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Stable Langmuir–Blodgett film deposition of polyaniline and arachidic acid

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Abstract

An experimental study was carried out to examine the stable Langmuir–Blodgett (LB) film deposition of mixtures of polyaniline (PA) and arachidic acid (AA) at different concentration ratios, with the aim of developing a systematic methodology for the production of quality PA/AA film at the highest deposition speed. The quality of LB film was examined before, during and after the film deposition process. Images of the PA/AA composite materials at air–liquid interface, based on the Brewster angle microscopy, revealed that a 50/50 concentration ratio of PA/AA composite layer produced the best LB film structure. The feasibility of LB film deposition was determined from dynamic contact angles which were measured by a flow visualization technique. The quality of the deposited film was judged by the transfer ratio and the atomic force microscopy images. The effect of pH was also examined, and it was found that the LB film deposition for the PA/AA system could only be carried out in a narrow range of pH. It was found that the deposited LB film of the PA/AA system had a high transfer ratio and improved surface roughness at the deposition speed 30 mm/min. This deposition speed is much higher than those previously reported.

Keywords: Langmuir–Blodgett film; Polyaniline; Arachidic acid; Brewster angle microscopy

1. Introduction

The Langmuir–Blodgett (LB) film deposition process has been considered as a potential technique for the production of ultra-thin films with controlled molecular orientation. The LB technique was mainly applied for amphiphilic molecules which had polar and non-polar parts [1,2]. There were few reports on LB films of non-amphiphilic molecules, due to processing difficulties and lack of product reliability. Recently, the LB technique was used to prepare conductive polymers such as polyaniline (PA), polypyrrole and polythiophene [3–5]. PA is a conducting polymer which is environmentally stable and easy to prepare. It has many potential industrial applications, such as serving as an electronic hole transport layer in polymer light emitting diode, as an anti-static and anti-abrasion agent and as a key component for smart windows [6–9]. Previous studies found that it was possible to carry out LB film deposition for emeraldine-based PA mixed with either *N*-methyl-pyrrolidone (NMP) or NMP/chloroform [10,11]. Porter et al. [12] studied different deposition conditions for making PA LB films, and examined the microstructures of the film using scanning force microscopy. They suggested that surface smoothness is more uniform at a surface pressure of 10 mN/m and a deposition speed of 1 mm/min. Several other authors also examined the LB film deposition of PA on different substrates and the deposited film quality was characterized by electrical, spectroscopic and electrochemical techniques [13–15]. Cheung and Rubner [16] first discovered that adding stearic acid (SA) to PA could improve the composite LB film deposition onto the substrate, and the molecular organization of the LB film was strongly influenced by the type of processing aides. They also found that the film fabricated from a PA/SA mixture was inhomogeneous and had a phase separation at the micron level. Dhanabalan et al. [17,18] analyzed composite LB films of PA and cadmium stearate, and found that the monolayer with 30–55% weight fraction of PA was quite stable for deposition and the PA molecules could be uniformly distributed within a monolayer. For higher PA concentration, the PA molecules were most likely to be squeezed out at the air–liquid interface. Riul et al. [19] displayed the atomic force microscopy (AFM) images of 16-mer polyaniline cadmium stearate composite LB film, and

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suggested that higher polymer content could increase the surface roughness and lower the conductivity of the composite film.

It is generally agreed that the addition of stearic acid to PA can assist the LB film deposition onto the solid substrate. However, previous studies were mostly carried out at deposition speeds lower than 5 mm/min, and the film quality was examined only after the completion of the LB deposition process. In the present study, the LB film deposition of PA/arachidic acid (AA) mixture was conducted at a much higher deposition speed, i.e., 30 mm/min. Different concentration ratios of PA/AA were examined. The images, based on Brewster angle microscopy (BAM), of the PA/AA system on the liquid–air interface were used to assess the quality of the deposited film. A flow visualization technique was employed to determine the dynamic contact angles which were used to determine the types of the LB film deposition [20]. The quality of the deposited film was further assessed with the measured transfer ratio (TR) and the atomic force microscopy images. The effects of pH of the sub-phase were also studied. Our attempt was to develop a methodology that the quality of LB film can be ensured step by step before, during and after the deposition.

2. Experimental details

Emeraldine-based polyaniline (PA; EB type Mw ca. 10,000) and arachidic acid (AA; 99% purity) were purchased from Sigma Aldrich Chemical Co. Both of these materials were used without further purification for the LB film deposition experiment. The coating solutions were prepared by dissolving PA in *N*-methyl-pyrrolidone (NMP; supplied by Riedel-deHaen) and AA in chloroform (supplied by J.T. Baker) with a concentration of 1.5 mg/ml. Microscope glass slides, chosen as substrates for LB film deposition, were soaked for about twenty minutes in an ultrasonic bath. The bath contained a mixture of equal portions of ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2). The substrates were then rinsed with de-ionized water, and purged with nitrogen gas. De-ionized water was obtained from a Milli-Q system (Millipore, Eschborn, Germany) and the resistance was controlled at 18.2 M/cm.

A solution of PA/AA at a fixed mass ratio was prepared and then spreading on a Nima 312 D mini-trough. The mini-trough was a precision-machined, computer controlled Langmuir trough with an area of 300 cm^2. It was equipped with a dipping well of area 50 mm × 20 mm and 75 mm deep, situated at the center of the trough. Two detachable teflon barriers were attached to compress the liquid surface toward the center of the trough. A Wilhelmy plate pressure sensor was used to detect the surface pressure. The temperature of the coating solution was maintained at 25 °C by a water circulator and a heater.

The Brewster angle microscopy (BAM, Nanofilm, Germany and Nima, UK) was developed to monitor ultra-thin or monolayer organic films at an air–liquid interface. With its excellent image quality and lateral resolution, it is an ideal instrument for online control and visualization of morphological film parameters such as homogeneity, stability and domain structures. It has a collimated beam of approximately 6 mm diameter, a wavelength 659 nm laser beam and an angle of incidence of about 52°–54° for aqueous sub-phases. The BAM was mounted on the mini-trough to observe the air-liquid interface. The images based on the BAM for different concentration ratios of PA/AA system could be used to judge the quality of the film before the deposition process. The BAM experiment was carried out using a fixed composition PA/AA solution. The solution was placed inside an ultrasonic vibrator for one hour to ensure thorough mixing, and then spread onto the sub-phase in the Nima mini-trough. After allowing 30 min for solvent evaporation, the two barriers began to compress the molecular layer at a speed of 20 cm^2/min. The BAM images were to be recorded 5 min after the surface pressure reached 25 mN/m. The surface pressure was then released by moving the barriers in the opposite direction at the same speed. The BAM images were again recorded one minute after releasing the surface pressure. The experiment was repeated with different durations for each step.

The experimental set-up for observing the dynamic contact angle is shown in Fig. 1. A dipper was mounted on the edge of a viewing cell. In order to observe the meniscus height of the coating solution, a Nikon Coolpix 4500 digital camera with a magnifying lens was set-up to magnify the interface. The dynamic contact angles were measured directly from the images captured during the upward and downward strokes of the dipper.

The LB film deposition experiment was initiated by spreading the coating solution onto the sub-phase. After allowing 30 min for solvent evaporation, the two moving barriers, set at a speed of 20 cm^2/min, were turned on to compress the molecular layer on the sub-phase. During the course of the experiment, an isothermal pressure vs. area (π–A) curve was generated in the Nima 312D mini-trough. The shape of the π–A curve displayed clearly the three distinctive regions of gas, liquid and solid states. The stability of a monolayer at the air–liquid interface could be examined by the relaxation curve which showed the variations of trough area at constant surface pressure. A pH probe (HTC200, Hotec) was used to measure the acidity of the sub-phase. A 0.05 M sodium hydroxide (NaOH) or a 0.05 M hydrogen chloride (HCl) solution was added to the sub-phase to adjust its pH.

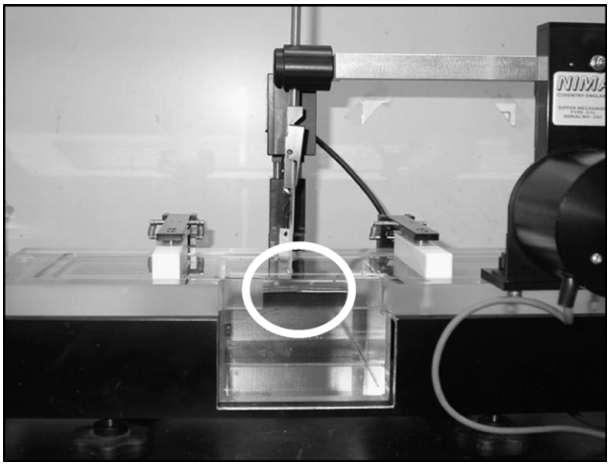

Fig. 1. The experimental set-up for visualizing the air–liquid interface during the immersion or the withdrawal operation.