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SHORT COMMUNICATION

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Improvement of wettability and detergency of polymeric materials by excimer UV treatment

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Abstract The 172 nm ultraviolet (UV) excimer light was exposed to polyethylene (PE), polypropylene, poly(ethylene terephthalate) and nylon 6 surfaces in ambient air. Changes in the contact angle and particle deposition in liquid due to UV treatment were investigated from the viewpoints of wettability and detergency. For all polymers, the wettability and the acid-base component of the surface free energy evaluated by the contact angle measurements increased remarkably by UV treatment of 1 min. From surface analyses of the polymer surfaces by X-ray photoelectron spectroscopy and atomic force microscopy, oxygen concentration was found to increase after UV treatment, whereas little topographical change was observed. The deposition of PE and nylon 12 particles onto the polymer surface was examined, in situ, in water, water/ethanol mixture, ethanol and n-heptane. Although the number of deposited particles was largely dependent on the kinds of the particle, the substrate and the liquid, a significant decrease in the deposition due to UV treatment was confirmed in any system.

Keywords Ultraviolet excimer light · Polymer surface · Contact angle · Surface free energy · Particle deposition

Introduction

Synthetic polymers possess many desirable physical and chemical characteristics, such as low dielectric constant, high strength-to-weight ratio, high formability, resistance to corrosion etc., in addition to their low cost. On the other hand, they have intrinsically low wettability and poor adhesion to various materials and hence required the surface treatment to increase their surface energies [1, 2]. Corona discharge [3–5] and flame [6] treatment processes are the most commonly proposed surface treatment of polymers. Plasma treatment [7–14] is another effective method for treating surfaces to enhance wettability and adhesion.

In the present paper, we are concerned with ultraviolet (UV) excimer treatment [15–21]. UV irradiation, which may introduce a high percentage of O functional groups onto polymer surfaces and enhance their surface energies, has been recently utilized as a surface modification technique. Four polymer samples, polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET) and nylon 6 (Ny6), were treated by exposure to an excimer UV lamp in air. The changes in wettability and surface free energy due to UV treatment were evaluated by contact angle measurements. The results were discussed in relation to the chemical and topographical changes at the film surface obtained by X-ray photoelectron spectroscopy and atomic force microscopy (AFM). Moreover, the influence of UV treatment on particle deposition onto the polymer surface in liquid media was investigated from the viewpoint of detergency.

Experimental

Materials

Polymer samples used were PE, PP, PET, and Ny6. For contact angle measurements and surface analyses, commercially available films of PE (Ohkura Kougyo, Japan), PP (Torayfan BO 2500, Toray, Japan), PET (EMBLET S-38, Unitika, Japan) and Ny6 (EMBLEM ON-25, Unitika, Japan) of 25–50 μm in thickness were chosen. PP and PET plates of 1 mm in thickness, supplied by Kureha Chemical Industry (Japan), were used for particle deposition experiments. Prior to use, all polymer samples were ultrasonically cleaned twice in water at 40 °C.

Spherical particles of PE (Seitetsu Chemical Industry Co. Ltd, Japan) and nylon 12 (Toray Co. Ltd, Japan) used had mean diameters of 4 μm and 5 μm, respectively [22, 23]. The particles were successively cleaned by extraction with water, ethanol and ethyl ether.

All chemicals used were extra pure grade reagents and used without further purification. Water was deionized and distilled using a Glass Still apparatus (Barnstead, Germany) and purified (resistivity of 18 MΩ cm) using an Easy Pure RF apparatus (Barnstead, Germany).

UV treatment

Polymer samples were irradiated with an UV excimer lamp at a wavelength of 172 nm in ambient air using a Xe_2 excimer vacuum UV apparatus (UER20–172, Ushio, Japan). The intensity of the UV excimer light at the upper window of the lamp house was determined to be 15.8 mW/cm^2 using a UV monitor system (UIT-150 and VUV-S172, Ushio, Japan). The sample surface was irradiated by the UV excimer light located 0.2 mm away from the window. The treatment time was 1 min because of the relatively high intensity UV radiation in the present system [24].

In the previous papers [24, 25], the hydrophobic recovery of the polymer film due to the reorientation and migration of polymer chains in the oxidized layer and the loss of volatile oxidized species to the atmosphere [26–28] was observed during 1 week after UV treatment. Therefore, the UV-exposed polymer samples were stored for 1 week prior to use.

Surface characterization

The polymer surfaces were characterized by X-ray photoelectron spectroscopy (XPS) using a spectrometer (Model 1600S, ULVAC-PHI, Japan) with 400 W Mg K_αX-ray source (1,253.6 eV). C1s, N1s and O1s core-level spectra from an area of 0.8×2.0 mm^2 were collected at a 45 ° take-off angle from the substrate normal. During the measurements, the pressure inside the analysis chamber was maintained below 5×10^{-6} Pa. The narrow XPS spectra were processed using Multipak software. All XPS binding energies were referenced to the C1s peak of adventitious carbon at a binding energy of 284.6 eV. The atomic concentrations of carbon, nitrogen and oxygen were calculated from the peak intensities and the atomic sensitivity factors of the respective elements given by PHI.

The AFM images were obtained with a Digital Instruments Model D3100 scanning probe microscope and Nanoscope IIIa. The AFM images were obtained in a tapping mode, and the mean roughness was determined from the data collected on an area of 1 μm^2.

Contact angle measurements

Contact angle measurements were carried out by the sessile drop technique using a video contact angle system (VCA-2500, ASC Products, USA). A 2–3 μl liquid drop was placed on the polymer film surface and was viewed using a CCD camera attached to a microscope. The contact angle and the drop base diameter were measured as a function of time from drop images stored every second in a computer. The advancing contact angle was obtained by extrapolating the measured angles to time-zero, because the contact angle linearly decreased with time and the drop diameter slightly increased in the initial stage.

The Lifshitz-van der Waals and acid-base components of the surface free energy of the polymer samples were determined from the advancing contact angles of three probe liquids (water, diiodomethane, and ethylene glycol) on the polymer films [29, 30].

Particle deposition experiment

Spherical particles of PE (1.6×10^9 particles/dm^3) and nylon 12 (1.5×10^9 particles/dm^3) were dispersed ultrasonically in water, water/ethanol mixture (volume ratio of 90/10), ethanol and n-heptane. The stability of the dispersion was observed to be relatively high, though the monodispersivity was not confirmed. As illustrated in Fig. 1, the PP or PE plate (5×30 mm^2) was perpendicularly immersed in the dispersion, which was filled in an optical quartz cell (10×10×45 mm^3). After standing for 24 h, microscopic photographs (see Fig. 1) were taken over 20 different areas (0.118 mm^2). The number of particles deposited onto the plate was counted and was regarded as the apparent equilibrium deposition [25].

All experiments were carried out in a room maintained at 25 ± 1 °C.

Results and discussion

Surface chemical composition and topography

Figure 2 gives the XPS and AFM results of the polymer films before and after UV treatment. The surface oxygen concentration was found to increase after UV treatment for all polymers. Especially for PE and PP, oxygen was detected only after UV treatment. Little topographical change due to UV treatment was observed for PP. In the case of PET, the surface roughness was small even after UV treatment, although the surface roughness increased by UV treatment.

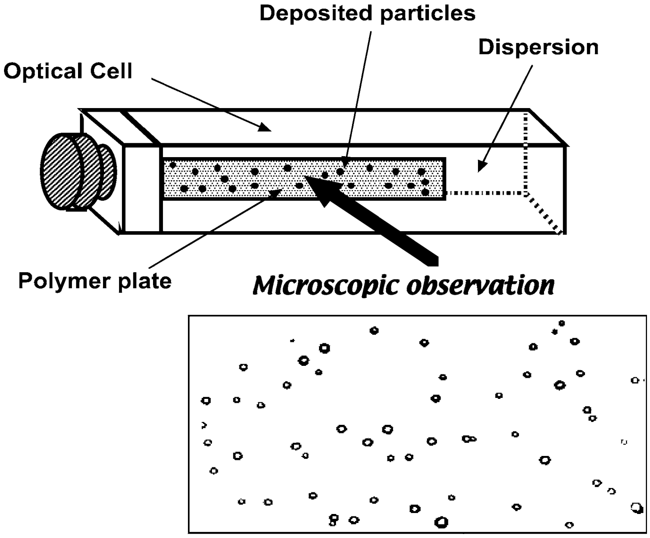


Fig. 1 Schematic diagram of particle deposition experiment and microscopic photograph of particles deposition onto the polymer surface

Wettability and surface free energies

The advancing contact angle of water on the polymer films as a measure of wettability is presented in Fig. 3. There was a considerable difference in contact angles among unexposed polymer films. The angle was the largest for PP followed by PE, PET and Ny6. This order is not in contradiction with the expectation from their chemical structures. For all polymers, the angle decreased (i.e. the wettability increased) by UV treatment.

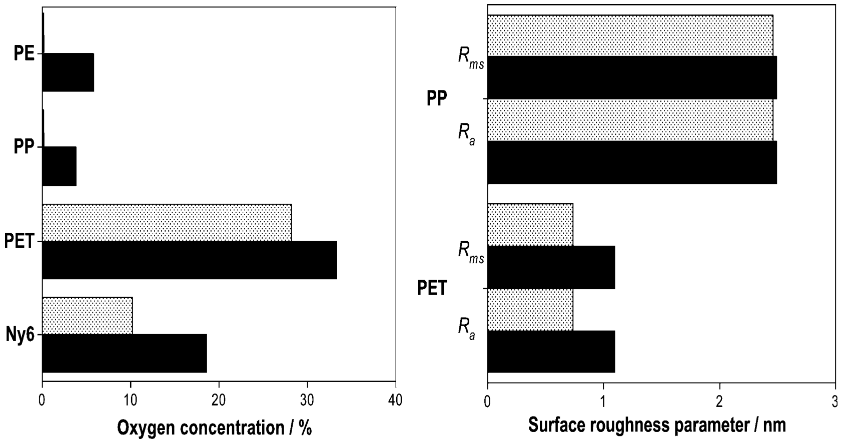
Figure 3 also gives the Lifshitz-van der Waals component (γ_s^{LW}) and the acid-base component (γ_s^{AB}) of the surface free energy of the polymer films. No significant change in the Lifshitz-van der Waals component due to UV treatment was observed. On the other hand, the acid-base component increased drastically by the treatment, which might cause an increase in adhesion of the polymer to other materials as well as in wettability.

By comparing the results in Fig. 3 with the XPS and AFM results in Fig. 2, it is clear that the improvement in the wettability of the polymer surfaces by UV treatment is caused not by the topographical change, but by the change in chemical composition at the surface.

Particle deposition

Figure 4 shows the number of particles deposited onto the polymer plate in water, water/ethanol mixture (volume ratio of 90/10), ethanol and n-heptane. The decrease in the deposition in water by the UV treatment can be caused by the increase in the wettability of the polymer plate as mentioned above. In addition, it may be attributed to the increase in the electrical double layer repulsion because of additional negative electric charge

Fig. 2 Oxygen concentration and roughness parameters (R_{ms}: root square mean roughness, R_a: mean roughness) for unexposed (*dotted columns*) and UV-exposed (*shaded columns*) polymer surfaces determined by XPS and AFM analyses



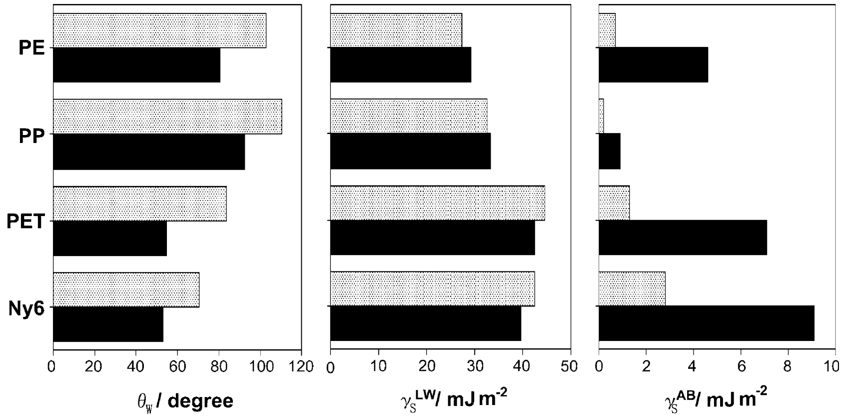


Fig. 3 Contact angle of water, θ_W, Lifshitz-van der Waals and Lewis acid–base surface free energies, γ_s^{LW} and γ_s^{AB}, for unexposed (*dotted columns*) and UV-exposed (*shaded columns*) polymer surfaces determined by the sessile drop technique

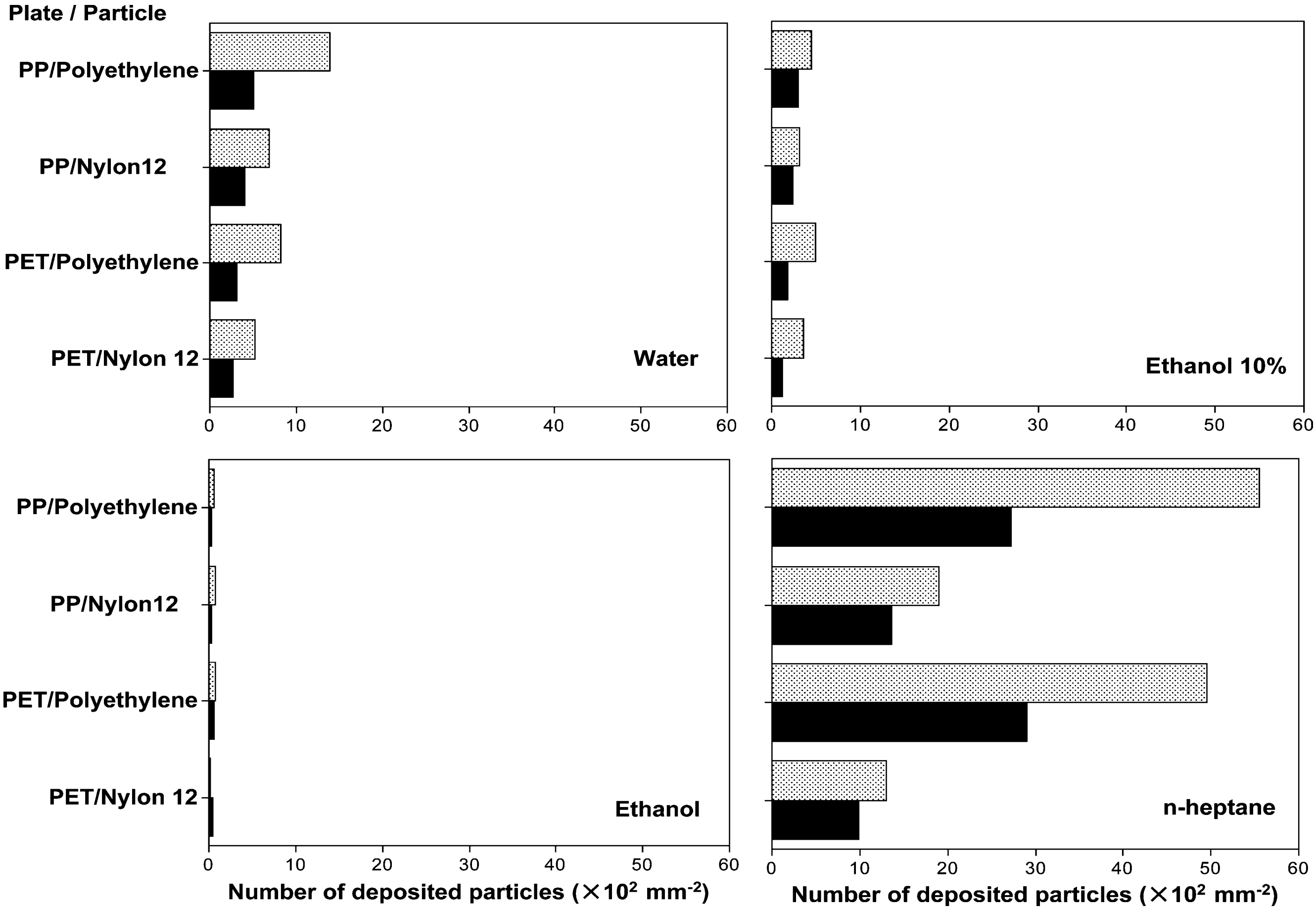


Fig. 4 Number of particles deposited onto unexposed (*dotted columns*) and UV-exposed (*shaded columns*) polymer surfaces in water, water/ethanol mixture (volume ratio of 90/10), ethanol and *n*-heptane

on the polymer surface due to the formation of functional groups as expected from XPS data.

For any plate and particle, the deposition decreased by the addition of ethanol to water and became extremely small in ethanol. In nonpolar n-heptane, a large number of particles were deposited onto any polymer plate. These results show that the particle deposition is largely dependent on the polarity of the liquid medium and can be prevented in liquids having intermediate polarity. In all liquids, the deposition was larger for PE particles than nylon particles, and for the PP plate than the PET plate. This indicates that the deposition can often take place between the particle and plate having small polarity.

In every system, the particle deposition decreased considerably after UV treatment. This suggests that the UV treatment of polymer surfaces is effective to prevent the particulate soil redeposition in aqueous and nonaqueous detergent systems.

Conclusions

The wettability and the surface free energy of PP, PE, PET and Ny6 were found to increase by 172 nm UV excimer light irradiation in air. XPS and AFM results showed that such increase is caused not by the surface topographical change, but by the increase in the surface oxygen concentration. The deposition of polymer particles onto the polymer surfaces in liquid media decreased drastically by UV treatment. Therefore, the UV treatment can be effective in preventing the particulate soil redeposition in the detergent system as well as for improving the wettability and the adhesion to other materials.

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