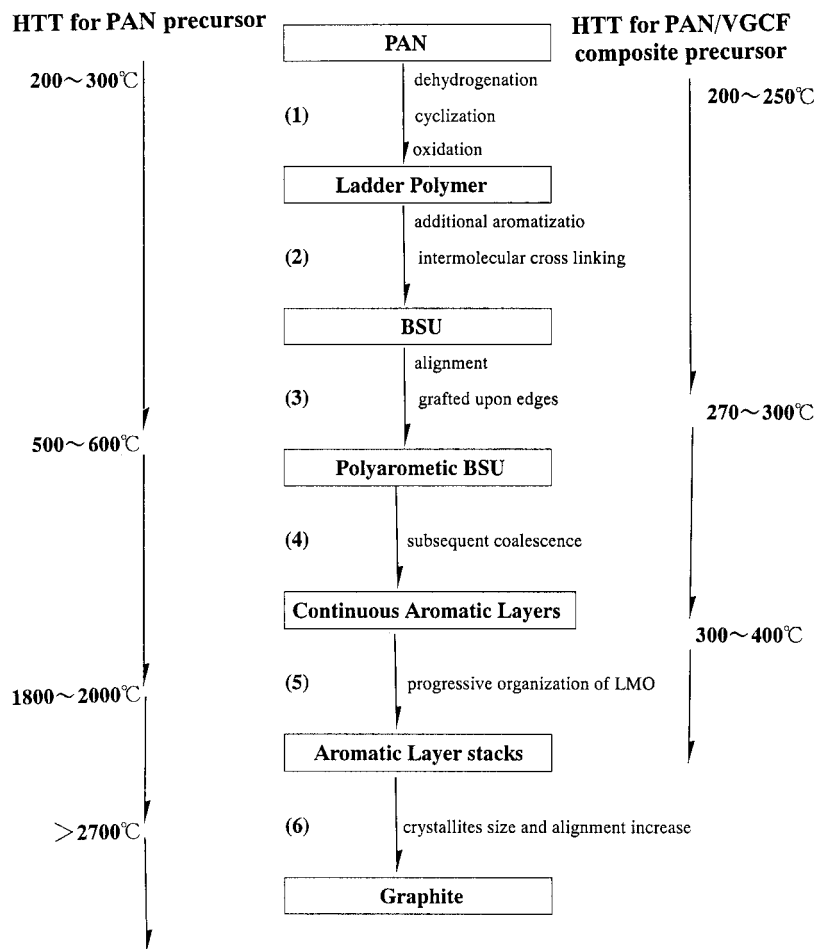


Figure 9 Morphology illustration for the two precursors of PAN and the PAN/VGCF composite during oxidative stabilization, carbonization, and graphitization.

CONCLUSIONS

Oxidative stabilization was carried out and studied for a new precursor, the composite of a high molecular weight PAN homopolymer and VGCF. It was found in this process of stabilization that the introduction of VGCF makes the precursor more endurable to heat treatment and of a higher modulus. The mechanism involved during the oxidative stabilization process was also discussed in terms of a morphology aspect according to the WAXD, IR, Raman spectra, and DSC measurements, in that the reactions such as cyclization, dehydrogenation, and oxidation take place and are shown in the DSC thermogram as a sharp peak around 260–280°C, forming the ladder structure. Although there is a slower initiation and propagation step of cyclization and dehydrogenation for the PAN/VGCF composite than that of the homopolymer, the oxidation step seems to occur before that of the homopolymer. The second peak appeared about 330°C in the DSC; although its origin could not be clearly explained from the IR spectra, it is speculated to correspond to the additional aromatization and certain

intermolecular crosslinking reactions, and the existence of VGCF was confirmed, which acts as an aromatic BSU during those reactions, promoted those reactions, and produced the turbostratic carbon layer stacks at much lower HTTs in the stabilization process, which could be realized only under the carbonization process and temperatures for the normal precursor.

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