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Flame Retardant Carbon Nanofiber and Carbon Nanotube Coatings

A. A. Cain,* E. A. Ellis,** J. C. Grunlan*

*Material Science and Engineering, 3123 Texas A&M University, 200 Mechanical Engineering, College Station, TX 77843
**Microscopy and Imaging Center, Texas A&M University, Biological Sciences Building Room Number 119, Mail Stop 2257, College Station, TX 77843-2257

Due to their ability to reduce volatilization of degradation products during heating, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) are interesting materials for use in nanocoatings to improve flammability resistance [1]. This behavior is commonly attributed to char formation due to nanoparticle aggregation at the surface of the substrate, which forms a protective shield from the fire [2]. Layer-by-Layer (LbL) deposition is an effective processing approach to form nanocoatings, but is difficult to thin section for electron microscopy. In this work, we present a consistent methodology for preparing samples of LbL assembled CNF and CNT-based thin films for transmission electron microscopy (TEM).

Specimens were prepared using the LbL assembly methodology reported by Park [3], with 0.05 wt.% CNF + 0.1 wt.% branched poly(ethylenimine) (PEI) or 0.1 wt.% PEI-functionalized multi-walled carbon nanotubes (PEI-MWNTs) as cationic aqueous solutions and 0.1 wt.% polyacrylic acid (PAA) as the anionic aqueous solution. The cationic solution was sonicated with a Misonix Ultrasonic Liquid Processor (XL-2000 Series) operating at 10W for two cycles of 10 minutes. All materials were used as received. Prior to polymerization, a thin layer of carbon was deposited with a Cresington Coater System 308R (Ted Pella, Inc., Redding, CA) in order to separate the PEI/PAA film from direct contact with the epoxy potting material and to explicitly differentiate the epoxy and polyethylene terephthalate (PET) substrate to the operator. Specimens were embedded in an epoxy resin with anhydride:epoxide ratio of 1:1 consisting of: Araldite 502 (2.74 g) and Quetol 651 (1.02 g), dodecenyl succinic anhydride (6.24 g), and benzyldimethylamine accelerator (0.2 mL) (Electron Microscopy Sciences, Hatfield, PA). Dow Corning Z-6040 Silane Solution was added at the rate of 0.2 mL/10 g of epoxy resin to increase adhesion with the thin film. The epoxy resin embedded specimen was polymerized overnight at 55°C. Gold sections were cut on an ultramicrotome and picked up on 200 mesh copper grids. Images were obtained with a JEOL 1200 EX TEM (JEOL USA Inc., Peabody, MA) operated at an accelerating voltage of 100 kV using a Scientific Instrument and Applications CCD camera (Duluth, GA). Magnifications were calibrated using a 2,160 lines per mm grafting replica (Electron Microscopy Sciences, Hatfield, PA).

Clear visualization of the nanoparticle morphology is critical to understand the mechanism responsible for flammability resistance. The TEM micrographs indicate that CNFs exhibit a range of orientations, with solid triangles in Figure 1a and hollow triangles in Figure 1b highlighting parallel and perpendicular orientations within the same four bilayer film, respectively. The PEI-MWNTs also exhibit random orientations, but show a distinct microstructure due to nanoparticle agglomeration. Previous LbL deposition studies with polymer and clay aqueous solutions found that highly ordered structures, such as the nanobrick wall structure [4], exhibit improved gas barrier properties, but may not necessarily exhibit improved flammability resistance [2].

Delamination is a significant obstacle when sectioning thin films, particularly those that vary in hardness. By incorporating silane into the embedding medium and matching the film hardness with that of the epoxy, delamination can be minimized, allowing effective morphological analysis. This approach has been applied to several different LbL films [2, 3, 4], and is shown here as a technique to reveal the initial pre-burned state of nanocoatings with enhanced flammability performance.

References

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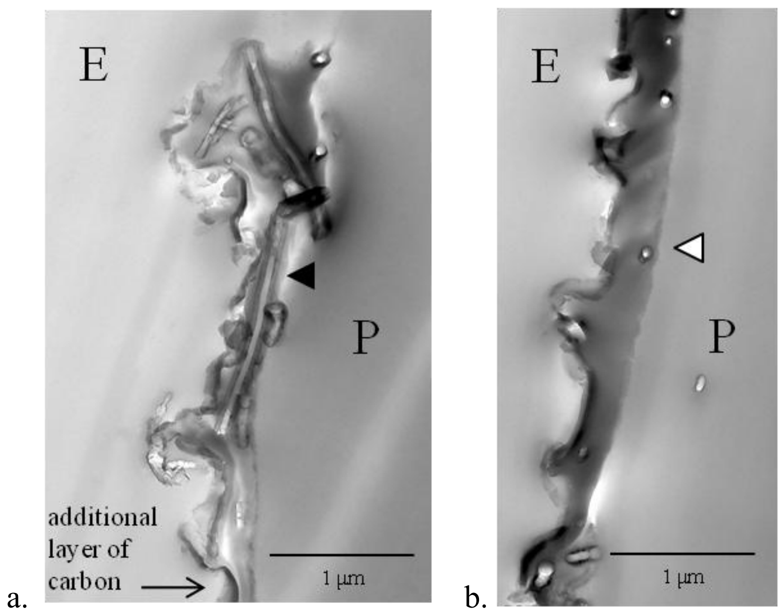

Fig. 1. TEM cross section of a [CNF+PEI / PAA]$_4$ thin film at low magnification.

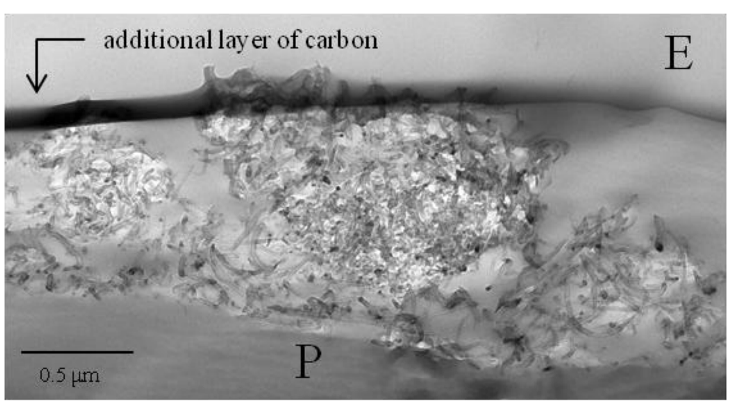

Fig. 2. TEM cross section of a [PEI-MWNT / PAA]$_4$ thin film at low magnification.

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