Quantitative appraisal of the interfacial anchoring state of polyaromatic hydrocarbons during the formation of C/C composites

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ABSTRACT

The preferred anchoring state for polycyclic aromatic hydrocarbons (PAHs) pyrolyzed onto carbon substrates has been studied by semi-quantitative methods, examining their interfacial lattice arrangements. The samples were prepared by decomposing petroleum pitch inside carbon nanotubes resulting in a variety of crystallinities forming one-dimensional C/C composites. Studies indicate that the preferred anchoring state of PAH molecules depends on the nature of the substrate. Accordingly the PAHs in mesophase pitch should exhibit a face-on orientation on the carbonaceous substrates, including a graphite sheet, glassy carbon, and pyrolytic carbon. However, it showed that the anchoring state (face-on or edge-on) of PAH units can be altered even on carbonaceous substrates. The results demonstrated that in C/C composites the anchoring state is predominantly determined by the relative degree of crystallinity of the pitch/carbon substrate, and can be semi-quantitatively estimated using the I_D/I_G ratio from Raman spectra. Face-on anchoring is preferred when the I_D/I_G ratio of substrate is smaller (higher crystallinity) than that of the pyrolyzed precursor, whereas edge-on anchoring is favored when it is larger. Such an estimation method is useful in tailoring microstructures in the fabrication of C/C composites using PAH precursors.

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1. Introduction

The investigation of the surface anchoring effect at the boundaries between polycyclic aromatic hydrocarbon (PAH) molecules/substrates attracts academic interest. There are two categories of surface anchoring states, edge-on and face-on, expounded by Hurt et al. [1–3]. The preference of the anchoring state is dependent on the competition between intermolecular forces within PAH molecules and between PAH units/substrate. Usually the sample is prepared by spreading and pyrolyzing the PAH precursor on the substrate for observation under a polarized optical microscope. However, the conventional method cannot provide direct evidence of the anchoring state in the vicinity of the boundary between PAHs/matrices. This is because the ordered anchoring region is sometimes on the scale of sub-micrometers and therefore beyond the optical resolution limit [2]. Another effective way to obtain information of interfacial anchoring states is...
to examine the arrangement of graphene layers within the sample using high-resolution transition electron microscopy (TEM). Since the penetration depth of electron beams at 200 kV is only tens of nanometers, the sample prepared for optical microscope analysis is not appropriate for TEM observation.

Recently, the template synthesis method using nanoporous anodic alumina (AAO) has been extensively applied to produce various one-dimensional carbon nanomaterials, like nanofibers [4–6] or nanotubes [7–9]. The microstructure of such nano-sized materials can be easily studied under TEM. In addition, it is known that the alignment of PAHs, which is affected by interaction with the surface of the substrate (the surface anchoring effect), can be extended into the sample body in the range of sub-micrometers [1,6]. Although the anchored molecules are restricted to the superficial region of a bulk material, the arrangement of the PAH molecules can dominate the entire microstructure as the dimension of the products approaches nanoscale. Therefore, such one-dimensional carbon nanomaterials are ideal intermediates to study the interfacial microstructure because of the pronounced anchoring behavior.

Present-day studies imply that the anchoring states of mesophase pitches depend on the type of substrate [1–3,10]. Edge-on anchoring is found on most substrates, whereas face-on anchoring is only observed on carbon, mica, polyimide, and silver. These reports also indicate that PAH molecules always exhibit a face-on orientation on a graphite-based surface and carbonaceous substrates, such as glassy carbon, carbon fibers, and pyrolytic carbon. The results inspired our interest in investigating whether PAHs can exhibit alternative anchoring states on a certain substrate and, if so, what interfacial anchoring patterns will be shown.

In this study, a variety of tubular carbon substrates were prepared and investigated for their preferred orientations of the graphene layers at the interface of pitch/carbon composites. The anchoring states of carbonized pitch in C/C composites were identified by high-resolution TEM and quantitatively characterized by Raman spectroscopy for their crystallinity.

2. Experimental

Thin carbon layers (5–50 nm) with different degrees of crystallinity were coated on a channel surface of AAO (Whatman Ltd.) becoming a carbonaceous substrate. Because each chemical vapor deposition (CVD) process has its own limitations, several kinds of depositions, such as acetylene decomposition (Samples B and D) [11,12], ethanol pyrolysis (Sample C [13,14], and Wurtz-type reaction (Sample E) [15–17] were employed to coat the AAO channels. The details of preparation can be found in Supporting Information. The adopted PAH precursor is isotropic petroleum pitch (A-240, Ashland Inc.), which is composed of hetero-PAH molecules. The precursor was spread on top of the templates with or without carbon coating for pyrolyzing the PAHs inside the channels during subsequent thermal treatment. In a tube furnace the temperature was held at 300 °C for half an hour under flowing Ar to soften the precursor, and then gradually raised to 700 °C for 2 h for the pyrolysis. The oxide template was removed by immersing in hydrofluoric acid. For the study of interfacial microstructure, all the products were annealed at 2500 °C to enhance their lattice orientation. The samples were characterized by high-resolution TEM (HRTEM, JEOL JEM-2010) and Micro-Raman scattering measurements (CHROMEX 501is: 488 nm).

3. Results and discussion

The petroleum pitch carbonized at 700 °C in the bare channels of AAO template without carbon coating (Sample A) was first examined. After leaching off the template, the product was found to be composed of uniform nanofilaments, as shown in Fig. 1a. Their diameter and length were evaluated to be 300 ± 50 nm and 60 μm, respectively, which accurately correspond to the channel size of the template. This implies that during the softening process, the channels of the template were fully impregnated with liquid-phase pitch, in which the alignment of PAH molecules is strongly influenced by the oxide inner surface of the channels. In the lattice image (Fig. 1b) it can be seen that the orientation of graphene layers is normal or oblique to the longitudinal axis of the nanofilaments. This suggests that the interaction between PAHs and alumina would result in an edge-on anchoring state. The result is in agreement with that of previous observations [5,18,19].

Carbon substrates made by coating carbon on AAO channels with different methods (Samples B–E) were obtained after the removal of template. Their appearance in scanning electron micrographs (SEM) is similar to that in Fig. 1a. However, in TEM (see Fig. S2) these substrates exhibit a tubular structure, and their hollow cores will be used in pitch-filling to form C/C composites with a core–shell structure. The diffraction spots in Fig. S2a can be assigned to the (0 0 2) lattice plane of graphite. It indicates that after graphitization the carbon substrate of Sample B comprises of graphite basal planes, whereas other samples show nanocrystalline carbon. In order to determine their interfacial anchoring state, the lattice images at the boundary of C/C composites (Samples B–E) were observed by high-resolution TEM. These core–shell materials were also treated at >2500 °C to develop crystallinity, thus enhancing the contrast of the lattice framework. Such a high-temperature treatment does not change the graphene orientation of the sample post-carbonization [2,20].

Fig. 2a (Sample B) shows that the arrangement of carbonized PAH units on the right side prefer to align parallel to the basal planes of the substrate on the left side, representing a face-on anchoring behavior. A similar result is seen with the pyrolysis of naphthalene polymer into multi-walled carbon nanotubes [21]. The lattice images become slightly clearer after thermal treatment, and the alignment tendency does not change (see Fig. 2b). As liquid-phase pitch carbonized in the channel coated with nanocrystalline carbon layer, the C/C interface becomes ambiguous and difficult to distinguish, as shown in Fig. S3a and c. After high-temperature treatment, the lattice alignment of PAH units in both Samples C and D can be discriminated as having a face-on anchoring preference (see Fig. S3b and d), in agreement with previous observations as well [1,2].
An entirely different result was obtained when the PAHs were carbonized on a carbon substrate with very low crystallinity (Sample E). After carbonization, an ambiguous C/C boundary with different lattice orientations can be roughly observed, as shown in Fig. 2c. In lattice images of Fig. 2d and e, the inclined edge-on anchoring from graphitized Sample E is shown. The semi-circular loops on the edge of the pitch filler imply that the dangling sites, rather than basal planes of PAH units, are exposed at the C/C interface, confirming edge-on alignment. Such loops on the surface of graphene edge are usually found in graphitized carbon materials [5,20]. Two sets of (0 0 2) diffraction spots exhibited in the...

Fig. 1 – (a) SEM and (b) high-resolution TEM images of carbon nanofilaments (Sample A) produced by carbonizing the pitch in the channels of nanoporous AAO. The lattice image exhibits an edge-on anchoring state.

Fig. 2 – Interfacial lattice images of PAHs pyrolyzed on graphite (Sample B) and nanocrystalline carbon (Sample E) substrates: Sample B after (a) carbonization, and (b) graphitization; Sample E after (c) carbonization, and (d) (e) graphitization. A dot line indicates where the C/C boundary is.
inset of Fig. 2d also signifies that at the C/C boundary it is composed of two groups of graphene stackings. The significant influence of surface anchoring effect in nanoscale can be manifest in Fig. S4. Even though the thickness of carbon shell (substrate) is only ~2% of the diameter of the nanofilament (see Fig. 2e), the appearance of the C/C composite is still substantially altered as the anchoring state changes. In nanoconfined environments, the enlarged elastic strain can dominate the anchoring arrangement as well. Four possible face-on configurations considering surface anchoring strength and elastic strain were proposed by Jian et al. [21]. The graphic microstructure of Sample E is disagreement with any proposed face-on configuration, indicating that two anchoring states can not be interchanged by internal elastic strain. In addition, edge-on state on disordered carbons might be affected by oxygen-containing functional groups on the surface of substrates. Although during thermal treatment most of adsorbed molecules should be expelled by reaction with carbons.

The degree of graphitization of all samples was determined by Raman scattering spectroscopy to systematically investigate the correlation between anchoring states and substrate crystallinity. Although the crystallinity of samples can be identified by the diffraction patterns of TEM as well, it is difficult to do quantitative comparison. Additionally, average grain size of samples can be estimated by peak width collected from X-ray diffractometer using Scherrer’s equation. However, as the crystallinity of carbon samples is low, only tiny (0 0 2) peak can be found in the pattern and others are hidden in the background. Therefore, the \( I_D/I_G \) ratio estimated from Raman pattern is suitable to semi-quantitatively denote the degree of graphitization of samples in a low-crystalline state. In this study, \( I_D/I_G \) ratios of samples were calculated as the ratio of peak heights using Breit–Wigner–Fano (BWF) + Lorentzian fits for comparison with Ferrari’s work [22]. The BWF function that has an asymmetric line shape, is given by:

\[
I(\omega) = I_0\left(1 + \frac{2(\omega - \omega_0)^2}{\omega_0^2}ight)^{-\frac{1}{2}}
\]

\[\omega_0 \text{ is the peak position, } I \text{ is the full width at half-maximum (FWHM), and } Q \text{ is the skewness coefficient.}
\]

The symmetrical Lorentzian shape is recovered in the limit as \( Q \to 0 \) [22–24]. Such a curve-fitting method is expounded to be satisfactory for the case of nanocrystalline and amorphous carbons [25]. All the fitting results were summarized in Table 1, including the \( I_D/I_G \) ratios obtained using a Gaussian fitting routine [26,27]. The correlation of the \( I_D/I_G \) ratios between using two kinds of fitting procedures is shown in Fig. S5.

In Raman spectra (Fig. 3a and b), the G-band (at 1550–1605 cm \(^{-1}\)) is attributed to the stretching-vibration mode of sp\(^2\) sites, such as in aromatic compounds or olefins (C=C chains), whereas D-band (near 1350 cm \(^{-1}\)) is caused by the breathing mode of those sp\(^2\) sites solely in aromatic rings. Ferrari et al. indicated that ranging from graphite (~100% sp\(^2\) sites) to tetrahedral amorphous carbon (~100% sp\(^3\) phase) visible Raman spectra can be elucidated using a three-stage model [22]. In our case while the G-band moves to the lower frequency, the \( I_D/I_G \) ratio decreases, and the FWHM of peak decreases as well. Therefore it can be concluded that all studied samples are composed of from micro- to nanocrystalline graphite without sp\(^3\) hybridization. The average \( I_D/I_G \) ratios of Sample A after pyrolysis (at 300 °C) and carbonization (at 700 °C) evaluated from Fig. 3a are 0.74 and 0.75, respectively. At the pitch/AAO interface the dispersive interaction between pitch/oxide is much weaker than the internal \( n-\pi \) bonding within PAH units, resulting in strong edge-on anchoring (see Fig. 1b). Typical Raman spectra of as-prepared carbon substrates before pitch-filling are shown in Fig. 3b. The average \( I_D/I_G \) ratio of Sample B is 0.15, indicating a well-developed graphite structure. The ratios of other samples with lower crystallinity were estimated to be in the range 0.60–1.09. Sample E has the highest \( I_D/I_G \) ratio, representing a very low-crystalline phase.

It was noted from the average \( I_D/I_G \) ratios, that if the crystallinity of carbon substrate (\( I_D/I_G \) ratio: 1.09, Sample E) is inferior to that of pyrolyzed pitch (\( I_D/I_G \) ratio: 0.74), the edge-on anchoring state is created. On the contrary, when the crystallinity of substrate is close to or better than that of pyrolyzed pitch, a face-on anchoring arrangement will be formed. Fig. 3c interprets that the interfacial microstructure is related to the \( I_D/I_G \) ratios (degrees of graphitization) of filler/substrate. This suggests that as the liquid-phase pitch pyrolyzes inside the carbon-coated channels, a competition in degree of order between self-assembling PAH molecules and the interfacial bonding with substrate will determine its ultimate anchoring state. Edge-on anchoring occurs on nanocrystalline carbon substrates because the PAH molecules assemble with themselves having higher surface energy than align along the substrate surface. As the degree of graphitization of substrate increases, the intermolecular attraction between pitch/substrate is enhanced, resulting in face-on anchoring to reach a lower energy conformation. An illustration of the two anchoring states at the boundary of pitch/carbon substrate is shown in Fig. 4. Such a semi-quantitative estimation method using

| Table 1 – Fitting parameters using BWF + Lorentzian and double-Gaussian fits for all samples. |
|------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                             | Sample A (300 °C) | Sample A (700 °C) | Sample B | Sample C | Sample D | Sample E |
| G-band position* (cm\(^{-1}\)) | 1598.5 | 1594.8 | 1587.0 | 1589.5 | 1602.2 | 1581.3 |
| FWHM* (cm\(^{-1}\)) | 75.1 | 72.1 | 119.9 | 76.0 | 53.1 | 20.0 |
| Peak ratio* (\( I_D/I_G \)) | 0.74 | 0.75 | 1.09 | 0.69 | 0.60 | 0.15 |
| Peak ratio* (\( I_D/I_G \)) | 2.60 | 2.73 | 4.11 | 2.63 | 2.45 | 0.42 |

* The parameters were obtained using BWF + Lorentzian fits, the \( I_D/I_G \) ratio was evaluated from the ratio of peak heights.

* The \( I_D/I_G \) ratio was evaluated from the ratio of integrated peak areas using two Gaussians.
Fig. 3 – Raman spectra measured from (a) pitch carbonized inside the channels of AAO, and (b) various carbon substrates before pitch-filling, (c) the $I_D/I_G$ ratios of samples versus their FWHM showing a linear relationship.

Fig. 4 – Comparative schemes: (a) face-on anchoring is preferred as the crystallinity of carbon substrate is better than that of pyrolyzed PAHs. (b) On the contrary edge-on anchoring will be created.
average $I_D/I_G$ ratios provides a simple and useful way to preprogram the microstructure of pitch/carbon composites. The interfacial texture in C/C composites deeply influences their physical and mechanical behavior [28,29].

4. Conclusions

The preferred anchoring state at C/C boundary in composites has been studied by directly observing their lattice orientation in high-resolution TEM. After examining the results of carbonized pitch on various carbon substrates, it has been demonstrated that the anchoring state is not only dominated by the nature of the substrates, but also the relative degree of crystallinity of pitch/carbon substrate. In addition, the resultant anchoring state can be determined by comparing the average $\frac{I_D}{I_G}$ ratio of pyrolyzed filler with that of carbon substrates from Raman spectra. When the carbon substrate has higher crystallinity than that of pyrolyzed pitch, the interfacial graphene orientation shows face-on anchoring, otherwise edge-on anchoring is preferred. This is helpful in understanding the microstructural patterns in C/C composites using PAHs as precursor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.11.024.

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