Application of the ion beam graft polymerization method to the thin film diagnosis

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Abstract

The ion beam graft polymerization (IBGP) method was applied to diagnosis of thin film of several tens μm or less thickness. After a sample stacked on polyethylene film was irradiated with proton beam, polyethylene was graft-polymerized with acrylic acid monomer. From observation of the graft-polymerized polyethylene, information inside the sample are obtained. Demonstrations of the diagnosis method were conducted for a leaf sample and a polyvinyl acetate film contained some voids. Using imitation samples made of metal and polymer sheets, some characteristics of this method was obtained. This method is useful for diagnosis for voids in thin film.

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Keywords: ion beam; graft polymerization; thin film; diagnosis

1. Introduction

Radiation graft polymerization is useful method to produce industrial materials. Generally, electron beams are utilized for this method. Ion track grafting had been developed by Betz (1995). In our laboratory, we have conducted the experiments to make a graft polymerized polymer with ion beams, such as proton, helium. The monomers react on the radicals generated by the ion beam irradiation. After polymerization reaction the graft chains are formed in the substrate. The ion beam graft polymerization (IBGP) method is useful and it can introduce the grafted chains with a functional base into the polymer at a vicinity of the surface, Taniike et al. (2011).

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There are many non-destructive diagnostic methods, e.g. supersonic echo, X-ray radiography among others, however these don't have sufficiently resolution for thin film analysis since interaction between sample material and probing beam is weak. On the other hand, the accelerator analyses are very powerful method for thin film diagnosis. But it is difficult to observe the voids inside of a thin film, because the analysis can only obtain the areal density. We have developed the diagnostic procedure method of a thin film with the ion beam graft polymerization. When a sample stacked on polyethylene film was irradiated with proton beam with enough energy, protons penetrate a sample and stop in the polyethylene. The range of the proton in polyethylene is a function of the size of the void that a proton passes. Thus, the polyethylene has information of the inside sample. After polyethylene is graft-polymerized with acrylic acid monomer, the information is appeared as existence of grafted polymer chains. Consequently, information inside the sample are obtained from observation of the grafted polyethylene. We examined this diagnostic method to analyze some samples made of metal and polymer. Some parameters in this method were obtained from the experiments.

2. Experimental Procedure

Samples and high density polyethylene film (HDPE) thickness is 50 μm, are irradiated with proton beams generated by the 1.7 MV tandem Pelletron accelerator at Kobe University (model 5SDH-2, NEC). Typical ion energy is 2.0 MeV, and the fluence is $2.0 \times 10^{12}$ cm$^{-2}$, and the fluence rate is $1.2 \times 10^{9}$ cm$^{-2}$s$^{-1}$, and the irradiation area is $1.5 \times 1.5$ cm$^2$. Fig. 1 shows schematic view of a sample irradiation a) and the cross sectional view b). Radicals are generated from the surface to ion range in HDPE. After an irradiation, the polyethylene is picked up from the holder and it is graft-polymerized by acrylic acid monomer. The IBGP procedure is described in a reference, Taniike et al. (2014). Samples, a leaf and a polyvinyl acetate resin were prepared to demonstrate this diagnostic method, and the imitation samples are prepared to measure the properties of this method.

3. Results and Discussions

3.1. An example of an observation in a sample with IBGP Method

A leaf sample and HDPE are stacked and irradiated by a 2.0-MeV proton. Then, the graft polymerization reactions are conducted to the irradiated HDPE. The HDPE has information of the inside sample. The information is obtained by HDPE observation. It looks like an ion beam radiography, and the results are shown in Fig. 2. A photograph of a clover leaf sample are shown in Fig. 2 a). The grafted HDPE was coloured in blue/green with Cu adsorption on the poly-acrylic acid. The inside structure of leaf is seen in Fig. 2 b). Polyvinyl acetate resin (bonding agent for wood) has many bubbles (voids). The bubbles in the thin film made of polyvinyl acetate could be also observed by this diagnostic method.
3.2. Observation of small holes inside thin film

To obtain the detection limit of the voids in the sample, we prepared some imitation samples. As shown in Fig. 3 a), a sheet with a hole was sandwiched by two sheets. Examples of the results are shown in Fig. 3. In these experiments the protons through the hole can arrive at HDPE, but the energy is small enough to penetrate three sheets. The reflected shapes of the holes are shown in a good contrast. In the case of all protons penetrate three sheets, the reflected shapes of the holes could be distinguished in a poor contrast.

Many samples were diagnosed in various combinations of the film thickness. The thickness of the thinnest sample whose hole could be observed was defined as smallest analyzable thickness. These thicknesses were listed in table 1. The thickness of polymer samples were larger than that of metal samples because of the difference in the stopping power. Sample thickness and the ratio of the smallest analyzable thickness and the sample thickness are also listed in table 1. In the case that the ratio is smaller than listed value the hole cannot be observed.

Observed graft polymerized area was broader than a hole area. The radius of graft polymerized area was proportional to the hole radius, and the experimental result of the dependence was shown in Fig. 4. The broadening of the radius was independent on the hole radius, and the broadening was constant of 11 μm. The value can be almost explained as ion struggling, propagation of the polymer chains, and expansion of graft polymerization area.

![Fig. 2. Observation of a leaf sample (clover).](image)

**Fig. 3. An example of the experimental results for the imitation samples.**

**Table 1. The smallest analyzable thickness of a hole and the ratio.**

<table>
<thead>
<tr>
<th>Sample Material</th>
<th>Smallest Analyzable thickness (μm)</th>
<th>Sample thickness (μm)</th>
<th>Hole ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>2</td>
<td>26 (= 12 + 2 + 12)</td>
<td>8</td>
</tr>
<tr>
<td>Titanium</td>
<td>2</td>
<td>22 (= 10 + 2 + 10)</td>
<td>9</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3</td>
<td>27 (= 12 + 3 + 12)</td>
<td>11</td>
</tr>
<tr>
<td>Polyimide</td>
<td>7.5</td>
<td>70.0 (= 50 + 7.5 + 12.5)</td>
<td>11</td>
</tr>
</tbody>
</table>
4. Conclusions

We have developed a diagnosis method for thin film with ion-beam-graft-polymerization method. To demonstrate this method some sample were analyzed. Inside structure of a leaf and bubbles in a polyvinyl acetate sample were observed. Some characteristics of the diagnosis were measured using imitation samples. Detectable limit of the void depth for metal and polymer imitation samples were measured. The radius of graft polymerized area was proportional to the radius of the hole. The broadening of the radius was 11 μm. We tried to observe a void with high resolution in depth direction. After a grafted HDPE was cut, the cross sectional view was observed by a microscope. The difference between grafted or not grafted area in depth direction was observed. The difference was corresponding to the void size. It is considered that this method is applicable for a thin/small void with high resolution.

Acknowledgements

This study was supported by A—STEP FS Stage Exploratory Research type, AS232Z02012B, JST and International Maritime Research Centre, Maritime Sciences, Kobe University.

References


Fig. 4. Dependence of the radius of graft polymerized area on the radius of sample hole.

\[
y = 1.00x + 11 \pm 1
\]

2 MeV p