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Study on peculiar carbon pattern formation from polymer blend thin films under electric fields

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ABSTRACT

In this study, we demonstrate the formation of a peculiar carbon pattern from polyacrylonitrile/poly(methyl methacrylate) (PAN/PMMA) blend thin films under external electric fields. When a spin-coated PAN/PMMA blend thin film was exposed to an electric field, the surface of the thin film facing air layer would fluctuate due to the electrohydrodynamic instability phenomenon induced by an electrostatic force. At the same time, the interface between PAN and PMMA would also become unstable because of the difference in the dielectric constants of PAN and PMMA. The microstructure of the PAN/PMMA thin film obtained after field exposure was influenced by the combined effect of the two phenomena. Subsequent controlled thermal treatment produced an unprecedented and peculiar carbon pattern, which remained intact during carbonization. The effect of experimental parameters such as field intensity, exposure time, and film thickness on the microstructure of the polymer precursor and resulting carbon pattern was investigated. This work provides a strategy to obtain carbon structures showing specific surface texture and certain properties that have been inaccessible by any other means.

1. Introduction

External electric fields can exert significant effects at the surface of polymeric thin films [1,2], and the use of these fields has been considered an elegant strategy and versatile tool for producing unique patterns in thin films [3,4]. One of the most influential effects of electric fields on thin films is an electrostatic pressure induced at interfaces due to a difference in dielectric constant [5]. Because of this force, the surface of the thin films becomes unstable and starts fluctuating, commonly referred to as the electrohydrodynamic (EHD) instability phenomenon [6–8]. In addition, interfaces existing inside the thin films tend to rotate along the direction of the applied electric field. Accordingly, the microstructures of the thin films are dramatically altered as a consequence of field exposure [9–18].

Therefore, unique pattern formation in polymeric thin films using electric fields has been extensively studied. Scale reduction in the EHD instability pattern has been pursued for more than a decade [19]. For example, the effect of incorporated nanocrystals on the EHD instability of polystyrene thin films was examined [5]. In addition, control over the microdomain structure in block copolymer thin films has been widely investigated by many research groups [8]. Subtle effects of surface functional nanoparticles on microdomain alignment behavior, in block copolymers under electric fields, were also studied in detail [9]. Theoretical approaches for revealing the underlying fundamentals of the field effects have also been consistently reported [20,21].

Although significant effort has been devoted to this research topic, the creation of distinctive carbon patterns has been scarcely reported [20,21]. Bae et al. reported the generation of a unique embossed carbon nanostructure by exposing polyacrylonitrile (PAN)-b-poly(methyl methacrylate) (PMMA) block copolymer thin films to an electric field [21].

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Structural evolution during field exposure was monitored by atomic force microscopy (AFM), as well as spectroscopic analyses, and a process window suitable for obtaining the unprecedented pattern was drawn. As an extension of those previous research activities, in this work, a peculiar carbon pattern generated from a PAN/PMMA polymer blend thin film was demonstrated. Both the EHD instability at the air/film surface and the electrostatic pressure at the PAN/PMMA blend interface played a role in pattern development. A controlled carbonization cycle produced an unprecedented carbon pattern without changing or disrupting the polymeric precursor structure. In parallel, the effects of field intensity, exposure time, and film thickness on the characteristics of the polymeric precursor and resulting carbon pattern were examined. It is expected that this work could provide a strategy for obtaining carbon structures with peculiar surface features and properties that are inaccessible by any other means.

2. Experimental

2.1. Materials

The PAN (M_n = 11.5 kg/mol) and PMMA (M_n = 15 kg/mol) were purchased from Polymer Source (Quebec, Canada) and used without further purification. A solvent (dimethylformamide; DMF) was purchased from Aldrich (St. Louis, MO, USA) and dried before use.

2.2. Spin coating of blend thin films

Equal amounts of PAN and PMMA were added to DMF to produce a final concentration of 3 wt%. PAN/PMMA (50/50 w/w) blend thin films were obtained by spin-coating the DMF solution (3 wt%) at 3000 rpm for 60 s on a passivated silicon substrate (International Wafer Source, Inc.). Before passivation, the silicon wafer was cleaned with acetone, ethanol, and toluene. Before spin-coating, the BCP solution and silicon substrate were heated to 85–90 °C for 10 min to reduce humidity.

2.3. Application of electric field

A schematic diagram of the apparatus is shown in Fig. 1. A silicon wafer coated with a blend thin film served as one electrode, and a glass sheet coated with a thin layer of indium tin oxide (ITO) served as the second electrode. The electrode spacing was controlled using polyimide (PI) spacers. A voltage was applied, and the assembly was heated well above the glass transition temperatures of the specific polymers (~100 and ~130 °C for PMMA and PAN). For PAN/PMMA blend thin film, it was found that 150–170 °C was appropriate for the experiment [22]. The assembly was then quenched to room temperature to freeze the microstructure. After each experiment, the upper glass electrode was removed manually.

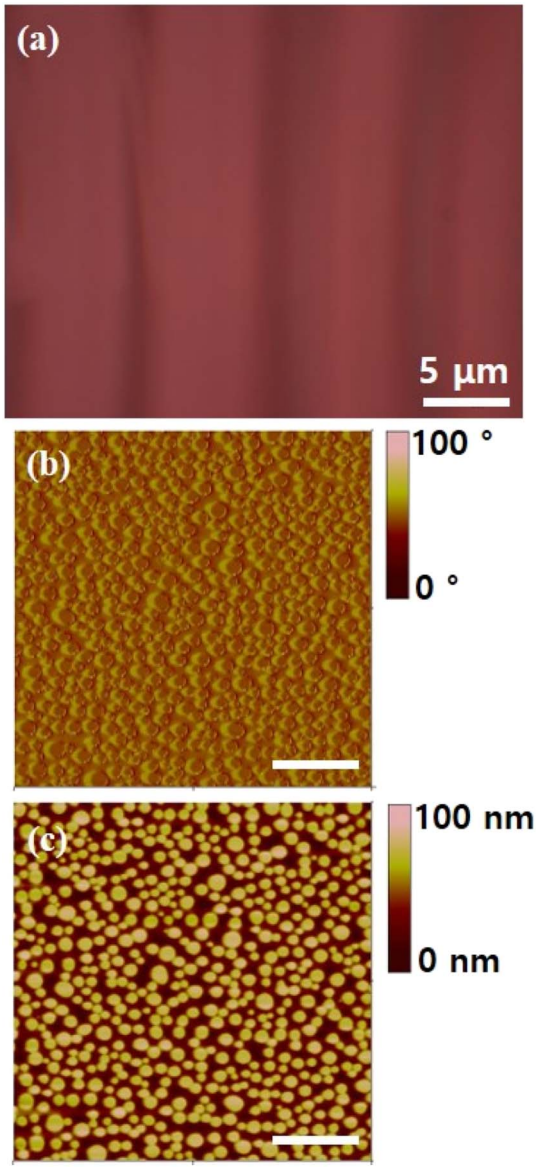

Fig. 2. (a) Optical microscopy (OM) and atomic force microscopy (AFM) phase (b) and height (c) images of the polyacrylonitrile/poly(methyl methacrylate)(PAN/PMMA) (50/50 w/w) blend thin film. (Scale bar is 5 μm).

2.4. Carbonization of thin films exposed to electric fields

The carbonization process was composed of four major steps: stabilization (1 °C/min to 300 °C), heating (3 °C/min to 800 °C), holding (1 h), and natural cooling. This cycle made it possible to improve the

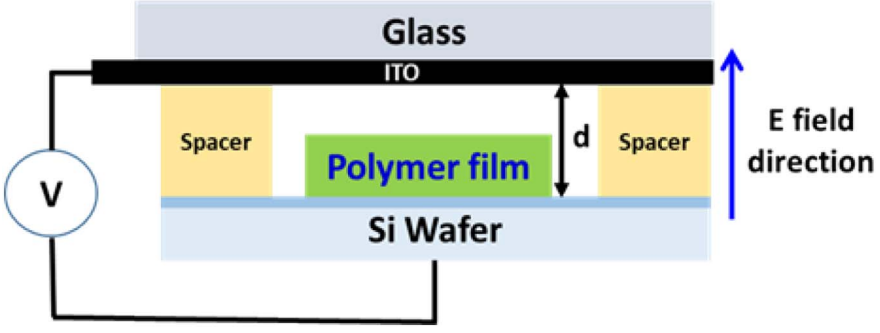

Fig. 1. Scheme of the experimental apparatus for application of electric fields to thin films.