

Evaluation of Carbonization Tar in Making High Performance Polyacrylonitrile-based Carbon Fibers

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ABSTRACT: The polyacrylonitrile carbonization tar is discussed in detail by using gas chromatographic-mass spectrometer and electron paramagnetic resonance. It is a viscous liquid that constitutes complicated condensed components resulting from polymer decomposition. It was demonstrated that the predominant products were acrylonitrile dimer and trimer species with trifle cyclohexane and cyclopentane. Moreover, the fragmentation course occurred in temperature range of 400–600°C and decomposed in 525°C most drastically. The formation of the tar could be regarded as random fragmentation

of linear chain segments among ladder structures accompanying with secondary decomposition. After adjusting the middle temperature carbonization technology, depending on the components and formation of tar, the high performance carbon fibers were obtained that had tensile strength of 4.2–4.5 Gpa, elongation at break 1.7%–1.8%, modulus 235–240 Gpa. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1255–1259, 2007

Key words: PAN tar; fibers; degradation; pyrolysis; stabilization

INTRODUCTION

It is well known that high quality polyacrylonitrile (PAN)-based carbon fibers are dependent on not only the nature of the precursors but also the stabilization stage and the carbonization stage. Many investigations have been devoted mainly to the basic understanding of the reaction kinetics,^{1–3} such as cyclization and crosslinking of the molecular chains of the thermally stabilized PAN fibers,⁴ and the examinations were generally confined to scanning electron microscopy,⁵ X-ray diffraction,⁶ transmission electron microscope,⁷ optical microscopy,⁴ Fourier transmittance infrared spectroscopy (FTIR),^{8,9} differential scanning calorimetry,¹⁰ nuclear magnetic resonance, and so on.^{11–14} However, these obtained results exhibited chemical structure transformation and small molecule products formation of PAN during heat treatment. The reports about the so-called carbonization tar for thermal degradation of PAN oxidized fibers in carbonization process were of little knowledge. Carbonization tar was byproduct in the course of PAN ladder polymer turning into network polymer, and it was a viscous liquid of the complicated condensed components. Formation mechanism of tar was expressed by chain random fragmentation accompa-

nying with secondary decomposition and partial mechanism.¹⁵ The residual tar made the fibers conglutinate together and melted into char in subsequent higher temperature on the fibers, which resulted in the decrease of tensile strength of carbon fibers. It was necessary to control the tar influence on carbon fibers to eliminate contamination of the tar.

EXPERIMENTAL

Spinning for PAN-based precursors

A copolymer consisting 95.4 wt % of acrylonitrile, 1.4 wt % of itaconic acid, and 3.2 wt % of methyl acrylate was produced by solution polymerization using DMSO as solvent and using AIBN (2,2'-azodiisobutyronitrile) as initiator; the intrinsic viscosity of the resulting polymer $[\eta]$ was 1.8; and the number-average molecular weight M_n of the resulting polymer was 170,000. The spinning dope with a concentration of 18% was spun to obtain PAN precursor in wet spinning way. The precursor had the tensile strength of 8.2 cN/dtex and the elongation at break of 11.0%.

Stabilization of PAN precursor

Samples were prepared by stabilizing the PAN-based precursor in the presence of air to different temperature, viz 190, 220, 240, 250, 260, 270, and 280°C zone in oven. Total drawing ratio in preoxidation process was 5.22%, with about 50 min of heat oxidation time.

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Collecting of the carbonization tar

The carbonization tar was collected from exhaust gas condenser pipe of self-designed carbonization furnace. The loss weight and change of exothermic and endothermic of the oxidized fibers were determined by the use of thermogravimetric analysis and high temperature differential thermal analysis, which were performed at a heating rate of 10°C/min in argon atmosphere on Netzsch STA 404 EP thermal analyzer.

Measurement and testing

Bruker Vector22 model FTIR spectrometer was used to characterize the selected PAN fibers, loading samples on KBr disks (0.5 mg sample with 200 mg KBr). KBr (high-quality purity, chemical reagent CO. of Peking) pelleting machine was employed to prepare samples.

A spot of concretionary tar was first dissolved by solvents, then filtrated into partial solution and mixed with the liquid portion dissolved by toluene and methyl alcohol to, respectively, make the corresponding full solutions of two kinds of solvents. The tar components were analyzed by Agilent GC-MSD 6890N-5973N of gas chromatographic-mass spectrometer (GC-MS). Decomposition products of the oxidized fibers pyrolyzed in faradic cracker were obtained by QP-5000G PyGC-MS. The sample was fragmented within 5 s at 650°C and the products were separated in chromatographic column at 50–250°C, with a heating rate of 6°C/min. It was ionized in mass spectrometer with 70 eV of the energy of electron beam in 260°C. The quantity change of free radical from chain thermal fragmentation was measured by JES-FA200 electron paramagnetic resonance (EPR) spectrometer at 350–600°C. Microwave frequency and power were, respectively, 8.99 GHz and 0.998 mW, magnetic intensity of field center was 320.916 mT, and sweep time and width were 1.0 min and 20.000 mT, respectively.

RESULTS AND DISCUSSION

Chemical structural change for the precursors

Figure 1 is the FTIR spectra of the stabilized fibers at different temperatures, which gives information related to the structural changes during the stabilization. Three prominent peaks at 1451.01 cm⁻¹, 2244.85 cm⁻¹, and 2936.58 cm⁻¹ in the spectrum of PAN fibers show that they originate from the bending vibration of methylene groups (CH₂), the stretch vibration of nitrile groups (C≡N), and methylene groups, respectively. With increasing the temperature, the distinct changes can be observed at 2936.58–2918.54 cm⁻¹, 2244.85–2236.95 cm⁻¹, and 1451.01–1446.45 cm⁻¹, and new peaks appear at 1594.68 cm⁻¹ and 1700 cm⁻¹, which can be attributed to the stretching

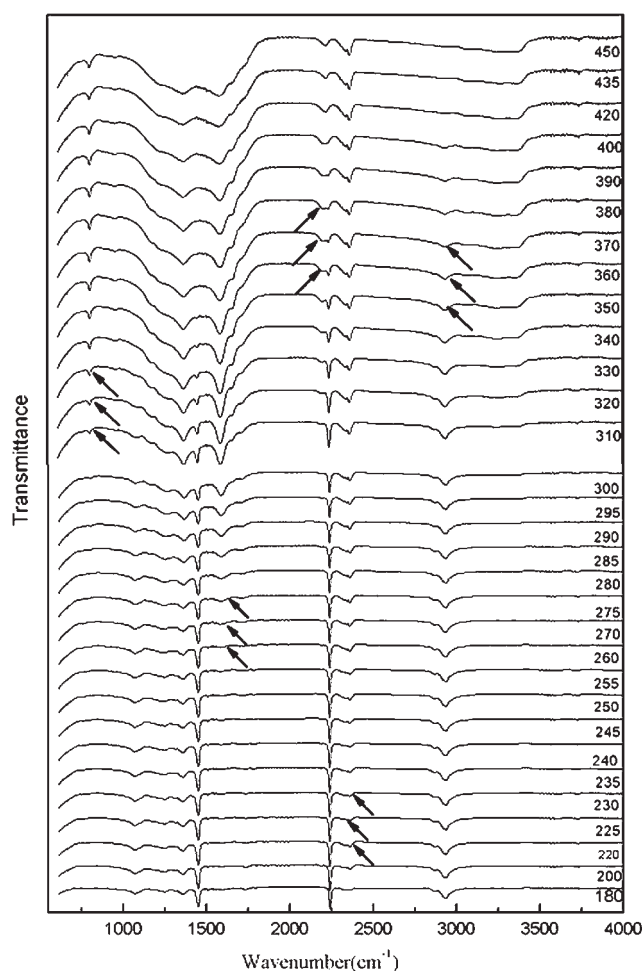


Figure 1 FTIR spectra of the stabilized fibers at various temperatures.

vibration of C=N and C=O groups, respectively. In spite of the structural changes observed in the stabilized fibers, C≡N and CH₂ groups have not yet thoroughly transformed into other structures. Further conversion will be continued with increasing treatment temperature or prolonging treatment time. There is no clear difference in chemical structure change for the self-made PAN precursors oxidation when compared with the other ones.

Formation of PAN carbonization tar

PAN precursor structure after oxidation was further evolved into graphite-like structure in carbonization process,¹⁶ but many polymer segments were fragmented into decomposition products, which occurred between cyclization and aromatization reactions. The DTA and TG curves of the PAN oxidized fibers, with a heating rate of 10°C/min in the range of 20–1400°C, in argon are shown in Figure 2. In PAN cyclization reaction, when the heating temperature (°C) exceeded 290°C, there was an exothermic peak at 326.2°C and an endothermic peak at

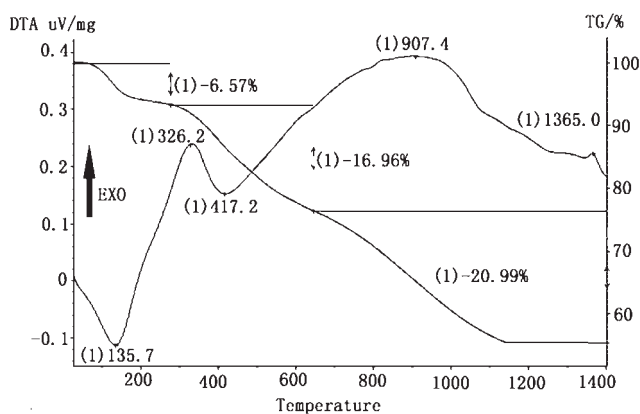


Figure 2 DTA and TG curves of PAN oxidized fibers.

417.2°C and subsequently an exothermic peak at 907.4°C. The exotherms with a peak at 326.2°C and 907.4°C were, respectively, attributed to intermolecular crosslinking and aromatization reaction of the fibers. The endothermic peak at 417.2°C was ascribed to the fragmentation process of the fibers. There was a 16.96% weight loss in TG curve in range of 300–640°C, because decomposition products from fragmentation volatilized away from the fibers in gas state and that the PAN carbonization tar was primary species of the decomposition products.

The exhaustive fragmentation course was elucidated by the EPR spectrum of the oxidized fibers. If energy in condensed system complied with Maxwell distribution, some bonds of molecule in excitation state would cleave when vibrational energy reached repulsive level with an increase of temperature.¹⁷ The bonds cleavage brought on chain free radicals and initiated fragmentation of polymer. On the basis of thermal degradation mechanisms of polymers of Lehrle¹⁸ and Schnabel,¹⁷ the forming tar of the PAN fibers degradation complied with random fragmentation mechanism accompanying with secondary decomposition, and it could be approved by EPR peak appearing in the oxidized fibers at different temperature.

The bonds thermal homolytic cleavage of the fibers polymer led to degradation process in carbonization. The polymer backbone chains fragmented into chain free radicals and the reaction of the radicals were manifested by unpaired electrons in carbonization temperature range, so the EPR curves characteristic to the unpaired electrons indicated the reaction course of the polymer. Each curve of from 1 to 8 measured at room temperature is shown, respectively, in Figure 3. It was shown that the curve was Lorentz linetype and single narrow spectra where there did not exist hyperfine separation. It was basically identical with free radical spectral line. The peak width appreciably became narrower with the increase in temperature and value of the peak presented a trend of augmenting first and then

diminished; the maximum value appeared at 525°C. The peak width change was mainly due to spin-spin interaction. With an increase of temperature, many unstable free radicals vanished to make “local magnetic field” that resulted from small magnets from unpaired electrons.¹⁹ So, the broadening effect reduced and the peak width became narrower. The change of peak value manifested variation of unpaired electrons quantity under the same testing condition, and the change of chain free radicals was attributed to random fragmentation. As temperature increased, the quantity of ruptured backbone chain increased gradually and reached maximum at 525°C and subsequently peak value became less. It has been testified that random fragmentation of the polymer backbone was enhanced with an increase of temperature and became most drastically up to 525°C, and the quantity of the free radicals descended sharply with the unpaired electrons consumption of H atoms abstraction/elimination.

Components analysis of carbonization tar

The tar was complicated mixture, and it was difficult to absolutely dissolve it by any kind of solvent. To detect its exhaustive components, it was, respectively, dissolved by toluene and methyl alcohol to prepare two kinds of solution after filtration. The components identified by GC-MS are summarized in Tables I and II.

By the analysis of peak value, it was observed that the nitriles were comparatively predominant and the quantitative contrast was shown by PyGC-MS analysis of the PAN fibers. It could be seen that the acrylonitrile dimer and trimer with nitriles and cyclohexane and cyclopentane products contained more car-

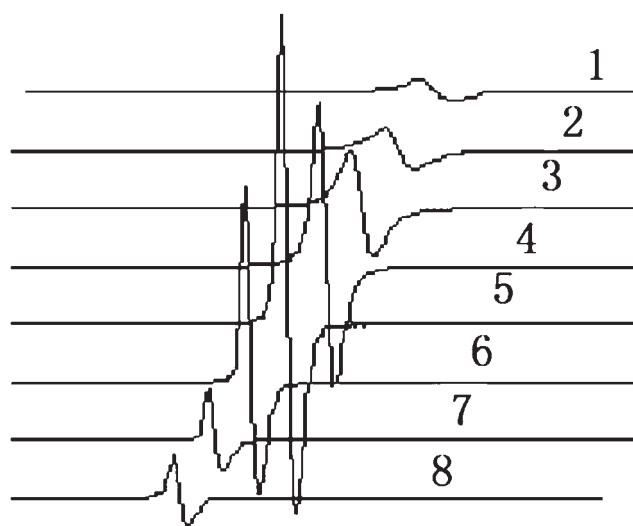


Figure 3 EPR spectrum of PAN oxidized fibers in different temperature: 1, 350°C; 2, 400°C; 3, 450°C; 4, 500°C; 5, 525°C; 6, 550°C; 7, 575°C; and 8, 600°C.

TABLE I
Tar Partial Components in Toluene Solution

Compound	Molecular weight	Retention times (min)
Trans-1,4-dimethyl-cyclohexane	112	4.93
1-Ethyl-2-methyl-cyclopentane	112	5.40
2-Methyl-bicyclo[2.2.1]heptane	110	5.49
Cis-1,2-dimethyl-cyclohexane	112	5.58
Ethylcyclohexane	112	5.71
1,1,3-Trimethyl-cyclohexane	126	5.83
Ethylbenzene	106	6.67
Cis-octahydro-pentalane	110	6.84
1,3-Dimethyl-benzene	106	6.96
Styrene	104	7.74
1,2,3-Trimethylbenzene	120	12.03
2-Cyano-benzeneacetonitrile	142	27.58
2,4-Bis (1,1-dimethylethyl)-phenol	206	29.96
Benzalmalononitrile	154	30.80
Cis-1,3-cyclohexanedicarbonitrile	134	31.34
N-(phenylmethylene)-benzenemethanamine	195	33.18
2,5-Bis(phenylmethylene)-cyclopentanone	260	37.67
3-Phenylnitropropane	165	40.19

bon atoms. There were less quinoline, pyrimidine, and ketone and hydroxybenzene products containing oxygen functional groups. Molecular weight of these compounds basically converged at 100–150.

The quantity comparison of tar compounds was denoted by following PyGC-MS testing of the oxidized fibers and is shown in Figure 4. The pyrolysis chromatographic peaks of the preoxidized fibers were semblable with the peaks of PAN before retention time of 30 min while the values of peaks were of difference. In Figure 4, the peak of 1 represented monomer series products of acrylonitrile, including acetonitrile, acrylonitrile, and methacrylonitrile. The peaks of 2, 3, and 4 represented dimer series of acrylonitrile, including succinonitrile, glutaronitrile, 2-

TABLE II
Tar Partial Components in Methyl Alcohol Solution

Compound	Molecular weight	Retention times (min)
Acetamide	59	2.29
3-Methyl-2,5-furandione	112	4.05
Butanedinitrile	80	4.66
3-Amino-acrylonitrile	70	5.16
Pentanedinitrile	94	5.92
2,3- Dimethyl- butanedinitrile	108	6.08
2-Methyl-pentanedinitrile	108	6.19
3- Methyl-pentanedinitrile	108	6.62
Hexanedinitrile	108	8.03
1,2-Benzenedicarbonitrile	128	9.31
2,6-Dicyanotoluene	142	10.89
1-Isoquinolinecarbonitrile	154	13.78
4-Methyl-3,5-pyridinedicarbonitrile	143	15.87
4-Amino-1,2-benzenedicarbonitrile	143	15.87
2-Ethyl-quinoline	156	16.58

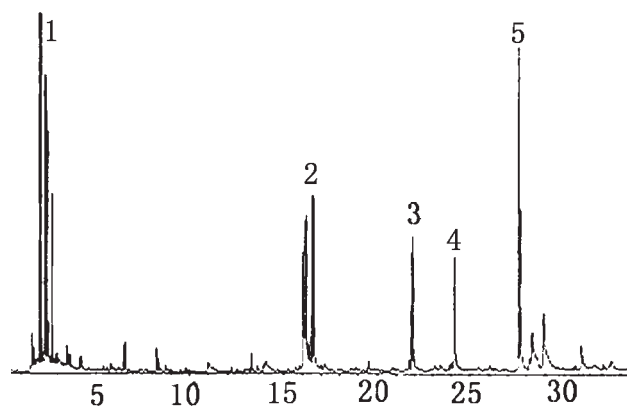


Figure 4 Pyrolysis gas chromatogram of PAN oxidized fibers.

methyl glutaronitrile, 1,3-dicyanobenzene, etc. The peaks of 5 and its nearby peaks represented trimer products, mainly including 1,3,5-tricyanobenzene and 2,6-dicyanobenzene. It could be concluded that acrylonitrile series oligomers were predominant components of PAN carbonization tar while cycloparaffin and pyrimidine, etc, largely appearing in the tar of toluene solution were inexistent in pyrolysis chromatogram.

Tar formation mechanism

Compared with PyGC-MS products of PAN precursor, there were no more complicated and degree of polymerization oligomers in the oxidized fibers chromatogram, which could be explained by that the fibers had more crosslinking interaction among molecular chains to withstand heat action. It was a clear fact that the PAN oxidized fibers were composed of cyclization structure and linear segments at intervals of few isolated conjugated structure, and the tar primarily came from linear segments fragmentation of the fibers. According to random thermal fragmentation, the primary tar products formation courses by

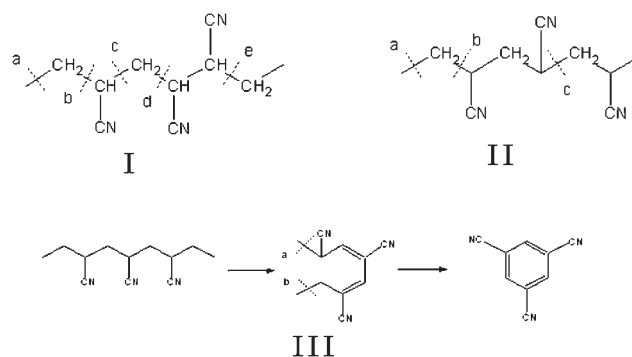


Figure 5 Random fragmentation mechanism of PAN oxidized fibers.

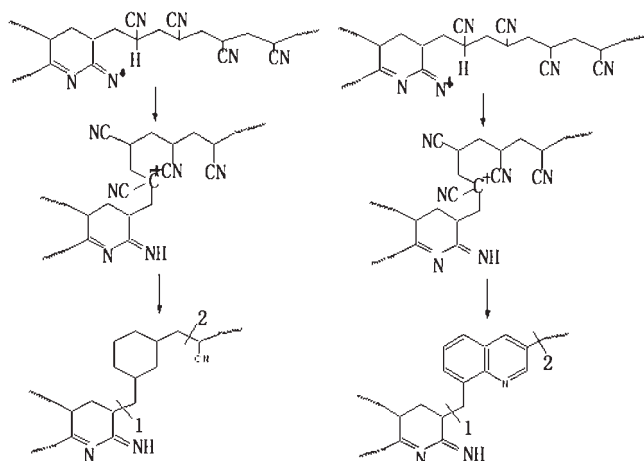


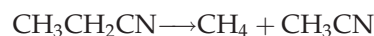
Figure 6 Formation of cycloparaffin and quinoline in PAN oxidized fibers fragmentation.

homolytic cleavage of the polymer backbone chain are described in Figures 5 and 6.

Monomer series such as acetonitrile, acrylonitrile, and methacrylonitrile were formed, respectively, by b and c, b and d, and a and d bonds homolytic cleavage in I course (Fig. 5). Succinonitrile as dimer series primary products formed by d and e bonds cleavage in I course. Glutaronitrile and 2-methyl glutaronitrile formed by b and c and a and c bonds cleavage in II course. 1, 3-dicyanobenzene of dimer product and 1,3,5-tricyanobenzene of trimer product were formed by a and b bonds cleavage in III course, in which chain segments of the linear polymer were activated to form ring structure and when β H atoms of methylene were of abstraction by adjacent free radicals, the cyanobenzene products were formed by closing loop. A small quantity of cycloparaffin and quinoline products were formed by random fragment of the backbone C—C bonds after secondary cyclization reaction had occurred. Cycloparaffin formed as a result of secondary cyclization arising in chain length of three acrylonitrile monomers, when β H atoms abstraction simultaneously occurred to cyclized segment benzene products came into being. When the secondary cyclization occurred in chain length of four acrylonitrile monomers accompanying with H atoms abstraction quinoline products would be formed. These courses are described in Figure 6.

Low molecular weight products were formed by secondary decomposition¹⁸ of fragmentation components of straight chain paraffin. For instance, acetonitrile and methane were formed by ethyl cyanide decomposition, as shown below. Other products

such as ethylene and acetamide were also formed in the secondary decomposition mechanism.



CONCLUSIONS

The PAN carbonization tar formed in temperature range of 400–600°C and most drastically in 525°C complying with random fragmentation mechanism. By GC-MS analysis of tar solution and PyGC-MS investigation of the oxidized fibers, the predominant species of the tar were acrylonitrile dimer and trimer series products with a trifle cyclohexane and cyclopentane products. The formation of the tar was regarded as random fragmentation of linear chain segments among ladder structures accompanying with secondary decomposition. After adjusting the middle temperature carbonization technology depending on the components and formation of tar, the high performance carbon fibers were obtained, with tensile strength 4.2–4.5 Gpa, elongation at break 1.7%–1.8%, and modulus 235–240 Gpa.

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