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PROPERTIES OF CARBONS DERIVED FROM
ACENAPHTHYLENE AND CINNAMYLIDENEINDENE

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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**PROPERTIES OF CARBONS DERIVED FROM
ACENAPHTHYLENE AND CINNAMYLIDENEINDENE**

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ABSTRACT

The effect of temperature and various additives on the properties of acenaphthylene (ACN) and cinnamylideneindene (CAI), and carbons derived from ACN and CAI, were studied. In thermal studies, a CAI polymer was found to be relatively stable for extended periods at 250° C, while significant property changes were noted for an ACN polymer under the same conditions. By blending various additives with ACN and CAI prior to pyrolysis, a wide variety of carbon properties were obtained, thus affording avenues to control these properties by modifying the precursors.

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SUMMARY

The primary goal of this study was to evaluate the properties of carbons derived from acenaphthylene (ACN) and cinnamylideneindene (CAI). Included in this study were: (1) an evaluation of the thermal stability of CAI and ACN polymers at 250° C; (2) a determination of the properties of carbon derived from CAI and ACN over the temperature range from 1,000 to 2,800° C; and (3) an evaluation of various additives to ACN and CAI by correlating the properties of the derived carbon with the additive type and content.

The primary conclusions reached from this study were: (1) the CAI polymer was relatively stable at 250° C for up to 28 days, while the ACN polymer showed some variation in physical properties during heating at 250° C for 28 days; (2) ACN and CAI produce carbons that densify at approximately 1,500 and 2,000° C, respectively, and undergo significant three-dimensional ordering between 2,000 and 2,800° C to yield highly crystalline carbons; and (3) properties of carbon derived from ACN and CAI can be modified over a wide range by blending additives with the respective materials prior to pyrolysis.

INTRODUCTION

Carbon has properties which are quite adaptable to demands brought by reactor, aerospace, and related technologies for specialty forms of structural materials. These properties include: (1) high-temperature heat resistance, (2) resistance to chemical attack, (3) constancy of properties with time, (4) a high strength-to-density ratio, and (5) a variety of forms into which the material can conveniently be made and the variety of properties that these forms can impact in structural applications.

As is characteristic of ceramic materials, properties of carbon are a function of microstructure (ie, crystal size, shape, and orientation). Carbon has versatility in that its crystallinity ranges from essentially amorphous to a well-ordered structure characteristic of natural flake graphite. Thus, control of carbon properties can be achieved by control of the crystalline parameters of size, shape, and orientation.

In general, organic materials which are infusible or become infusible prior to pyrolysis do not tend to produce graphitic carbon. This type of material is characterized by thermosetting resins or highly crosslinked polymers. On the other hand, thermoplastic materials or materials with a low degree of crosslinking provide viscosities that are conducive to molecular rearrangement and reorientation prior to pyrolysis; and, thus, tend to form graphitic carbon unless stable, nonplanar intermediates are formed.

Efforts in this study at the Oak Ridge Y-12 Plant^(a) are directed toward correlations between the precursor properties and the properties of a derived carbon. By knowing the relation between precursor properties and precursor-derived carbon properties, control over the latter may be exercised. This control involves two aspects: (1) reproducibility, with emphasis on the use of synthetic raw materials as carbon precursors; (2) manipulative control, which would make it possible to make carbon with specific and preselected properties by the appropriate choice of precursors and processing conditions.

This report describes an evaluation of the properties of two synthetic precursors—cinnamylideneindene (CAI) and acenaphthylene (ACN). Properties of carbons derived from these two materials, as well as properties of carbons derived from blends of CAI and ACN with various additives, were determined in an effort to correlate the precursor properties with the properties of the derived carbons.

(a) Operated by Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

CARBONS FROM ACENAPHTHYLENE AND CINNAMYLIDENEINDENE

MATERIALS

Synthetic Compounds

Acenaphthylene (ACN) was obtained from usual chemical supply sources. Upon carbonization and subsequent graphitization, ACN:

Acenaphthylene

yields a highly graphitic carbon.

Cinnamylideneindene (CAI) was prepared by the room-temperature condensation of indene with cinnamaldehyde in the presence of an alcoholic base.⁽¹⁾ The structure of CAI is:

Cinnamylideneindene

Since earlier studies have indicated that some inorganic substituents (ie, residual potassium hydroxide) have an effect on the properties of CAI-derived carbon,⁽²⁾ efforts were made to use CAI with a minimum inorganic contaminant. The CAI used in this study contained less than 100 ppm potassium, as analyzed by X-ray fluorescence spectroscopy. Carbon derived from this CAI is highly graphitic.

Isotruxene (ITX):

Isotruxene

was prepared by the reaction of indene and 1,4-naphthoquinone in the presence of a tertiary amine.⁽¹⁾ Properties of carbon derived from ITX correspond to those of a fine-grain, isotropic carbon with a low order of graphiticity.

The synthesis of p-xylylideneindene (XYN) was accomplished by the room-temperature reaction of indene with terephthalaldehyde in the presence of an alcoholic base.⁽¹⁾ The structure of XYN shows a highly conjugated system of unsaturated bonding:

p-Xylylideneindene

Upon carbonization and subsequent graphitization, a noncrystalline carbon is obtained from XYN.

Furfurylideneindene (FAI):

was prepared by the room-temperature condensation of indene and furfural in the presence of an alcoholic base.⁽³⁾ Carbon derived from FAI is noncrystalline.

Reagents

Pyromellitic dianhydride was obtained from the usual chemical supply sources and used as received.

METHODS

Polymer Properties

Polymers examined in this study were prepared by one of two methods: (1) heating approximately two kilograms of the specified material in a stainless steel beaker under a slight flow of argon, with heating times ranging from 7 to 28 days; or (2) autoclaving the respective blends in a gas pressure autoclave for two hours at 300 or 340° C in nitrogen at an initial (room-temperature) pressure of 300 psi.

Polymer average molecular weight data were obtained with a Hewlett-Packard high-temperature vapor pressure osmometer (Model 302), using sucrose octaacetate as the calibration standard.

Gel permeation chromatographic (GPC) scans were obtained from a Waters Associates Model 200 gel permeation chromatograph. The polymers were dissolved in reagent-grade tetrahydrofuran and eluted on a column packed with Styrogel, a styrene-divinylbenzene polymer supplied by Waters Associates.

Pitch softening points, benzene insolubles, and Conradson carbon residues were determined according to ASTM D-36-66, ASTM D-2317, and ASTM D-189-65, respectively, while oxygen contents were determined by neutron activation.

Carbon Properties

Carbonization consisted of heating 30 grams of the precursors or precursor blends (prepared using a Waring blender) in a three-inch-diameter crucible to 1,000° C under an inert gas atmosphere. This procedure was rate controlled and required approximately 60 hours. Other samples containing 200 grams of precursor powders were heated in four-inch-diameter stainless steel beakers. Coke yields were calculated as the percent residue after the 1,000° C carbonization step. Some of the samples received a precarbonization air cure, which consisted of heating the samples in air to 250° C using a programmed heating cycle covering a period of approximately 50 hours. After the air cure, the samples were carbonized in 30-gram batches, as described previously.

Helium densities were calculated by determining the volume of weighed samples by the displacement of helium.

Metallographic samples were mounted in epoxy resin and placed under vacuum to remove adherent air bubbles and to impregnate the flakes. The mounted specimens were then ground successively on silicon carbide grits of 240, 320, 400, and 600 size. After cleaning to remove loose adherent silicon carbide, the samples were polished with Linde A (0.3 micrometer Al₂O₃ powder), suspended in water on Pellon cloth on a Syntron vibrating polisher. This work was followed by a final polish on the Syntron with Gamel cloth and a water suspension of Linde B (0.05 micrometer Al₂O₃ powder). The samples were then cleaned in flowing water with a cotton swab and blown dry with compressed air. Photomicrographs were made using sensitive-tint illumination on a Bausch and Lomb Research 1 metallograph.

A Siemen's Crystalloflex IV recording diffractometer with copper K_α radiation was used to obtain the X-ray diffraction data. An internal standard of sodium chloride was analyzed with each sample. Interlayer spacings were calculated from the X-ray data using the methods described by Ruland.⁽⁴⁾ The degree of graphiticity of the carbons was also expressed in terms of a g factor defined as follows by Maire and Mering:⁽⁵⁾

$$d_{002} = g(3.355) + (1 - g)3.44.$$

STUDY OF ACENAPHTHYLENE AND CINNAMYLIDENEINDENE

Properties of Acenaphthylene and Cinnamylideneindene Polymers as Functions of the Heat-Treatment Time at 250° C

Baking formed pieces to 750 - 900° C is accompanied by a loss of some of the pitch binder phase, resulting in a loss in apparent density and the development of porosity. These characteristics can be improved by pitch impregnation prior to graphitization. To be useful for impregnation, the pitches must be extremely fluid at the temperature of impregnation and free of suspended particles. Economical considerations prefer that the impregnation pitch have properties which allow indefinite storage of the pitch at the impregnation temperature.

Properties of an acenaphthylene polymer (ACN-340) and cinnamylideneindene polymer (CAI-340) were determined with respect to the heating time at 250° C in efforts to determine if degradation of the polymers occurred during the time of study. The polymers, prepared by autoclaving ACN and CAI for two hours at 340° C and 300-psi pressure (initial room-temperature nitrogen pressure), were heated under a slight flow of argon for 28 days with sampling occurring every seven days. Data obtained are listed in Table 1 and illustrated in Figures 1 through 3.

Figure 1. GEL PERMEATION CHROMATOGRAPHIC SCAN SHOWING MOLECULAR DISTRIBUTION TYPICAL OF THAT OBTAINED FROM CAI-300 THAT WAS HEAT TREATED AT 250° C.

GPC scans of the CAI-340 polymers revealed little change in the molecular distribution as the heat-treatment time increased. A GPC scan, typical of that obtained from the CAI-340, is given in Figure 1.

Significant changes in the molecular distribution of the ACN-340 polymer were noted with heat-treatment time, as indicated by the GPC scans presented in Figure 2. Comparison of the scans shows a shift to a lower-molecular-weight species with a significant increase in dimer and trimer content, indicating degradation on heating at 250° C.

As indicated in Figure 3, softening points of the CAI-340 sample increased slowly as the heat-treatment time increased, probably due to the loss of volatiles and lower-molecular-weight constituents. Softening points of the ACN-340 sample decreased to a minimum with heat-treatment time at 250° C, indicating that some degradation of the original polymer occurs upon heating. This trend corresponds nicely to the change in

Table 1
 PROPERTIES OF ACENAPHTHLYENE AND CINNAMYLIDENEINDENE POLYMERS AS FUNCTIONS
 OF THE HEATING TIME AT 250° C

Sample	Heating Time at 250° C (days)	Softening Point ⁽¹⁾ (° C)	Benzene Insolubles ⁽²⁾ (%)	Carbon Residue ³⁾ (%)	Coke Yield ⁽⁴⁾ (%)	X-Ray Diffraction Data ⁽⁵⁾		
						d ₀₀₂ (Å)	L _c (Å)	g Factor
Acenaphthylene Polymer								
A	0	210.5	0.25	38.9	42	3.364	650	0.884
B	7	150.8	1.38	42.2	46			
C	14	130.0	-	46.4	49			
D	21	169.8	-	57.5	61			
E	28	224.5	47.2	77.5	77	3.362	700	0.907
Cinnamylideneindene Polymer								
A	0	67.2	0.04	33.7	46	3.374	300	0.767
B	7	100.2	0.34	39.1	50	3.373	450	0.779
C	14	109.0	0.33	40.1	52	3.371	400	0.802
D	21	121.8	0.08	42.3	53	3.373	350	0.779
E	28	126.2	0.15	43.3	53	3.371	300	0.802

(1) Ring and ball method, ASTM D-36-66.

(2) ASTM D-2317.

(3) Conradson, ASTM D-189-65.

(4) Carbonized to 1,000° C in an inert atmosphere.

(5) Obtained after firing for one hour at 2,800° C.

Figure 2. GEL PERMEATION CHROMATOGRAPHIC SCANS SHOWING THE MOLECULAR DISTRIBUTIONS OF ACN-340 DURING HEAT TREATMENT AT 250° C. (Scans are in the Order of Increasing Molecular Size)

molecular distribution noted in the GPC scans in Figure 2. For heating times longer than 14 days, loss of volatiles and lower-molecular-weight species resulted in an increase in the softening point.

Conradson carbon residues and coke-yield values for the CAI-340 samples appear to reach maximum values of approximately 44 and 53 percent, respectively, as the heat-treatment time at 200° C increased. Since little change in the molecular distribution was noted as the heating time increased, little variance in carbon residues and coke yields was expected. Thus, after an initial weight loss due to volatiles and lower-molecular-weight species, carbon residues and coke yields were reasonably constant for the CAI-340 samples as the heating time increased.

Figure 3. PROPERTIES OF ACN-340 AND CAI-340 AS FUNCTIONS OF THE HEAT-TREATMENT TIME AT 250° C.

Coke yields and carbon-residue values of the ACN-340 samples increased rapidly as the heating time at 250° C increased. Thus, the dimer and trimer, formed in increasing amounts during the study, must be quite stable compared to the other species present. Upon carbonization, lower-molecular-weight species and volatiles were still lost, but coke yields and carbon residues increased due to the increased amount of dimer and trimer present.

As noted in Table 1, interlayer-spacing (d_{002}) and crystallite-size (L_c) values showed no significant change as the heat treatment time increased. Microstructures typical of the carbons derived from the ACN-340 and CAI-340 samples are given in Figure 4.

In summary, there were significant changes in the physical properties of the ACN-340 upon extended time at 250° C. Extended heat treatment at 250° C results in the increasing formation of dimer and trimer polymer constituents which, in turn, causes variations in polymer properties and the carbon properties of coke yield and carbon residue. However, changes in the CAI-340 were not drastic relative to the original values and probably reflect the loss of volatiles upon extended heat treatment. Carbon crystallinity and the degree of graphiticity were not visibly altered in either the ACN-340 or CAI-340 system as the heat treatment time increased. Thus, CAI-340 could be applicable for uses involving impregnations, while ACN-340 may require alteration of process requirements if used for extended periods.

Properties of Carbons Derived from Acenaphthylene and Cinnamylideneindene as Functions of Temperature

Properties of carbons derived from cinnamylideneindene (CAI) and acenaphthylene (ACN) were measured as a function of temperature over the range from 1,000 to 2,800° C. The 1,000° C carbons were obtained by heating the raw materials on a programmed cycle to 1,000° C, with a two-hour hold time at the maximum temperature. Successive heat treatments involved heating aliquots of the 1,000° C carbons to the respective temperature by use of a carbon induction furnace. All of the samples, except for the 2,800° C samples, were heated at the maximum temperature for thirty minutes. The 2,800° C samples were heated for one hour at temperature. The resulting carbon data are presented in Table 2.

As noted in Figure 5, helium densities of ACN-derived carbons increased to an apparent maximum as the temperature increased from 1,000 to 1,500° C, then decreased to a fairly constant value over the temperature range from 1,700 to 2,500° C. This density decrease was probably due to shrinkage and closing of pore entrances. Helium densities of CAI-derived carbons were essentially constant as the temperature increased to 1,800° C. In the temperature range from 1,800 to 2,200° C, the helium density of the CAI-derived carbon increased, indicating a volume contraction. Above 2,200° C, helium density values were essentially constant.

Interlayer-spacing values of the ACN-derived carbons revealed a slow growth of the graphitic structure as the temperature increased to 2,000° C. In the temperature range from 2,000 to 2,500° C, three-dimensional ordering occurred as the d_{002} values decreased from 3.423 to 3.372 Å. Ordering occurred at a much slower rate above 2,500° C. Corresponding L_c values

I487-1

I92-5

Figure 4. MICROSTRUCTURES OF TYPICAL CARBONS (AFTER 2,800° C) DERIVED FROM ACN-340 AND CAI-340. (Sensitivity: 250X)

Table 2
 PROPERTIES OF CARBONS DERIVED FROM ACENAPHTHYLENE
 AND CINNAMYLIDENEINDENE AS FUNCTIONS
 OF THE TEMPERATURE

Temperature ⁽¹⁾ (° C)	Helium Density ⁽²⁾ (gms/cm ³)	X-Ray Diffraction Data		
		d ₀₀₂ (Å)	L _c (Å)	g Factor
<u>Cinnamylideneindene</u>				
1,000	1.88	(3)	-	-
1,250	1.97	(3)	-	-
1,500	2.08	(3)	-	-
1,760	2.04	3.4160	58	0.279
2,020	2.14	3.4292	95	0.062
2,480	2.22	3.3812	114	0.684
2,800	2.22	3.3640	230	0.881
<u>Acenaphthylene</u>				
1,000	1.97	(3)	-	-
1,250	2.14	(3)	-	-
1,500	2.24	3.4292	41	0.062
1,760	2.14	3.4250	87	0.087
2,020	2.16	3.4190	141	0.244
2,480	2.16	3.3730	236	0.779
2,800	-	3.3622	385	0.905

(1) Samples heated for 30 minutes at the indicated temperature in an Astro Model 1000A furnace. Samples at 2,800° C heated for one hour in a carbon-induction furnace.

(2) Density obtained by helium displacement.

(3) No measurable peaks on the X-ray diffractions scans.

increased slowly in the temperature range from 2,000 to 2,500° C, and more rapidly at temperatures above 2,500° C. The d₀₀₂ and L_c values for the 2,800° C carbons are those of a highly graphitic carbon. Figure 4 contains a photomicrograph which shows the microstructure that is typical of carbons obtained from ACN.

Interlayer-spacing values for carbon derived from CAI indicated an apparent maximum in disorientation as the temperature increased to 2,000° C, though helium-density values indicated an increase in the degree of crystallinity and orientation for this region. Variance in the d₀₀₂ values probably does not go through a maximum and, thus, should resemble the data obtained for the ACN carbons. Since the carbons from both CAI and ACN have such a low order of graphiticity in this region, X-ray diffraction scans tend to be quite diffuse. Thus, the d₀₀₂ and L_c values obtained in this region contain a higher degree of error than the helium-density values.

At temperatures above 2,000° C, crystallite growth processes predominate and the variance in the d₀₀₂ values again resemble that noted for the ACN-derived carbons, though L_c values increased at a much slower rate than the L_c values for ACN-derived carbons. The interlayer-spacing and crystallite-size values of the 2,800° C carbon are those of a highly graphitic structure, though less graphitic than that obtained from ACN. A microstructure typical of carbon derived from CAI can also be seen in Figure 4.

Figure 5. PROPERTIES OF CARBONS DERIVED FROM ACENAPHTHYLENE AND CINNAMYLIDENEINDENE AS FUNCTIONS OF TEMPERATURE.

In summary, it can be said that the densification at 1,400 to 1,600°C and the ordering of the crystal structure above 2,000°C of carbon derived from ACN are quite common to graphitizing carbons. Though CAI-derived carbons densify in the temperature range from 1,800 to 2,100°C, ordering of the crystal structure also occurs in the temperature range corresponding to graphitizing carbons. Carbon data indicate that CAI-derived carbon is of a lower order of graphiticity than is ACN-derived carbon.

Properties of Carbons Derived from Blends of Acenaphthylene with Pyromellitic Dianhydride

Thermal degradation of pyromellitic dianhydride (PMDA) results in the production of highly reactive, short-lived benzyne intermediates:

The usefulness of PMDA as a crosslinking agent for controlling the degree of fluidity and/or molecular mobility of carbon precursors during polymerization and pyrolysis has been reported in earlier reports.^(2, 6) For example, properties of carbon derived from CAI/PMDA blends reflected a decreasing degree of graphiticity as the PMDA content increased.⁽²⁾

Blends of ACN and PMDA were carbonized to determine if the properties of ACN-derived carbons could be altered by the addition of PMDA. The resulting carbon data are listed in Table 3.

As noted in Figure 6, coke yields increased steadily as the PMDA content increased, while the graphitic properties decreased with increasing PMDA content. Thus, the amount of crosslinking and/or nonplanarity occurring during polymerization and pyrolysis increased as the PMDA content increased.

Microstructures, shown in Figure 7, also reveal the decrease in graphitic character as the PMDA content increased. Little microstructural change was noted among carbons from blends containing up to 20 percent PMDA. However, as the PMDA content increased from 20 to 30 and 40 percent, significant decreases in crystallinity were observed. Carbons from blends containing PMDA concentrations of 40 percent or higher were noncrystalline. Thus, the addition of PMDA to ACN alters the properties of the carbon derived from ACN in a reproducible and controllable manner.

Table 3
PROPERTIES OF CARBONS DERIVED FROM
ACENAPHTHYLENE/PYROMELLITIC
DIANHYDRIDE MIXTURES

Sample	PMDA Content (%)	Coke Yield ⁽¹⁾ (%)	X-Ray Diffraction Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	30	3.3622	385	0.905
B	10	35	3.3616	379	0.912
C	20	37	3.3644	336	0.879
D	30	38	3.3684	232	0.833
E	40	50	3.4268	40	0.078
F	50	46	(3)	-	-

(1) Obtained after heating to 1,000° C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800° C.

(3) No measurable peak at the 002 plane.

Properties of Carbons Derived from Blends of Acenaphthylene and Cinnamylideneindene with Furfurylideneindene

Furfurylideneindene (FAI), a thermosetting indene derivative which yields a noncrystalline carbon on graphitization, was blended with ACN and CAI in efforts to utilize the

Figure 6. PROPERTIES OF CARBONS DERIVED FROM ACENAPHTHYLENE/PYROMELLITIC DIANHYDRIDE MIXTURES AS FUNCTIONS OF THE PYROMELLITIC DIANHYDRIDE CONTENT.

thermosetting properties of the FAI as a crosslinking agent. Data for the carbonized blends are presented in Table 4.

Acenaphthylene/Furfurylideneindene Mixtures - As indicated in Figure 8, coke yields gradually increased as the FAI content increased, while no significant change in the degree of graphiticity occurred for compositions corresponding to less than 60 percent FAI. For FAI contents greater than 60 percent, a rapid decrease in the degree of graphiticity was observed.

(a) 20% PMDA.

MS-71-0839-8

(b) 30% PMDA.

MS-71-0839-9

(c) 40% PMDA.

101 8

Figure 7. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ACENAPHTHYLENE/PYROMELLITIC DIANHYDRIDE MIXTURES. (Sensitive Tint; 250X)

Figure 8. PROPERTIES OF CARBON DERIVED FROM ACENAPHTHYLENE/FURFURYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE FURFURYLIDENEINDENE CONTENT.

Table 4
PROPERTIES OF CARBONS DERIVED FROM MIXTURES OF
FURFURYLIDENEINDENE WITH ACENAPHTHYLENE
AND CINNAMYLIDENEINDENE

Sample	FAI Content (%)	Coke Yield (%)	X-Ray Diffraction Data		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
Cinnamylideneindene					
A	0	32	3.3628	248	0.898
B	10	36	3.3634	129	0.891
C	20	39	3.3656	142	0.865
D	30	44	3.3724	88	0.786
E	40	46	3.3720	93	0.791
F	50	48	3.3782	103	0.719
G(1)	50	50	3.3684	135	0.833
H(1)	60	45	3.3730	107	0.779
I(1)	70	50	3.3828	77	0.665
Acenaphthylene					
A	0	30	3.3622	385	0.905
B	10	33	3.3622	423	0.905
C	20	35	3.3634	380	0.891
D	30	39	3.3634	385	0.891
E	40	41	3.3656	357	0.865
F	50	42	3.3656	301	0.865
G	60	51	3.3672	229	0.847
H	70	53	3.3724	120	0.786
I	80	54	3.3880	108	0.605

(1) Samples consisted of 200-gram blends.

Microstructures of carbons after 2,800° C (Figure 9) were highly crystalline for compositions containing up to 60 percent FAI. However, as the FAI content increased to 70 and 80 percent, the crystallinity decreased to a more homogeneous, smaller-grain microstructure and a fine-grain, homogeneous microstructure, respectively. Thus, properties of ACN-derived carbon can be altered by the inclusion of FAI. However, since concentrations of FAI greater than 60 percent are necessary to invoke noticeable changes in microstructure, possible applications of this system are limited to those uses which can tolerate the high levels of oxygen present.

Cinnamylideneindene/Furfurylideneindene Mixtures - Coke yields of carbons derived from CAI/FAI mixtures also increased steadily as the FAI content increased, as indicated in Figure 10. The degree of graphiticity decreased more rapidly with increasing FAI content than was noted for the ACN/FAI system. Thus, it appears that CAI was more susceptible to the crosslinking characteristics of the FAI during polymerization.

Microstructures of the 2,800° C carbon also revealed a decrease in graphiticity as the FAI content increased (Figure 11). Microstructures decreased in crystallinity from a highly crystalline carbon typical of CAI to a fine-grain, homogeneous carbon.

Thus, the copolymerization of CAI and FAI resulted in an increased amount of crosslinking and/or nonplanarity in the polymeric system as the FAI content increased. However, less FAI was necessary to effect noticeable microstructural and graphitical changes in the CAI than was required for the ACN system, indicating a greater degree of miscibility and/or interaction between the CAI and FAI during polymerization.

In order to economically obtain the quantities of carbon necessary to fabricate parts, large batches of the precursor blends must be carbonized. To determine if carbon properties were altered by batch sizes, blends of CAI and FAI containing 50, 60, and 70 percent FAI were carbonized in 200-gram quantities. Data are recorded in Table 4 and shown in Figures 10 and 12. These data indicated that by increasing the batch size an increase in the degree of graphiticity was obtained. For example, carbon derived from a 200-gram CAI/FAI mixture containing 60 percent FAI was similar in microstructure and graphitic properties to carbon from a 30-gram CAI/FAI mixture containing 40 percent FAI.

FAI was also blended with autoclave-polymerized CAI (CAI-340) to determine if the properties of the resulting carbons were altered. Blends of the FAI and CAI-340 were prepared by adding FAI to molten CAI-340 with stirring. After stirring the mixture for approximately five minutes, the blend was allowed to cool to room temperature. Carbonization consisted of heating 30 grams of the blend to 1,000° C in an inert atmosphere, followed by heat treating the carbons for one hour at 2,800° C. Carbon data are presented in Table 5.

Coke yields of the blends increased gradually as the FAI content increased (Figure 13), probably indicative of the increased crosslinking and/or nonplanarity in the polymer system during polymerization and pyrolysis. Coke yields of the FAI/CAI-340 blends are higher than coke yields of the FAI/CAI blends; due, probably, to the loss of volatiles during the autoclaving and blend-preparation steps.

(a) 60% FAI.

I91-10

(b) 70% FAI.

I91-11

(c) 80% FAI.

I91-12

Figure 9. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ACENAPHTHYLENE/FURFURYLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

Figure 10. PROPERTIES OF CARBON DERIVED FROM CINNAMYLIDENEINDENE/FURFURYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE FURFURYLIDENEINDENE CONTENT.

Table 5

PROPERTIES OF CARBONS DERIVED FROM BLENDS OF FURFURYLIDENEINDENE AND AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE

Sample	FAI Content (%)	Coke Yield ⁽¹⁾ (%)	X-Ray Diffraction Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	47	3.3672	270	0.847
B	10	50	3.3720	169	0.791
C	20	49	3.3708	149	0.805
D	40	53	3.3770	128	0.733
E	50	55	3.3806	110	0.691

(1) Obtained after heating to 1,000° C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800° C.

The degree of graphiticity of the 2,800° C carbons decreased in a gradual manner as the FAI content increased, as indicated by Figure 13 and the microstructures shown in Figure 14. Thus, carbon crystallinity decreased from a highly crystalline, heterogeneous microstructure to a fine-grain, homogeneous microstructure as the FAI content increased from 0 to 50 percent.

Of interest was the fact that FAI has a similar effect on carbons derived from monomeric CAI and CAI-340. Since one mode of interaction (copolymerization) was eliminated by the

(a) 0% FAI.

(b) 20% FAI.

(c) 40% FAI.

(d) 50% FAI.

Figure 11. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMYLIDENEINDENE/FURFURLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

143118

(a) 50% FAI.

193-5

(b) 60% FAI.

193-6

(c) 70% FAI.

193-7

Figure 12. MICROSTRUCTURES OF CARBON (AFTER 2,800° C) DERIVED FROM LARGE BATCHES OF CINNAMYLIDENEINDENE/FURFURYLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

Figure 13. PROPERTIES OF CARBONS DERIVED FROM MIXTURES OF FURFURYLIDENEINDENE AND POLYMERIC CINNAMYLIDENEINDENE AS FUNCTIONS OF THE FURFURYLIDENEINDENE CONTENT.

use of CAI-340, a decreased reactivity of FAI with CAI-340 was expected. Since the effects were similar to each other, little copolymerization of the two materials must occur, although the two materials remain miscible in each other.

The relationship between carbon properties and the chemistry of the polymeric precursor system can be better illustrated by examining the data obtained from the autoclave polymerization of CAI and FAI.

Blends of CAI and FAI were autoclaved for two hours at 300°C and an initial (room-temperature) nitrogen pressure of 300 psi. Properties of the resulting polymers and derived carbons are listed in Table 6. Figure 15 contains a composite GPC scan showing the variation in molecular distribution as the FAI content was varied. As the FAI content increased, the average molecular size increased, which is indicative of an increased degree of crosslinking to form higher-molecular-weight entities. Average-molecular-weight values, shown in Figure 16, reinforce the argument that higher-molecular-weight entities are formed, in that the average molecular weights of the polymers increased steadily as the FAI content increased. Ring-and-ball softening points of the polymers increased rapidly due to the increased concentration of the higher-molecular-weight components.

As would be expected, oxygen contents of the polymers increased as the FAI content increased. As noted with the polymers, properties of carbon derived from these polymers correspond to the graduated change from a thermoplastic to a thermosetting polymer system. Coke yields after 1,000°C increased steadily as the FAI content increased. Crystallite-size and g-factor values obtained for the 2,800°C carbons decreased as the FAI content increased, further indicating a trend to a more crosslinked and/or nonplanar system.

Figure 14. MICROSTRUCTURES OF CARBON DERIVED FROM MIXTURES OF FURFURYL IDENEINDENE AND AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE. (Sensitive Tint; 250X)

Table 6
 PROPERTIES OF POLYMERS PREPARED BY AUTOCLAVING MIXTURES OF
 CINNAMYLIDENEINDENE AND FURFURLIDENEINDENE

Sample(1)	FAI Content (%)	Softening Point (° C)	Polymer Average Molecular Weight(2)	Oxygen Content(3) (%)	Coke Yield(4) (%)	Carbon Data(5)		
						d ₀₀₂ (Å)	L _c (Å)	g Factor
A	0	50	421	0.66	44	3.3662	230	0.858
B	25	85	555	2.01	47	3.3656	127	0.865
C	50	125	663	2.99	53	3.3816	106	0.679
D	75	195	856	4.47	61	3.3916	73	0.563
E	100		(6)	5.65	75	3.4148	70	0.293

- (1) Samples autoclaved for two hours at 300° C and 300 psi (initial N₂ pressure).
 (2) Determined by vapor pressure osmometry.
 (3) Determined by neutron activation.
 (4) Carbonized in an open, four-inch-diameter boat and in an argon atmosphere on a programmed cycle to 2,800° C. Samples contained 30 grams of polymer.
 (5) Obtained after heating for one hour at 2,800° C.
 (6) Sample contained 79 percent insolubles, making molecular weight determination biased.

Figure 15. GEL PERMEATION CHROMATOGRAPHIC SCANS OF AUTOCLAVE-PRODUCED POLYMERS OF CINNAMYLIDENEINDENE AND FURFURLIDENEINDENE.

Microstructures of the 2,800° C carbons, shown in Figure 17, also indicated a graduated decrease in carbon crystallinity as the FAI content increased. Thus, the crystallinity changes

Figure 16. PROPERTIES OF AUTOCLAVED BLENDS OF CINNAMYLIDENEINDENE AND FURFURLIDENE-INDENE.

from a highly crystalline, heterogeneous structure typical of the CAI-derived carbon to a noncrystalline structure typical of the FAI-derived carbon.

(a) 0% FAl.

(b) 25% FAl.

(c) 50% FAl.

(d) 75% FAl.

Figure 17. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTCLAVED BLENDS OF CINNAMYLIDENEINDENE AND FURFURLIDENEINDENE.
(Sensitive Tint; 250X)

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In summation, addition of FAI to CAI and ACN allows for control of properties of the respective derived carbons.

Properties of Carbons Derived from Blends of Acenaphthylene and Cinnamylideneindene with p-Xylylideneindene

The high degree of conjugation present in p-xylylideneindene (XYN) results in crosslinking characteristics which hinder molecular mobility in the stages prior to pyrolysis and thus produces a thermosetting rather than a thermoplastic material. Consequently, upon heating to 1,000° C and subsequent firing at 2,800° C, a noncrystalline carbon is obtained from XYN. Efforts to control the properties of the carbons led to the copolymerization of ACN and CAI with XYN in order to utilize the potential crosslinking character of XYN. Data obtained for the blends are listed in Table 7.

Table 7
PROPERTIES OF CARBONS DERIVED FROM MIXTURES OF
p-XYLYLIDENEINDENE WITH CINNAMYLIDENEINDENE
AND ACENAPHTHYLENE

Sample	XYN Content (%)	Coke Yield ⁽¹⁾ (%)	X-Ray Diffraction Data ⁽²⁾		
			d ₀₀₂ (Å)	L _c (Å)	g Factor
<u>Cinnamylideneindene</u>					
A	0	37	3.3582	114	0.951
B	10	38	3.3668	147	0.851
C	20	44	3.3708	79	0.805
D	30	44	3.3730	70	0.779
E	40	48	3.3782	63	0.719
F	50	53	3.3834	67	0.658
G	60	56	3.3846	57	0.644
<u>Acenaphthylene</u>					
A	0	30	3.3622	385	0.905
B	10	37	3.3662	305	0.858
C	20	42	3.3712	180	0.798
D	30	45	3.3690	204	0.826
F	40	49	3.3668	270	0.851
F	50	51	3.3684	218	0.833
G	60	54	3.3650	201	0.872
H	70	55	3.3764	126	0.740
I	80	57	3.3834	98	0.658

(1) Obtained after heating to 1,000° C in an inert atmosphere.

(2) Obtained after firing for one hour at 2,800° C.

Acenaphthylene/p-Xylylideneindene Mixtures - Coke yields of carbons derived from ACN/XYN blends increased steadily as the XYN content increased to 80 percent (Figure 18), while g factors of the corresponding 2,800° C carbons were more erratic. The crystallinity decreased to an apparent minimum as the XYN content increased from 0 to 20 percent and increased somewhat in the composition range corresponding to 30 to 60 percent XYN. Compositions containing greater than 60 percent XYN rapidly decreased in crystallinity.

Figure 18. PROPERTIES OF CARBONS DERIVED FROM ACENAPHTHYLENE/p-XYLYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE p-XYLYLIDENEINDENE CONTENT.

Microstructures shown in Figure 19 also reveal the transition in crystallinity with increasing XYN content. A subtle decrease in crystallinity was evident as the XYN content increased from 10 to 50 percent, while increasing the XYN content 70 to 80 percent resulted in carbons with a significant decrease in crystallinity.

The gradual increase in coke yields as the XYN content increased implied a gradual increase in the crosslinked character of the precursor blend. However, X-ray data revealed that the degree of crosslinking and/or nonplanarity in the precursor during polymerization and/or pyrolysis was erratic for XYN concentrations lower than 60 percent. For higher concentrations (70% or greater), the degree of crosslinking and/or nonplanarity appeared to increase rapidly as the XYN content increased.

Cinnamylideneindene/p-Xylylideneindene Mixtures - As noted in Figure 20, coke yields of CAI/XYN blends increased steadily as the XYN content increased, while the degree of graphiticity decreased gradually with increasing XYN. Thus, the degree of crosslinking in the CAI/XYN precursor system must be increasing with increasing XYN content.

Microstructures of the 2,800° C carbons, shown in Figure 21, revealed a gradual decrease in carbon crystallinity from a highly crystalline carbon typical of CAI to a fine-grain, homogeneous carbon as the XYN content increased from 0 to 50 percent.

Copolymerization of the CAI/XYN blends apparently include enough miscibility of one precursor in the other to allow the thermosetting character of XYN to decrease the molecular reorientations necessary to produce carbon of high graphiticity. Thus, the CAI/XYN system affords carbon which has reproducible and controllable properties.

(a) 10% XYN

MS-71-0838-6

(b) 50% XYN.

MS-71-0838-10

(c) 70% XYN.

192-2

(d) 80% XYN.

192 3

Figure 19. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ACENAPHTHYLENE/p-XYLYLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

Figure 20. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEINDENE/*p*-XYLYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE *p*-XYLYLIDENEINDENE CONTENT.

Properties of Carbons Derived from Blends of Acenaphthylene and Cinnamylideneindene with Isotruxene

Isotruxene (ITX), which yields a carbon of low graphiticity, was blended with CAI and ACN in efforts to alter the properties of the highly graphitic carbons derived from these two precursors. Carbon data obtained from these blends are listed in Table 8.

Acenaphthylene/Isotruxene Mixtures - Coke yields of carbons derived from the ACN/ITX mixtures, and coked without a prior air cure, varied only slightly as the ITX content in the blend increased (Figure 22), while coke yields of the air-cured samples increased rapidly for blends containing greater than 40 percent ITX. As also indicated in Figure 22, the graphiticity of the corresponding 2,800° C carbons decreased slowly as the ITX content increased. Air-cured samples were of a higher order of graphiticity than samples coked without an air cure.

Microstructural transitions, shown in Figure 23, reflect the decrease in graphiticity as the ITX content increased in blends coked without an air cure. Samples decreased in crystallinity from highly crystalline carbon typical of ACN to a somewhat fine-grain, less-crystalline carbon typical of ITX. As expected from an examination of Figure 22, microstructures of carbons derived from air-cured ITX/ACN mixtures revealed little change in crystallinity as the ITX content increased (Figure 24).

(a) 0% XYN.

(b) 10% XYN.

(c) 20% XYN.

(d) 30% XYN.

(e) 40% XYN.

(f) 50% XYN.

Figure 21. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM DIFFERENT CINNAMYLIDENEINDENE/p-XYLYLIDENEINDENE MIXTURES.
Sensitive Tint: 250X

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Table 8
 PROPERTIES OF CARBON DERIVED FROM MIXTURES OF ISOTRUXENE WITH
 CINNAMYLIDENEINDENE AND ACENAPHTHYLENE

Sample	ITX Content (%)	Coke Yield (%)		Carbon Data					
				With an Air Cure			Without an Air Cure		
		With an Air Cure	Without an Air Cure	d ₀₀₂ (Å)	L _c (Å)	g Factor	d ₀₀₂ (Å)	L _c (Å)	g Factor
Cinnamylideneindene									
A	0	46	36	3.3708	154	0.805	3.3678	215	0.840
B	10	-	38	-	-	-	3.3650	152	0.872
C	15	-	37	-	-	-	3.3668	212	0.851
D	20	45	38	3.3752	125	0.753	3.3662	196	0.858
E	25	-	37	-	-	-	3.3628	160	0.898
F	40	48	41	3.3628	380	0.898	3.3622	342	0.905
G	60	53	38	3.3628	365	0.898	3.3616	383	0.912
H	80	58	38	3.3622	395	0.905	3.3764	106	0.740
I	100	60	36	3.3640	271	0.884	3.3758	121	0.747
Acenaphthylene									
A	0	30	30	3.3588	> 1,000	0.944	3.3588	807	0.944
B	20	30	31	3.3594	640	0.937	3.3594	723	0.937
C	40	31	32	3.3600	398	0.930	3.3594	521	0.937
D	60	42	31	3.3604	560	0.926	3.3622	350	0.905
E	80	54	34	3.3628	289	0.898	-	-	-
F	100	60	36	3.3640	271	0.884	3.3758	121	0.747

Figure 22. PROPERTIES OF CARBONS DERIVED FROM ACENAPHTHYLENE/ISOTRUXENE MIXTURES AS FUNCTIONS OF THE ISOTRUXENE CONTENT.

(a) 40% ITX.

G313-2

(b) 60% ITX.

G313-3

(c) 80% ITX.

G313-4

(d) 100% ITX.

G313-5

Figure 23. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ACENAPHTHYLENE/ISOTRUXENE MIXTURES. (Sensitive Tint; 250X)

(a) 20% ITX.

G314-1

(b) 80% ITX.

G314-4

Figure 24. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM A R-CURED ACENAPHTHYLENE/ISOTRUXENE MIXTURES. (Sensitive Tint; 250X)

Thus, air curing blends of ITX/ACN affords a method of increasing the coke yield while altering the graphitic properties only slightly. Samples coked without an air cure yield changing graphitic properties and little change in coke yield as the ITX content in the blends increased.

Cinnamylideneindene/Isotruene Mixtures - Properties of carbons derived from CAI/ITX blends are illustrated as a function of their ITX content in Figure 25. Coke yields of the air-cured sample increased with increasing ITX content, while coke yields of the uncured samples were essentially constant with composition. Corresponding g factors reveal a transition in graphiticity with changing composition. This transition occurred over a relatively narrow composition range for both air-cured and uncured samples. However, the specific composition at which the transition occurred differed with the cure conditions. Thus, the transition occurred over a composition range corresponding to samples containing 60 to 80 percent ITX for uncured samples, while a transition in the air-cured samples occurred at compositions corresponding to 20 to 40 percent ITX. For both cured and uncured samples, changes at other compositions were minimal.

Figure 25. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEINDENE/ISOTRUXENE MIXTURES AS FUNCTIONS OF THE ISOTRUXENE CONTENT.

Microstructures, shown in Figures 26 and 27, also reveal the transition in carbon crystallinity as the ITX content changed. Thus, air-cured samples from CAI/ITX mixtures change at ITX contents greater than 60 percent from a coarse-grain, more graphitic carbon to a fine-grain, less graphitic carbon (Figure 26), while the reverse transition occurs for uncured samples at ITX contents greater than 20 percent (Figure 27).

(a) 0% ITX.

G316-1

(b) 20% ITX.

G316-2

(c) 40% ITX.

G316-3

Figure 26. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AIR-CURED CINNAMYLIDENEINDENE/ISOTRUXENE MIXTURES. (Sensitive Tint; 250X)

(a) 60% ITX.

G315-4

(b) 80% ITX.

G315-5

Figure 27. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMYLIDENEINDENE/ISOTRUXENE MIXTURES. (Sensitive Tint; 250X)

In summary, air curing blends of CAI and ITX resulted in a gradual increase in coke yields as the ITX content in the blend increased, and an apparent minimum in crystallinity in the composition range corresponding to 0 to 40 percent ITX. Uncured samples yielded essentially constant coke-yield values and showed a decrease in crystallinity in the composition range corresponding to 60 to 80 percent ITX.

CONCLUSIONS

The data in this report show the versatility of acenaphthylene (ACN) and cinnamylideneindene (CAI) as carbon precursors. Thermal data show that a CAI polymer has adequate stability for extended periods at elevated temperatures as, for example, would be necessary for impregnating applications. Thermal data of an ACN-polymer show less potential for impregnating applications. Versatility of the precursors was demonstrated by the ability to modify properties of the ACN and CAI-derived carbons by inclusion of various additives. These blends can be used to produce carbons that cover a wide range of crystalline properties.

REFERENCES

- (1) Smith, W. E., Napier, B., Jr, and Harper, W. L.; *Preparation and Characterization of Hydrocarbon Derivatives of Indene*, Y-1712; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; April 21, 1970.
- (2) Smith, W. E., Horne, O. J., Jr, Napier, B., Jr, Larson, E. A., and Harper, W. L.; *Properties of Carbon Derived from Indene Compounds*, Y-1790; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; September 15, 1971.
- (3) Wuest, H. M.; "Isomerism of Benzfulvenes and Indenes", *Ann*, pp 415, 291 (1918).
- (4) Ruland, W.; "X-Ray Diffraction Studies on Carbon and Graphite", *Chemistry and Physics of Carbon*, 4, p 1, Edited by P. L. Walker, Jr; Marcel Dekker, Inc, New York (1968).
- (5) Maire, J., and Mering, J.; *Proceedings of the Fourth Carbon Conference*, p 345; Pergamon Press, New York (1960).
- (6) Horne, O. J., Jr, Smith, W. E., and Napier, B., Jr; *Properties of Carbon Derived from Petroleum Pitches*, Y-1875; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; June 21, 1973.

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