SURFACE MODIFICATION OF POLYTETRAFLUOROETHYLENE WITH ArF EXCIMER LASER IRRADIATION

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PTFE surface property was modified from hydrophobicity to high wetting ability by ArF excimer laser irradiation in Monosodium L-Glutamate Monohydrate (L-Glutamate) solution and in ethyl alcohol solution. The wetting ability of the processed surface was examined by the water contact angle method. The contact angle of the film was improved from 120 degree to 0 degree. By XPS analysis it was shown that amino groups, carbonyl groups, ethylene linkages were substitutionally formed with the release of fluorine atom on the surface. These hydrophilic molecules formed on the processed surface are believed to make the surface hydrophilic. The processed surface showed its original appearance without any stain and physical damage. Spatial resolution of 1 μ m is obtained with this method.

1. Introduction

Researches of the surface property modification have been increasing in order to develop new functional surface property on polymer materials. Although Fluorocarbon polymer films such as polytetrafluoroethylene (PTFE) are used in many applications for their excellent properties such as heat resistivity and solvent resistivity, their applications are limited by the chemical inactivity of their surface property. It has been demanded to develop the surface property modification method on the PTFE surface. In order to activate the PTFE surface, defluorine method in alkaline metallic solution [1] and plasma etching method [2] were reported. These methods do not give satisfactory results, since the processed surface becomes partially stained and rough and it is difficult to specify the activation area with these methods. We have developed the surface modification method of PTFE which enables the formation of hydrophilic surface selectively on the PTFE surface without any stain and physical damage. The method consists of ArF excimer laser irradiation in L-

Glutamate solution and alcohol solution. The processing method and results are described.

2. Processing method

Fig. 1 shows schematic diagram of experimental setup. PTFE film floating on various kinds of solution was irradiated by patterned ultraviolet light which was generated by excimer laser with mask imaging optical system. Distilled water solution of ethyl alcohol and Monosodium L-Glutamate Monohydrate was used. Their concentrations in weight % were varied from 0 to 90%. High Power Excimer Laser (L5000, HAMAMATSU PHOTONICS K. K.) was used for ArF excimer laser source (wavelength: 193 nm, pulse duration: 15 nsec). Fig. 2 and Fig. 3 show the Excimer Laser and the Laser Microprocessing Unit (C4540, HAMAMATSU PHOTONICS K. K.), respectively. The PTFE film used were 50 μm in thickness (TOMBO 9001, NICHIASU Co. Ltd.), which transmitted approximately 30 % of the incident UV light. Laser irradiation on the PTFE films was operated at the fluence of 0-90 mJ/cm^2 with 1000-6000 shots at 50 Hz. Surface activation process occurred at the interface of the PTFE film and the solution with the UV light penetrated through the PTFE film.

The chemical structure of the PTFE film was analyzed by X-ray photoelectron Spectroscopy (XPS, ESCA 5400: PERKIN-ELMER Co. Ltd.). And wetting ability of the film surface was examined by measuring the water contact angle of the PTFE.

Fig. 1 Schematic diagram of experimental setup

Fig. 2 High power excimer laser (L5000)
maximum output power : 80 watts
continuous operation : 16 hours
beam size : 27 x 10 mm

Fig. 3 Laser microprocessing unit (C4540)
minimum processing size: ϕ 1 μ m

3. Results and analysis of the experiment

By optical mask imaging system, minimum spatial resolution of 1 μm was obtained with the laser microprocessing unit (C4540). Such fine spatial resolution can not be achieved by the usual method with alkaline metallic solution and plasma etching method. Fig. 4 shows one of the examples of the processed PTFE film. An optical test chart mask of line and space was used. The pattern copied on the film was decorated by water color ink after processing. It can be seen the spatial resolution of 50 μm with this conventional decoration method.

Fig. 4 An example of the processed PTFE film
The pattern copied on the film was decorated by water color ink. Spatial resolution of 50 μm is seen with this conventional decoration method.

1) L-Glutamate solution

Fig. 5 shows the water contact angle of PTFE processed surface as the concentration of L-Glutamate solution is changed. It can be seen that the contact angle is drastically improved from 120 degree to 0 degree when the concentration of L-Glutamate solution is 1-5 %. Fig. 6 shows the contact angle versus the energy density (fluence) of the UV pulse per various solution concentrations. From these results it can be seen that there is optimum fluence and solution concentration for the process. The minimum contact angle of approximately 0 degree can be achieved at the fluence of 10-20 mJ/cm^2 and the concentration of 2.9 %.

Fig. 5 The water contact angle of PTFE as functions of the concentration of L-Glutamate solution
laser fluence : 10 mJ/cm^2
number of laser pulses : 1000 pulses
laser repetition frequency : 50 Hz

Fig. 6 The water contact angle of PTFE as functions of the laser fluence at three different concentration of L-Glutamate solution
number of laser pulses : 1000 pulses
laser repetition frequency : 50 Hz

2) Ethyl alcohol solution

Fig. 7 shows the contact angle as the concentration of ethyl alcohol solution is changed. The contact angle is improved from 120 degree to 0 degree when the concentration is 15-25 %. Fig. 8 shows the contact angle versus the fluence per various solution concentrations. As in the case of L-Glutamate solution, there is also an optimum processing condition for the process with ethyl alcohol solution. The minimum contact angle of approximately 0 degree is achieved at the fluence of 10-40 mJ/cm² and the concentration of 20%.

Fig. 7 The water contact angle of PTFE as functions of the concentration of ethyl alcohol solution

laser fluence : 15 mJ/cm²
 number of laser pulses : 3000 pulses
 laser repetition frequency : 50 Hz

Fig. 8 The water contact angle of PTFE as functions of the laser fluence at three different concentration of ethyl alcohol solution

number of laser pulses : 3000 pulses
 laser repetition frequency : 50 Hz

3) XPS analysis of the processed PTFE surface

By measuring the water contact angle of the processed film, we confirmed the formation of hydrophilic surface on the film. We investigated the chemical compositional change of the photo modified film surface by X-ray photoelectron spectroscopy (XPS). Fig. 9 and Fig. 10 show depth profile data of atomic concentration on the processed films of the zero contact angle with L-Glutamate solution and ethyl alcohol solution, respectively. The depth profile data were obtained by Argon ion etching in the XPS chamber. From both Figures, it can be seen that the fluorine concentration (F/C) is much decreased and the oxygen concentration (O/C) is increased on the surface. And defluorine process occurs more and up to deeper portion with L-Glutamate solution than with ethyl alcohol solution.

In order to identify the hydrophilic group of the processed surface, spectrum analysis of C_{1s} spectra was performed. It was found that the C_{1s} spectra of the surface processed both with L-Glutamate solution and ethyl alcohol solution have five peaks. These peaks are identified to the following peaks; $-CH_2$ (286.3 eV), $-OH$ (287.9 eV), $-CF$ (289.1 eV), $-C=O$ (290.3 eV) and $-COOH$ (291.0 eV). And the surface processed with L-Glutamate solution has the peak of $-NH_2$ (400.5 eV) in addition to above peaks. The dominant component of C_{1s} spectra observed on the unprocessed PTFE film surface is the peak of $-CF_2$ (292.3 eV).

Fig. 9 Depth profile of atomic concentration of the film processed with L-Glutamate solution

Fig. 10 Depth profile of atomic concentration of the film processed with ethyl alcohol solution

4. Conclusions and Discussions

The new surface property modification method on the PTFE film was investigated. The modification method consists of ArF excimer laser irradiation on the PTFE film surface in L-Glutamate solution and ethyl alcohol solution. It was shown that by the water contact angle measurement the hydrophobic property of the PTFE film surface can be modified to the hydrophilic one with this method very effectively. It was also found that there were optimum processing conditions with both L-Glutamate solution and ethyl alcohol solution. These processing conditions are 1-5 % concentration of L-Glutamate solution at the laser fluence of 10-20 mJ/cm² and 15-25 % concentration of ethyl alcohol solution at the laser fluence of 10-40 mJ/cm². With these processing conditions, the minimum contact angle of approximately zero was achieved. By the XPS analysis, it was found that the fluorine atomic concentration on the processed surface was much reduced by

comparing to unprocessed surface. And it is also shown that the processed hydrophilic PTFE surface has hydrophilic molecules such as amino groups, carbonyl groups and ethylene linkages. Since the level of the laser fluence is not so high as to induce laser abrasion process, any physical damage was not observed on the processed PTFE surface.

We believe the mechanism of the formation of hydrophilic surface on PTFE with ArF excimer irradiation as follows. Incident photons of ArF laser (6.43 eV) cut C-F molecular bonds of PTFE and deplete fluorine atoms at the surface at first step. Then the dangling bonds on the surface formed by this process are terminated by such groups as amino groups, carbonyl groups and ethylene linkages in solution. These hydrophilic molecules make the surface hydrophilic. On the contrary, the formation of hydrophilic surface on PTFE by alkaline metallic solution method and Plasma etching method is based on anchoring effect which is obtained by roughing process of the PTFE surface.

Application of the new surface modification method can be expected for its excellent features such as non physical damage on the processed surface and selective processing area. And moreover, spatial resolution of 1 μm is obtained by this method. Since the hydrophilic surface has low surface energy, adhesiveness of the PTFE surface will be improved very much. This will make PTFE application diverse and various applications can be expected for the combination of reciprocal properties (hydrophobicity and hydrophilicity). Artificial blood vessel is one of major applications of this technology.

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