

PITCH WETTING ON MODEL BASAL AND EDGE-PLANE SURFACES

Phillip Wapner[†], Kengqing Jian^{††}, Yuming Gao^{††},
Gregory Crawford^{††}, Robert Hurt^{††}, Wesley Hoffman^{†††}

[†] ERC Inc., Edwards CA, 93524 USA, ^{††}Brown University, Providence, Rhode Island, 02912 USA, ^{†††}Air Force Research Laboratory, Edwards, CA, 93524 USA

Introduction

The wetting behavior of pitch plays an important role in the impregnation process for composites [1], in deposition and fouling within processing equipment for heavy hydrocarbons, and in the synthesis of new carbon forms derived from the infiltration of pitch into porous templates [2]. While there have been many studies of pitch rheology, especially under conditions relevant to fiber spinning [3], there have been few systematic studies of the true wetting behavior of pitch [4] or mesophase pitch [5]. At *Carbon2003* we presented first studies of pitch wetting and spreading on the HOPG basal plane used as a model for understanding pitch interactions with basal surfaces [6]. Here we extend the work to carbon edge-plane surfaces in an attempt to bracket the spectrum of real carbon surfaces, which contain widely varying fractions of basal and edge sites. The present work focuses on flat substrates with future work targeted at the more complex case of fiber and fiber-bundle wetting.

Flat edge-plane surfaces

Flat, fully-dense carbon edge-plane surfaces are needed for these fundamental droplet spreading and wetting studies. HOPG edge surfaces were early candidates, since HOPG was used in our prior work on basal plane wetting [6]. It was found, however, that HOPG edge surfaces have a complex folded structure (see Fig. 1), that we believe would exhibit significant basal plane character in wetting studies.

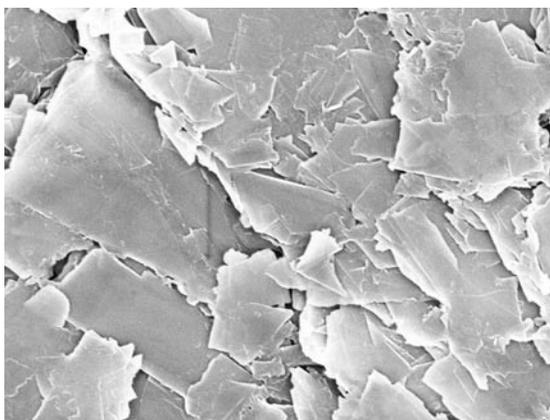


Figure 1. SEM micrograph of nominal HOPG edge surface, showing the folded mesostructure with large patches of basal surface terminating at edge-plane fracture lines. These surfaces are unsuitable as model edge-plane surfaces due to the majority of basal sites observed by wetting agents.

Another possible source of all-edge carbons surfaces are liquid crystal derived carbon films, where edge-on anchoring of the polyaromatic precursors at the free surface is "covalently captured" to produce carbons with exposed edge planes[7]. These films can be made from AR mesophase (Fig. 2), but this precursor requires oxidative stabilization prior to carbonization and the resulting carbon films are not typically fully dense [7]. A new and promising liquid crystalline precursor for the fabrication of thin carbon films is indanthrone disulfonate (Fig. 2).

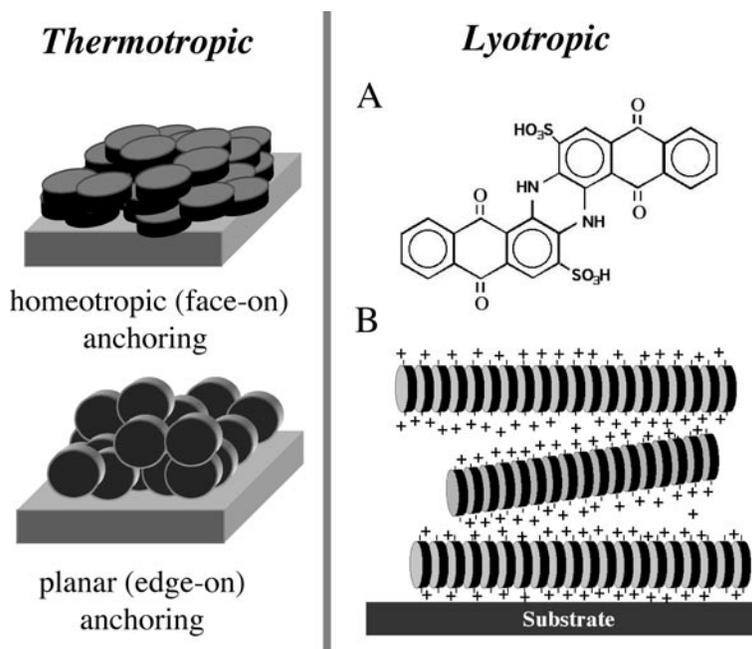


Figure 2. Liquid crystalline precursors and their surface anchoring states. AR-mesophase is a thermotropic LC, whose surface anchoring states vary with substrate. Indanthrone disulfonate (A) is a lyotropic precursor, which assembles in aqueous solution into massive π -stacked rod-like aggregates (B). Entropic forces cause bulk alignment of the aggregates at high concentration ($> \sim 4\%$) and also cause parallel alignment in the vicinity of substrates as shown.

Indanthrone is a polyaromatic dye that can be sulfonated to introduce hydrophilic sites on the disk periphery. In such compounds the polyaromatic faces remain hydrophobic, and this leads to extensive π -stacking in aqueous solution [8]. In indanthrone disulfonate solutions, this face-to-face stacking is extensive, leading to long rod-like aggregates of ~ 1.5 nm in diameter and about 300 nm in length (~ 200 aspect ratio) [9], while proton dissociation imparts negative charge that aids in aggregate dispersion (see Fig. 2). The liquid crystallinity in this material arises by rod alignment driven by entropic forces associated with electrostatic repulsion and size exclusion [9]. This LC system is classified as lyotropic, since the rod alignment is induced by increase in concentration rather than decrease in temperature as in thermotropic liquid crystals. The same entropic forces cause rod alignment parallel to surfaces, as this configuration decreases the excluded volume at the LC/substrate interface [8, 9]. The rod alignment is further improved when the solutions dry and the liquid crystalline order is converted to solid crystalline order in the deposited film.

In this work we fabricate all-edge carbon films from indanthrone using both bar and spin coating and then utilize the films as model substrates for pitch wetting studies.

Experimental

Films from indanthrone disulfonate (Optiva, Inc. South San Francisco) were formed on quartz from 7.5 wt% aqueous solution either by spin coating (rotation rate: 500 rpm for 20 seconds and then 5000 rpm for 30 seconds) or Meyer-bar coating. After drying the films were carbonized by slow heating to 700 °C in inert gas flow. The procedure for the wetting experiments was described in detail previously [6]. Briefly, the experiments used the naphthalene-derived AR mesophase (HP grade) supplied courtesy of Mitsubishi Gas Chemical. The mesophase was first dried under vacuum for 24 hours at 125 °C then cooled to ambient temperature and loaded into a custom designed hot-syringe system at the AFRL laboratories [6]. Single drops of AR mesophase are formed by pressurization and then allowed to fall onto the substrate. Its spreading is observed with an InfiniVar™ continuously-focusable microscope from Edwards Scientific, Inc. that is equipped with a high-resolution CCD video camera which feeds a video signal at 30 frames/second to an FTA 100 Drop Shape Analyzer. The FTA 100 is manufactured by First Ten Angstroms, Inc., of Portsmouth, VA and its software reduces the data to actual contact angles.

Results and Discussion

No information could be found on the carbonization behavior of indanthrone disulfonate, so preliminary experiments were done on bulk samples. These experiments showed a 60% carbon yield at 700 °C and the retention of sharp edges that indicate solid-state carbonization. Thin films were then formed by spin coating (Figs. 3,4) and Meyer-bar-coating (Fig. 5) of indanthrone disulfonate aqueous solutions followed by drying and direct carbonization at 700 °C. Oxidative stabilization was not required, which is consistent with the absence of a fluid phase during the carbonization of bulk samples. Both samples are 100% anisotropic (Fig. 4,5) indicating edge-on anchoring of the molecular disks. This is consistent with the expected parallel alignment of the rod-like aggregates near any flat surface driven by configurational entropy (Fig. 1). The spin coated films are thin (200 - 300 nm) and partially transparent, but fully dense. Their front surfaces appear grey and quite flat giving clear specular reflections (Fig. 3).

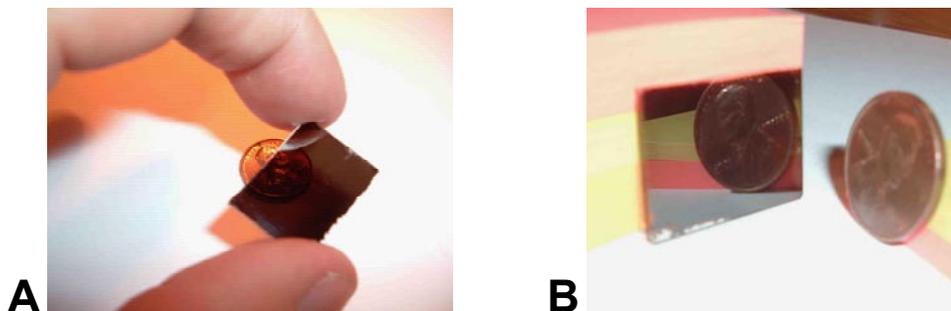


Figure 3. Macroscopic appearance of carbon thin films on quartz made from spin coating aqueous solutions of indanthrone disulfonate followed by heating at 700 °C. The films are sufficiently thin to be partially transparent (A), and sufficiently flat to exhibit specular reflection (B).

The spin coated films show a fascinating optical texture under polarized light. A small central region of these films near the starting droplet shows radial graphene layer order, but this quickly gives way to the random, multi-domain structure seen in Fig. 4 that constitutes most of the film. The surface is entirely anisotropic as expected, since the parallel anchoring of rod-like aggregates at both the top and glass surface effectively forces the molecular disks into a perpendicular arrangement. The multi-domain structure shows some regions of spatial periodicity (see Fig. 4). The optical texture of the films is essentially identical before and after carbonization, indicating that the discotic order is effectively “captured” by the simple thermal carbonization step. These films are 100% anisotropic locally, but are effectively isotropic over length scales much larger than the domain size (about 30 micrometers).



Figure 4. A. Top surface of carbon thin film prepared by spin coating indanthrone disulfonate liquid crystalline solutions and heating. Optical micrograph with simple polarized illumination. The surface is uniform, dense, and 100% anisotropic consisting of small (30-50 micron) edge-on domains with alternating in-plane orientation. In some regions of the surface, the liquid crystalline domains appear in nearly regular spatial patterns (see white arrows). B. Sketch of the edge-on symmetry of these carbon films.

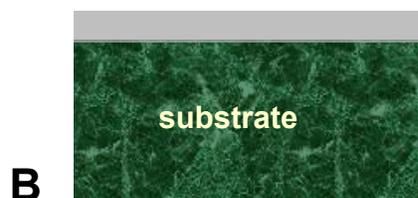


Figure 5 shows carbon films formed by Meyer-bar coating of indanthrone disulfonate solutions. Polarized light microscopy shows that the graphene layers here lie preferentially perpendicular to the rubbing direction, consistent with alignment of the original rod-like precursor aggregates parallel to the rubbing direction. These carbon films are thus fully edge-on, but also possess long range orientational order in the substrate plane. This homogeneous alignment is believed to occur by extensional and shear flow in the open microchannels at the bar/substrate interface. The carbon films here are about 1 micron in thickness, are also made without stabilization, and are fully dense. The AFM analysis of Fig. 6 gives a root-mean-square surface roughness of 2.6 nm. Again the discotic molecular order is preserved upon carbonization, indicating that the intermolecular forces in the discotic film are strong enough to hold the molecular assembly intact until the point of thermal decomposition and covalent cross linking.

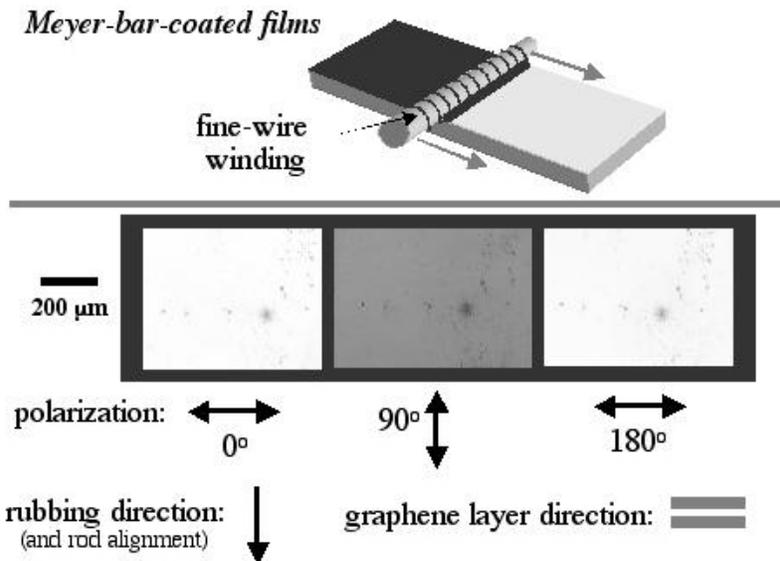


Figure 5. Formation and structure of homogeneously ordered carbon thin films made by bar coating of lyotropic liquid crystal. Extensional and shear flow in the inter-wire gaps during rubbing aligns the rod-like aggregates parallel to the rubbing direction, which secondarily aligns the disks in the transverse direction. The images are optical micrographs of the carbonized (700 °C) films with illumination polarized as shown and fixed photograph exposure. Imperfections and surface dust confirm a common location for all images. Note the image sequence was taken by *sample* rotation at fixed polarization, and the 90/180 images above were digitally rotated back to 0° for comparison.

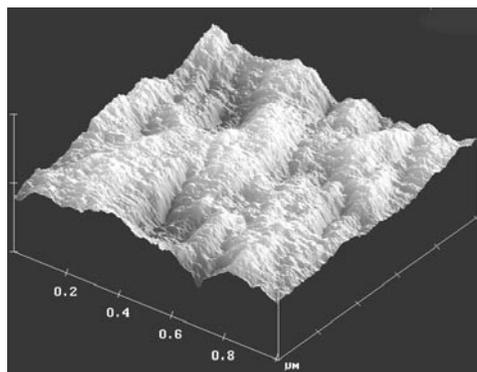


Figure 6. Atomic force micrograph of 1 micron square region of homogeneous, bar-coated lyotropic thin film carbonized at 700 °C. The root mean square roughness is 2.6 nm.

Wetting results

Figure 7 shows previous results of dynamic contact angle on freshly cleaved HOPG basal planes. Spreading times in this study were strongly temperature dependent, varying from about 1 second at 371 °C to well over 100 sec at 325 °C. This data was compared to the dynamic droplet spreading theory of DeGennes, and it was

concluded that viscosity plays a key role in practical pitch wetting behavior [6] due to significant viscous dissipation in the thin wedge-shaped region at the leading edge of the spreading droplet (Fig. 7b).

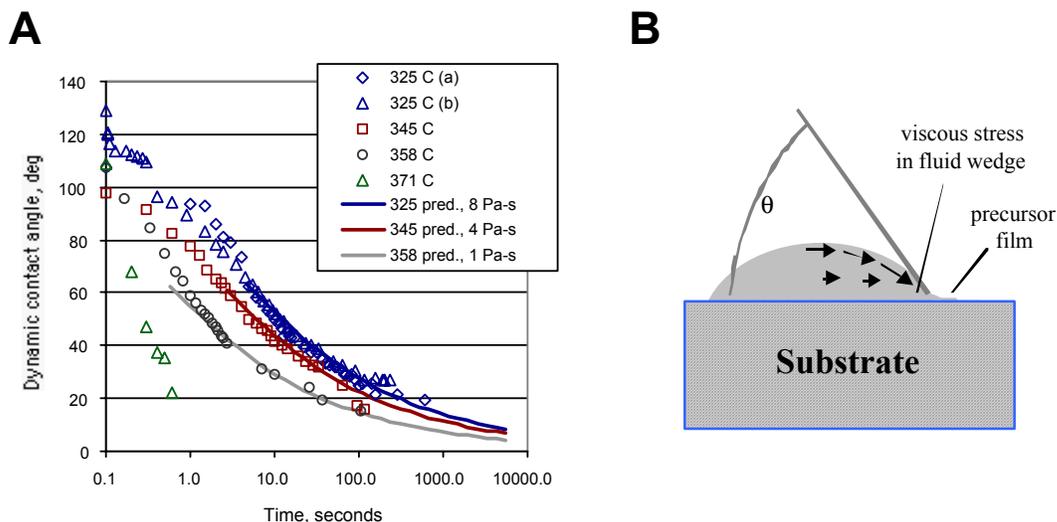


Figure 7. A. Dynamic contact angles for AR mesophase on freshly cleaved HOPG basal plane using the preheated droplet technique: Symbols: experimental measurements, Lines: dynamic spreading theory predictions for viscosities given in legend. B. fluid mechanical stresses in the wedge-shaped leading edge that is believed to govern spreading velocity in pitch.

Figure 8 compares this spreading data on basal surfaces with new data obtained on the all-edge carbon thin films. The edge-plane data was taken at 350 C and lies close to the HOPG basal data at similar temperatures (345 C, 358 C). Edge-plane surfaces can have a highly variable functional group composition depending on their treatment and post-carbonization exposure. This data was taken on the as-produced films, carbonized and quenched in nitrogen and then exposed to room air. More work is underway to study the effect of surface chemistry on the wetting of the new all-edge carbon thin films.

Conclusions

Indanthrone disulfonate is a promising new liquid crystalline precursor for advanced carbon materials. It can be solvent processed into ordered discotic films that carbonize in the solid state with preservation of the molecular order even without oxidative stabilization. All-edge films can be made with either random in-plane orientation (by spin coating) or unidirectional in-plane orientation (by Meyer bar coating).

Preliminary work on the wetting of AR mesophase on these model all-edge surfaces shows similar behavior to HOPG basal plane wetting. The early to intermediate stages of the wetting process is dominated by spreading kinetics, which are a strong function of pitch viscosity and thus temperature. More work is needed to understand if and how carbon surface structure and chemistry affects wetting data at long times

and equilibrium contact angles. Future work will exploit the reactivity of the all-edge films to examine the effects of surface oxidation, after which experiments will begin on the three-dimensional problem of fiber and fiber-bundle wetting.

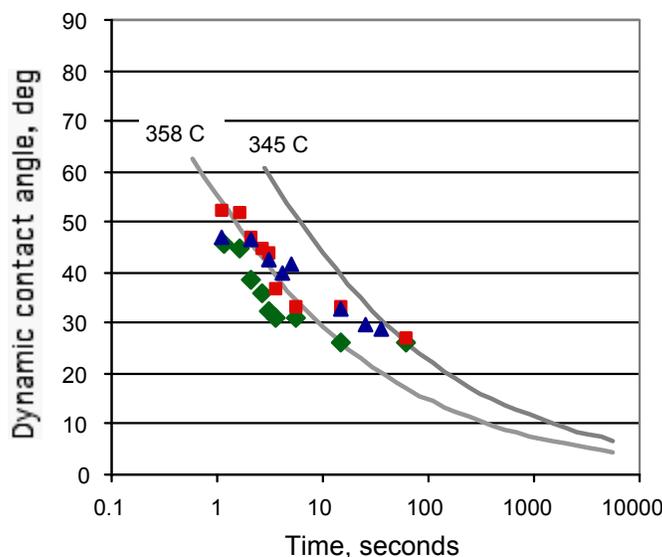


Figure 8. Comparison of AR wetting/spreading data on basal and edge surfaces. Points: measurements at 350 C on as-produced top surface of all-edge carbon thin films made by spin-coating Indanthrone disulfonate. Lines: previous measurements on HOPG basal surface at similar temperatures.

Acknowledgements

Financial support was provided by the Chemistry and Materials Directorate, Air Force Office of Scientific Research as well as the National Science Foundation under NIRT Grant CMS-0304246.

References

- [1] Wapner PG, Hoffman WP, Jones S, US Patent 6,309,703, 2001.
- [2] Jian K., Shim H-S, Schwartzman A, Crawford GP, Hurt, RH, *Adv. Materials* 2003; 15(2) 164-167.
- [3] Yoon, S-H, Korai Y, Mochida I, Kato I, *Carbon* 1994; 32(2) 273-280.
- [4] Heintz EA, *Carbon* 1986; 24 (2) 13-134.
- [5] Hurt RH, Krammer G, Crawford GP, Jian K, Rulison C., *Chem. of Materials* 2002; 14 4558-4565.
- [6] Equilibrium and Non-Equilibrium Effects in Pitch Wetting, P.G. Wapner, R.H. Hurt, Gernot Krammer, W.P. Hoffman: *Carbon* 2003, Oviedo, Spain.
- [7] Jian K., Xianyu H., Eakin J., Gao Y., Crawford G.P., Hurt R.H., "Orientationally Ordered and Patterned Discotic Films and Carbon Films from Liquid Crystal Precursors," *Carbon*, in press, 2004.
- [8]. Iverson IK, Casey SM, Seo W, Tam-Chang S. *Langmuir* 2002; 18(9): 3510-3516.
- [9]. Dembo A, Ionov A, Lazarev P, Manko A, Nazarov V. Lyotropic dye-water mesophases formed by rod-like supramolecules. *Molec. Mater.* 2001; 14(4): 275-290.