We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Polyimide-Derived Graphite Films with High Thermal Conductivity

Guanming Yuan and Zhengwei Cui

Abstract

Nowadays, polyimide-derived graphite films with high thermal conductivity have been increasingly applied in many cutting-edge fields needing thermal management, such as highly integrated microelectronics and wireless communication technologies. This chapter first introduces a variety of functional graphite films with high thermal conductivity of 500–2000 W/m K in the planar direction, then provides the preparation technology (including lab-scale preparation and industrial production) and quality control strategy of high-thermal-conductivity graphite films, which are derived from a special polymer- polyimide (PI) by carbonization and graphitization treatments through a suitable molding press in a vacuum furnace. The morphology, microstructure and physical properties as well as the microstructural evolution and transformation mechanism of PI films during the whole process of high-temperature treatment are comprehensively introduced. The nature of PI precursor (e.g., the molecular structure and planar molecular orientation) and preparation technics (e.g., heat-treatment temperature and molding pressure) are critical factors influencing their final physical properties. Currently challenged by the emerging of graphene-based graphite films, the latest developments and future prospects of various PI-derived carbons and composites (beyond films) with high thermal conductivity have been summarized at the end. This chapter may shed light on a promising and versatile utilization of PI-derived functional carbon materials for advanced thermal management.

Keywords: polyimide, graphite film, preparation, structure, property, high thermal conductivity, thermal management

1. Introduction

Highly oriented graphite film has excellent electrical and thermal conductivity properties, and is an ideal material indispensable for the development of modern science and technology. It has a very broad application prospect in thermal management field such as modern microelectronic packaging-integration and 5 G wireless communication technologies. In the early 1960s, scientists had used high-temperature pyrolysis deposition technology to prepare highly oriented pyrolytic graphite (HOPG), however, the material needs to be prepared at high temperature (up to 3400-3600°C) and high pressure (10 MPa), the production cycle is long and the production cost is high. Thus, the wide application of such material is subject to certain restrictions [1]. Subsequently, Japanese scientists had initially discovered that polyimide (PI) film with a golden appearance as shown in **Figure 1a** did not melt during the carbonization process and maintained the original film shape,
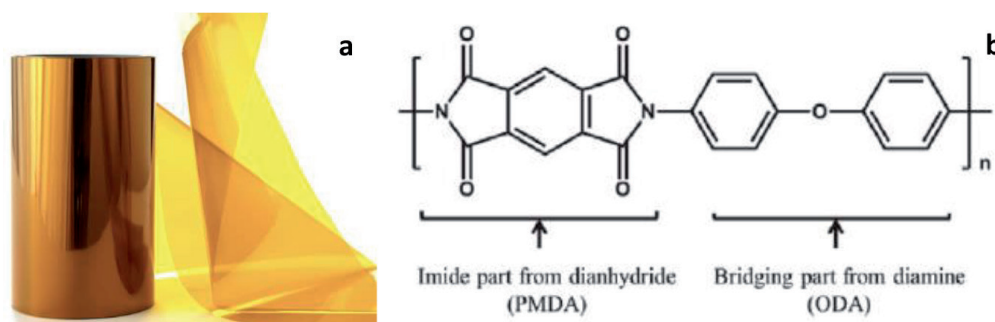
Figure 1.
(a) Optical appearance and (b) a molecular repeating unit of Kapton PI film [2].
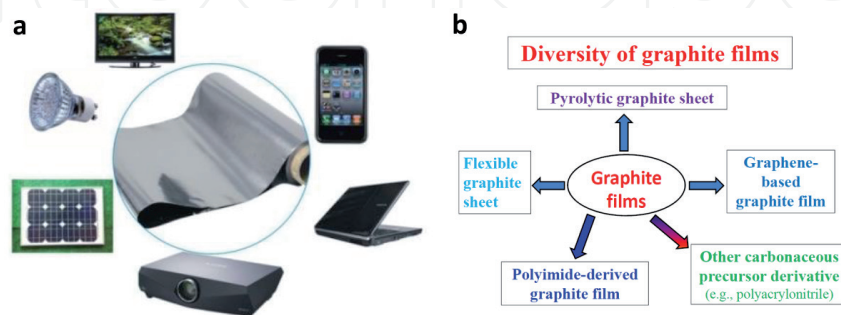
Figure 2.
(a) Wide heat-dissipation application of PI-derived graphite films in advanced microelectronics and (b) a variety of graphite films classified by different precursors.

after high-temperature (2800-3200°C) graphitization treatment, a highly oriented graphite film with a structure close to single crystal graphite can be obtained [3, 4]. Nowadays, PI developed as a thermoresistant polymer has been widely used in different fields, for instance, aromatic PI is often employed as an excellent carbonaceous precursor to prepare various carbon materials with different morphologies (e.g., fiber, film, foam and block) [2]. This is because aromatic PI has many advantages such as wide range of well-defined molecular structure as shown in **Figure 1b**, relatively high crystallinity and carbon yield.

Recently, PI-derived graphite films with high thermal conductivity in the planar direction ranging in 500–1900 W/m K have been successfully produced and practically applied in heat dissipation of many microelectronic devices as shown in **Figure 2a**. This is attributed to the extensive research on the composition, structure and properties of PI polymer film and related high-temperature heat treatment process have been conducted to improve the thermal conductivity of resultant graphite films and reduce the production cost [2–13]. It is well-known that the thermal conductivity of graphite films is greatly affected by many factors (the quality of PI film precursor, film thickness and heat treatment temperature, etc.). In addition, the microstructural evolution and transformation mechanism [4, 6, 12] of PI polymer during high-temperature heat treatment, the capability of forming an ordered graphite structure and the relevant control strategy need to be further understood. This will make the application of graphite films for thermal management move forward [2, 4, 11].

2. Diverse graphite films with high thermal conductivity

Generally, high-thermal-conductivity graphite films can be divided into two main types (natural graphite-derived and artificial synthetic films) and several

subdivided categories as shown in **Figure 2b** according to different raw materials: oriented pyrolytic graphite sheet, flexible graphite sheet, graphene-based graphite film, PI-derived graphite film and other carbonaceous precursor derivative.

HOPG sheet refers to polycrystalline graphite film with a high bulk density of ~2.20 g/cm^3 and highly oriented graphene layers stacking along the c-axis direction, similar to single crystal graphite as shown in **Figure 3** [14]. Its room-temperature thermal conductivity along the a-axis direction of the graphite sheet reaches up to 1600–2000 W/m K [15]. Recently, through a facile and feasible chemical vapor deposition on transition metal substrates, the prepared graphite films possess a high thermal conductivity of 600–1570 W/m K [16, 17].

Flexible graphite sheet is prepared by using natural flake graphite as raw material through several procedures as follows. Firstly, strong acidification treatment for chemical intercalation, then washing, drying and high-temperature expansion to obtain high-expanded graphite worms, and finally calendering and pressing treatment processes. The thermal conductivity of flexible graphite sheet can be adjusted in the range of 200–600 W/m K according to the bulk density and sheet thickness [18, 19]. Because this material does not require high-temperature graphitization and the preparation process is simple, the production cost is relatively low, and it can be used not only as a high-temperature sealing material, but also as a heat dissipation pad for the interface between electronic devices and heat sinks. In addition, the thin graphite sheet has a certain degree of flexibility and can be bent and rolled for storage as shown in **Figure 4**, which accelerates its low-cost industrial production. However, the mechanical properties of flexible graphite sheet decrease with the increase of thickness. So it is suitable for fields where material strength, toughness and flexural properties are not very high.
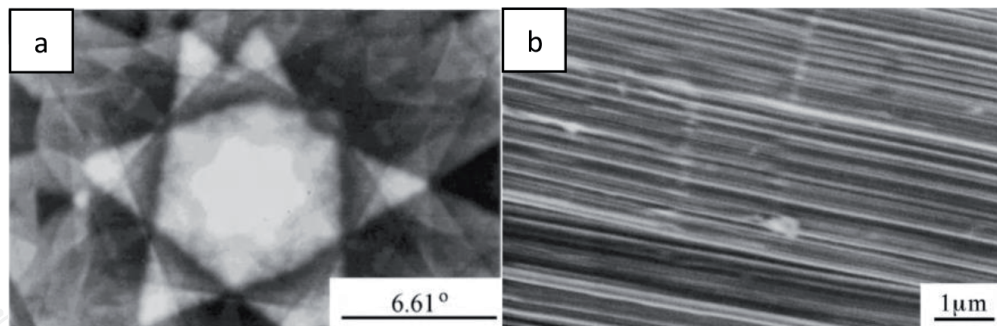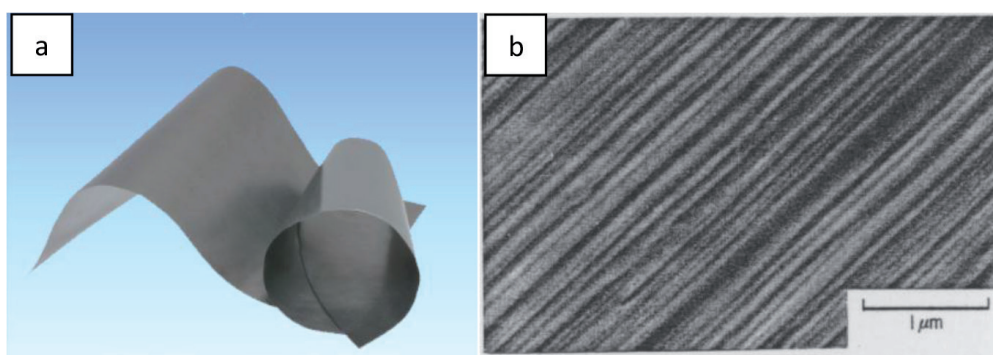

Figure 3.
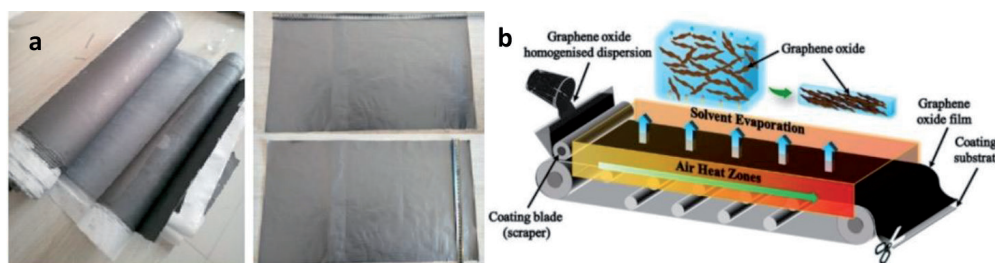*(a) Electron channeling pattern and (b) SEM image of HOPG [14].*
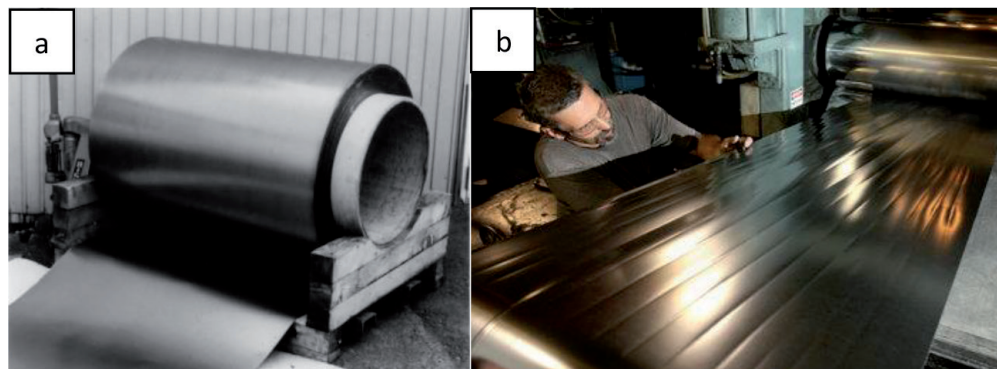
Figure 4.
Optical photographs of (a) flexible graphite sheet rolled for store in Nihon carbon and (b) GrafTech graphite sheet production line.

Figure 5.
(a) Optical photograph and (b) microscopic image of PI-derived thermal pyrolytic graphite sheet (PGS) produced by Panasonic Industry [20].

Figure 6.
(a) Optical photograph of large-scale preparation of graphene laminated films [21] and (b) the schematic of film fabrication process [22].

PI graphite film with high crystallinity and preferred orientation is similar to HOPG as shown in **Figure 5** and has a high thermal conductivity up to 1900 W/m K in the planar direction [2]. The thermal conductivity of the pyrolytic graphite sheets developed by Panasonic Industry is reported to be 700-1950 W/m K according to their bulk densities (0.85–2.13 g/cm^3) and sheet thicknesses (0.10–0.01 mm) [20]. Obviously, the thermal conductivity of graphite sheets is greatly affected by its bulk density, thickness and pyrolysis process. As a rule, the greater the thickness is, the lower the thermal conductivity is.

Recently, there has been numerous studies on making graphene or its precursor (e.g., graphene oxide and reduced graphene oxide) into graphite films as shown in **Figure 6a** [21–23]. This extensive research greatly improves the thermal conductivity of graphene-based films up to 2000 W/m K and promotes their various applications [23]. Although the production cost of large-area high-quality graphene films with high thermal conductivity is still high at this stage, the large-scale fabrication in science and industry is rising [21, 22].

3. Preparation technology of graphite films

3.1 Lab-scale preparation

At present, a batch-scale preparation method, i.e., multi-sheet carbonization by laminated molding in a small-sized vacuum induction furnace as shown in **Figure 7a**, is generally adopted to prepare sheet-like PI-derived graphite films with different sizes. However, this method shows obvious disadvantages such as relatively high production cost, low preparation efficiency, and particularly large energy consumption. Moreover, the size of the films is limited by the graphite
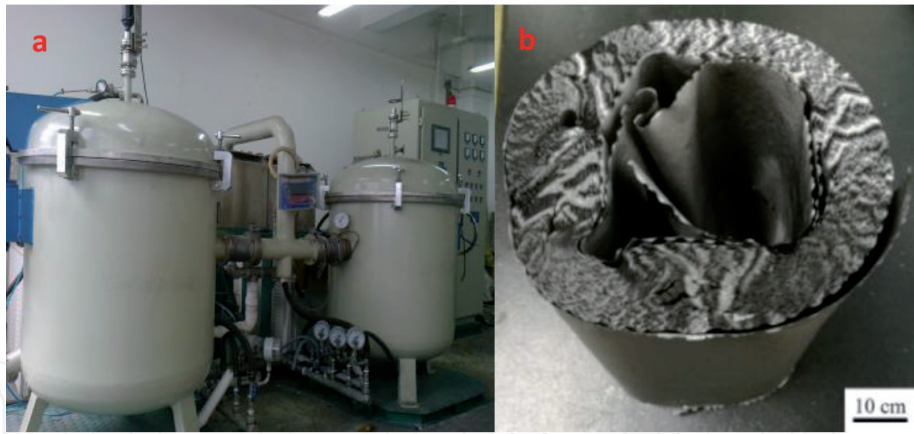
Figure 7.
Optical photographs of (a) a lab-scale vacuum induction furnace and (b) roll-shaped graphite film prepared from PI film.

mold (which needs to repeatedly endure severe condition under high temperature and high pressure) and the size of the heat treatment furnace.

3.2 Industrial production

In general, the industrial production of PI-derived graphite films is carried out in multiple sets of large-sized vacuum induction furnace. The emerging advanced rolling-carbonization technology, i.e., directly performing carbonization-graphitization treatment on the roll-shaped organic PI films, could obtain a roll-shaped graphite films with a large size as shown in **Figure 7b** by controlling the heat treatment process of tightly rolled films. This technology can significantly improve the production efficiency of graphite films, reduce the production cost and improve their mechanical properties.

3.3 New fabrication technology

With the rapid development of graphene and graphene-based materials throughout the world, some new methods, new processes and new technologies [21, 22, 24–27], such as molecular welding, molecular assembling, flow coating and centrifugal casting, as shown in **Figures 6b** and **8**, have been increasingly developed to fabricate graphene-based graphite films with high thermal conductivity for thermal management application. This will surely provide some reference for the preparation strategy of PI-derived graphite films. It is possible to take advantage of continuous high-temperature carbonization technology as shown in **Figure 8b** to fabricate large-scale PI-derived graphite films at a low cost in the future.
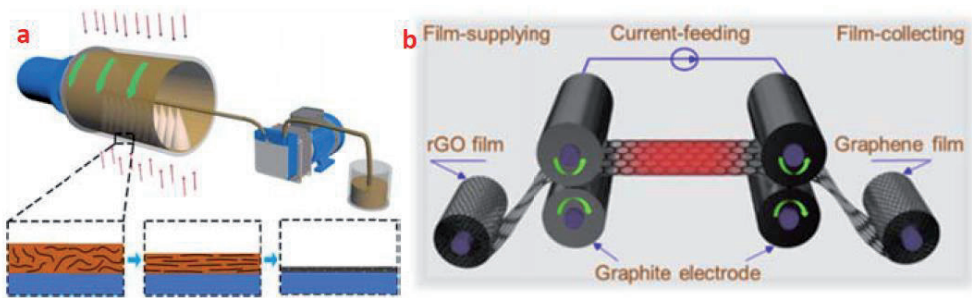
Figure 8.
Schematics of producing graphene-derived films by different methods (a) the continuous centrifugal casting [26] and (b) the pressurized roll-based production by Joule heating [27].

## 4. Morphology, structure and properties of PI-derived graphite films

The uniform PI raw film (DuPont Kapton) with a golden color shrinks significantly after 1000°C carbonization and 3000°C graphitization under proper pressure in a vacuum furnace, and the shrinkage rate in the planar direction is about 15% × 15%. The color of the film changes from yellow to black and gray as shown in **Figure 9a–c**, the carbonized and graphitized samples are brittle and flexible (can be bent at a certain angle >90° at many times), respectively. The molding-press and its pressing strength on the PI films have an important role on the final quality of resultant graphite films as shown in **Figure 9d–f**.

As shown in **Figure 10**, the surface of 1000°C-carbonized carbon films (with a thickness of 50 μm for the raw film) is smooth and the thickness is still uniform, the internals of carbon films exhibit an amorphous carbon structure. After 2000°C graphitization, a local chaotic layered structure can be observed in the cross-section of the films [28]. When the graphitization temperature reaches 2400°C, the cross-section of the films presents a more uniformly oriented layered structure, and as the graphitization temperature further increases up to 3000°C, the layered structure becomes more flatted and ordered, and the graphite-like crystal structure is nearly perfect.

The thickness and the nature of the PI films have a significant impact on the capability of forming a graphite-like crystal structure. As shown in **Figure 11a–c**, the PI film with a thickness of 50 μm completely forms a graphite-like layered structure with high crystallinity, and the degree of preferred orientation of the graphene layers is high. The PI films with thicknesses of 75 and 100 μm display a partial graphite-like layered structure and nearly amorphous structure with low crystallinity and poor crystalline orientation, respectively. Some small holes appear on the cross-section of graphite film, which may be related to the removal of non-carbon elements during the high-temperature graphitization process. Moreover, the nature of PI films (e.g., the variety of polymer constituent and molecular structure
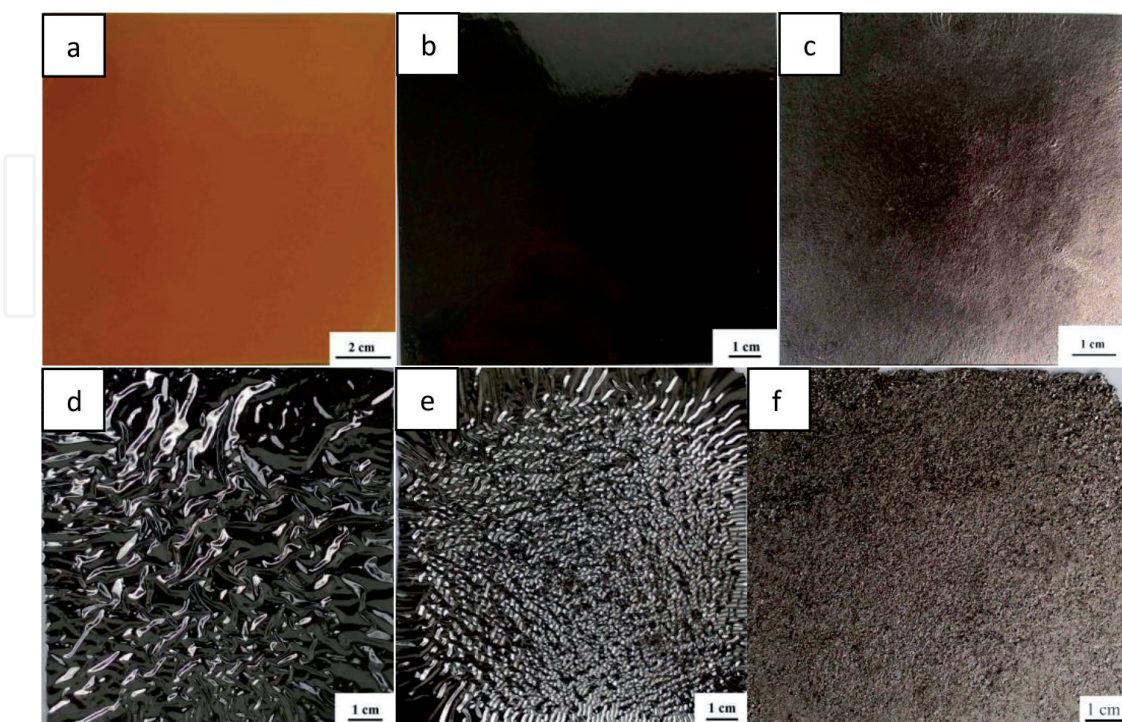
Figure 9.
Optical photographs of (a) PI raw film, its (b, d and e) 1000°C-carbonized and (c and f) 3000°C-graphitizatized samples made by various molding-press treatments ((b and c) suitable pressure; (d) no pressure; (e) insufficient pressure; and (f) excessive pressure).
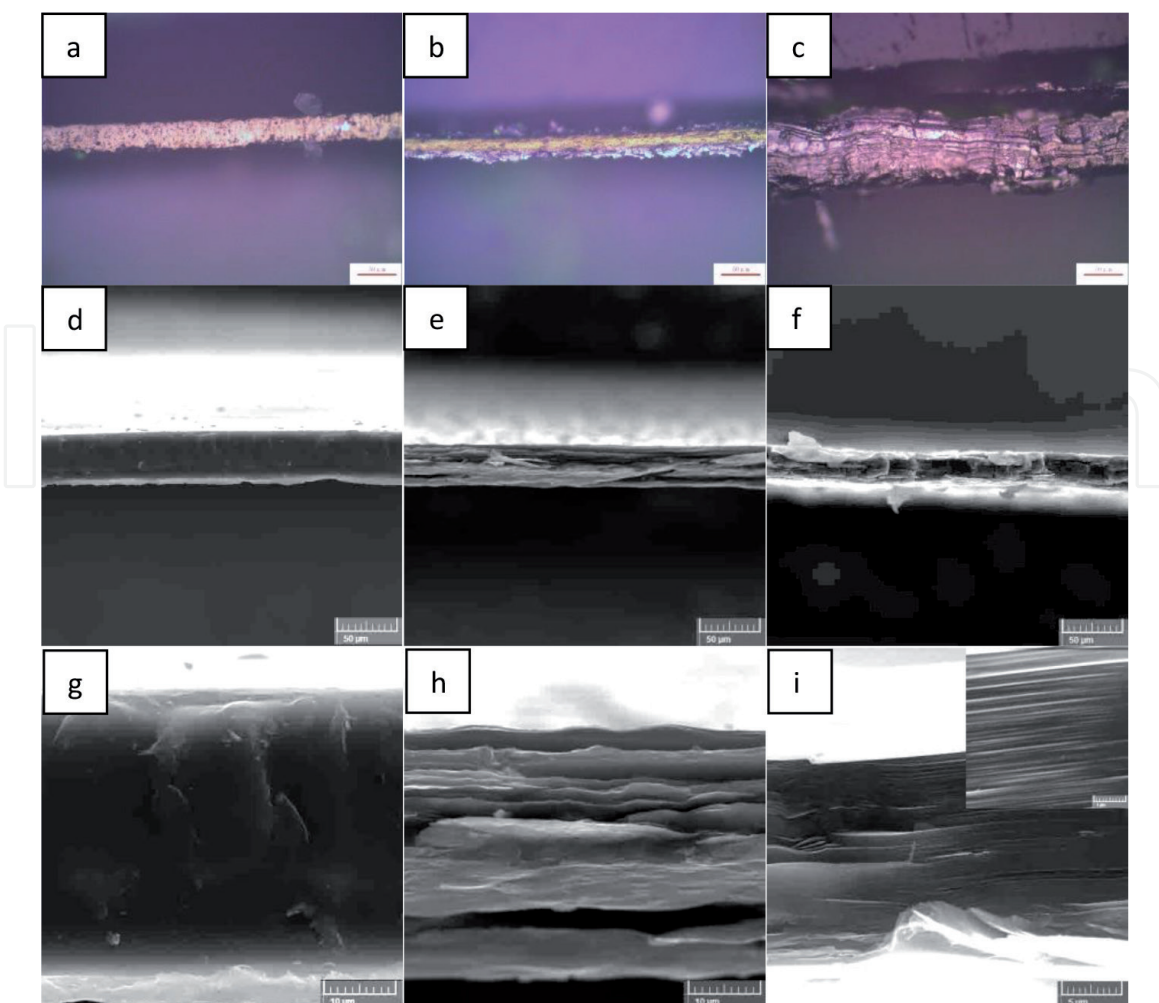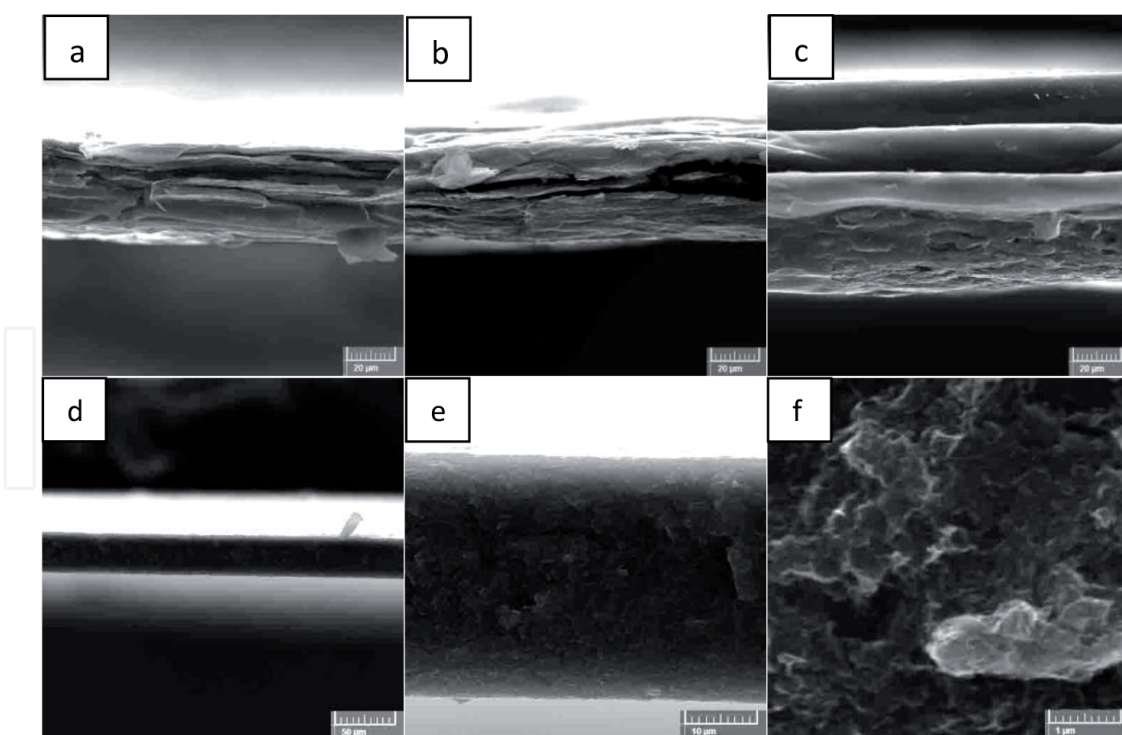
Figure 10.
(a–c) PLM and (d–i) SEM images of the transversal section of PI films heat-treated at different temperatures ((a, d and g) 1000; (b, e and h) 2400; and (c, f and i) 3000°C), (g–i) are high magnification images of (d–f), respectively, and the top right inset in i is the corresponding enlargement.

in various PI films produced by different manufacturers) is very critical to prepare highly oriented graphite films, which has been demonstrated in **Figure 11d–f**.

The PI laminated sample with a good graphite-like crystal structure as shown in **Figure 12** could be prepared by a hot-press method at 2400°C under a certain pressure. It has a uniformly layered structure in the cross-section, and the stacking of PI films is regular and orderly. The PI monolayer film inside the laminated sample still maintains its complete sheet-like structure, which is conducive to the high efficient conduction of heat in the two-dimensional direction of the plane. The PI-derived laminates can be used as a bulk thermally conductive material to further expand the application field of graphite films, but the controllable preparation of such large-size and ultra-thick bulk materials (e.g., blocks) is still difficult [4].

It can be seen from the XRD patterns as shown in **Figure 13a–c** that the PI raw film has a certain degree of orientation owing to the arrangement of aromatic molecules. With the rise of heat treatment temperature, the intensity of diffraction peak of the (002) crystal plane of the PI sample continues to increase. Meanwhile, the microcrystallite accumulation height (Lc) and graphitization degree (g) listed in **Table 1** increase step by step. After 3000°C graphitization, the interlayer spacing d_{002} (0.336 nm) is close to the theoretical value of single crystal graphite (0.3354 nm). The ratio of the two peaks (D and G) as shown in **Figure 13d** gradually decreases, especially the D peak of 2400°C-graphitized sample completely disappears, which indicates that a three-dimensional ordered graphite structure forms in the graphite film, the content of amorphous carbon and structural defects
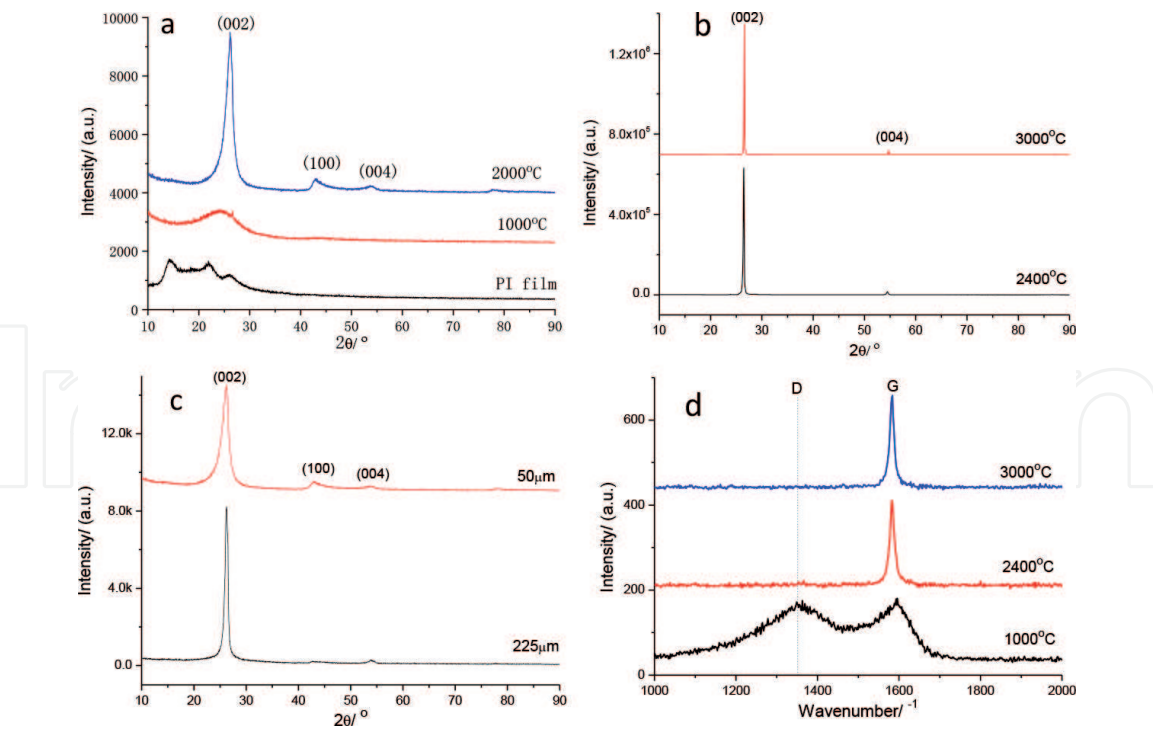
Figure 11.
SEM images of the transversal section of 3000°C-graphitized films derived from Kapton PI films with different thicknesses of ((a) 50, (b) 75, (c) 100 μm) and other brand PI film with a thickness of 50 μm at different enlargements (d–f).
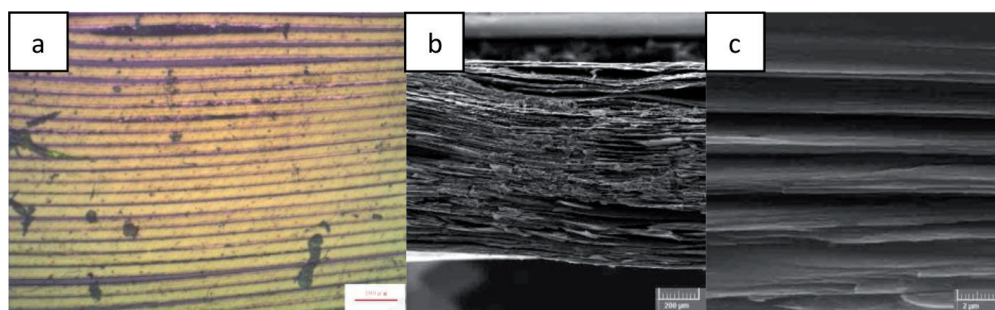
Figure 12.
(a) PLM and (b and c) SEM images of the transversal section of PI film-stacked block made by a suitable molding-press treatment at 2400°C.

is very low, and the graphite crystalline size is large [29]. It is worth noting that the microcrystalline size and g of graphite films are affected significantly by the nature (e.g., the extent of biaxial stretching on the original film) and thickness of PI films. The microcrystals in the thick graphite films grow and crystallize slowly, and their preferred orientation is relatively low. As a comparison, the graphite films made from other brand PI show an amorphous structure after graphitization at 3000°C, their microcrystals are small and disordered. The higher the heat-treatment temperature is, the easier the structural transformation completes. Graphitization treatment results in the better growth and crystallization of graphite microcrystals and the preferable orientation of graphene layers in the graphite films.

Figure 14a shows the room-temperature electrical resistivities of the Kapton PI films after heat treatment at different temperatures. It can be seen that the electrical resistivities of the PI films decrease significantly with the increase of the heat treatment temperature, indicating that the electrical conductivities increase rapidly. The PI film is a polymer insulating material and its volume electrical resistivity is as high as 10^{16} Ω cm. After 1000°C carbonization treatment, the electrical resistivity
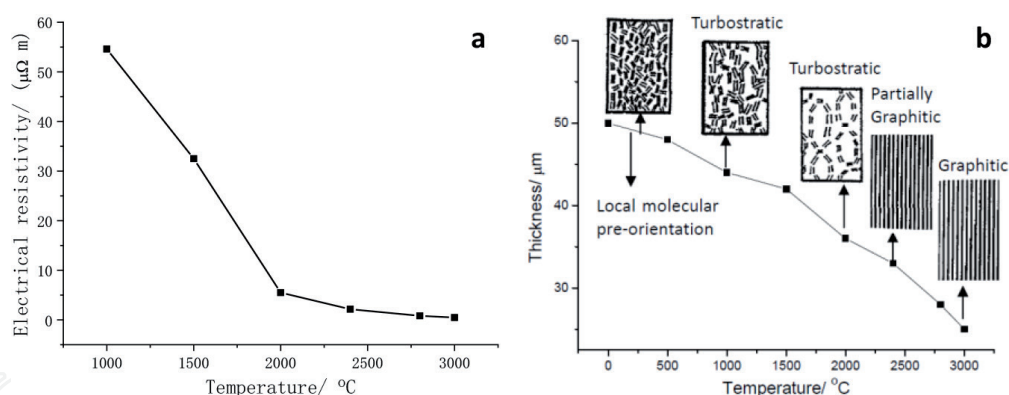
Figure 13.
(a–c) XRD patterns and (d) Raman spectra of various PI films ((a, b and d) Kapton; (c) other brand) heat-treated at different temperatures.

Sample	$2\theta_{002}/°$	d_{002}/nm	Lc/nm	g/%
PI raw film	25.94	0.343	2.03	10
PI-1000°C-50 μm	24.37	0.365	3.06	—
PI-2000°C-50 μm	26.12	0.341	5.63	34
PI-2400°C-50 μm	26.44	0.338	39.83	70
PI-2800°C-50 μm	26.50	0.337	50.95	82
PI-3000°C-50 μm	26.56	0.336	65.94	93
PI-3000°C-100 μm	26.33	0.338	49.71	70
PI-3000°C-50 μm[a]	26.22	0.340	12.42	47
PI-3000°C-225μm[a]	26.01	0.342	5.63	23
Single crystal graphite	26.58	0.3354	>100	100

[a]*Other brand PI film.*

Table 1.
Microcrystalline parameters of various PI films heat-treated at different temperatures.

reduces by 18 orders of magnitude, to about 54.6 μΩ m, because the PI film has undergone structural changes at this time, most of the heteroatoms are eliminated, and the carbon content increases significantly. At this stage, a local hexagonal-like carbon layer structure forms in the interior of carbon film. The electrical resistivities of the graphitized samples at 2000 and 2800°C are 5.5 and 0.82 μΩ m, respectively. The decline is not very large due to the fact that the conductive path in PI film has been formed around 2000°C. Further graphitization is only to improve its three-dimensional ordered structure with highly preferred orientation as shown in **Figure 10**. The electrical resistivity of the 3000°C-graphitized PI film is as low as 0.48 μΩ m, which is very close to the theoretical electrical resistivity of single crystal graphite (0.4 μΩ m) in the planar direction [30]. With the rise of heat treatment

Figure 14.
(a) Room-temperature electrical resistivities of PI films heat-treated at different temperatures in the planar direction and (b) micro-structural evolution and transformation mechanism model from PI polymer to ordered graphite film during high-temperature treatment reproduced from [6].

temperature, the g of PI films continues to increase as listed in **Table 1**, and its internal graphene layered structure with highly preferred orientation is conducive to the transmission of electrons [2, 4].

From the above discussion on the morphology and microstructure of the PI films heat-treated at different temperatures, a microstructural change model from PI polymer to ordered graphite at each stage is shown in **Figure 14b** [6]. The heat-treatment process can be roughly divided into four stages: the first stage (500-1000°C), the second stage (1000-2000°C), the third stage (2000-2400°C) and the fourth stage (2400-3000°C). The whole process reflects that the internal structure of the PI film gradually changes from a disorderly amorphous structure to a highly crystalline graphite structure as the heat treatment temperature progresses [4].

According to the relevant empirical formulas [31], the thermal conductivity of 3000°C-graphitized graphite films (with a thickness of ca. 25 μm) is calculated to be 1143 W/m K. Measured by a laser thermal conductivity meter (NETZSCH LFA 457), its room-temperature thermal diffusion coefficient is ~700 mm^2/s, and the corresponding thermal conductivity is measured to be 994 W/m K (the bulk density and specific heat are about 2.0 g/cm^3 and 0.71 J/g K, respectively). This excellent conduction performance is attributed to the highly ordered three-dimensional graphite structure of this film material.

5. Influencing factors on thermal conductivity of graphite films

It is well-known to all that the high-thermal-conductivity of carbon materials comes from the strong C—C covalent bonding between carbon atoms and the highly ordered graphite structure stacked by graphene layers and mainly results from the anharmonic vibration of the elastic lattice (i.e., the mutual interaction of phonons) to transfer heat [32]. Single crystal graphite has a hexagonal network layered structure and an anisotropic thermal conductivity, as shown in **Figure 15a**, its thermal conductivity along the a-axis direction (as high as 2000 W/m K) is much greater than that along the c-axis direction [33]. However, for carbon materials with a disordered graphite structure, the graphene layers with different sizes are stacked randomly, a lower thermal conductivity will yield unexpectedly. There are many critical factors governing the heat-dissipation performance of graphene-assembling carbon materials, such as microcrystalline size, crystalline orientation, structural defects (e.g., vacancies and substitution) and wrinkle deformation in graphene layers as shown in **Figure 15b** [34].
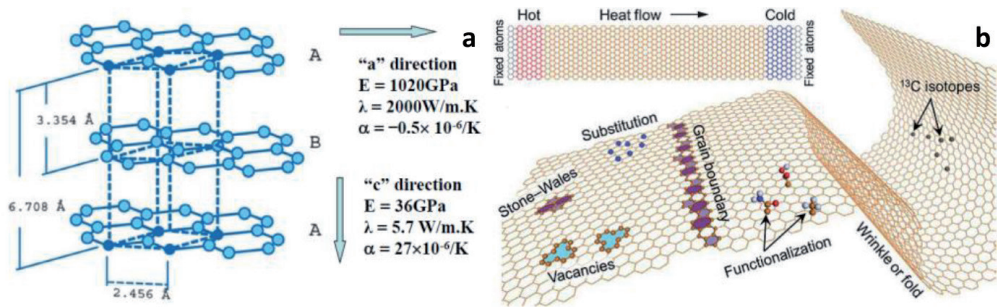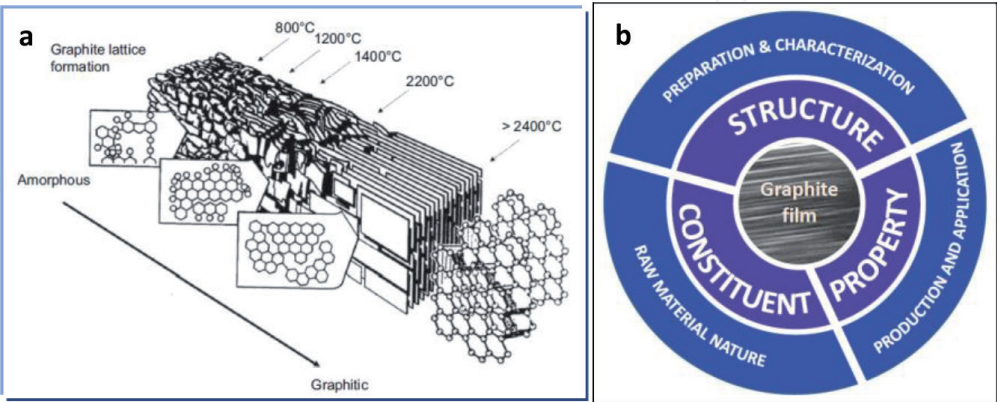
Figure 15.
(a) Crystal structure of perfect graphite with anisotropic thermal conductivity reproduced from [33] and
(b) key factors determining heat dissipation of graphene-assembling film materials [34].

Usually, organic carbonaceous compounds are used as raw materials to prepare carbon materials. Under low temperature at about 300-1000°C, the component containing H, O, N and other non-C elements in organic compounds is gradually decomposed, and C-containing aromatic molecules continue to cyclize and aromatize, which forms C-rich material (i.e., carbon material), and finally through the graphitization process up to 3000°C, pure C material, i.e., graphite material can be obtained. Most of the chemical reactions during the carbonization of precursors are accompanied by the evolution of various gases—different hydrocarbons, carbon oxides, and H_2 [35]. It is important to timely remove the pyrolytic gases from the stress-stacked PI films in the highly sealed furnace. The conversion from PI polymer film to graphite film is a typical process of solid phase carbonization. Its prominent characteristic is the similarity in morphology (and shape) of raw material and final product without experiencing a fusion process, which is different from that of liquid phase carbonization [36]. Therefore, selecting proper carbonaceous precursors (e.g. Kapton PI film) and appropriate heat treatment process (e.g., high temperature graphitization under a suitable pressure and duly degassing treatment) to control the growth, accumulation and orientation of graphite microcrystals inside the carbon materials as shown in **Figure 16a** [37], are essential for obtaining graphite films with high thermal conductivity.

As a result, the thermal conductivity of graphite films mainly depends on the nature of the polymer films and their capability of forming an ordered graphite structure through high-temperature heat treatment as diagramed in **Figure 16b**. There are three mainly important conditions for obtaining graphite films with high thermal conductivity as follows [2, 4, 7, 28]. Firstly, high carbon content in the large

Figure 16.
(a) Marsh-Griffiths model of carbonization-graphitization process on a carbonaceous precursor [37] and
(b) a diagram of quality control strategy for high-thermal-conductivity graphite films.

molecules and high carbon yield after carbonization treatment. Secondly, the quality of polymer films (e.g., the constituents and structure of aromatic molecules, high molecular planarity and suitable stiffness as well as molecular orientation degree through the role of biaxial stretching treatment, appropriate film thickness). Thirdly, heat treatment process control (e.g., heating treatment procedure, molding-press condition, non-carbon elements escape, and final graphitization temperature).

6. Latest developments of PI-derived carbons with high thermal conductivity

6.1 Modification of PI precursor to improve the flexibility of graphite films

There is no denying that the PI-derived graphite films with high thermal conductivity after graphitization treatment have a certain degree of brittleness as shown in **Figure 17a** due to their high stiffness (modulus) and high crystallinity and crystalline orientation, which undoubtedly limits their wide applications. It is difficult to achieve high thermal conductivity and ideal mechanical properties for the graphite films (e.g., internally contradictory indices like high modulus (associating with thermal conductivity) and high flexibility are hardly satisfied simultaneously) except a few reports such as Refs [2, 11, 39, 40]. Nowadays, the modification by doping of PI precursor with graphene (and graphene oxide) and other precursors (e.g., polyacrylonitrile) is a good strategy to improve the flexibility of graphite films with high thermal conductivity [38, 41–43] as shown in **Figure 17b**. It is interesting to note that various striking cranes with good flexibility as shown in **Figure 18** made with different raw materials by different methods and processes have been successfully prepared [2, 19, 38, 43].

6.2 Versatile forms of PI-derived carbons

Recently, many new forms of PI-derived carbons (including carbon fibers, carbon foams, carbon aerogels and carbon blocks as shown in **Figure 19**, which are beyond graphite films) with a feature of high thermal conductivity have been fabricated [44–51]. This extensive and intensive research on PI polymer will expand its application areas. Especially, ultrathick graphene film with a high thickness up to 200 μm while retaining a high thermal conductivity of 1200 W/m K has been achieved [52], which will stimulate the preparation of ultrathick (e.g., millimeter-scale) PI-derived graphite films or large graphite blocks.
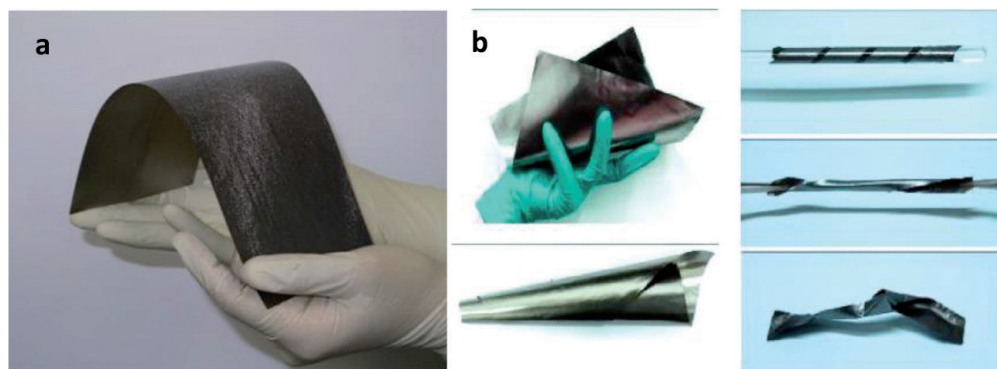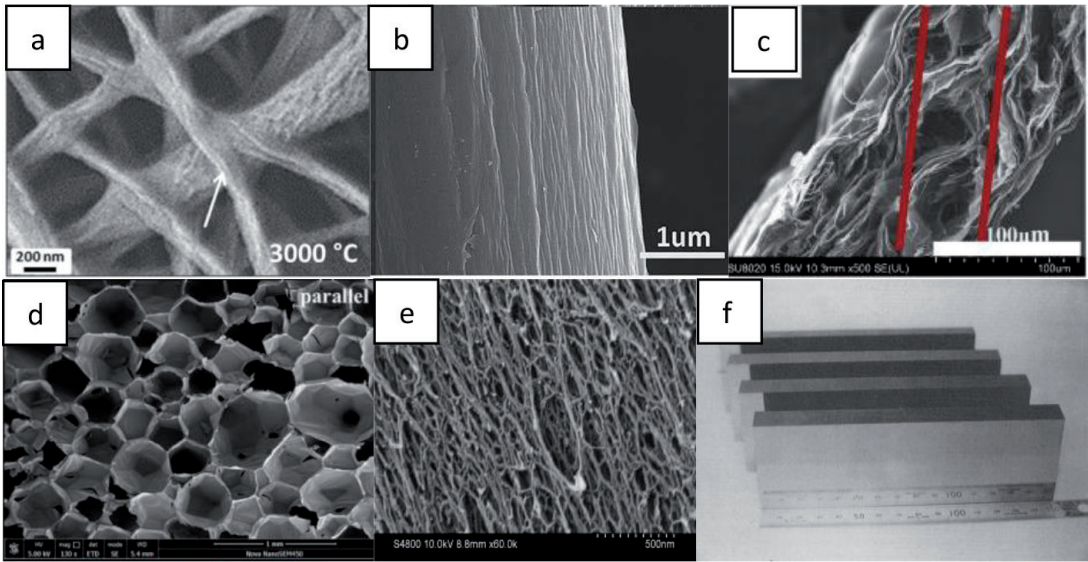

Figure 17.
Optical photographs of (a) highly-oriented PI-derived graphite thin sheet with improved manual handling [11] and (b) superflexible (bending, curling, enwinding, twisting, and knotting) graphene films [38].
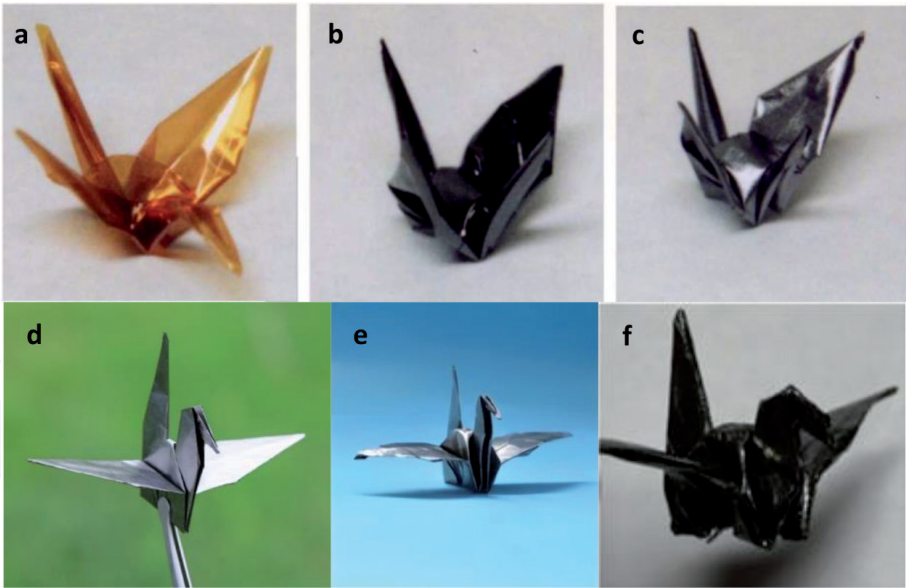
Figure 18.
Optical photographs of evolutional crane made of a PI film (a) and after carbonization (b) and graphitization (c) treatments showing good shape-retention and flexibility [2] and (b) various cranes derived from superfoldable graphene film (d) [38], polyacrylonitrile-derived graphite film (e) [43] and flexible graphite sheet (f) [19].
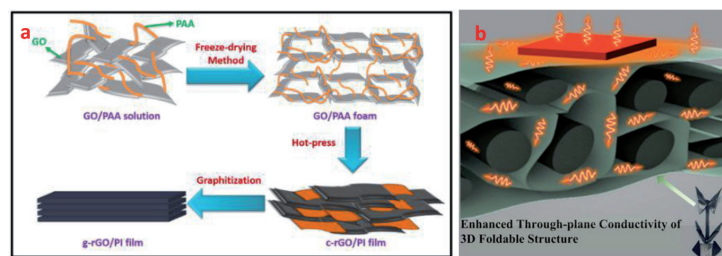

Figure 19.
(a–e) SEM images of various PI-derived carbons with high thermal conductivity ((a) carbon nanofibers [44], (b) carbon microfibers [45], (c) carbon bubbles [46], (d) carbon foams [47], (e) carbon aerogels [48]) and (f) optical photograph of highly oriented graphite blocks prepared from PI [49].

6.3 PI-derived composite materials

It is well accepted that graphene-based carbon films as thermal management materials can boost the heat-dissipation performance of film materials in the planar direction [21–23, 32–34, 38–41, 53, 54]. Through new functional composite technologies (e.g., chemical interaction as shown in **Figure 20a** [53], and modification treatment through doping or hybridizing with other carbonaceous precursors (graphene, carbon nanotube, etc.) and non-carbon fillers such as BN) [53–56], the thermal conductivity and mechanical flexibility of resultant graphite films can be both enhanced. Furthermore, in the through-plane direction, a superhigh thermal conductivity up to 150 W/m K can be obtained by novel structure design as shown in **Figure 20b** [54]. This affords carbon materials with a feature of three-dimensional

Figure 20.
(a) A diagram of preparing composite films through the covalent bonding between graphene oxide and PI [53] and (b) a 3-D hybridized structure of composite carbon film made with graphene oxide and PI [54].

high thermal conductivity (it is beyond the traditional graphite materials with high thermal conductivity only in the planar direction [32]), which will further promote the wide practical applications of carbon materials in thermal management [22, 23, 53–55, 57–59].

7. Conclusions

In a lab-scale study, the Kapton PI-derived graphite films (with a thickness of 50 μm for raw film) show a three-dimensional ordered structure consisting of graphene layers with highly preferred orientation and prefect graphite crystals after graphitization at 3000°C. Their electrical resistivity and thermal conductivity at room temperature in the planar direction are 0.48 μΩ m and ~ 1000 W/m K, respectively. The nature of PI precursor (the molecular structure, planar molecular orientation and film thickness, etc.) and preparation technics (e.g., heat-treatment temperature and molding pressure) have a critical influence on the final conduction performance of graphite films.

In the early time, limited by preparation technology, the thickness of PI-derived graphite films were mainly 20–50 μm, and their thermal conductivity in the planar direction was mostly 300–1000 W/m K. With the continuous improvement of production technology, high-thermal-conductivity graphite film products become more abundant, and some are even industrialized. The 10 μm-thin graphite films can approach a high thermal conductivity of 1900 W/m K. Currently, the thickest product (derived from graphene) is about 200 μm, and its thermal conductivity could reach about 1200 W/m K. However, there is still no breakthrough in the preparation of millimeter-thick graphite films and PI-derived graphite blocks with large sizes. In the future, as the application range widens, the market demand for high-thermal-conductivity graphite films will be more diversified, and the diverse products will also be developed in the direction of wider thickness and higher thermal conductivity.

The emerging modification treatment and composite technology provide a promising strategy not only to improve the comprehensive performance (e.g., high thermal conductivity and good mechanical flexibility) of PI-derived graphite films but also to prepare a variety of new forms of PI-derived carbon materials with high thermal conductivity. Furthermore, polymer-derived carbon materials with a significant feature of three-dimensional high thermal conductivity can be achieved by novel structure design.

At present, high-thermal-conductivity graphite films have been widely used in smart phones, successfully solving the heat dissipation problem of various electronic products. In the near future, with the development of miniaturization and thinning of electronics, high-thermal-conductivity graphite films and other carbon composites with good flexibility will be promisingly used in the field of thermal

management as next-generation heat-dissipation components for highly integrated microelectronics, 5 G wireless communication, and high-power smart devices.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Author details

Guanming Yuan[1,2]* and Zhengwei Cui[1,2]

1 The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

2 Hubei Province Key Laboratory of Coal Conversion and New Carbon Materials, Wuhan University of Science and Technology, Wuhan, China

*Address all correspondence to: yuanguanming@wust.edu.cn

IntechOpen

References

[1] Inagaki M. New Carbons Control of Structure and Functions. Oxford: Elsevier Science Ltd; 2000. pp. 35-39. DOI: 10.1016/B978-008043713-2/50010-8

[2] Inagaki M, Ohta N, Hishiyama Y. Aromatic polyimides as carbon precursors. Carbon. 2013;61:1-21. DOI: 10.1016/j.carbon.2013.05.035

[3] Burger A, Fitzer E, Heym M, et al. Polyimides as precursors for artificial carbon. Carbon. 1975;13(3):149-157. DOI: 10.1016/0008-6223(75)90225-0

[4] Inagaki M, Takeichi T, Hishiyama Y, Oberlin A. High quality graphite films produced from aromatic polyimides. In: Thrower PA, Radovic LR, editors. Chemistry and Physics of Carbon. Volume 26. New York: Marcel Dekker, Inc; 1999. pp. 245-333.

[5] Hishiyama Y, Yoshida A, Kaburagi Y. Graphite films prepared from carbonized polyimide films. Carbon. 1992;30(3):333-337. DOI: 10.1016/0008-6223(92)90027-T

[6] Bourgerette C, Oberlin A, Inagaki M. Structural and textural changes from polyimide Upilex to graphite: Part III. Journal of Materials Research. 1993;8(1):121-130. DOI: 10.1557/JMR.1993.0121

[7] Hishiyama Y, Nakamura M, Nagata Y, et al. Graphitization behavior of carbon film prepared from high modulus polyimide film: synthesis of high-quality graphite film. Carbon. 1994;32(4):645-650. DOI: 10.1016/0008-6223(94)90085-X

[8] Kaburagi Y, Hishiyama Y. Highly crystallized graphite films prepared by high-temperature heat treatment from carbonized aromatic polyimide films. Carbon. 1995;33(6):773-777. DOI: 10.1016/0008-6223(95)00009-3

[9] Hishiyama Y, Igarashi K, Kanaoka I, et al. Graphitization behavior of Kapton-derived carbon film related to structure, microtexture and transport properties. Carbon. 1997;35(5):657-668. DOI: 10.1016/S0008-6223(97)00021-3

[10] Zhong DH, Sano H, Kobayashi K, Uchiyama Y. A study of film thickness dependence of the graphitizability of PMDA–ODA polyimide-derived carbon film. Carbon. 2000;38(15):2161-2165. DOI: 10.1016/S0008-6223(00)00075-0

[11] Murakami M, Tatami A, Tachibana M. Fabrication of high quality and large area graphite thin films by pyrolysis and graphitization of polyimides. Carbon. 2019;145:23-30. DOI: 10.1016/j.carbon.2018.12.057

[12] Kato T, Yamada, Y, Nishikawa Y, et al. Carbonization mechanisms of polyimide: Methodology to analyze carbon materials with nitrogen, oxygen, pentagons, and heptagons. Carbon. 2021;178:58-80. DOI: 10.1016/j.carbon.2021.02.090

[13] Murashima K, Kawashima Y, Ozaki S, et al. Modified-edge-support heat treatment method of polyimide for crystalline, large-area, and self-standing ultrathin graphite films. Carbon. 2021;181:348-357. DOI: 10.1016/j.carbon.2021.05.036

[14] Inagaki M, Kang FY. Materials Science and Engineering of Carbon: Fundamentals. 2nd Edition. Beijing: Tsinghua University Press; 2014. p. 265. DOI: 10.1016/C2013-0-13699-9

[15] Bertram A, Beasley K, Torre W. An overview of navy composite developments for thermal management. Naval Engineers Journal. 1992;104(4):276-285. DOI: 10.1111/j.1559-3584.1992.tb01170.x

[16] Zheng Q, Braun PV, Cahill DG. Thermal conductivity of graphite thin

films grown by low temperature chemical vapor deposition on Ni (111). Advanced Materials Interfaces. 2016;3(16):1600234. DOI: 10.1002/admi.201600234

[17] Kato R, Hasegawa M. Fast synthesis of thin graphite film with high-performance thermal and electrical properties grown by plasma CVD using polycrystalline nickel foil at low temperature. Carbon. 2019;141:768-773. DOI: 10.1016/j.carbon.2018.09.074

[18] Hu KS, Chung DDL. Flexible graphite modified by carbon black paste for use as a thermal interface material. Carbon. 2011;49(4):1075-1086. DOI: 10.1016/j.carbon.2010.10.058

[19] Hou SY, He SJ, Zhu TL, et al. Environment-friendly preparation of exfoliated graphite and functional graphite sheets. Journal of Materiomics. 2021;7(1):136-145. DOI: 10.1016/j.jmat.2020.06.009

[20] Thermal protection sheet (Graphite Sheet (PGS)/PGS applied products/ NASBIS). https://industrial.panasonic.com/ww/products/pt/pgs

[21] Wu TS, Xu YL, Wang HY, Sun ZH, Zou LY. Efficient and inexpensive preparation of graphene laminated film with ultrahigh thermal conductivity. Carbon. 2021;171:639-645. DOI: 10.1016/j.carbon.2020.09.039

[22] Chen S, Wang Q, Zhang M, et al. Scalable production of thick graphene films for next generation thermal management applications. Carbon. 2020;167:270-277. DOI: 10.1016/j.carbon.2020.06.030

[23] Song NJ, Chen CM, Lu CX, et al. Thermally reduced graphene oxide films as flexible lateral heat spreaders. Journal of Materials Chemistry A. 2014;2(39): 16563-16568. DOI: 10.1039/C4TA02693D

[24] Li HL, Dai SC, Miao J, et al. Enhanced thermal conductivity of graphene/polyimide hybrid film via a novel "molecular welding" strategy. Carbon. 2018;126:319-327. DOI: 10.1016/j.carbon.2017.10.044

[25] Akbari A, Cunning BV, Joshi SR, et al. Highly ordered and dense thermally conductive graphitic films from a graphene oxide/reduced graphene oxide mixture. Matter. 2020;2(5):1198-1206. DOI: 10.1016/j.matt.2020.02.014

[26] Zhong J, Sun W, Wei Q, et al. Efficient and scalable synthesis of highly aligned and compact two-dimensional nanosheet films with record performances. Nature Communications. 2018;9(1):3484. DOI: 10.1038/s41467-018-05723-2

[27] Liu YJ, Li P, Wang F, et al. Rapid roll-to-roll production of graphene films using intensive Joule heating. Carbon. 2019;155:462-468. DOI: 10.1016/j.carbon.2019.09.021

[28] Yuan GM, Li XK, Dong ZJ, et al. Preparation and characterization of graphite films with high thermal conductivity. Functional Materials. 2015;46(17):17097-17101. DOI: 10.15541/jim20160156

[29] Tuinstra F, Koenig JL. Raman spectrum of graphite. Journal of Chemical Physics. 1970;53(3):1126-1130. DOI: 10.1063/1.1674108

[30] Dutta AK. Electrical conductivity of single crystals of graphite. Physical Review. 1953;90(2):187-192. DOI: 10.1103/PhysRev.90.187

[31] Lavin JG, Boyington DR, Lahijani J, et al. The correlation of thermal conductivity with electrical resistivity in mesophase pitch-based carbon fiber. Carbon. 1993;31(6):1001-1002. DOI: 10.1016/0008-6223(93)90207-Q

[32] Taylor R. The thermal conductivity of pyrolytic graphite. Philosophical Magazine. 1966;13(8):157-166. DOI: 10.1080/14786436608211993

[33] Norley J. The role of natural graphite in electronics cooling. Electronics Cooling Magazine. 2001. http://www.electronics-cooling.com/2001/08/the-role-of-natural-graphite-in-electronics-cooling

[34] Pop E, Varshney V, Roy AK. Thermal properties of graphene: fundamentals and applications. MRS Bulletin. 2012;37(12):1273-1281. DOI: 10.1557/mrs.2012.203

[35] Inagaki M, Kang FY, Toyoda M, Konno H. Advanced Materials Science and Engineering of Carbon. Beijing: Tsinghua University Press; 2013. p. 68. DOI: 10.1016/C2012-0-03601-0

[36] Yuan GM, Cui ZW. Preparation, characterization, and applications of carbonaceous mesophase: a review. In: Ghamsari MS, Carlescu I, editors. Liquid Crystals and Display Technology. IntechOpen; 2020. pp. 101-120. DOI: 10.5772/intechopen.88860

[37] Marsh H. Introduction to Carbon Science. London: Butterworths; 1989. pp. 7-8.

[38] Peng L, Xu Z, Liu Z, et al. Ultrahigh thermal conductive yet superflexible graphene films. Advanced Material. 2017;29 (27):1700589. DOI: 10.1002/adma.201700589

[39] Wang N, Samani MK, Li H, et al. Tailoring the thermal and mechanical properties of graphene film by structural engineering. Small. 2018;14(29):1801346. DOI: 10.1002/smll.201801346

[40] Wang B, Cunning BV, Kim NY, et al. Ultrastiff, strong, and highly thermally conductive crystalline graphitic films with mixed stacking order. Advanced Materials. 2019;31(29):1903039. DOI: 10.1002/adma.201903039

[41] Ma LR, Wang YX, Wang YY, et al. Graphene induced carbonization of polyimide films to prepared flexible carbon films with improving-thermal conductivity. Ceramics International. 2020;46:3332-3338. DOI: 10.1016/j.ceramint.2019.10.042

[42] Wang K, Li MX, Zhang JJ, Lu HB. Polyacrylonitrile coupled graphite oxide film with improved heat dissipation ability. Carbon. 2019;144: 249-258. DOI: 10.1016/j.carbon.2018.12.027

[43] Huang HG, Ming X, Wang YZ, et al. Polyacrylonitrile-derived thermally conductive graphite film via graphene template effect. Carbon. 2021;180:197-203. DOI: 10.1016/j.carbon.2021.04.090

[44] Yan H, Mahanta NK, Wang BJ, et al. Structural evolution in graphitization of nanofibers and mats from electrospun polyimide–mesophase pitch blends. Carbon. 2014;71:303-318. DOI: 10.1016/j.carbon.2014.01.057

[45] Li A, Ma ZK, Song HH, et al. The effect of liquid stabilization on the structures and the conductive properties of polyimide-based graphite fibers. RSC Advance. 2015;5:79565-79571. DOI: 10.1039/C5RA10497A

[46] Tao ZC, Wang HB, Lian PF, et al. "Graphitic bubbles" derived from polyimide film. Carbon. 2017;116: 733-736. DOI: 10.1016/j.carbon.2017.02.044

[47] Ou AP, Huang Z, Qin R, et al. Preparation of thermosetting/thermoplastic polyimide foam with pleated cellular structure via in situ simultaneous orthogonal polymerization. ACS Applied Polymer Materials. 2019;1(9):2430-2440. DOI: 10.1021/acsapm.9b00558

[48] Feng JZ, Wang X, Jiang YG, et al. Study on thermal conductivities of aromatic polyimide aerogels. ACS Applied Materials & Interfaces. 2016;8(20):12992-12996. DOI: 10.1021/acsami.6b02183

[49] Murakami M, Nishiki N, Knakamura K, et al. High-quality and highly oriented graphite block from polycondensation polymer films. Carbon. 1992;30(2):255-262. DOI: 10.1016/0008-6223(92)90088-E

[50] Wang JM, Li QX, Liu D, et al. High temperature thermally conductive nanocomposite textile by "green" electrospinning. Nanoscale. 2018;10:16868-16872. DOI: 10.1039/C8NR05167D

[51] Kausar A. Emerging polyimide and graphene derived nanocomposite foam: research and technical tendencies. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry. 2021;58(10):643-658. DOI: 10.1080/10601325.2021.1934011

[52] Zhang XD, Guo Y, Liu YJ, et al. Ultrathick and highly thermally conductive graphene films by self-fusion. Carbon. 2020;167:249-255. DOI: 10.1016/j.carbon.2020.05.051

[53] Zhu Y, Peng QY, Qin YY, et al. Graphene-carbon composite films as thermal management materials. ACS Applied Nano Materials. 2020;3(9):9076-90887. DOI: 10.1021/acsanm.0c01754

[54] Li YH, Zhu YF, Jiang GP, et al. Boosting the heat dissipation performance of graphene/polyimide flexible carbon film via enhanced through-plane conductivity of 3D hybridized structure. Small. 2020;16(8):1903315. DOI: 10.1002/smll.201903315

[55] Ning Wen, Wang ZH, Liu P, et al. Multifunctional super-aligned carbon nanotube/polyimide composite film heaters and actuators. Carbon. 2018;139:1136-1143. DOI: 10.1016/j.carbon.2018.08.011

[56] Ou XH, Chen SS, Lu XM, Lu QH. Enhancement of thermal conductivity and dimensional stability of polyimide/boron nitride films through mechanochemistry. Composites Communications. 2021,23:100549. DOI: 10.1016/j.coco.2020.100549

[57] Loeblein M, Bolker A, Tsang SH, et al. 3D Graphene-infused polyimide with enhanced electrothermal performance for long-term flexible space applications. Small. 2015;11(48):6425-6434. DOI: 10.1002/smll.201502670

[58] Wang Y, Wang HT, Liu F, et al. Flexible printed circuit board based on graphene/polyimide composites with excellent thermal conductivity and sandwich structure. Composites Part A: Applied Science and Manufacturing. 2020;138(44):106075. DOI: 10.1016/j.compositesa.2020.106075

[59] Luo XH, Guo QG, Li XF, et al. Experimental investigation on a novel phase change material composites coupled with graphite film used for thermal management of lithium-ion batteries. Renewable Energy. 2020;145:2046-2055. DOI: 10.1016/j.renene.2019.07.112