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EFFECT OF CROSSLINKING ADDITIVES ON
THE PROPERTIES OF CARBONS DERIVED
FROM SELECTED PRECURSORS

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MASTER

**UNION
CARBIDE**

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
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Oak Ridge Y-12 Plant

P.O. Box Y, Oak Ridge, Tennessee 37830

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ABSTRACT

A study has been made of the effect of various crosslinking additives on the properties of carbons derived from several precursors. Included in the group of additives were: furfurylideneindene, furfurylidene fluorene, p-xylylideneindene, p-xylylidene fluorene, pyromellitic dianhydride, H-Resin Type 3, dicyclopentadiene, and norbornadiene. By blending one of these additives with either a synthetic or commercial carbon precursor, a wide variety of carbon properties was obtained, thus affording avenues to control these properties by a controlled modification of the precursors.

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SUMMARY

The primary goal of this study was to evaluate the crosslinking capability of various materials by correlating properties of carbons derived from blends of the additive and a well-characterized precursor with the additive type and content. Included in the group of additives were: furfurylideneindene (FAI), furfurylidene fluorene (FAF), p-xylylideneindene (XYN), p-xylylidene fluorene (XYF), pyromellitic dianhydride (PMDA), H-Resin Type 3 (H-3), dicyclopentadiene (DCPD), and norbornadiene (NBD). Blends of these additives with an appropriate precursor resulted in carbons exhibiting a wide range of properties. Crosslinking agents that were found to be effective with the following precursors in producing controlled carbon with homogeneous properties were: (1) acenaphthylene-H-3 resin and DCPD; (2) cinnamylideneindene-FAF, XYF, DCPD, and NBD; (3) cinnamylidene fluorene-FAI, XYN, and PMDA; (4) Ashland-240 Pitch-XYF and NBD.

INTRODUCTION

Nuclear applications

Recent developments associated with reactor and aerospace technology place emphasis on strong, low-density materials such as carbon. Thus, there is a renewed interest in carbon and particularly in those factors which influence its properties.

Properties of carbon are largely determined by the molecular structure of the precursor materials and the reaction mechanisms which the precursors undergo to become carbon. In general, the ability of a precursor to yield a graphitic structure depends upon the precursor's ability to assume the planar aromatic structure characteristic of the graphite unit cell. Thus, processes such as bond cleavage, molecular rearrangements, cyclization, aromatization, and dehydrogenation are involved in the transition of a precursor to carbon. Factors which prevent these processes from occurring in a prescribed order and at prescribed rates favor the formation of a nongraphitic carbon, and varying degrees of inhibition would result in varying graphiticity. Materials which "thermoset" into highly crosslinked polymers do not tend to rearrange prior to pyrolysis due to the reduced degrees of molecular freedom. These materials do not tend to yield graphitic carbon. However, thermoplastic materials or materials with a low degree of crosslinking allow viscosities in which molecular rearrangements with reorientations can occur, and tend to form graphitic carbons unless stable, nonplanar intermediates are formed.

Efforts in this study at the Oak Ridge Y-12 Plant^(a) are directed toward correlating carbon properties with precursor properties. By knowing the relation between precursor properties and precursor-derived carbon properties, control over the latter may be exercised.

This report describes an evaluation of the effect of various crosslinking additives on carbons derived from several precursors. Properties of carbons derived from blends of the precursor and crosslinking additives were determined in efforts to correlate carbon properties with precursor composition.

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

EFFECT OF ADDITIVES ON PRECURSOR-DERIVED CARBONS

PRECURSOR MATERIALS

Acenaphthylene

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

Acenaphthylene

yields a highly crystalline carbon. Factors which influence the properties of ACN-derived carbon have been the subject of earlier reports.^(1,2)

Cinnamylideneindene

Cinnamylideneindene (CAI) was prepared by the room-temperature condensation of indene with cinnamaldehyde in the presence of an alcoholic base.⁽³⁾ The structure of CAI is:

Cinnamylideneindene

Properties of carbon derived from CAI are those of a highly crystalline, heterogeneous carbon. Factors which influence the properties of CAI-derived carbon have been presented in earlier reports.^(1 - 4)

The CAI polymer used in this study (CAI-340) was prepared by heating the monomer in a gas-pressure autoclave for two hours at 340° C. Carbon derived from CAI-340 is also highly crystalline.

Cinnamylidenefluorene

Cinnamylidenefluorene (CAF):

Cinnamylidenefluorene

was prepared by slowly adding 300 milliliters of a methanolic solution containing 198 grams of cinnamaldehyde to 1500 milliliters of a methanolic solution containing 166 grams of fluorene (an indene analogue):

Fluorene

and 50 grams of potassium hydroxide.⁽⁵⁾ The reaction mixture was heated under reflux during the addition and for one hour afterward. On cooling, a light-yellow, crystalline solid was collected, representing a product yield of 63 percent. Carbon derived from CAF is highly crystalline.⁽⁴⁾

α -Methylcinnamylideneindene

Preparation of α -methylcinnamylideneindene (MCAI):

α -Methylcinnamylideneindene

involves the reacting of indene and α -methylcinnamaldehyde (3:2 molar ratio) in the presence of methanol and tetramethylammonium hydroxide (TMAH) solutions. In practice, indene (58 gms) was added to a solution of methanol (300 mls) and TMAH (55.8 gms of 20% TMAH in methanol), and the aldehyde (49 gms) was subsequently added in one portion. After stirring for one hour, the bright-yellow product (MP = 83° C) was collected by filtration. Product yields were approximately 20%. Carbon derived from MCAI is highly crystalline.

Isotruxene

Isotruxene (ITX) was prepared by the reaction of indene and 1,4-naphthoquinone in the presence of a tertiary amine.⁽³⁾ Properties of carbon derived from ITX correspond to those of a fine-grain, isotropic carbon with a low order of graphiticity. The ITX used in this study was oxidatively polymerized by heating for 40 hr at 300° C with an air flow of 300 cm³/min. This pretreatment results in a polymeric form of ITX and yields a highly crystalline carbon on carbonization and subsequent graphitization.⁽⁴⁾

Ashland-240 Pitch

The Ashland-240 pitch (A-240) was a petroleum distillate fraction obtained from the Ashland Oil Company. A highly crystalline carbon is obtained from A-240. Properties of carbon derived from A-240 are the subject of an earlier report.⁽⁶⁾

Barrett's 15-V Pitch

Barrett's 277 15-V Pitch (15-V) was obtained from the Barrett Division of the Allied Chemical Corporation. Carbon derived from 15-V is highly crystalline.

CROSSLINKING MATERIALS

Furfurylideneindene

Furfurylideneindene:⁽⁷⁾

Furfurylideneindene

was prepared by the dropwise addition of furfural (32 gms) to indene (58 gms) in a methanol (300 mls)/TMAH (55.8 gms) solution. The reaction exothermed as the furfural was added and the product formed only after the reactants had cooled to approximately

30° C. The yellow product (MP = 80° C) was collected by filtration. Product yields were approximately 40%. A noncrystalline carbon was obtained from FAl.

Furfurylidenefluorene

Furfurylidenefluorene (FAF):

Furfurylidenefluorene

was prepared by the dropwise addition of a solution of furfural (144 mls) and methanol (100 mls) to a refluxing solution of fluorene (166 gms), potassium hydroxide (50 gms), and methanol (1,500 mls).⁽⁵⁾ Reflux conditions were necessary, due to the decreased reactivity of the methylene group compared to indene. The reaction mixture was stirred under reflux for one hour after the aldehyde addition, then poured, while hot, into two approximately equal fractions and allowed to cool. Approximately 2000 milliliters of water were added to each of the fractions, and the resulting solutions filtered and dried. A light-yellow, crystalline solid with a melting point of approximately 85° C was collected at 50% of the theoretical yield. Upon carbonization and subsequent graphitization, a noncrystalline carbon was obtained.

p-Xylylideneindene

Synthesis of p-xylylideneindene (XYN):

p-Xylylideneindene

was accomplished by the room-temperature reaction of indene with terephthalaldehyde in the presence of an alcoholic base⁽³⁾. The structure of XYN shows a highly conjugated system of unsaturated bonding. Upon carbonization and subsequent graphitization, a noncrystalline carbon is obtained from XYN.

p-Xylylidene fluorene

p-Xylylidene fluorene (XYF):

p-Xylylidene fluorene

was prepared by adding terephthalaldehyde (87 gms) in one portion to a refluxing mixture of fluorene (207.5 gms), potassium hydroxide (50 gms), and methanol (1700 mls). After refluxing and stirring for two hours after aldehyde addition, the solution was filtered and the yellow precipitate (MP = 160° C) collected and dried. Product yield was 78 percent of theoretical. A noncrystalline carbon was obtained from XYF.

H-Resin Type 3

H-Resin Type 3 (H-3) is a thermosetting resin available from Haveg Industries, Inc. Due to the chemical nature of the resin, heating rates during carbonization must be slow (~ 50/min or less).

Pyromellitic Dianhydride

Pyromellitic dianhydride (PMDA) was obtained as a white powder from the usual chemical supply sources. No carbon residue was observed when PMDA was heated to carbonization temperatures.

Dicyclopentadiene

Dicyclopentadiene (DCPD):

Dicyclopentadiene

was obtained from the usual chemical supply sources and used as received. No carbon residue was observed when DCPD was heated to carbonization temperatures. When heated in a gas-pressure autoclave for two hours at 340° C and an initial room-temperature nitrogen pressure of 300 pounds per square inch, a heterogeneous carbon with a fine-grain and noncrystalline region was obtained.

Norbornadiene

Norbornadiene (NBD):

Norbornadiene

was purchased from the usual chemical supply sources and used as received. Carbon derived from autoclaved NBD is described in a later section of this report (page 34).

METHODS

Precarbonization Treatment

Blends involving DCPD and NBD were heated for two hours at 340° C and an initial room-temperature nitrogen pressure of 300 pounds per square inch in a gas-pressure autoclave prior to carbonization. All other blends were carbonized as mixed and received no precarbonization treatment.

Carbonization and Graphitization

Carbonization usually consisted of heating 30 grams (when available) of the precursors or precursor blends in a three-inch-diameter crucible to 1000° C under an inert atmosphere. For all the blends, except those involving the H-3 resin, this procedure was rate controlled and required approximately 60 hours. Carbonization of the H-3 resin containing blends was also rate controlled, but approximately 150 hours were required for completion of the cycle. Coke yields were calculated as the percent residue after the 1000° C carbonization step.

After carbonization, samples were fired for one hour at 2800° C by using a carbon induction furnace. The resulting samples were then evaluated by metallography and X-ray diffraction.

Evaluation of Carbon Properties

Metallographic samples were mounted in epoxy resin and placed under vacuum to remove adherent air bubbles and to impregnate 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 ($0.3\ \mu\text{m}\ \text{Al}_2\text{O}_3$ powder) while 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 ($0.05\ \mu\text{m}\ \text{Al}_2\text{O}_3$ 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.⁽⁸⁾ The degree of graphiticity of the carbons was also expressed in terms of a g factor defined as follows by Maire and Mering:⁽⁹⁾

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

DISCUSSION

Evaluation of Furfurylideneindene as a Crosslinking Additive

As reported previously,^(2,6) furfurylideneindene (FAI) was an effective crosslinking agent for cinnamylideneindene (CAI), acenaphthylene (ACN), and Ashland-240 pitch. In this study, FAI was blended with α -methylcinnamylideneindene (MCAI) and cinnamylidene fluorene (CAF) in efforts to utilize the thermosetting properties of the FAI as a crosslinking agent for these two precursors.

α -Methylcinnamylideneindene/Furfurylideneindene Blends - As indicated in Figure 1, coke yields of MCAI/FAI blends increased gradually with increasing FAI content. Examination of the 2800°C carbons by metallography indicated no significant microstructural changes as the FAI concentration increased to 40 percent. Apparently, copolymerization of MCAI and FAI is significantly hindered by the presence of the branched methyl group so that the effect of crosslinking was not reflected in the carbon properties.

Figure 1. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEFLUORENE/FURFURYLIDENEINDENE AND α -METHYLCINNAMYLIDENEINDENE/FURFURYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE FURFURYLIDENEINDENE CONTENT.

Cinnamylidene fluorene/Furfurylidene indene Blends - As also shown in Figure 1, coke yields of CAF/FAI blends increased steadily as the FAI content increased, while the degree of graphiticity decreased rapidly with increasing FAI content. Thus, the degree of crosslinking in the CAF/FAI system must be increasing with increasing FAI content.

Microstructures of the 2800° C carbons, seen in Figure 2, revealed a gradual decrease in crystallinity from a highly crystalline carbon typical of CAF to a fine-grain, homogeneous carbon as the FAI content increased from 0 to 40%.

In summary, the copolymerization of CAF and FAI resulted in an increased amount of crosslinking and/or nonplanarity in the polymeric system as the FAI content increased, while no significant amount of interaction was noted for the MCAI/FAI blends.

Evaluation of Furfurylidene fluorene as a Crosslinking Additive

Furfurylidene fluorene (FAF) was blended in binary mixtures with heat-treated isotruxene (ITX), A-240, ACN, and CAI in efforts to evaluate FAF as a crosslinking agent for these precursors.

Blends of Furfurylidene fluorene with Heat-Treated Isotruxene, Acenaphthylene, and Ashland-240 Pitch - As noted in Figure 3, coke yields of heat-treated ITX/FAF, A-240/FAF, and ACN/FAF mixtures decreased steadily with increasing FAF content. Metallographic examination of the 2800° C carbons derived from these respective blends revealed no visible change in microstructure with increasing FAF content, indicating that little or no crosslinking interaction occurred for these mixtures.

Blends of Furfurylidene fluorene with Cinnamylidene indene - As can be seen in Figure 4, coke yields and g factors of CAI/FAF blends slowly increased and decreased, respectively, indicating some effect of the FAF on CAI-derived carbons. Microstructures of the 2,800° C carbons (see Figure 5) indicated a subtle decrease in carbon crystallinity with increasing FAF content.

Thus, FAF was not an effective crosslinking additive for heat-treated ITX, A-240, and ACN, while being only moderately effective for CAI. Decrease in the reactivity of FAF when compared with FAI was expected since the ethylene linkings of the five-atom ring are rendered more inactive by the extra benzene nuclei.

Evaluation of p-Xylylidene indene as a Crosslinking Additive

Effect of p-xylylidene indene (XYN) on the properties of carbons derived from CAI, ACN, and A-240 has been reported previously.^(2,6) Efforts to further evaluate XYN as a crosslinking additive involved the evaluation of properties of carbons derived from MCAI/XYN and CAF/XYN blends.

α-Methylcinnamylidene indene/p-Xylylidene indene Blends - Coke yields increased steadily for mixtures of MCAI and XYN as the XYN content increased (Figure 6). Crystallinity of the 2800° C carbons, as indicated by the g factor, indicated a gradual decrease in crystallinity with increasing XYN content. Microstructures of the 2800° C carbons

(a) With 0% FAI.

J257-1

(b) With 10% FAI.

J257-2

(c) With 20% FAI.

J257-3

(d) With 30% FAI.

J257-4

(e) With 40% FAI.

J257-5

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

(Figure 7) revealed a subtle decrease in crystallinity as the XYN content increased from 30 to 40%. As reported previously,⁽²⁾ blends of CAI and XYN containing 40% XYN resulted in a fine-grain, homogeneous carbon. Therefore, as noted for the MCAI/FAI blends, the branched methyl group resulted in a decreased reactivity between the MCAI and XYN, requiring higher concentrations of XYN to effect a significant decrease in carbon crystallinity.

Cinnamylidenefluorene/p-Xylylideneindene Blends - Coke yields and g factors of CAF/XYN blends, reported in Figure 8, increased and decreased, respectively, with increasing XYN content. Microstructures of the 2800° C carbons (seen in Figure 9) reveal a decrease in carbon crystallinity from a highly crystalline carbon typical of that derived from CAF (Figure 2, View a) to a fine-grain, homogeneous carbon derived from the blend containing 30% XYN. A similar effect was noted for carbons derived from CAI/XYN blends.⁽²⁾

In summary, copolymerization of CAF and XYN resulted in an increased amount of crosslinking which altered the properties of the carbon derived from CAF. Subtle changes in properties of MCAI-derived carbon were effected by the inclusion of XYN.

Evaluation of p-Xylylidene fluorene as a Crosslinking Additive

Effectiveness of p-xylylidene fluorene (XYF) as a crosslinking additive for CAI, heat-treated ITX, ACN, and A-240 was determined by evaluating the properties of carbon derived from mixtures of the respective precursor with XYF. A certain decrease in reactivity of XYF compared to XYN was expected, due to the presence of the additional benzene rings in the XYF.

Acenaphthylene/p-Xylylidene fluorene Blends - Coke yields of ACN/XYF blends varied only slightly and were in the range from 38 to 40%. Metallographic examination of the 2800° C carbons revealed no visible change in microstructure with increasing XYF content, indicating little or no interaction between the two. A similar trend was noted for ACN/XYN mixtures.⁽²⁾

Cinnamylideneindene/p-Xylylidene fluorene Blends - Coke yields of carbons derived from CAI/XYF blends were essentially constant over the XYF concentration range studied

Figure 3. COKE YIELDS OF CARBONS DERIVED FROM BINARY MIXTURES OF FURFURYLIDENEFLUORENE WITH HEAT-TREATED ISOTRUXENE, ASHLAND-240 PITCH, AND ACENAPHTHYLENE AS FUNCTIONS OF THE FURFURYLIDENEFLUORENE CONTENT.

(Figure 10), while the degree of graphiticity, as indicated by the g factor, decreased rapidly with increasing XYF content. Microstructures of the 2800° C carbons, shown in Figure 11,

indicated a decrease in crystallinity from a highly crystalline, heterogeneous carbon to a fine-grain, homogeneous carbon. Properties of CAI-derived carbons are affected similarly by the inclusion of XYN.⁽²⁾

Figure 4. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEINDENE/FURFURYLIDENEFLUORENE BLENDS AS FUNCTIONS OF THE FURFURYLIDENEFLUORENE CONTENT.

Heat-Treated Isotruxene/p-Xylylidene fluorene Blends - Coke yields and g factors of carbons derived from heat-treated ITX/XYF blends appeared to obtain a maximum at a XYF content of approximately 15%, and then both properties decreased with increasing XYF content (Figure 12). Microstructures, shown in Figure 13, revealed the decrease in carbon crystallinity with increasing XYF content, indicating some interaction between the XYF and heat-treated ITX.

Ashland-240 Pitch/p-Xylylidene fluorene Blends - Coke yields and g factors of carbons derived from A-240/XYF blends decreased slowly with increasing XYF content (Figure 14). A subtle change in the texture of the 2800° C carbon can be seen in Figure 15 as the XYF content increased from 20 to 40%. Carbon properties of A-240/XYN blends⁽⁶⁾

varied more noticeably than properties of carbons derived from these A-240/XYF blends.

In summary, XYF was an ineffective crosslinking additive for ACN, while being only moderately effective for CAI, heat-treated ITX, and A-240. Thus, the effectiveness of XYF as a crosslinking additive is less than that of its indene homologue, XYN.

Evaluation of H-Resin Type 3 as a Crosslinking Additive

Further efforts to control the properties of derived carbons led to the evaluation of a thermosetting resin [H-Resin Type 3 (H-3 resin)].^(b) Binary mixtures of H-3 resin with ACN, CAI, heat-treated ITX, A-240, Barrett-277 15-V Pitch (15-V), and a CAI polymer (CAI-340) were carbonized in efforts to determine if the properties of the respective derived carbons were altered. Figures 16 and 17 point out that there was an increase in the coke yields of the binary mixtures as the H-3 resin content increased.

(b) Obtained from Haveg Industries, Inc.

(a) With 20% FAF.

J250-5

(b) With 30% FAF.

J250-6

(c) With 40% FAF.

J250-7

Figure 5. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMYLIDENEINDENE/FURFURLIDENEFLUORENE MIXTURES. (Sensitive Tint; 250X)

Figure 6. PROPERTIES OF CARBONS DERIVED FROM α -METHYLCINNAMYLIDENEINDENE/p-XYLYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE p-XYLYLIDENEINDENE CONTENT.

(a) With 30% XYN.

J249-7

(b) With 40% XYN.

J249-9

Figure 7. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM α -METHYLCINNAMYLIDENEINDENE/p-XYLYLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

Figure 8. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEFLUORENE/p-XYLYLIDENEINDENE MIXTURES AS FUNCTIONS OF THE p-XYLYLIDENEINDENE CONTENT.

(a) With 10% XYF.

J257-6

(b) With 20% XYF.

J257-7

(c) With 30% XYF.

J257-8

Figure 9. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMYLIDENEFLUORENE/p-XYLYLIDENEINDENE MIXTURES. (Sensitive Tint; 250X)

Figure 10. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEINDENE/p-XYLYLIDENE-FLUORENE BLENDS AS FUNCTIONS OF THE p-XYLYLIDENEFLUORENE CONTENT.

(a) With 0% XYF.

J255-9 (b) With 20% XYF.

J255-10 (c) With 30% XYF.

J255-11 (d) With 40% XYF.

J255-12

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

Figure 12. PROPERTIES OF CARBONS DERIVED FROM HEAT-TREATED ISOTRUXENE/p-XYLYLIDENE-FLUORENE MIXTURES AS FUNCTIONS OF THE p-XYLYLIDENEFLUORENE CONTENT.

(a) With 20% XYF.

J256-10

(b) With 30% XYF.

J256-11

(c) With 40% XYF.

J256-12

Figure 13. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM p-XYLYLIDENEFLUORENE/HEAT-TREATED ISOTRUXENE MIXTURES. (Sensitive Tint; 250X)

Figure 14. PROPERTIES OF CARBONS DERIVED FROM ASHLAND-240 PITCH/p-XYLYLIDENEFLUORENE BLENDS AS FUNCTION OF THE p-XYLYLIDENEFLUORENE CONTENT.

Figure 15. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ASHLAND-240 PITCH/p-XYLYLIDENEFLUORENE MIXTURES. (Sensitive Tint; 250X)

Acenaphthylene/H-3 Resin Blends -

Microstructures of the ACN/H-3-derived carbons fired for one hour at 2800° C (Figure 18) revealed a rapid decrease in crystallinity from a highly crystalline carbon typical of that obtained from ACN to an extremely fine-grain carbon derived from the blend containing 20% H-3 resin. Blends containing greater than 20% H-3 resin were noncrystalline. Thus, H-3 resin was an effective crosslinking agent for ACN.

Blends of H-3 Resin with Cinnamylideneindene, Heat-Treated Isotruxene, Ashland-240 Pitch, and 15-V Pitch -

Microstructures of the 2800° C carbons derived from binary mixtures of H-3 resin with CAI (Figure 19), heat-treated ITX (Figure 20), A-240 pitch (Figure 21), and 15-V pitch (Figure 22) revealed similar two-phase carbons containing crystalline and noncrystalline regions. Since H-3 resin (melting point of approximately 75° C) thermosets rapidly at temperatures of approximately 120° C, interaction between the resin and CAI (melting point of 190° C) was expected to be minimal.

Decreased reactivity of ITX conferred by heat treatment overrides the possible interaction between the ITX and H-3 resin which could have occurred due to the lower melting point of the ITX pitch (130 - 150° C). Microstructures of blends of H-3 with A-240 (softening point of approximately 110° C - Figure 21) and 15-V (softening point of approximately 87° C - Figure 22) reflected the decreased reactivity of the pitches and/or the immiscibility of the H-3 resin and pitches during polymerization and pyrolysis.

Polymeric Cinnamylideneindene/H-3 Resin Blends - Since H-3 had no effect on the properties of CAI-derived carbons, interest was focused on the potential crosslinking effect of H-3 resin on a lower melting polymer of CAI. The polymer (CAI-340) had a ring-and-ball softening point of 67° C. Thus, by sacrificing some amount of relative reactivity upon changing the monomer to polymer, a system was obtained in which both the H-3 resin and CAI-340 were fluid prior to reaching the thermosetting temperature of the resin.

Figure 16. COKE YIELDS OF BINARY MIXTURES OF H-3 RESIN WITH ACENAPHTHYLENE, CINNAMYLIDENEINDENE, AND HEAT-TREATED ISOTRUXENE AS FUNCTIONS OF THE H-3 RESIN CONTENT.

Figure 17. COKE YIELDS OF BINARY MIXTURES OF H-3 RESIN WITH ASHLAND-240 PITCH AND 15-V PITCH AS FUNCTIONS OF THE H-3 RESIN CONTENT.

(a) With 0% Resin.

J26-3

(b) With 10% Resin.

J7-1

(c) With 20% Resin.

J7-2

Figure 18. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM ACENAPHTHYLENE/H-3 RESIN BLENDS. (Sensit ve Tint; 1250X)

(a) With 0% Resin.

J26-5

(b) With 10% Resin.

J7-4

Figure 19. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMYLIDENEINDENE/H-3 RESIN BLENDS. (Sensitive Tint; 250X)

(a) With 0% Resin.

J27-4

(b) With 10% Resin.

J8-4

(c) With 30% Resin.

J8-6

(d) With 40% Resin.

J27-3

Figure 20. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM BLENDS OF HEAT-TREATED ISOTRUXENE AND H-3 RESIN. (Sensitive Tint; 250X)

(a) With 0% Resin.

J27-2

(b) With 20% Resin.

(c) With 30% Resin.

J8-3

(d) With 40% Resin.

J27-1

Figure 21. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM BLENDS OF ASHLAND-240 PITCH AND H-3 RESIN. (Sensitive Tint; 250X)

(a) With 0% Resin.

J2E-1

(b) With 10% Resin.

J28-2

(c) With 30% Resin.

J28-4

(d) With 40% Resin.

J28-5

Figure 22. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM BLENDS OF 15-V PITCH AND H-3 RESIN. (Sensitive Tint; 250X)

Blends of CAI-340 and H-3 resin were prepared by heating the CAI-340 until fluidity was obtained and then adding, with stirring, the H-3 resin. The blends were then carbonized and heated to the graphitizing temperatures.

Carbon data, reported in Figure 23, indicated a rapid increase in coke yields with increasing H-3 content, along with a rapid decrease in the degree of graphiticity of the derived carbons as indicated by the g factor.

Microstructures, as seen in Figure 24, also indicated a rapid decrease in crystallinity from a highly crystalline, heterogeneous carbon typical of that obtained from CAI-340 to a fine-grain, homogeneous carbon derived from the blend containing 20% H-3. Blends containing greater than 20% H-3 resulted in noncrystalline carbons.

Therefore, in contrast to the relative unreactivity of the CAI monomer, CAI-340 must be quite susceptible to the crosslinking effects of the H-3 during pyrolysis, despite a loss of reactivity incurred by using the polymer.

In summary, H-3 resin was an effective additive for the controlled variation of properties of carbons derived from CAI-340 and ACN. For H-3 to be an effective crosslinking additive for other precursors, the precursor must be: (1) relatively reactive, and (2) fluid and miscible with the resin prior to the thermosetting temperature of the resin ($\sim 120^{\circ}\text{C}$).

Evaluation of Pyromellitic Dianhydride as a Crosslinking Additive

The structure of pyromellitic dianhydride (PMDA) is such that thermal degradation results in the production of highly reactive benzyne intermediates:

These highly reactive benzyne intermediates should be useful as crosslinking agents for controlling the degree of fluidity and/or molecular mobility of the carbon precursors during polymerization and pyrolysis, which should allow for control of the carbon properties. Usefulness of PMDA as a crosslinking additive for CAI and A-240 has been previously reported.^(2,4,6) Blends of PMDA with MCAI and CAF were carbonized to determine if PMDA could be used to obtain control of the properties of carbon derived from these two precursors.

α -Methylcinnamylideneindene/Pyromellitic Dianhydride Blends - Coke yields of carbons derived from MCAI/PMDA blends increased to an apparent maximum at a PMDA content of approximately 30%, as indicated in Figure 25, while the g factors of the 2800°C carbons indicated a rapid decrease in crystallinity with increasing PMDA content. Microstructures of the 2800°C carbons, shown in Figure 26, also revealed the transition in crystallinity from a highly crystalline carbon typical of that obtained from MCAI to a fine-grain homogeneous carbon. Similar results were noted for CAI/PMDA blends.⁽⁴⁾

Cinnamylidene fluorene/Pyromellitic Dianhydride Blends - Coke yields of CAF/PMDA blends continue to increase as the PMDA content increased to 30% (Figure 27). The degree of graphiticity, as indicated by the g factor, decreased quite rapidly, indicating interaction between the PMDA and CAF. Microstructures of the 2800° C carbons, shown in Figure 28, indicated a decrease in crystallinity as the PMDA content increased, much in the same manner as the CAI/PMDA blends.⁽⁴⁾ Thus, the inclusion of PMDA was an effective means for controlling properties of carbon derived from MCAI and CAF.

Evaluation of Dicyclopentadiene as a Crosslinking Additive

Efforts to obtain carbon property control have led to the search for organic systems which contain reactive double bonds which could give rise to crosslinking characteristics that lead to thermosetting rather than thermoplastic materials. This present study involved the evaluation of dicyclopentadiene (DCPD) as a crosslinking agent. Due to the volatility of dicyclopentadiene under normal carbonization conditions employed in this study, the binary mixtures of DCPD and the precursor were heated in a gas-pressure autoclave prior to carbonization. Coke yield data obtained from autoclaved CAI/DCPD and ACN/DCPD blends are illustrated in Figure 29.

Acenaphthylene/Dicyclopentadiene Blends - As indicated in Figure 29, coke yields of ACN/DCPD blends were essentially constant for concentrations of DCPD less than approximately 67%, while the coke yields increased rapidly as the DCPD content approached 100%. Microstructures of the respective carbons after firing to 2800° C indicated a decrease in crystallinity as the DCPD content increased (Figure 30).

Blends containing 33 and 50 percent DCPD yielded highly crystalline, heterogeneous carbons, while a fairly homogeneous, fine-grain structure was obtained from the blend containing 67% DCPD. As indicated in Figure 30, View d, carbon derived from autoclaved DCPD was heterogeneous, containing areas of varying degrees of crystallinity.

Cinnamylideneindene/Dicyclopentadiene Blends - Coke-yield values of autoclaved CAI/DCPD blends were fairly constant as the dicyclopentadiene content increased to 50% (Figure 29), but increased from approximately 33 to 73% as the dicyclopentadiene increased to 100%. Microstructures of the respective carbons after firing for one hour at 2800° C indicated a decrease in crystallinity as the dicyclopentadiene content increased (Figure 31).

Carbon derived from the polymerized blend containing 33% dicyclopentadiene was heterogeneous, showing areas with flow lines and areas of a fine-grain microstructure

Figure 23. PROPERTIES OF CARBONS DERIVED FROM BLENDS OF H-3 RESIN AND AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE.

(a) With 0% H-3 Resin.

J111-1

(b) With 10% H-3 Resin..

J111-2

(c) With 20% H-3 Resin.

J111-3

Figure 24. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM BLENDS OF H-3 RESIN AND AUTOCLAVE-POLYMERIZED CINNAMYLIDENEINDENE. (Polarized Light; 250X)

Figure 25. PROPERTIES OF CARBONS DERIVED FROM α -METHYLCINNAMYLIDENEINDENE/PYROMELLITIC DIANHYDRIDE MIXTURES AS FUNCTIONS OF THE PYROMELLITIC DIANHYDRIDE CONTENT.

(a) With 0% PMDA.

J249-1

(b) With 10% PMDA.

J249-10

(c) With 20% PMDA.

J249-11

Figure 26. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM α -METHYLCINNAMYLIDENEINDENE/PYROMELLITIC DIANHYDRIDE MIXTURES. (Sensitive Tint; 250X)

Figure 27. PROPERTIES OF CARBONS DERIVED FROM CINNAMYLIDENEFLUORENE/PYROMELLITIC DIANHYDRIDE MIXTURES AS FUNCTIONS OF THE PYROMELLITIC DIANHYDRIDE CONTENT.

(a) With 10% PMDA.

J259-1

(b) With 20% PMDA.

J258-2

(c) With 30% PMDA.

J258-3

Figure 28. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM CINNAMYLIDENEFLUORENE/PYROMELLITIC DIANHYDRIDE MIXTURES. (Sensitive Tint; 250X)

(Figure 31, View a). As the dicyclopentadiene content in the preautoclaved blend increased to 50 and 67%, the 2800° C carbons exhibited increasing homogeneity and decreasing grain size (Figure 31, Views b and c). Thus, properties of carbons derived from autoclaved ACN and CAI can be altered by the addition of DCPD to the precursor prior to the autoclaving step.

Evaluation of Norbornadiene as a Cross-linking Additive

Norbornadiene (NBD) was another organic compound which was evaluated in efforts to obtain carbon property control.

Properties of Carbon Derived from Autoclaved Norbornadiene - A black, fluffy powder was obtained in 50% yield from NBD autoclaved for two hours at 340° C and at an initial room-temperature nitrogen pressure of 300 pounds per square inch. A coke yield of 88 percent was noted after the powder was heated to 1000° C. As indicated in Figure 32, the NBD-derived carbon was uniformly spherical, with some evidence of sphere agglomeration. Sphere diameters were approximately 0.75 micrometer, as estimated by scanning electron microscopy.

X-ray diffraction data obtained on the carbon fired for one hour at 2800° C resulted in an interlayer-spacing (d_{002}) value of 3.405 Å and a crystallite-size (L_c) value of 140 Å.

Metallographic examination of the 2800° C carbon was quite difficult, due to the fine particle size of the powder. From an examination of the photomicrograph of Figure 33, a higher degree of graphiticity was expected than was indicated from X-ray data. The structure appeared to be that of a medium-to-fine-grain homogeneous carbon. Metallographic examination of the black powder prior to carbonization at 1000° C revealed a microstructure similar in appearance to that noted for the 2800° C carbon. Thus, the microstructure of the NBD carbon was established at a very early stage of pyrolysis and was essentially maintained on firing to higher temperatures.

Blends of NBD with CAI and A-240 were autoclaved and carbonized to determine if the properties of the carbon derived from these two precursors could be altered by the addition of NBD.

Cinnamylideneindene/Norbornadiene Blends - As indicated in Figure 34, coke yields of CAI/NBD blends increased rapidly for NBD contents greater than 50%, while coke yields of A-240/NBD blends were essentially constant over the NBD concentration range from 0 to 75%.

Figure 29. COKE YIELDS OF AUTOCLAVED BLENDS OF DICYCLOPENTADIENE WITH ACENAPHTHYLENE AND CINNAMYLIDENEINDENE AS FUNCTIONS OF THE DICYCLOPENTADIENE CONTENT.

(a) With 33% DCPD.

I372-10

(b) With 50% DCPD.

I372-9

(c) With 67% DCPD.

I372-11

(d) With 100% DCPD.

I161-2

Figure 30. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVED ACENAPHTHYLENE/DICYCLOPENTADIENE BLENDS. (Sensitive Tin; 250X)

(a) With 33% DCPD.

I372-3

(b) With 50% DCPD.

I372-1

(c) With 67% DCPD.

I372-2

Figure 31. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVED BLENDS OF DICYCLOPENTADIENE AND CINNAMYLIDENEINDENE. (Sensitive Tint; 250X)

(a) At 3,000X.

SM-38543

(b) At 10,000X.

SM-38542

(c) At 20,000X

SM-38541

Figure 32. SCANNING ELECTRON MICROGRAPHS OF CARBONS (AFTER 1,000° C) DERIVED FROM AUTOCLAVED NOBORNADIENE.

J207-1A

Figure 33. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVED NOBORNADIENE. (Polarized Light; 250X)

Microstructures of carbons (after 1000° C) derived from autoclaved CAI/NBD blends revealed a rapid decrease in crystallinity as the NBD content increased from 50 to 75% (Figure 35), indicating some crosslinking effect of the NBD. All carbons derived from CAI/NBD mixtures containing 50% or less NBD contained highly crystalline microstructures. Since the microstructural changes are noted at such a high NBD concentration, the mechanism evoking the change could be one of dilution rather than crosslinking.

Ashland-240 Pitch/Norbornadiene Blends - As noted in Figure 36, carbons derived from autoclaved A-240/NBD mixtures decreased in crystallinity as the NBD content increased. Subtle changes are evident as the NBD content increased from 25 to 50%, while a fairly homogeneous, fine-grain carbon was obtained from the blend containing 75% NBD. Again, dilution of the precursor is suspected to be the mode of reactivity rather than crosslinking due to the presence of at least two phases in the sample after autoclaving.

Figure 34. COKE YIELDS OF AUTOCLAVED BLENDS OF NORBORNADIENE WITH CINNAMYLIDENEINDENE AND ASHLAND-240 PITCH AS FUNCTIONS OF THE NORBORNADIENE CONTENT.

(a) With 50% NBD.

J318-5

(b) With 75% NBD.

J318-6

Figure 35. MICROSTRUCTURES OF CARBONS (AFTER 1,000° C) DERIVED FROM AUTOCLAVED BLENDS OF CINNAMYLIDENEINDENE AND NORBORNADIENE. (Sensitive Tint; 250X)

(a) With 25% NBD.

J318-1

(b) With 50% NBD.

J318-2

(c) With 75% NBD.

J318-3

Figure 36. MICROSTRUCTURES OF CARBONS (AFTER 1,000° C) DERIVED FROM AUTOCLAVED ASHLAND-240 PITCH/NOBORNADIENE MIXTURES. (Sensitive Tint; 250X)

In summary, autoclaving NBD resulted in a fluffy, carbonaceous powder which, in turn, yielded a high coke yield on heating to 1000° C. A homogeneous, medium-to-fine grain structure was noted for the 340, 1000, and 2800° C samples. Microstructural changes in carbons derived from autoclaved CAI/NBD and A-240/NBD mixtures occur only at high concentrations of NBD (~ 75%) and are probably effected by the dilution of the precursor with NBD. Thus, little or no control of properties of CAI or A-240-derived carbon was obtained by the inclusion of NBD.

CONCLUSIONS

Data presented in the report show the effect of various crosslinking additives on the properties of carbons derived from selected precursors. It was found that H-3 resin and dicyclopentadiene were effective crosslinking additives for acenaphthylene. Properties of carbons derived from cinnamylideneindene were altered by the addition of furfurylidene-fluorene, p-Xylylidene-fluorene, or norbornadiene to the precursor prior to carbonization. Furfurylideneindene, p-xylylideneindene, and pyromellitic dianhydride were found to be effective crosslinking additives for cinnamylidene-fluorene. Properties of carbons derived from Ashland-240 pitch were altered by the addition of p-xylylidene-fluorene and NBD. Thus, by selecting the appropriate precursor and additive, carbons with a wide range of crystalline properties can be produced in a controlled and reproducible manner.

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