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Surface modification of polymers by ion irradiation at the solid–liquid interface

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ABSTRACT

An ion irradiation system in liquid has been developed using a tapered glass capillary with a thin window at the tip. Irradiation at a solid–liquid interface is interesting because it can be applied to novel analysis, radiation testing, and surface modification processes. In this study, polyethylene and polytetrafluoroethylene were irradiated with H^+ ions in an aqueous solution containing acrylic acid monomers. The irradiated surfaces which were originally hydrophobic became hydrophilic due to the surface layer formed by the acrylic acid polymer.

1. Introduction

Ion irradiation in a liquid has a high potential in areas such as biological radiation resistance assays, corrosion testing of nuclear materials, elemental microanalysis in wet environments, and in surface modification. We have developed an ion irradiation system in liquid using a tapered glass capillary with an end window, and have succeeded in irradiating part of a cell's nucleus under an optical microscope [1].

The ion beam is focused and guided using an electric field formed by the self-organized charging of the inner wall of the glass capillary when the energy of the ion is small [2,3]. Small angle scattering by the inner wall of the tapered glass capillary is dominant in the high-energy region [4]. Beam focusing using a glass capillary is a promising method to obtain a microbeam easily at a very low cost.

The thin end window at the tip of the capillary enables the entire beam line to be kept under vacuum, and at the same time, the transmitted beam can be injected into a liquid and directed to the target. In this study, we irradiated polyethylene (PE, $-[CH_2CH_2]_n-$) and polytetrafluoroethylene (PTFE, $-[CF_2CF_2]_n-$) solutions, expecting a large modification effect compared with irradiation in a vacuum. Radiation graft polymerization is a popular surface modification method for grafting monomers using radicals formed by electron or gamma ray irradiation [5–7]. By using ion irradiation, we expected that a high-density grafting of monomers would be achieved owing to the high ionization efficiency of the ions.

2. Experimental

Pulling on both sides of a heated borosilicate glass tube with an inner diameter of 0.8 mm produced a tapered glass capillary. The outlet diameter could be controlled from <1 μm to several hundred micrometers. The end window of the capillary was fabricated by shaping caulked glass using a focused ion beam (FIB). Fig. 1a and b shows optical microscope images before and after FIB shaping near the capillary outlet, respectively. A scanning ion microscopy (SIM) image of the exit of the window during FIB shaping is shown in Fig. 1c, showing that a flat and smooth surface was maintained. Large-diameter windows (>100 μm) were fabricated by pasting a polyimide (Kapton) thin film (7 μm thick) at the end of the capillary using epoxy adhesive. The tip of the capillary was inserted into a container filled with a liquid (Fig. 2).

A hydrogen ion beam extracted from a cesium sputter ion source was accelerated to 3 MeV using the Pelletron Accelerator at RIKEN, Japan. The beam was transported into the capillary holder via an analyzing magnet. The beam was injected into one side of the tapered glass capillary and passed through the thin window. The range of the 3 MeV H^+ ions in water after passing through the window composed of either 5 μm thick glass or 7 μm thick Kapton was calculated to be 140 μm using the SRIM software package. The irradiation was performed with the distance of the capillary tip to the sample being about 100 μm. At this distance, the average energy of the H^+ ions was calculated to be 1.3 MeV.

The liquid we chose to use was an aqueous acrylic acid (AAc, CH_2CHCO_2H) solution in concentrations between 0 and 10 wt.%. Acrylic acid readily combines with itself or other monomers by reacting at its double bond site to form hydrophilic polymers.

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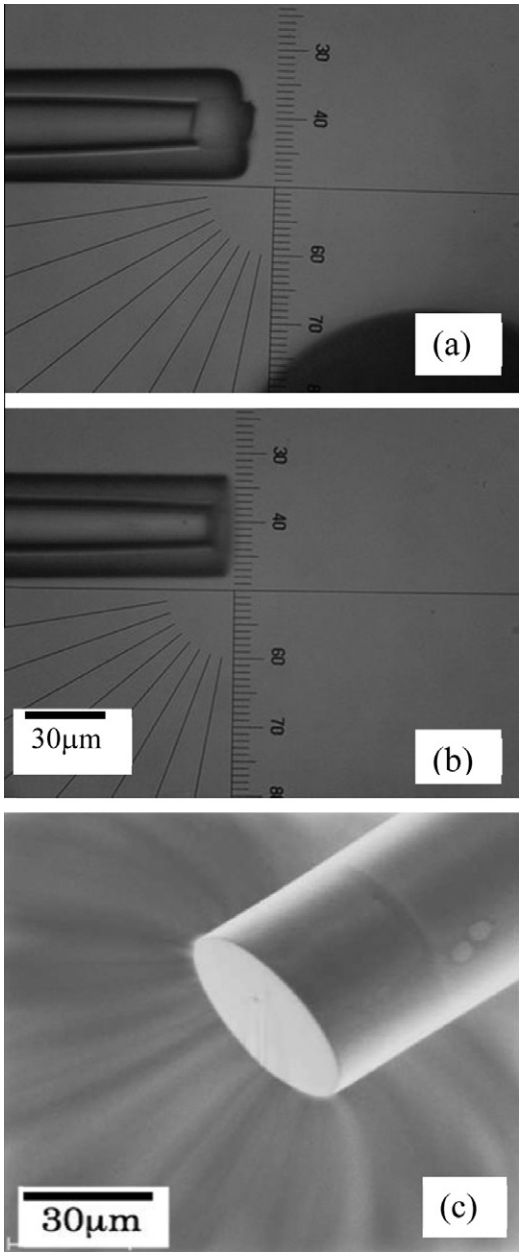

Fig. 1. Micrographs of the glass capillary with an end window: (a) with caulked glass, (b) after FIB shaping, and (c) a SIM image formed during FIB shaping.

PE and PTFE sheets were cut into 10×10 mm^2 pieces and fixed to flat silicon substrates. Beam scanning was performed by moving a stage containing the hanging sample at a speed of 2 or 10 μm/s.

The irradiated samples were washed with running water and then dried. Surface characterization was performed using a confocal microscope and an FT-IR spectrometer equipped with a microscopic attenuated total reflection (ATR) attachment. The affinity of water to the irradiated surface was observed using water droplet tests. Samples irradiated using a capillary with an outlet diameter of 200 μm were used for the surface characterization experiments.

3. Results and discussion

At the inlet of the capillary, the beam current density was typically 100 nA/cm^2, while at the outlet it was enhanced to 2.5 μA/cm^2 (total current of 0.2 nA using a capillary of 100 μm diameter) by the focusing effect. Irradiation in water that did not contain any

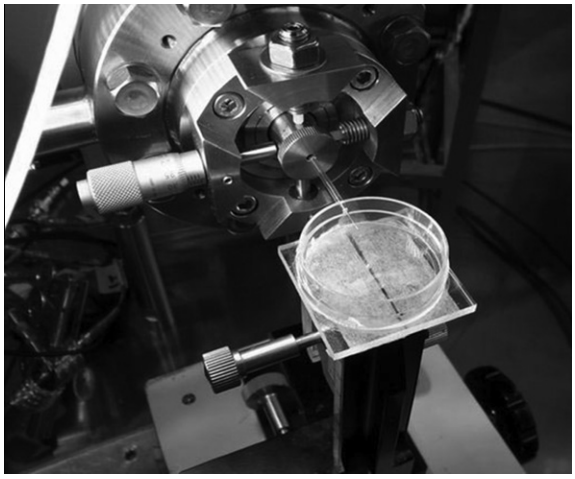

Fig. 2. A glass capillary fixed at the end of the beamline and inserted into a container filled with liquid.

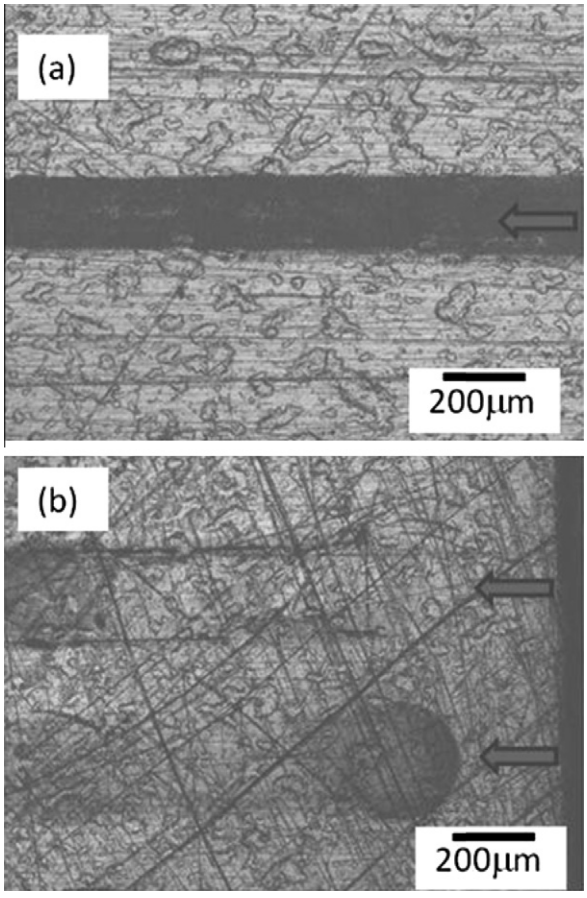

Fig. 3. A polyethylene surface irradiated in an aqueous acrylic acid solution using a scanning speed of 2 μm/s: (a) 10 wt.% and (b) 5 wt.%.

AAc solute showed a slight trace on the PE and PTFE surfaces, and no marked changes were observed in either the water affinity or in the FT-IR spectra. Microscope observations during the long irradiation time (>1 min) without beam scanning showed the formation bubbles of detached gas from the PE and PTFE, and the formation of a circular hole having the same diameter as the beam on the sample surface. The formation of large bubbles was suppressed by scanning the beam.