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Preparation, Characterization, and Applications of Carbonaceous Mesophase: A Review

Guanming Yuan and Zhengwei Cui

Abstract

Carbonaceous mesophase with a nematic liquid crystal structure possesses an easily graphitizable characteristic and can be used as a promising raw material to prepare anisotropic carbon and graphite materials with high performance and multifunction. Therefore, the carbonaceous mesophase occupies a pivotal and irreplaceable position in many frontier and cutting-edge fields. The controllable preparation and characterization of carbonaceous mesophase derived from a model molecule (i.e., naphthalene) are presented, especially the formation, development, and transformation of anisotropic liquid crystalline mesophase in the synthetic naphthalene pitch during the process of liquid-phase carbonization (350–450°C). The increasing applications of naphthalene-based carbonaceous mesophase as an ideal precursor material for fabricating representative advanced carbon materials with high added value (e.g., mesophase pitch-derived coke, mesocarbon microbeads, mesophase pitch-based carbon foam, high-modulus mesophase pitch-based carbon fibers, and high-thermal-conductivity carbon-based composites, etc.) are reviewed in detail in this chapter.

Keywords: carbonaceous mesophase, liquid crystal, carbon materials, preparation, characterization, applications

1. Introduction

The research on carbonaceous mesophase can be traced back to the 1960s, when Books and Taylor found there was liquid-crystalline phase (i.e., mesophase spheres) in the thermal conversion of carbonaceous feedstocks, which opens a new era in the research of liquid-phase carbonization and the development of carbon material industry [1]. Up to now, carbonaceous mesophase has been studied for more than 50 years and has always been the research hotspot and focus in the field of carbon materials [2–5]. Mesophase pitch has long been recognized as a liquid crystal in a defined temperature range (e.g., 200–400°C) and exhibits both lyotropic and thermotropic nature, which is different from ordinary polymers and isotropic pitch [2]. It is well known that the mesophase pitch with a nematic liquid crystal structure possesses an easily graphitizable characteristic and can be preferentially aligned under mechanical force shearing after melting; thereby it is regarded as a basic raw material for preparing high-performance carbon and graphite materials with controllable structure of forming an ordered graphite, which provides a feasible route to prepare graphite-like materials [2]. In addition to the high carbon yield and potential price advantage (owing to the relatively low cost of carbonaceous raw materials) of

Figure 1.

Main promising applications of carbonaceous mesophase as an excellent precursor for making a wide variety of industrial and engineering carbon products.

mesophase pitch, it has become a high-quality precursor material for fabricating high-performance and multifunctional carbon materials as shown in **Figure 1**, such as mesophase pitch-based coke, needle coke, high-power graphite electrodes, meso-carbon microbeads (MCMBs), mesophase pitch-based carbon foam, mesophase pitch-based carbon fibers with high modulus and thermal conductivity, good binder and impregnating agent for high-thermal conductivity carbon-based composites, etc. Therefore, there is no doubt that mesophase pitch occupies a pivotal and irreplaceable position in various fields, such as defense, military, aerospace, cutting-edge technology, high-end industrial manufacturing, etc. [2, 3, 5].

2. Preparation of carbonaceous mesophase

The formation of mesophase pitch is a phase inversion process (transformed from isotropic to anisotropic), which is a result in which the pitch precursor undergoes thermal decomposition and thermal polycondensation to a certain extent. Nowadays, either thermal polycondensation of commercial coal-tar pitch and petroleum pitch (or even their certain soluble fractions) or catalytic polymerization of some aromatic substances is commonly used to prepare the carbonaceous mesophase [5]. It needs to be emphasized that carbonaceous precursors for the preparation of high-performance mesophase pitch are very crucial. Although commercial coal-tar pitch or petroleum pitch or heavy oil is very cheap and easy to obtain, these feedstocks are normally a complex mixture including with some heteroatoms and inorganic ash (~0.2 wt.%), which makes a spinnable mesophase pitch difficult to prepare [6–8]. So far, it is still very hard to massively produce cheap mesophase pitch with high quality, especially for continuously melt spinning high-performance carbon fibers. In recent 30 years, small model aromatic compounds (such as naphthalene, methylnaphthalene, anthracene, etc.) have been widely used to synthesize spinnable mesophase pitch by catalyzing with superacid, HF-BF_3 . The obtained naphthalene-derived mesophase pitch possesses characteristics of high purity, controllable molecular structure, and ideal physical property [3, 9–11]. However, the severe corrosion problem and potential operating risk of using HF-BF_3 as a catalyst will unfortunately limit its widespread use (and such a mesophase pitch product named “AR” as shown in **Figure 2(a)** is now no longer available from, e.g., Mitsubishi Gas Chemical Company).

Figure 2.
 Optical photographs of (a) pellet and (b) block-shaped carbonaceous mesophase pitch derived from naphthalene.

Figure 3.
 Flow diagram of catalytic thermal polymerization of naphthalene molecule to form carbonaceous mesophase pitch ((LT) a low temperature of $\sim 200^{\circ}\text{C}$ and (MT) a mid temperature of $\sim 430^{\circ}\text{C}$).

In the meantime, a mild catalyst AlCl_3 has been selectively used to prepare the mesophase pitch from the simple molecules and achieve the anticipated catalytic polymerization effect in spite of a trace of residual catalyst (e.g., 300–1000 ppm) inevitably intermingled in the mesophase pitch [3, 12–14]. **Figure 3** shows the flow diagram of catalytic thermal polymerization of naphthalene molecule to prepare carbonaceous mesophase pitch as shown in **Figure 2(b)** by a two-step reaction process at a liquid-phase carbonization temperature of $350\text{--}450^{\circ}\text{C}$ for a certain period of time. It could be concluded that some carbonaceous precursors (e.g., naphthalene) have undergone four stages of liquid-crystalline sphere development and transformation and finally formed a bulk liquid-crystalline mesophase from an isotropic matrix as illustrated in **Figure 4** under a suitable reaction condition (i.e., reaction temperature and time) [2, 15, 16]. The general four-stage conversion of liquid crystals during the whole process is diagramed as follows: (I) generation of optically anisotropic spheres in isotropic matrix, (II) growth of anisotropic spheres in isotropic matrix, (III) coalescence of anisotropic spheres in isotropic matrix, and (IV) deformation and disintegration of anisotropic coalesced spheres to form bulk liquid-crystalline mesophase.

However, it has been demonstrated that the formation, development, and transformation of liquid-crystalline anisotropic spheres (i.e., nucleation, growth, coalescence and deformation and orientation) in an isotropic pitch matrix are unconcerted and inhomogeneous during the process of liquid-phase carbonization as shown in **Figure 5** [16]. Furthermore, it is not easy to obtain a 100 vol.% anisotropic mesophase pitch (i.e., bulk mesophase) both with a fine flow optical texture and an acceptable softening point less than 300°C for subsequent fiber spinning. This mainly depends on the carbonaceous precursors (e.g., molecular unit size, the flatness of molecules and the chemical reactivity, etc.) and the suitable thermal reaction conditions adopted [2, 15, 16].

Figure 4.
Schematic illustration of the formation and development process of bulk liquid-crystalline mesophase under a suitable reaction condition (scale bar in PLM micrographs is 100 μm).

Figure 5.
(a) Polarized light microscope (PLM) micrograph of the naphthalene-based synthetic pitch and (b) SEM image of broken surface of the pitch-derived coke showing an unsynchronized and inhomogeneous conversion of liquid-crystalline anisotropic spheres.

3. Characterization of carbonaceous mesophase

Mesophase pitch consists of a large variety of polycyclic aromatic hydrocarbons and maintains the molecular ordering (i.e., optical anisotropy), which is an important precursor for high-performance industrial carbon materials. Characterizing the structures and properties of carbonaceous mesophase plays a significant role in its quality control, process optimization, and applications [5, 17, 18]. Only through effective measurement of the molecular weight distribution and quantitative description of the structural characteristic as well as the multi-scale evaluation of the thermophysical nature will the understanding, controllable preparation, and applications of carbonaceous mesophase be updated. The common instruments used for characterizing carbonaceous mesophase are as follows: Fourier-transform infrared spectrometer (FTIR), elemental analyzer, nuclear magnetic resonance

Figure 6.
 FTIR patterns of (a) naphthalene pitch and (b) its derived mesophase pitch.

Figure 7.
¹H-NMR spectra of the soluble fractions from (a) naphthalene pitch and (b) its derived mesophase pitch.

Figure 8.
 MS spectra of (a) naphthalene pitch and (b) its derived mesophase pitch.

(NMR), flight mass spectrometer (MS), polarized light microscope, capillary rheometer, X-ray diffractometer, Raman spectrum, thermogravimetric, differential scanning calorimetry, etc.

The carbonaceous mesophase pitch prepared by AlCl₃ catalytic thermal polymerization of naphthalene has a relatively high aromaticity (the aromatic index is about 0.70)

Figure 9. Typical PLM micrographs of the (a, b) as-received, (c) melted, and (d) melt-stirred naphthalene-based AR mesophase pitch.

and a regular planar molecular structure constructed by a number of naphthenic structure, as well as a relatively large molecular weight of ~ 2600 g/mol, consisting of mesogen units (a ladder-shaped molecular structure) formed by ~ 20 naphthalene molecules through thermally induced aromatic growth [3, 10, 11] according to the analyses of **Figures 6–8**. The suitable softening point ($260\text{--}280^\circ\text{C}$) and appropriate H/C mol ratio ($0.52\text{--}0.60$), as well as high liquid-crystalline mesophase content (100 vol.%) and ideal fine flow texture as displayed in **Figures 9** and **11**, are the significant characteristics of such carbonaceous mesophase. The analysis results of other characterizations are not shown here (refer to previous work [2, 3, 10, 11, 15, 18]).

4. Texture and properties of carbonaceous mesophase as a liquid crystal

The as-received liquid-crystalline AR mesophase pitch as shown in **Figure 9(a, b)** possesses a streamline “fibrous” texture with highly preferred orientation visible via orthogonal observation by rotating the object stage of the PLM. Following melting and melt-stirred treatments at 320°C as shown in **Figure 9(c, d)**, respectively, the optical texture of the melting pitch is nearly maintained, and the conformation and orientation of the macromolecules in the melt-stirred pitch are disrupted to become partially disordered or turbulent (severely deformed) depending upon the degree of stirring [19]. The purpose of this thermo-stirring treatment is to investigate the influence of liquid-crystalline texture of mesophase pitch precursors on the morphology, microstructure, and physical properties of resulting carbon fibers as shown in **Figure 10**.

It can be found that the as-prepared naphthalene-based mesophase pitch as being transmitted from the reaction autoclave to a metal plate at a molten status

Figure 10.
Schematic of the microstructure evolution from mesophase pitch precursor to transverse texture-controlled carbon fibers as degree of melt-stirring increases.

Figure 11.
(a) Optical photograph of a naphthalene-based synthetic pitch with good wire-drawing performance and (b) PLM micrograph of the drawn pitch fiber.

Figure 12.
Typical (a) molten flow curve of distance-temperature and (b) viscosity-temperature curve of naphthalene-based AR mesophase pitch.

exhibits good wire-drawing performance and ideal viscoelastic property and the unwittingly drawn wires (i.e., large-diameter pitch fibers) possess an orderly liquid-crystalline texture as shown in **Figure 11**, which is closely related to its plastic flowing behavior and low apparent viscosity upon melting as shown in **Figure 12**. This is favorable for pitch melt spinning and other rheology applications [5].

5. Applications of carbonaceous mesophase

5.1 Carbonaceous mesophase-derived coke

It is well known that pitch-derived coke is mainly used to make carbon and graphite electrodes equipped within electric arc furnaces for steelmaking, and mesophase pitch-derived coke (or needle coke) has an overwhelming advantage to produce graphite electrodes with high and ultrahigh power [5, 20].

It can be clearly seen that mesophase pitch-derived coke exhibits a well-oriented texture as shown in **Figure 13(a, b)**, which is closely related to the formation and development of flow-type liquid crystalline in carbonaceous mesophase products during the process of delayed coking [5]. In contrast, coarse-grained mosaic texture is presented in the coke derived from commercial coal-tar pitch as shown in **Figure 13(c, d)** [16, 20]. Thus it can be concluded that the carbonaceous feedstocks have a significant influence on the optical texture and microstructure of resulting coke, which depends on the development and evolution of carbonaceous mesophase during the liquid-phase carbonization process.

Figure 13.
(a, c) Optical photographs and (b, d) PLM micrographs of mesophase pitch-derived coke (a, b) and coal-tar pitch-derived coke (c, d).

5.2 Carbonaceous mesophase-based mesocarbon microbeads

As a special type of carbon material, MCMB has some outstanding physical and chemical properties that other carbon materials do not have due to its unique spherical morphology and lamellar structure. Therefore, MCMB can be widely applied to various fields, such as high-performance liquid chromatography column materials, high-specific surface area activated carbon materials, high-efficiency lithium ion battery anodes, high-density and high-strength graphite materials, etc. [5, 21].

Under suitable thermal reaction conditions, homogeneous liquid-crystalline spheres with an identical diameter of $\sim 10\ \mu\text{m}$ which appeared in the optically isotropic pitch matrix can be achieved as shown in **Figure 14(a)**, which is closely related to the effective control of the polymerization degree of naphthalene molecules. Through subsequent separation, infusibilization, and carbonization treatments, uniform-sized MCMBs as shown in **Figure 14(b)** can be easily obtained by starting with a simple naphthalene molecule.

5.3 Carbonaceous mesophase-based porous carbon and carbon foam

Recently, many researchers have used mesophase pitch as a raw material to prepare porous carbon materials (e.g., ultrahigh surface area activated carbon, mesoporous carbon, and hierarchical porous carbon) with controlled microstructure and morphology [22, 23]. The large specific surface area, rich pore structure and excellent adsorption performance of porous carbon materials provide excellent supporting characteristics for various transition metal and precious metal catalysts. Porous carbon support can resist the severe corrosion in harsh environments such as acid, alkali and salts, and greatly improve the adsorption performance and catalytic efficiency, and thus has broad applications [24].

Mesophase pitch-based carbon foam is a new type of porous carbon material prepared by foaming mesophase pitch as shown in **Figure 15**. Owing to its low density, high thermal and electrical conductivity, fire resistance, microwave absorption, noise reduction, low thermal expansion coefficient, chemical resistance, etc., carbon foam is extremely suitable for heat transfer systems, such as aerospace vehicles and satellites, rocket launching platforms, large heat exchangers, and computers in chemical plants [25–27]; therefore, such carbon foam sees promising application prospects.

Figure 14.
(a) PLM micrograph of anisotropic liquid-crystalline carbonaceous spheres generated from naphthalene-based synthetic pitch and (b) SEM image of homogeneous MCMBs derived from the spherical liquid crystals.

Figure 15.
(a) Optical photograph and (b) PLM micrograph of carbon foam derived from naphthalene-based mesophase pitch.

5.4 Carbonaceous mesophase-based carbon fibers

Mesophase pitch-based carbon fibers firstly reported by Singer in 1978 are the most successful high-end product for the development and application of carbonaceous mesophase, which are derived from spinnable mesophase pitch by melt spinning, oxidative stabilization, and carbonization and graphitization treatments [28]. The inherent alignment structure of liquid crystal molecules is preserved within the as-spun pitch fibers. Upon high-temperature graphitization, the graphite crystals are preferentially oriented along the fiber axis, so the final fibers have super high Young's modulus (up to a theoretical value of graphite, 1000 GPa) and excellent axial electrical (as low as $1.0 \mu\Omega \text{ m}$ in electrical resistivity) and thermal conductivity (exceeding 1000 W/m K). Thus they are now being widely used in aviation, aerospace, nuclear, and other high-tech fields, in which polyacrylonitrile-based carbon fibers have a certain limitation [3, 5, 29–33]. At present, only the United States (Cytac Industries Incorporated) and Japan (Mitsubishi Chemical Corporation and Nippon Graphite Fiber Corporation) have mature manufacturing technology ranging from the precursor materials to the final products (i.e., mesophase pitch, high-performance carbon fiber continuous filaments, and carbon fiber composites). The morphology of commercial carbon fibers usually includes three types of forms, i.e., continuous filament, chopped fiber, and ground fiber powder.

The round-shaped carbon fibers with different diameters and large-sized ribbon-shaped carbon fibers (sectional width $\sim 2 \text{ mm}$, thickness $\sim 10 \mu\text{m}$) as shown in **Figure 16** can be successfully prepared from the AR mesophase pitch owing to its good spinnability. It is worthy to point out that most large-diameter carbon fibers with a radial transverse texture are inclined to spit in the subsequent high-temperature heat treatment. The ribbon-shaped carbon fibers can efficiently solve the crack problem and maintain their shape and structure without any damage. The carbon crystalline structure and layered orientation parallel to the ribbon main surface are obviously better than those of round fibers. The axial electrical resistivity and thermal conductivity of the round and ribbon fibers graphitized at 3000°C are measured to be as low as $1.1\text{--}1.30 \mu\Omega \text{ m}$ and about $900\text{--}1000 \text{ W/m K}$ at room temperature [19, 34–36].

5.5 Carbonaceous mesophase-based carbon composites

Mesophase pitch-based carbon (graphite) fibers are often used as ideal functional fillers for preparing various carbon-based composites with high thermal conductivity [5, 37–41], which can be widely utilized in the field of thermal management [32, 33]. The thermal conductivity of these carbon-based composites depends not only on the

Figure 16.
 (a, c) Optical photographs and (b, d) SEM micrographs of round- (a, b) and ribbon-shaped carbon fibers (c, d) derived from naphthalene-based AR mesophase pitch.

conduction performance of carbon fibers themselves and their loading amount, as well as laying or weaving architecture in the composites, but also on the physical properties of matrix materials involved (i.e., the resin, mesophase pitch, or pyrolytic carbon).

In the previous work, the mesophase pitch-based graphite fiber (long filament) reinforced one-dimensional (as shown in **Figure 17(a)–(c)**) and two-dimensional ABS resin composites with a large size of 10 cm × 10 cm × 0.3–2 cm can reach a high thermal conductivity of ~500 W/m K [37, 38]. However, the thermal conductivity of composites reinforced by shortcut carbon fibers and milled fiber powders as shown in **Figure 17(d, e)** is only 10–20 W/m K, which can be used as heat paste or thermal grease for interfacial heat dissipation. Using various mesophase pitch-based graphite fibers (i.e., round-shaped and ribbon-shaped fibers) as a reinforcing filler and the same mesophase pitch as a binder, ultrahigh thermal conductivity (700–900 W/m K) of the one-dimensional C/C composites as shown in **Figures 18** and **19** could be realized [39, 40]. However, it is disadvantage to use phenolic resin as a binder to prepare high-thermal-conductivity materials owing to its non-graphitizable nature (i.e., a typical hard carbon) as shown in **Figure 20**. By comparison, the mesophase pitch-derived carbon after high-temperature treatment exhibits good crystallinity, high graphitization degree, and orderly stacked graphene sheets as shown in **Figure 18(d)**, which is very important to improve the directional thermal conductivity performance. It is worth noting that the pyrolytic carbon with a highly oriented texture deposited on the mesophase pitch-based graphite fibers as shown in **Figure 21** is also found to markedly increase the thermal conductivity of C/C composites [41].

It is interesting to note that mesophase pitch is a promising binder (due to its good flow orientation performance in the molten state, easily graphitizable

Figure 17. (a) Optical photograph, (b–d) PLM micrographs, and (e) SEM image of ABS resin composites reinforced by unidirectional (b, c) and disordered (d, e) mesophase pitch-based carbon fibers ((b, c) are, respectively, imaged perpendicular and parallel to the fiber axis).

Figure 18. (a) Optical photograph, (b) PLM micrograph, and (c)–(e) SEM images of unidirectional carbon/carbon composites reinforced by mesophase pitch-based carbon fibers using mesophase pitch as a binder ((b)–(d) are imaged perpendicular to the fiber axis, and (e) is imaged parallel to the fiber axis).

Figure 19.
(a) Optical photograph, (b, c) PLM orthogonal micrographs, and (d) SEM image of unidirectional carbon/carbon composites reinforced by mesophase pitch-based ribbon fibers using mesophase pitch as a binder.

Figure 20.
(a) PLM micrograph and (b) SEM image of unidirectional carbon/carbon composites reinforced by mesophase pitch-based carbon fibers using phenolic resin as a binder.

characteristic, etc.) for large-scale fabricating natural flake graphite-molded blocks by using the cheap and available natural graphite flakes as a raw material. The prepared graphite blocks with a high bulk density of 1.9 g/cm³ possess a highly preferred structural orientation perpendicular to the hot-pressing direction as shown in **Figure 22** and a high thermal conductivity of 500–600 W/m K in plane two-dimensional direction [42, 43].

Figure 21.
(a) Optical photograph, (b) PLM micrograph, and (c) SEM image of unidirectional carbon/carbon composites reinforced by mesophase pitch-based carbon fibers using pyrolytic carbon as a “binder.”

Figure 22.
(a) Optical photograph, (b) PLM micrograph, and (c) SEM image of natural flake graphite-molded blocks perpendicular to the hot-pressing direction using mesophase pitch as a binder.

5.6 Other applications

It is well known that carbon materials are important materials for the preparation of various batteries. From ancient dry batteries to today’s high-efficiency fuel cells, as well as new high-energy storage batteries being developed, pitch-based carbon materials are playing an increasingly important role. Mesophase pitch is an easily graphitizable carbonaceous precursor. After high-temperature heat treatment, its three-dimensional stack structure is very regular, and mesophase pitch can be transformed into a high-crystalline graphite. The necessary energy of intercalating lithium ions into the carbon layers is relatively low, and thus such material has a large lithium insertion depth and reversible capacity [44, 45], especially carbonaceous mesophase-derived coke after spheroidizing and coating treatments as shown in **Figure 23(a)** which can significantly improve the cycle stability and service life of the battery.

By the same token, using the easily graphitized mesophase pitch-derived carbon as a raw material, a large-sized graphene (or a few layers of graphene sheets) with uniform thickness and good transparency as shown in **Figure 23(b)** can be successfully prepared through a special technique (i.e., molten salt ion intercalation stripping), which can realize the size and thickness control of carbon layers. The preparation method seems to be very simple and easy to operate and thus will have a good prospect.

In addition to being used as a high-quality raw material for the above-mentioned carbon materials, carbonaceous mesophase can also be used to prepare some novel and value-added carbon materials such as miracle graphene [46], carbon quantum dots [47], good binder for high-performance magnesia carbon bricks [48], fluorinated pitch [49], etc.

Figure 23.
 Typical (a) SEM image of carbonaceous mesophase-derived spherical coke used as Li-ion battery anodes and (b) TEM image of carbonaceous mesophase-derived graphene with a relatively large size.

6. Conclusions

In this chapter, the preparation, characterization, and applications of naphthalene-based carbonaceous mesophase are reviewed. With the continuous advancement of preparation techniques and characterization methods, the understanding of the molecular structure, molecular weight, molecular weight distribution, aggregation texture, and rheology property of mesophase liquid crystals will be deepened, and finally the comprehensive understanding of the carbonaceous mesophase (including the formation mechanism, molecular dynamic law and high-efficiency control) from molecular and micro and macro scales could be realized, which will maximize the performance of carbonaceous mesophase-derived carbon products with desirable performance, multi-versatility, and high added value, thus to promote the theoretical foundation of carbonaceous mesophase and accelerate its broad applications in various fields.

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Conflict of interest

The authors declare no conflict of interest.

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