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REVIEW ARTICLE

Coal Derived Carbons†

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1. INTRODUCTION

Research on carbonaceous solid materials is a very important area—an area which has been overlooked to a considerable extent in universities and also to a considerable extent on the national scene relative to its importance. Carbonaceous materials fall in gaps between metals, polymers, and ceramics. Persons working in these latter areas more or less disclaim responsibility for research on carbons.

I want to consider a particular precursor for the production of carbonaceous solids. One thing which is fortunate about carbon is that there are many organic precursors we can start with. We are going to consider coal as a precursor. This is one of the more important precursors used for the production of carbons. I want to consider producing two types of carbons from coal. One type will be that which has high microporosity; and by microporosity, we are talking about small pores, pores less than about 2 nm in size. Materials of this type have wide commercial applications at the moment; and, I think, have a splendid growth potential. For example, activated carbon, which is used to remove impurities from gas and water streams, is an important application of microporous carbons. Carbons as catalyst supports and molecular sieve carbons for the separation of molecules are areas which have considerable potential.

On the other hand, I am going to jump all the way to carbons that have very small microporosity. These are represented by the more graphitic materials—materials like carbon composites, electrodes for production of steel, and electrical brushes. The interesting fact about carbons is that we can, in essence, have a whole range of materials from those containing considerable microporosity to those containing essentially no microporosity. I will focus primarily on these two extremes.

The carbons being considered are polycrystalline materials. In other words the artifacts are composed of a number of crystallites. The building block in all these carbons will be primarily the, if you will, pseudographitic building block, in other words, where the carbon atoms have trigonal bonding (Fig. 1). It involves strong covalent bonding in the basal plane to three adjacent carbon atoms and weak Van der Waals bonding between basal planes. One thing that distinguishes carbons from each other is crystallite size—the average crystallite size of a carbon or the average extent of this condensed ring structure which can be measured by X-ray diffraction. But even more important is the crystallite alignment, because this is going to determine, for example, extent of microporosity in the carbon.

If we look again at this crystallite, we really have a very exciting situation. Due to the bonding being highly anisotropic in this crystallite, all the properties that can be mentioned about a solid are going to be highly anisotropic in this crystallite. They are going to differ markedly, the properties in the basal plane from those perpendicular to the basal plane. However, if we have no crystallite alignment in the artifact, in other words if we have completely random crystallite alignment, the properties in the artifact are going to be completely isotropic even though the building block has properties which are the most anisotropic of any solid which exists. As we increase this crystallite alignment from random to increasingly preferred, we are going to realize increasingly the anisotropic properties in the crystallite (in the building block).

I will be emphasizing a couple of these properties, one is microporosity. If these building blocks are very poorly aligned, they pack very poorly; and porosity exists between these building blocks. If the crystallite size is small, the void size between these building blocks is going to be small. There is going to be microporosity. On the other hand, if we go to a very high crystallite alignment, as we will for example in some carbon fibers which we will consider later, we are not going to have any significant amount of porosity between the crystallites or building blocks. Therefore, the microporosity in the fiber will be very

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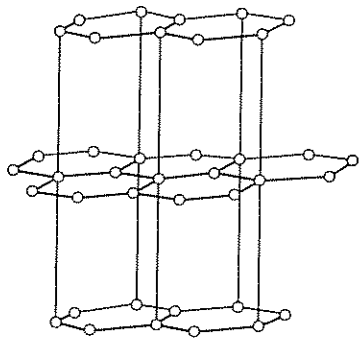

Fig. 1. The graphite crystal structure.

small. It is the understanding of how one can start with an organic precursor and from that precursor, by thermal treatment for example, convert it to a carbonaceous solid having a controlled alignment of crystallites, which represents the very heart of the materials science of carbon materials.

It turns out that the temperature range which we will be particularly interested in during thermal treatment is from about 400 to 600°C. This is the temperature range, for most organic solids, where we are going to begin losing hydrogen, be producing free-radicals, which are going to condense into larger molecular units, leading ultimately to a solid material. It is in this temperature range that crystallite alignment is going to be determined. Even though many of these carbons are eventually going to be seeing much higher temperatures of heat treatment, it is the setting of crystallite alignment below 600°C which is primarily going to determine the structure and the ultimate properties of the carbonaceous material. This is the temperature range we want to focus on in producing carbons from coal. We are going to consider first the production of carbons of high microporosity from coal.

2. CARBONS OF HIGH MICROPOROSITY

Now, there are many models of coal. The model I am considering is the so-called Wiser model (Fig. 2). There are two or three things that I want to emphasize about this precursor. First, the building blocks are primarily aromatic and hydroaromatic. The amount of aromatic to hydroaromatic structure varies with the rank of the coal. Second, there are heteroatoms at the edges of the building blocks (oxygen, sulfur, hydrogen and nitrogen), which are going to be liberated as we thermally treat this precursor at higher temperatures. Thirdly, and perhaps most important, is the extent of cross-linking between the building blocks. We can point out a couple of important cross-links in coal; one is a methylene cross-link, CH_2. The other cross-link is an oxygen ether cross-link. Consider the implication of cross-links. As the number of cross-links increases, the apparent molecular weight of the coal increases. The coal is going to change from a thermoplastic material which softens as we heat it up towards 600°C to a thermosetting material, as the number of cross-links in the original coal increases and as the number formed during thermal treatment increases. Additional cross-links are thought to form during thermal treatment as a result of condensation of hydroxyl and carboxyl groups in the coal, for example.

Now it turns out that coal is a microporous material. Most of the surface area and most of the pore volume in coals, going all the way from anthracite through the bituminous coals of Illinois to lignites, are located in pores less than 2 nm in size. So, if you were assigned the problem of converting a coal to a microporous carbon, you would certainly say that we want to preserve the microporosity in the coal. What that means is that we want the coal to behave as a thermosetting material. In other words, as we heat the coal up, we do not want it to soften. We do not want the building blocks to have an opportunity to

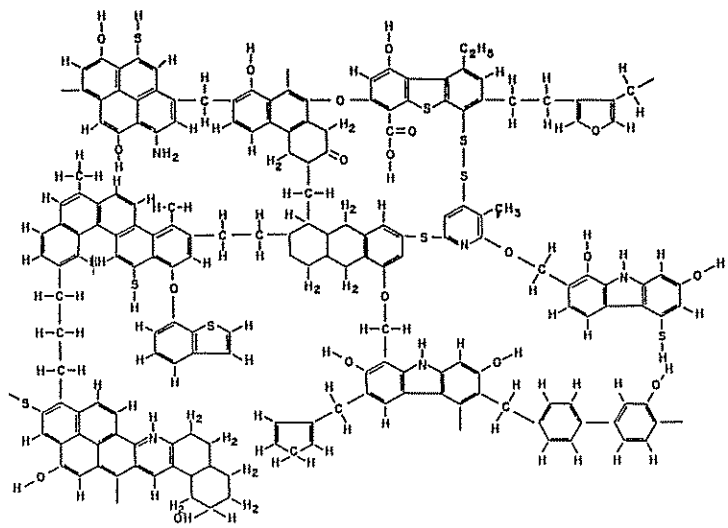

Fig. 2. A representation of bituminous coal structure.

thermally align and pack better and, consequently, lose much of the microporosity which existed in the original coal.

The problem with essentially all bituminous coals, including Illinois bituminous coals, is that they are to a considerable extent thermoplastic materials. In other words, when they are heated, they begin to soften at about 400°C, to flow to a considerable extent, and thereby are not going to produce the large microporosity which we desire. Some pretreatment of the coal is necessary to convert it from a thermoplastic to a thermosetting precursor. I want to consider some possible pretreatments.

We will consider the swelling of coal (bituminous coals) during heating and the effect which some interesting pretreatments have on reduction of this swelling. The swelling is caused by a combination of release of volatiles and softening of the coal. The volatiles exert pressure and expand the material.

Let us look at one interesting pretreatment. This is some work we have done at The Pennsylvania State University in the taking of bituminous coal to temperatures of about 100–150°C and exposing it to air. At this temperature, carbon or coal gasification is insignificant. There is an increase in weight as oxygen is added to the coal. It is thought that oxygen interacts primarily with some of the hydrogen to produce additional hydroxyl groups in the coal. Then as the pretreated coal is heated to higher temperatures in the range of 400–600°C, we get condensation of these adjacent hydroxyl groups liberating water and leaving behind an oxygen atom which produces an additional ether cross-link in the coal. The coal is converted increasingly to a more thermosetting material as more oxygen is added. Let us see how effective this pretreatment is.

What we are looking at here is volume expansion, and some coals expand considerably upon heating (Fig. 3). For example, this particular hvA bituminous coal, upon heating in N_2, expanded over 700% (seven times). Curve A is for the original coal which has not been preoxidized, and you see at about 500°C a very sizable expansion. Now as we go from curves B to G, we added increasing amounts of oxygen by air exposure at 150°C—0.3 weight % for sample B and 2.0% for sample G. Swelling is progressively removed as we add more oxygen until sample G shows no swelling. We can increase the thermosetting character of the coal in a very sensitive way. I might say that the activated carbon industry uses this approach as one of the steps in converting bituminous coals to activated carbons. Bituminous coals are the main precursor for production of activated carbons in the United States.

There are a couple other approaches we can use which we might look at. Some Polish workers[2] recently took a bituminous coal and treated it at room temperature with either concentrated HCl, concentrated HF, or their mixtures. Following acid treatment, the coal was exhaustively washed with distilled water. It is found that these acid pretreatments markedly reduce the swelling (and thus fluidity) of the coal upon heating. There is another interesting effect brought about by acid treatment. Treatment in HCl removes some mineral matter from the coal. Treatment in HF removes more mineral matter, and treatment in both acids removes essentially all the mineral matter. In many applications of the final product, this is highly desirable.

Consider another possible pretreatment which we have been studying at Penn State. Dr. R. Khan, for his Ph.D. thesis, looked at the effect of potassium carbonate (K_2CO_3) addition. Exxon Corporation, in their catalytic coal gasification process, has been adding K_2CO_3 to coal, primarily as a catalyst for its steam gasification. The interesting thing that they noted was that K_2CO_3 addition markedly reduces the fluidity of bituminous coals upon subsequent heating. Khan finds also that the addition of 20% K_2CO_3 to an Illinois bituminous coal sharply reduces its swelling. The Exxon group leaves the K_2CO_3 in the low temperature 600°C char that they produce. It serves as a catalyst for subsequent gasification of the char with steam to produce CO and H_2. Thus K_2CO_3 addition to the original coal serves two functions. It converts the bituminous coal to a thermosetting precursor—thereby retaining a high surface area in micropores upon heat treatment. It also serves as a catalyst to enhance the rate of reaction of steam with char active sites located in these micropores. Most of the potassium can be ultimately removed from the char by water washing.

Now we have our microporous char produced at about 600°C. There may be some additional things we would like to do to the char to make it a more valuable commercial product. One thing is to open up closed microporosity, because, typically, coals and their chars not only have in them microporosity which is open but also a significant amount of microporosity which is closed, in pores less than about 0.5 nm in size. These micropores are not useful because they are smaller than the size of most molecules. What we frequently do is to now selectively remove carbon atoms from this microporous, low temperature carbon by gasification in steam, CO_2, or air. Removal of carbon atoms has two results. One, we increase the average size of the micropores which are already open to the adsorbate or the gas. Second, we open up closed pores.

Let us look, quantitatively, at what happens to the pore volume in a coal char as we remove carbon atoms by gasification[3]. We can determine the pore volume open to He by measuring a He density (by He displacement) and a particle (apparent) density (by Hg displacement). In an anthracite char the starting particle density is about 1.55 g/cc (Fig. 4). As we gasify away carbon atoms, using CO_2 at 850°C up to a carbon burn-off of about 63%, there is a linear decrease in particle density. By contrast, the He density of the starting char is about 1.90 g/cc. As gasification proceeds and closed pores are opened up, there is less volume to displace He; and, as a con-

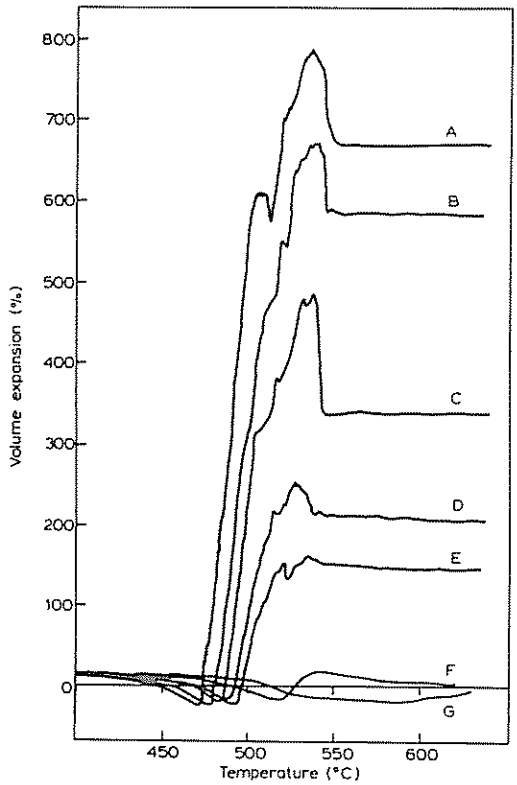

Fig. 3. Dilatometer data for an hvA coal preoxidized to different levels in air prior to heating in N_2[1].

sequence, the He density increases. Upon gasification to 63% burn-off, it approaches 2.15 g/cc, which is close to the true density of the carbon crystallites composing the remaining char. The specific pore volume in the char remaining in cc/g, is the difference of the reciprocals of the particle density and the helium density. Specific pore volume continues to increase as we increase carbon burn-off. We primarily increase micropore volume.

Let us now consider what happens to surface area as we gasify our coal char[3]. We will measure surface area using N_2 adsorption at 77 K. We will start with 1.0 g of char. The original char has a low N_2 surface area (Fig. 5). As gasification proceeds and closed pores are opened and open pores are enlarged in size, surface area increases more sharply than we lose weight; that is, the surface area remaining increases up to a point. At some point, as pore walls begin being reacted away and the total number of open pores begins to decrease with further gasification, the surface area generated begins to decrease. Typically for coal chars, the surface area generated goes through a maximum at a carbon burn-off of about 40%.

Today there is considerable interest in molecular sieve carbons for the separation of molecules of different sizes and shapes. Coal chars are viable precursors for the production of molecular sieves. If instead of gasifying a char to high burn-offs, to produce an activated carbon (of relatively large pore size), we restrict burn-off to low levels, we can produce a molecular sieve. The amount of burn-off depends upon the size of the molecules we wish to separate. We have studied, for example, the effect of small levels of burn-off of an anthracite char on the ease of penetration (diffusion) of CH_4 into the micropores of the char[4]. At a burn-off level of about 7%, CH_4 diffusion is activated, with an activation energy of about 28 kJ/mole (Fig. 6). Upon additional gasification to about 8% total burn-off, there is a large increase in the rate of CH_4 diffusion into the char and a decrease in activation energy for the diffusion to about 12 kJ/mole. Another 1% increase in char gasification to a total burn-off of about 9% results in another substantial increase in CH_4 accessi-

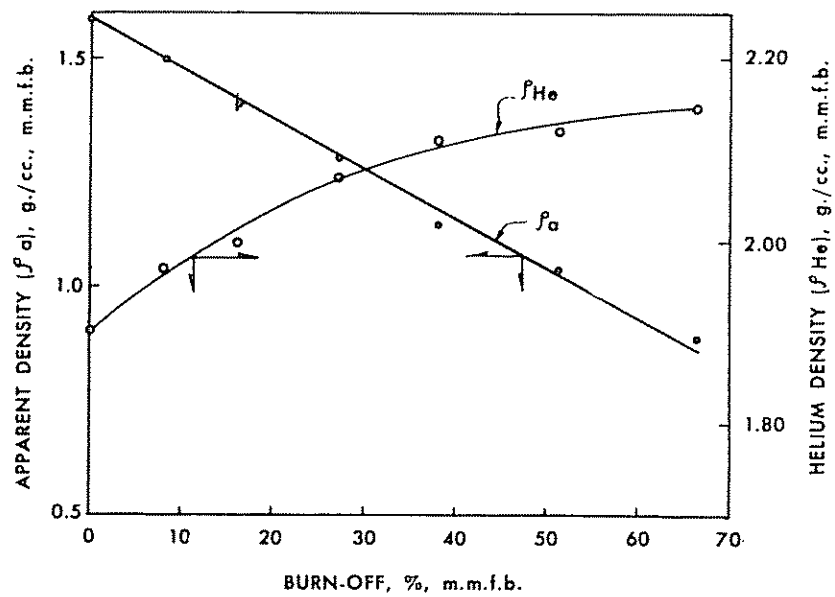

Fig. 4. Variation of densities with burn-off of anthracite char in CO_2 at 850°C[3].

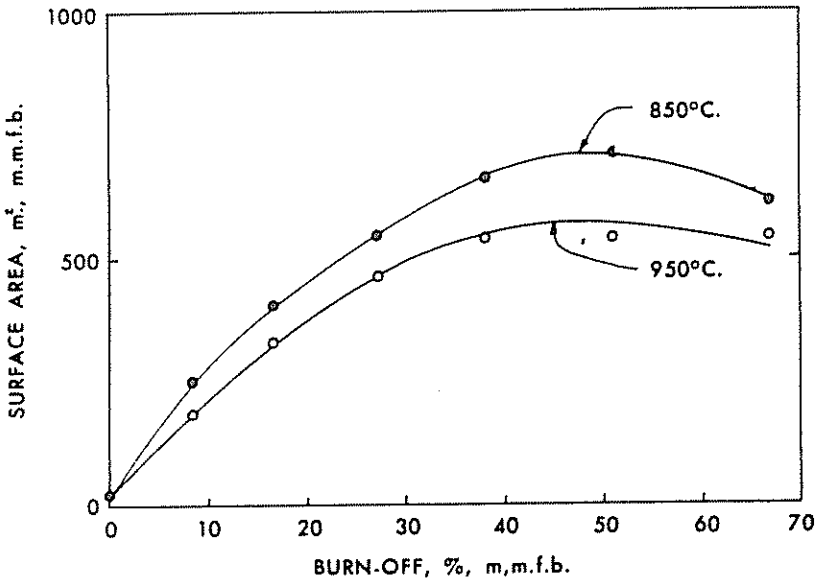

Fig. 5. Variation of surface area with burn-off of 1.0 g of anthracite char in CO_2 at 850°C and 950°C[3].

bility into the micropores. Diffusion is no longer activated, since the pore size no longer closely approximates the molecular size of CH_4. Rather diffusion is in the Knudsen regime, where the diffusion coefficient is proportional to $T^{0.5}$. Clearly small amounts of burn-off of a coal char can change its molecular sieving characteristics tremendously. Well, I think this emphasizes the real possibilities, if you will, of molecular engineering—controlling the size of openings to let molecules in, which we want to let in, and not let molecules in, which we do not want to let in.

3. CARBONS OF LOW MICROPOROSITY

So much, in rather short order, for microporous materials from coal, let us move to the other end. Let us consider more graphitic materials and materials which have in them a negligible amount of total porosity and also microporosity. These will be materials of excellent crystallite alignment. In this case, we are not going to use coal as a precursor; we are going to use a coal by-product, a coal tar, which is obtained upon the pyrolysis of coal. The reason we are going to do this is that if we want to produce very graphitic carbons we ordinarily do not want any significant amount of inorganic constituents in these carbons. In the case of coal itself, we have a considerable amount of inorganic constituents. Therefore, we are going to take an overhead material, a coal tar, produced during coal pyrolysis. We are going to convert it to a coal tar pitch by selective distillation to produce one of the important precursors for the production of graphitic materials.

The interesting thing about coal tar pitches is that they contain a large number of different organic compounds, derived from the large number of different building blocks found in coals. An area that we have found to be of considerable interest and an area again where I think there is a lot of fundamental research which can be done is to look at the behavior of a number of the important compounds which are in coal tars and coal tar pitches, to understand their conversion to carbonaceous solids. We have studied four compounds: anthracene, phenanthrene, biphenyl and phenazine. They are all contained in significant amounts in coal tars and coal tar pitches.

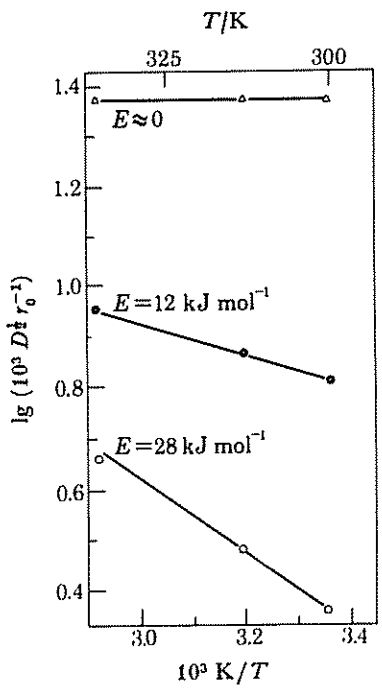

Fig. 6. Effect of burn-off of an anthracite char on ease of diffusion of methane into the micropores. Burn-offs (%): ○, 6.9; ●, 8.0; △, 9.1.

Studying the carbonization of these molecules demonstrates different principles of the carbonization process. Anthracene is a linear, planar aromatic molecule consisting of three benzene rings. Upon heating to about 450°C (in an autoclave to prevent its vaporization), it commences losing hydrogen at the 9,10 positions forming free radicals. These radicals condense producing a larger molecule—9,9′ bianthryl. Continued loss of hydrogen, free radical production and then radical condensation lead to increasingly large, planar molecules and, eventually, low-temperature coke.

Phenanthrene also consists of three benzene rings and is a planar molecule, but is branched. It is an isomer of anthracene. It also undergoes the loss of hydrogen and radical condensation reactions to ultimately produce large planar aromatics and then coke. However, branched aromatics are much less reactive than are linear aromatics. Thus, phenanthrene undergoes the loss of hydrogen at a rate some 100 times more slowly than does anthracene; its carbonization rate and, hence, rate of formation of low temperature coke is much less than that of anthracene.

Phenazine is a linear aromatic, like anthracene. However, nitrogen is substituted for carbon in the middle benzene ring (in the 9,10 positions). The presence of nitrogen accelerates the loss of hydrogen, free radical production, and thus enhances the rate of carbonization over that of anthracene.

Biphenyl contains two benzene rings which are not condensed but instead connected by a single carbon–carbon bond. It is a nonplanar molecule with free rotation around the carbon–carbon bond. Hence, upon its carbonization nonplanar free radicals are produced, which upon condensation lead to larger nonplanar molecules. As we will see, this has important implications as to the morphology of the cokes and structure of carbons which can be produced, compared to the situation when the other three aromatics are used as precursors.

Consider the carbonization of a precursor which behaves as a thermoplastic material upon heating and forms planar intermediates (as does anthracene). We can observe the carbonization process in reflected polarized light. At some temperature the compound melts (128°C for anthracene), forming an isotropic liquid. As temperature is increased to about 450°C, the viscosity of the liquid decreases or mobility of the molecules increases. At about 450°C, hydrogen is lost from reactive positions in some of the molecules, free radicals form, and condensation reactions occur. Eventually, the planar molecules become large enough in size to realize sufficient Van der Waals attraction between them to promote their alignment. At this point, anisotropic spheres (called anisotropic mesophase) appear, dispersed in the isotropic liquid. As carbonization continues the size and number of these spheres increase. Their ultimate coalescence leads to the formation of mosaic regions and, then, low temperature coke. Interestingly, biphenyl, which does not lead to planar intermediates upon carbonization, is not a precursor for anisotropic mesophase or ultimately coke having an anisotropic morphology. Rather, it leads to an isotropic coke and, ultimately, an isotropic high temperature carbon of small crystallite size.

We can do molecular engineering using mixtures of compounds as precursors. For example, if we start with phenanthrene and biphenyl, we can produce cokes and high temperature carbons of variable crystallite alignment and microporosity. The greater the phenanthrene content is in the mixture the better the crystallite alignment in the carbon, the larger its crystallite size, the higher its density, and the smaller its microporosity[5]. Figure 7 shows how the addition of biphenyl to phenanthrene sharply reduces crystallite growth in the low temperature carbon formed upon its heat treatment at 2800°C[6].

So far we have been talking about pure aromatic precursors leading strictly to carbonaceous solids. However, we may want one or more metals dispersed in our carbon. We may want to produce a composite. To do this we simply add one or more organo–metallic compounds into our original recipe. In addition to taking part in the carbonization process, they will ultimately lead to the addition of metal(s) of some particle size and morphology to the carbon. Such addition can radically change all properties of the carbon. For example, the addition of varying amounts of vinyl ferrocene (VF) to furfuryl alcohol (FA) results in the production of carbons of variable crystallinity, mechanical, and electrical properties[7]. The addition of 10% (by weight) of VF converted FA from a nongraphitizable to a graphitizable precursor upon heat treatment to 2500°C.

Let us now consider carbon fibers and carbon composites. Carbon composites are going to be one of the most important materials of the 21st century.

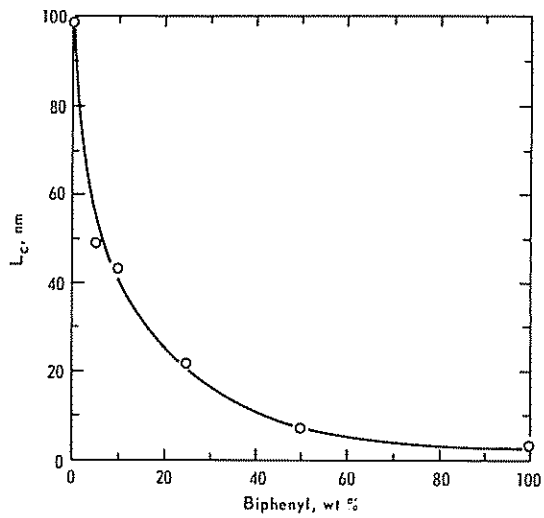

Fig. 7. Change in average crystallite height of the 2800°C carbon with the starting composition of the phenanthrene–biphenyl system[6].

They have the highest strength to weight ratio of any solid; this is extremely important for aerospace applications. They will probably be increasingly important in land transportation applications also. What structural property do we want in our composite to achieve a high strength to weight ratio? We want very high crystallite alignment, high basal plane alignment parallel to the axis of the carbon fibers. This will result in negligible porosity within the fiber. Most of the early fibers were produced using rayon and polyacrylonitrile as precursors.

More recently, in the United States, Union Carbide Corporation has pioneered the use of coal tar pitches and petroleum pitches as precursors for carbon fibers. Essentially, a carbon composite is composed of about 50% fibers bonded together by about 50% polymer or 50% pitch carbon. Bonding between the fiber surface and matrix is of extreme importance in determining the final properties of the composite. Basal planes of carbon crystallites are quite inert and bond poorly to other surfaces, whereas edges of basal planes are quite reactive and bond well. Thus, the extent of crystallite alignment in the fiber surface is an important property which will determine the extent of bonding.

Let us look at the Union Carbide approach to producing pitch fibers. What do we do? Well, the first thing we do, which is extremely important, is to get the solid's content of the pitch very low. Inorganic impurities, for example, are going to retard good coalescence of mesophase and, subsequently, good crystallite alignment. Further, upon taking the fibers to high temperatures to effect additional crystallite growth and alignment, inorganic impurities will volatilize from the fibers leaving behind unwanted voids. They will act as sources of stress concentration and reduce the tensile strength of the fiber. Most of the inorganic impurities in coal tars are present in fine particles of coke dust entrained with the tar during the coal coking operation. What has to be done, at a very minimum, is to filter the heated (liquid) coal tar to remove most of the solids. The second thing that we do is to produce some mesophase, to produce about 50% highly aligned material in the isotropic media, by heating to about 450°C[8]. Then we go through an agitation and spinning step, selecting a temperature where the viscosity of the pitch has a desirable value, that is, about 50 P. Upon drawing, the mesophase tends to align even better and to, synergistically, enhance alignment of the material which is still isotropic.

We have good alignment in the pitch fiber after drawing, and we want to preserve it. To achieve this, we heat at low temperatures in air, adding a little oxygen to the fiber. The oxygen forms some cross-links so that when we begin heating to higher temperatures the material does not soften and lose the good alignment which was achieved in the spinning step. Lastly, we heat at higher temperatures to further increase crystallite size and crystallite alignment in the fibers.

It is helpful to study fiber structure in polarized light. Most fibers that are produced commercially are in the range of 5–15 μm in diameter. In polarized light you see considerable domain structure or mosaic structure, if you will, running parallel to the fiber axis. In other words, within the 10 μm fiber you see finer fibrils or finer domain regions. Even though carbon crystallites have their basal planes running essentially parallel to the fiber axis, two extreme morphologies can still exist and are identified by microscopy. In one we have a radial structure, with the surface of the fiber being composed predominantly of crystallite edges. In the other, we have an onion-like structure in which the fiber surface is composed predominantly of basal planes. Frequently, pitch fibers show a random mixture of these two morphologies. An understanding of how to achieve a controlled morphology is of vital importance in controlling subsequent fiber–matrix interaction and all properties of the composite. This is an area of very active research today.

Let us look at some data from Union Carbide on properties of pitch fibers, in this case pitch fibers P-25 and P-120. Fiber P-25 was heated to about 1800°C, whereas P-120 was heated to about 2800°C. As you increase temperature of heat treatment, you increase crystallite size and enhance crystallite alignment. As discussed, in the single crystal of graphite, the mechanical properties are highly anisotropic. Young's modulus and tensile strength are much higher in the basal plane than perpendicular to the basal plane. In fact, the problem perpendicular to the basal plane is a low shear modulus. As we increase crystallite alignment, by going to higher heat treatment temperatures, we are going to increase Young's modulus parallel to the fiber axis. Indeed, it goes from about 140 GPa for fiber P-25 to 820 GPa for fiber P-120. Single crystal graphite has a Young's modulus of about 1000 GPa within the basal plane.

We see that in carbon fibers of high crystallite alignment the Young's modulus approaches that of the graphite single crystal rather closely. This is not true of tensile strength. Whereas the single crystal has measured values of about 20 GPa within the basal plane, P-120 has a tensile strength of only 2.2 GPa in the axial direction. Further, the value does not increase much upon increasing heat treatment temperature from 1800°C to 2800°C. Tensile strength is primarily determined by defects in the structure, that is points of stress concentration. Its value is a function of length of fiber tested or probability of finding a flaw. This is why it is so important to start with clean precursors and to spin the fibers in an environment of low dust concentration.

The selection of fiber heat treatment temperature depends upon the stiffness desired in the fiber and the composite. Since Young's modulus increases much more with increasing heat treatment than does tensile strength, strain at failure decreases with increasing heat treatment temperature. The fiber becomes more brittle. For example, for P-120 fiber, strain at failure

is only about 0.2%; the fiber is quite brittle. Also as you increase crystallite alignment and Young's modulus in the axial direction, you sacrifice some shear modulus perpendicular to the fiber axis. In some cases you may want somewhat higher shear modulus and sacrifice some Young's modulus. Again, this can be controlled by a change in maximum heat treatment temperature of the fiber.

4. CONCLUSIONS

We have talked about the large variability of coal as a precursor for carbons as we go from anthracite to bituminous to lignite. We can produce carbons of large variability in properties, like microporosity, by pretreating the coal and changing the nature of the precursor with which we start. We can also use the overhead tar resulting from pyrolysis of coal as a precursor. We can produce a wide variety of carbons which, today, have important commercial applications. For tomorrow, there is great promise of producing new carbons of still greater commercial applications.

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