Wrinkling of Polymeric Surface by Electron Irradiation

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1. Introduction

Surface wrinkling is a widely observed phenomenon characterized by flat surface waves on a micrometer or nanometer scale, which can take on different morphologies, such as hexagonal, peanut-shaped and lamellar forms. [1] In particular, the wrinkling of polymer surfaces is of great interest in both science and technology as it addresses potential applications such as tunable optical devices, switchable wettability, dry adhesion, biosensors, drug delivery, tissue engineering, microfluidic channels, and flexible electronics. The wrinkling phenomenon is achieved by various methods; however, one of the basic mechanisms for its occurrence is the application of stress. The stress can be induced by chemical, thermal or mechanical approximation.

In the case of the mechanical approach, a wrinkled surface is obtained by stretching and releasing, [1] but this method has limitations in producing wrinkled surfaces with large areas and in controlling wrinkle morphology. As to the case of the chemical or thermal approach, the wrinkling process generally requires the preparation of a double-layered structure using a thin polymer film and the application of strain-entrainment stress. In particular, this stress is derived in the thermal approach from the difference of the thermal expansion coefficient of the two layers. The chemical approach also uses a bilayer structure, but the stress is obtained by swelling a layer by solvent injection. These methods, while effective, require time-consuming and complicated steps in the fabrication of a bilayer structure, such as the like. As coating, thermal deposition and sputtering. They also require additional steps, such as heat application and solvent injection, in the application of stress. Moreover, they require the use of various materials, including both organic and inorganic materials, to make crumpled surfaces, and the methods appear to be severely limited to the use of thin films. [2]

Although previously mentioned techniques for producing wrinkled polymer surfaces have been developed, the production of patterned, wrinkled surfaces in which wrinkles are formed only on desired areas of a surface is still a challenge. Such structuring of wrinkled surfaces is very important in their application to tissue engineering and microfluidic channels. [3]

In this work, we propose a novel approach to producing wrinkled surfaces by blasting an electron beam onto polymers. The electron beam generates a bilayer polymer structure and at the same time provides heat to the polymer surface to create stress so that no further steps are required to produce wrinkled surfaces. In addition, this approach allows the structuring of wrinkled surfaces by selectively irradiating areas on the polymer surface. The method also offers other very advantageous features, such as the ability to be used on samples having complex shapes or large surface areas.

2. Methods

Four different polymers, polymethyl methacrylate (PMMA) (Goodfellow ME303031), polypropylene (PP) (Goodfellow PP303030), polystyrene (PS) (Goodfellow ST313200), and polyethylene (PE) (Goodfellow ET323250) were used in this study. The polymer plates having a thickness of 3 mm were cut into 1×1 cm^2 samples, followed by washing with isopropyl alcohol and drying with nitrogen gas. The samples were irradiated with an electron beam emitted from a thermionic electron gun in a vacuum of 10^{-6} Torr was

generated. The energy of the electron beam was set at 50 keV and the diameter of the beam was 1.5 cm.

The morphology and surface structure of the irradiated polymers were characterized using an optical microscope (OM, Park Systems XE-70) and an Atomic Force Microscope (AFM, Park Systems XE-70) in tapping mode. Mean and standard deviation values of wrinkle width and height were determined by averaging 10 AFM measurements at various locations on the sample surface. The depth to which a 50 keV electron beam acts on the polymers was determined by Raman spectra of an irradiated polymer. The Raman spectra were measured at various positions of the cross section of the irradiated polymer using a dispersive Raman spectrophotometer (HORIBA Jobin Yvon ARAMIS) equipped with an Ar ion laser. The spot size of the laser was 2 μm and the laser power of less than 0.5 mW was used to avoid damaging the polymer during the measurement. The temperature at the polymer surface during electron irradiation was measured using thermal labels (Nichiyu). Glass transition temperatures of the irradiated polymers were obtained using a cryogenic differential scanning calorimeter (DSC, NETZSCH DSC 204 F1). Thin (0.05 mm thick) polymer films were used and heated at a rate of 10 ° C / min to 200 ° C to measure the glass transition temperature.

3. Results

All original polymer samples had flat surfaces (1a, c, e, h). Interestingly, however, when PMMA was electron beam irradiated at a current density of 2.12 μA / cm^2 for 60 minutes, a wrinkled surface was created over the entire polymer surface (Fig. 1b). A similar wrinkled surface but with a smaller pleat width and height was also observed with PP when the polymer was irradiated under the same conditions used for PMMA irradiation. In contrast, no crumpled surfaces were formed on PS and PE when irradiated under the above conditions. Even at a higher current density of 4.24 μA / cm^2 for 60 min, PS and PE left their original flat surfaces without wrinkling.

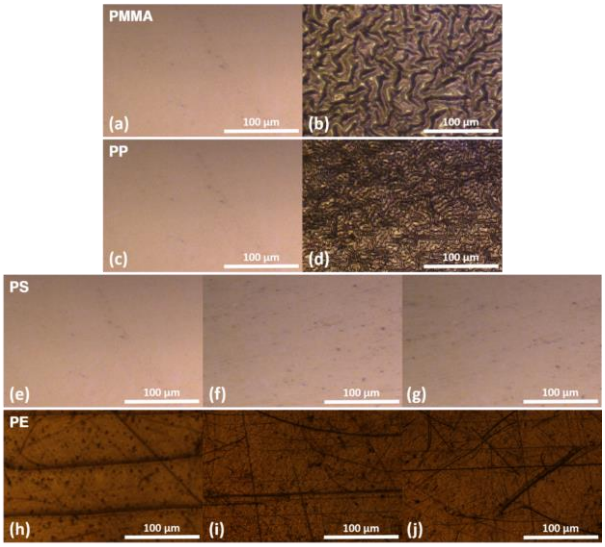

Figure 1

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