

Surface Treatment of Polymers by Simultaneous Exposure to VUV and Nanometer-Sized Particles in Helium Atmosphere

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A new surface treatment for polymers in helium at atmospheric pressure was demonstrated. By focusing the strong absorption of vacuum ultra-violet light at the wavelength between 60nm and 80nm for polymers and high transparency in helium gas of the vacuum ultra-violet light at the wavelength over 50.4nm, we developed the new process for surface treatment of polymers for making bonds between polymer surfaces and painting over polymer surfaces in helium atmosphere by simultaneous exposure to VUV and nanometer-sized particles.

Keywords: surface treatment, polymer, VUV, nanometer-sized particles, helium

1. Introduction

Because of their easy treatment, light-weight, and low consumer energy, polymers have been used in various products. Despite the versatility of many polymers, they have limitations to many applications because almost all plastics are composed of non-polar and long-chain molecules, and their surfaces have very low free energy and are essentially inert. Unlike high surface energy materials, such as metals and ceramics, plastics are lack of the availability of bonding sites offered by charged ions distributed over the surface. Without such a molecular attraction, liquid fails to wet the surface, resulting in poor adhesion and coverage on the polymer surface. This is especially troublesome when painting and making bonds on to the polymer. Recently, a lot of studies looking at modification of polymer surfaces using UV lasers, UV lights and electron beams have been reported [1-3]. Most of those studies have concentrated on changing in polymer shape and quality. And also, surface activation of the polymer by conventional surface treatments such as UV exposure or plasma treatment, is lost within a few days [4,5]. While, the surface treatment by laser ablation with vacuum ultra-violet (VUV) light in a vacuum, makes it possible to improve adhesion characteristics of polymer surfaces [6]. However, there has been a strong demand to make this processing in the atmosphere. Therefore a surface treatment of polymers in one atmospheric pressure gas has been studied.

Here, we show the new surface treatment of polymers, the exposure to VUV and nm-sized particles at the same time, without changing polymer shape or quality in 1 atm helium atmosphere.

2. VUV generation

The calculated transmittance of VUV for typical industrial polymers showed the strong absorption, which comes from carbon 2p electrons in polymers, at the wavelength of about 75 nm. Also it is well-known that the polymer surface gets activation quickly just after exposure to VUV without deformation.

Here, we've developed VUV and nanometer-particles source of laser produced plasma for simultaneous exposure to polymers without deformation and quick losing of the surface activity.

For VUV generation, mainly a carbon disc target was irradiated with a pulsed laser of 532nm wavelength, a pulse duration of 7 ns, a repetition rate of 10 Hz, and an energy of 1 J, delivered by the YAG laser system (Spectra Physics Pro-290). The laser beam was focused on a spot between 0.2 mm and 4mm on the target using a spherical lens. The irradiation intensities were approximately between 0.8×10^9 and 4.0×10^{11} W/cm².

In a laser-produced plasma with this irradiated intensity, extended emission spectra between soft X-ray and infrared were generated, but in this irradiation intensity, a stronger VUV emission was observed. The VUV spectrum was observed using a VUV spectrometer shown in experimental set-up (Fig. 1) with a diffraction grating of 1200 grooves/mm (HITACHI model 001-0437) and a back-illuminated X-ray CCD camera (IP Lab. PI-SX 1024) as the detector. The VUV spectra from the laser-produced plasma of the irradiated typical targets for a single laser shot were obtained. Some intense VUV lines were observed at wavelengths between 40 nm and 80 nm for carbon at the intensities between 4.0×10^9 and 4.0×10^{11} W/cm² shown in Fig. 2. Considering diffraction efficiency, mirror reflectivity, and slit size, the total energy of VUV lines between 60 nm and 80 nm was more than 10 mJ on the target per single shot at the intensity of 4.0×10^9 W/cm²

in the plasma. The energy of VUV light located 10 cm from the VUV source for 5 seconds exposure, which is more than 0.8 mJ/cm^2 , was sufficient for activating polymer surfaces [7].

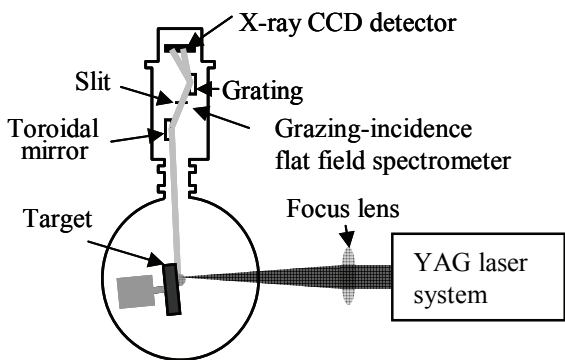


Fig. 1 Block diagram of a grazing incidence flat field spectrometer equipped with a toroidal mirror for measuring spectra from the plasma on the target.

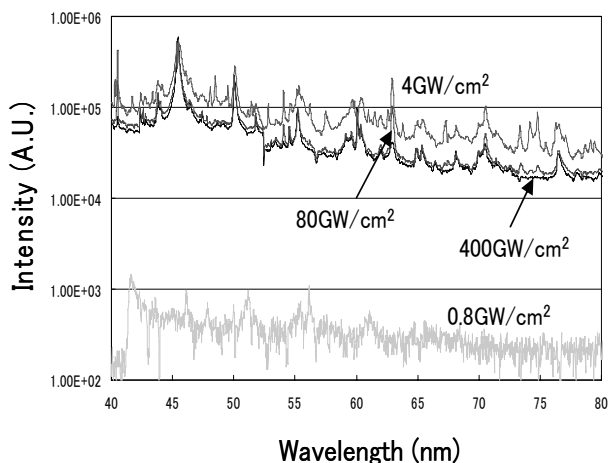


Fig. 2 VUV spectra at wavelength between 40 nm and 80nm from a carbon target irradiated with the intensity between 0.8 and $4.0 \times 10^{11} \text{ W/cm}^2$.

3. Ablated particles

The ablated particles from the irradiated targets such as aluminum, copper and carbon in vacuum were observed by scanning electron microscopy (SEM) and transmittance electron microscopy (TEM). The deposited thicknesses of the deposited ablated particles were measured with a surface-profiler (Dektak3ST VEECO/SLOAN Technology).

Figure 3 shows the SEM images of ablated particles from carbon, copper and aluminum targets. Almost all ablated particles from a carbon target were not observed

by SEM and TEM due to their small size of less than a few nanometers. However, for copper and aluminum submicron-sized particles were observed especially in the normal direction of the target surface. The thicknesses of the copper targets, a few nanometer and submicron-sized spherical particles were observed. The surface profiles of the deposited particles of carbon, copper and aluminum for 20,000 times laser shots in vacuum were measured. The thicknesses of the deposited ablators of carbon, copper and aluminum were about 50 nm, 80 nm and 600 nm, respectively.

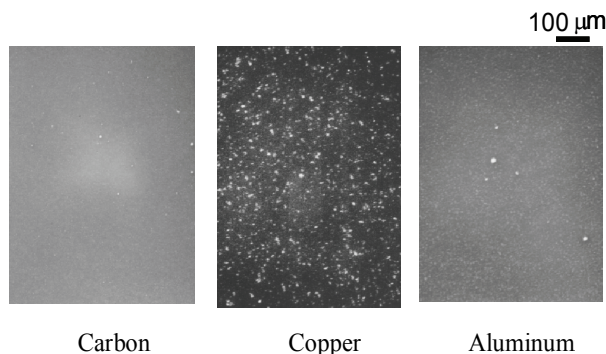


Fig. 3 SEM image of ablated particles on a silicon substrate from the copper target for 100 laser shots.

4. Atmosphere

The transmittance (T) of a gas under atmospheric pressure was estimated by the following equation:

$$T = \exp(-2r_0\lambda\phi f_2) \quad (1)$$

Here, r_0 is the classical electron radius, λ is the wavelength, ϕ is the number of gas atoms per unit volume, and f_2 is the imaginary part of the atomic scattering factor [8]. From calculation of transmittance of VUV light with eq. (1) for various gases, some gas except helium showed a strong absorption for VUV light at the wavelength between 60 nm and 80 nm, which improve adhesion characteristics of a polymer surface. From this result, it is clear that helium gas is appropriate as atmospheric gas for the surface treatment with VUV [9].

On the other hand, a mean free pass of an ablated particle scattered in helium gas of one atmospheric pressure is about $3.5 \times 10^{-5} \text{ cm}$ for a carbon, and considering the representative distance between carbon target and the polymer substrate, 3 cm, which is the typical distance in our experiment, a few of ablated particles will arrive at a polymer substrate with keeping more than 1% of initial kinetic energy. In the case of a carbon cluster comprising carbon atoms more than several hundred, cluster particles arrive at a polymer substrate with keeping higher than 60% of the initial kinetic energy, because of little

decrement of kinetic energy by a collision to a helium atom [9].

The thickness of the deposited ablated particles from carbon, copper and aluminum targets irradiated with a pulsed laser on silicon substrates in one-atmospheric helium gas were measured with a surface profiler. Each target was irradiated 36,000 times with the focused second-harmonic laser beam (wavelength: 532 nm, pulse duration: 7 ns, energy/pulse: 1 J, repetition rate: 10 Hz) from the Nd-YAG laser system in one-atmospheric helium gas. The irradiation intensity was estimated to be about $4.6 \times 10^9 \text{ W/cm}^2$. Measured surface profiles of the deposited particles on silicon substrates compared with that in vacuum ($\sim 10^{-3} \text{ Pa}$) are shown in Fig. 4.

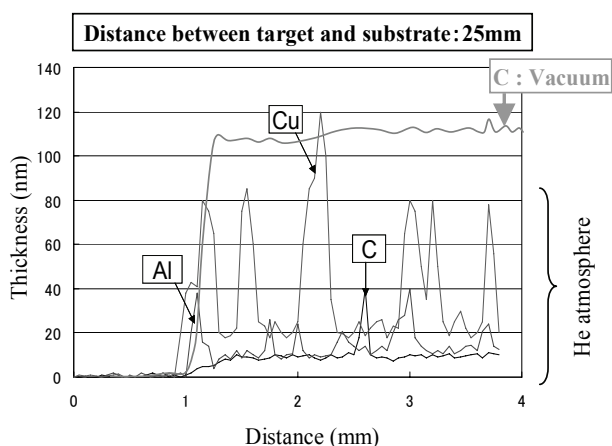


Fig. 4 The surface profiles of the deposited particles of carbon, copper and aluminum.

For a copper target, large peaks, which seem to depend on about 100 nm deposited particles were observed. The thickness of the deposited particles for a carbon target was about 10 nm, which was about 1/10 the thickness in vacuum. And also, a few particles with a size of more than 10 nm in helium atmosphere were observed. These experimental results did not agree with the estimation from the calculation result of arrival to the substrate for only a carbon cluster consisting of more than several hundred carbon atoms. But, from these experimental results, it was expected that a polymer surface should be exposed to VUV light and scattered particles, which are necessary for improving of the polymer surface, even in one-atmospheric helium gas.

5. Surface treatment of polymers

Polymer surfaces were simultaneously exposed to VUV and nanometer-sized particles from laser-produced plasma in order to improve the adhesion property in helium atmosphere. An experimental setup for the polymer surface treatment is shown in Fig. 5. Laser beam

delivered from Nd-YAG laser system was focused elliptically to a spot with a longer axis of about 4 mm and a shorter axis of about 1 mm on a carbon target at an angle of 60 degrees between the target normal and the laser beam. The irradiated intensity was estimated to be about $4.6 \times 10^9 \text{ W/cm}^2$. Droplets from the target are scattered mainly in the normal direction of the target surface. Avoiding depositing droplets on the polymer sample, the target and the polymer sample were set up at the off-axis in the chamber. A rotated carbon disc used as a target by a motor was irradiated by the focused laser beam. Polypropylene (TORAY) plates used as polymer substrates were rotated for uniform exposure. The surface of a substrate was covered with flowed helium gas.

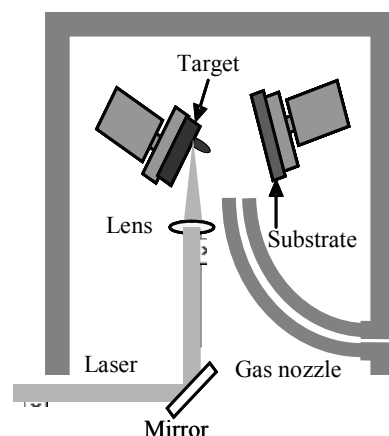


Fig. 5 Schematic set-up for the surface treatment.

6. Estimation of treated polymers

The treated samples were coated with a conventional paint directly. R320U-40(NIHON B-CHEMICAL) was used as a paint. Some painted samples were left for one day in the oven at 293K and other samples were dipped for 10 days in the water bath at 313K. Some samples for the tensile test were bonded to metal rods by an epoxy adhesive. After drying, bonded samples were pulled by a testing machine (Instron. Co.). Others were used for the cross-cut test of the painted film.

The results of the tensile tests are shown in Fig. 6.

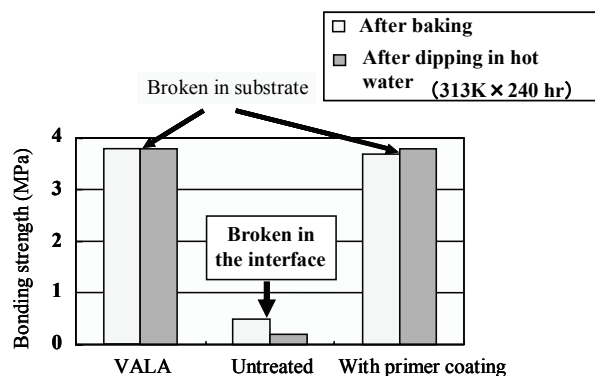


Fig. 6 Bonding strength of the treated samples, the untreated samples and conventional primer coated samples

The metal rod was pulled off from all samples exposed to VUV and nm-particles at more than 3.5 MPa, and the surfaces of polymers were broken off as well as samples with conventional primer coating. However, in the case of untreated samples, the metal rod was pulled off from the surfaces of polymers without breaking polymer surfaces themselves at less than 0.5 MPa.

After baking the painted samples at 363K for 20 min. and dipping them for 10 days in a water bath at 313K, samples were cross-cut with the knife and pull off with the stuck tape (cross-cut test).

Figure 7 shows the one of results of the cross-cut test for samples after dipping in hot water.

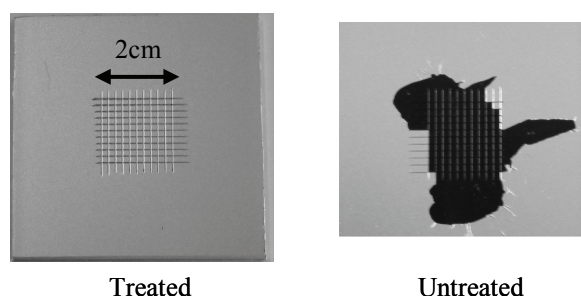


Fig. 7 Appearances of dipped samples after cross-cut test.

The coating films were not torn off from the treated polymer surfaces. On the other hand, without the treatment, the films were easily torn off from the polymer substrates. And also, the samples without dipping hot water were estimated by cross-cut test in the same way. As a result, the treated sample in a helium gas showed enough adhesion strength.

7. Discussion

For understanding the correlation between the procedure and the adhesion improvement of polymer surfaces, the polymer surface with VUV and nm-particles, with nm-particles, and with only VUV were analyzed by XPS. The photoelectron spectra of C1s electron of treated surfaces of polymer films with VUV and with only VUV has broadening in higher energy sides. And after the 10 day-treatment only the spectrum with VUV and nm-particles has broadening in higher energy sides [6][9]. This broadening of photoelectron spectrum indicates the bindings of carbon atoms to gas molecules. It is well-known that the broadening at higher energy side in XPS spectrum of C1s depends on the bonding between carbon and oxygen or hydro-oxygen. And this broadening at the higher energy side was more remarkable when the polymer left longer after the treatment. The adhesion

improvement of the polymer surface treated with VUV is caused by the creation of these bonds of the polymer surface. And we assumed that the ablated nm-particles caused to keep the adhesion improvement of polymer surfaces for long time.

8. Conclusion

By focusing the strong absorption for polymers and high transparency in helium gas of the vacuum ultra-violet light in the wavelength region between 60nm and 80nm, we developed the new process for surface treatment of polymers in helium atmosphere by simultaneous exposure to VUV and nanometer-sized particles.

This new surface treatment makes it possible to paint directly on a polymer without conventional primer.

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