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Water nanocondensation on polymer single crystal-decorated buckypaper

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ABSTRACT

Condensation on the surfaces of single-walled carbon nanotube (SWCNT) buckypaper and polymer single crystal-decorated buckypaper was monitored *in situ* using an environmental SEM (ESEM). Water vapor was pumped into the chamber, and backside cooling was used to control sample surface temperature. In this way, condensation could be imposed on the sample. It was found that, due to the different wetting states, condensation contact angles of all the samples are significantly lower than the static contact angles measured by the sessile drop method. The polyethylene (PE) single crystal-decorated buckypaper also strongly resists water vapor condensation, thereby precluding flooding below the fog point. Our results show that the heterogeneous surface structure plays a key role in determining water condensation.

1. Introduction

Carbon nanotube (CNT)-based membranes and coatings have shown considerable merit for use in both the control and sensing of humidity [1–6]. CNT-based surfaces have been used to detect analytes from the gas phase [7–9] and functionalized to control wetting behavior [10,11]. Water vapor rejection has also been demonstrated: aligned CNTs have been shown to selectively reject water vapor from a gas mixture [6]. To explain this behavior, a three-stage condensation, agglomeration, rejection mechanism whereby water droplets nucleate and are collected on impurities until they can roll off of the barrier into a collection vessel, has been suggested. In the case of semicrystalline polymers, water wetting behavior is sensitive to crystalline structure and morphology [12,13]. We have previously shown that by decorating CNTs with polymer single crystals [14–16], a novel hybrid material could be produced which was termed “nanohybrid shish kebab” (NHSK), where CNTs served as the shish and polymer single crystals formed kebabs on the CNTs [15]. Simple vacuum filtration of NHSK dispersions allowed the formation of free-standing NHSK paper that mimics buckypaper, with controlled pore sizes. The NHSK paper is electronically conductive with controllable water wetting because of the hierarchical roughness and well-tuned local chemistry [17]. Further modifying these materials with PTFE broadened the range of wetting behaviors that could be accessed, suggesting additional applications [18,19].

To better understand the wetting behavior of water on NHSK paper, it is desired to investigate the condensation process *in situ*. Previous work showed that wetting under ESEM closely simulates the conditions in the vicinity of a cathode catalyst layer [20]. Yu et al. and Zhang et al. used this technique to explore the conditions at the catalyst layer [21,22]. Addressing the general issue of microcondensation on rough surfaces, Jung and Bhushan used ESEM to study droplet formation on wafers patterned with pillars of different geometry and pitch coated with a monolayer of 1,1,-2,2,-tetrahyrdoperfluorodecyltrichlorosilane, and showed how roughness impacts the formation of condensation drops [23]. ESEM has also been used to study water condensation on lotus leaves and to study spatial control of heterogeneous nucleation of water [24–26]. In this paper, the behavior of water molecules condensed from the vapor phase on SWCNT buckypaper and NHSK paper was explored. We show that incorporating polymer single crystals onto SWCNT sidewalls is an effective means to tune wetting behavior and detailed analysis of ESEM wetting behaviors revealed how water condensation was affected.

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2. Experimental

2.1. Preparing NHSK paper

Fig. 1 shows the experimental process. High-density PE (MFI 12 g/10 min), 1,2-dichlorobenzene (DCB, 99% manufacturer's spec.), isopropanol, and rinse solvents were purchased from Aldrich and used as received. SWCNT, “purified” grade, were purchased from Unidym. In a typical experiment, 24 mg SWCNT would be placed in a 250 mL round-bottom flask with 120 g DCB, in the expectation that the final crystallization solution would contain approximately 50% of the original CNT content and 85% of the original DCB (0.01 wt.% SWCNT). 2 vol.% isopropanol was added to prevent sonopolymer functionalization of the CNTs. Separately, a desired quantity of PE was added to a 100 mL round bottom flask with an appropriate amount of DCB, purged with N_2, and heated to dissolution under a N_2 blanket. The CNT solution was bath sonicated for 90 min, tip sonicated for an additional 30 min, and then divided up into centrifugation vials and centrifuged for 20 min at 10,000 rpm. The supernatant was collected and equilibrated to the PE dissolution temperature (130 °C) for 8–10 min. The PE solution was then cast into the CNT dispersion and the combined solution was mixed for 3 min before quenching to the crystallization temperature, 88.5 °C, and would remain at this temperature for 120 min. Isothermal filtration was performed 3× after the initial rinse. The filtered solution was then quenched to room temperature. Samples were filtered over 0.2 μm PTFE membranes from Savillex. For pure buckypaper, this filtration step had to be done immediately after centrifugation to mitigate aggregation of the CNTs.

2.2. Characterization

Surface characterization of the SWCNT buckypaper and NHSK paper was done on a Zeiss Supra 50VP operating at 1 keV in secondary electron detection mode. *In situ* characterization of buckypaper and NHSK paper surfaces was performed in an FEI XL30 Environmental SEM in wet mode using a cooling stage from Peltier. Samples were stuck to the stage by first wiping on a small amount of vacuum grease and then gently unfurling the sample over the greased surface. The sample was cooled to 1 °C and recordings were made during a step-ramp pressure increase. Starting at a vapor pressure of 3.0 torr (62% relative humidity), the pressure was ramped 0.1 torr/min until condensation would appear on the surface and remain on the surface without evaporating. Sessile drop contact angles (CAs) were recorded on a Sony XC-HR90 camera with a C-mount lens. A minimum of 5 droplets (using 10 μL droplets of distilled water from Aqua Solutions, Inc.) were individually measured to analyze sessile drop CAs.

3. Results and discussion

3.1. Surface properties of SWCNT buckypaper and NHSK papers

Fig. 2 shows the appearances of SWCNT buckypaper and polymer single crystal-decorated SWCNT paper surfaces. It can be seen that the SWCNT buckypaper (Fig. 2a) forms a dense mat with openings dotting the surface: this is due to SWCNT bundling and SWCNTs connecting separate bundles as tie chains, forming a web-like network. Decorating CNTs with PE single crystals to form NHSK structures provides functionalization, allowing tube–tube separation [16,27–36]. Vacuum filtration of the NHSK suspension led to the formation of porous buckypaper analogs called “NHSK paper.” Samples designated as NHSK-*n*, where *n* is the percentage of CNTs in the sample, are shown in Fig. 2c,e,f. With increasing PE content from Fig. 2c–e, the surface roughness increases and the static contact angle (sCA) increases from 117.8° to 138.1°. Further increasing the PE content by increasing PE lamellar size leads to the mechanical instability of the PE crystallites, which in turn, causes the surface features to collapse. This is reflected in the shapes of sessile drops placed on the surfaces of these films and the sCA decreases to 117.1°. SWCNT buckypaper is slightly hydrophilic. The sCA of buckypaper was found to be 83.6 ± 2.7°. NHSK papers are statically hydrophobic and dynamically non-sliding. This has been attributed to the nanoscale Cassie and micro-scale Wenzel wetting

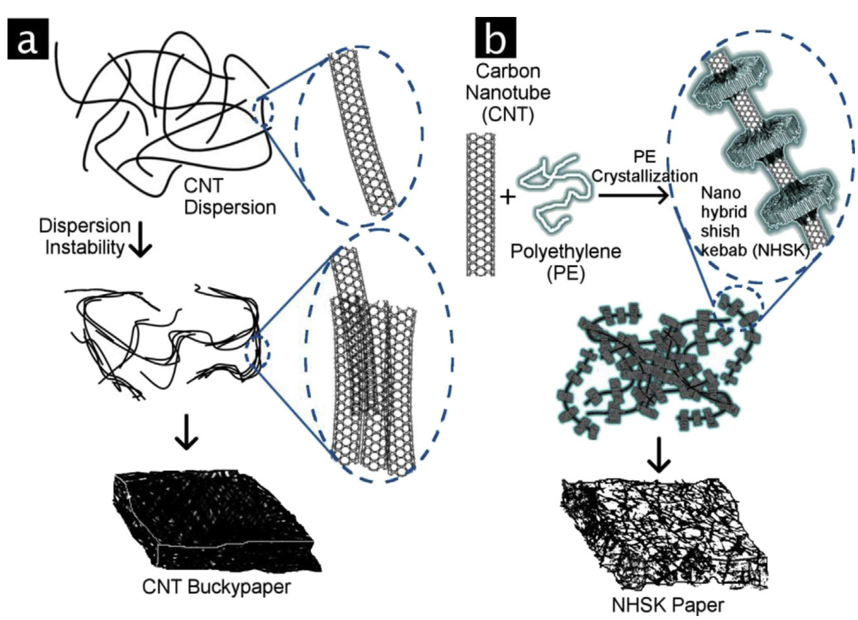

Fig. 1. Deposition of SWCNT buckypaper and NHSK paper. a) Dispersed CNTs flocculate in solution during vacuum filtration. A nonwoven mat of SWCNT bundles is thus produced. b) Solution crystallization of PE forms a physical functionalization to prevent reaggregation of SWCNTs. The initial ratio of PE to SWCNT in solution dictates the kebab size. This hybrid structure is termed “nano hybrid shish kebab” (NHSK). Vacuum filtration of NHSK produces a porous nonwoven mat with regular features on the 10–100 nm length scale, termed “NHSK paper.”