

Surface Modification of Polyolefine by UV Light/ozone Treatment

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SYNOPSIS

The surface modification of polyethylene (PE) and polypropylene (PP) was investigated by UV light/ozone (UVO) treatment. The surface oxygenation was determined by electron spectroscopy for chemical analysis (ESCA). As shown from ESCA spectra, after UVO treatment, oxygen-containing functional groups, such as carbonyl, carboxyl, and ether groups, were produced in the sample surface. The dependence of oxygenation extent (as measured by O_{1s}/C_{1s} value of ESCA spectra) on different experimental conditions, such as irradiation time, temperature, and O_2 flow rate, was obtained. It was shown that after UVO treatment at suitable conditions the surface properties of polyolefine samples, such as hydrophilicity, adhesion property, and dyeability, were improved remarkably. Furthermore, UVO treatment in short time does not have notable effect on the ageing property. It was concluded that UVO treatment is a promising technique to modify polyolefine surface properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyolefine, in particular polyethylene (PE) and polypropylene (PP), are the most widely used synthetic polymers. For most of them, the outermost surface is hydrophobic and inert due to a preponderance of nonpolar bonds. Extensive work to develop practical and economical method for surface modification of polyolefine has been carried out by many workers. For improvement of adhesivity, dyeability, and wettability, surface photografting modification in gas-phase or liquid-phase has received wide attention.¹⁻⁶ Surface treatment of polyolefine with ozone has also been actively studied.⁷⁻⁹ However, there are still some technical or economical problems to be resolved for industrial use of these methods.

Recently, an alternative surface modification method named ultraviolet light/ozone (UVO) treatment has been developed in Canada and Japan.¹⁰⁻¹³ In this method the polymer surface was exposed to UV in a flow of an oxygen gas containing ozone. After the UVO reaction of polyolefine, there ap-

peared oxidation groups such as $-C-O-$ and $-C=O$ groups in their surface, the contact angle to water of PP reduced to ca. 30° ¹³ and the adhesion property of PE fiber to epoxy resin matrix improved.¹² The present study was undertaken to proceed the surface analysis of polymer with Electron Spectroscopy for Chemical Analysis (ESCA) and specify the suitable experimental condition of UVO treatment to produce significant changes in the polyolefine surface. It is hoped that the results presented in this work will contribute to a technical and commercial practice successfully.

EXPERIMENTAL

Materials

In this work different kinds of samples (film, sheet, and fiber) were used for investigating the efficacy of UVO treatment. LDPE films ca. $90 \mu\text{m}$ thickness were supplied by Beijing Twelfth Plastic Plant. They were extracted with acetone for 2 days before use. LDPE and PP sheets of 0.5 mm thickness were prepared by pressing the resin powder at 170° and 180° , respectively, between two PET sheets. LDPE and PP powder without any additives were supplied by

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Beijing Second Auxiliary Plant and Yanshan Petrochemistry Company, respectively. PP fiber was supplied by the Institute of Chemistry, Academia Sinica.

UVO Treatment

UVO equipment is schematically illustrated in Figure 1. It consists of two parts: 1) ozone generator; 2) ultraviolet light irradiation apparatus. The ozone concentration in oxygen gas was varied by changing the generator voltage and the oxygen flow rate. The amount of ozone produced was determined by passing the gas through acidified potassium iodide solution at different O_2 flow rate and titrating the liberated iodine with 0.1N sodium thiosulfate solution. The concentration of ozone under different oxygen flow rate is shown in Table I.

The polymer sample was placed in the irradiation reactor. An oxygen gas containing ozone was passed through the reactor when the reactor was heated to a specified temperature. Then the sample was irradiated through a quartz window for a definite time.

Measurements

After UVO treatment, the following analyses and tests of samples were carried out:

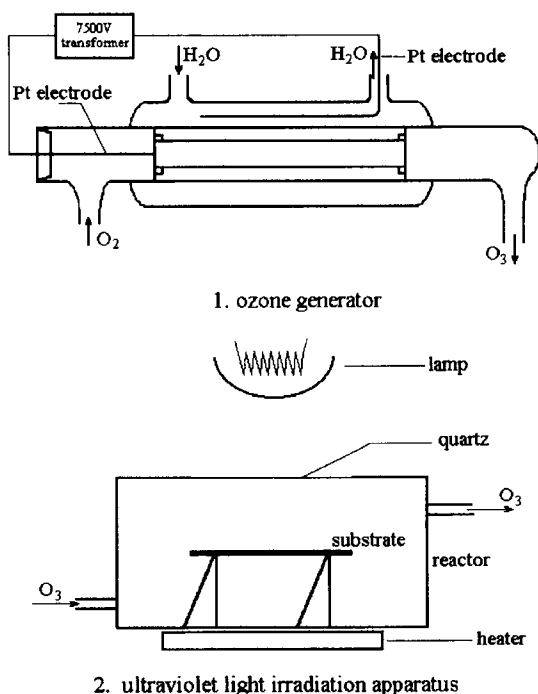


Figure 1 UVO equipment.

Table I Ozone Flow Rate of Different Oxygen Flow Rate

Oxygen Flow Rate (L/min)	$Na_2S_2O_3$ (mL)	Ozone Flow Rate (mL/min)
0.5	4.00	4.5
1.0	9.57	10.7
2.0	10.00	13.0
3.0	14.83	17.0
4.0	15.25	17.1
5.0	16.16	18.0
7.0	18.00	20.3

1. ESCA analysis. The ESCA spectra were recorded on a ES-300 Spectrometer with a Mg K α X-ray radiation source.
2. Contact angle measurement. The contact angles to water of the modified samples were measured on a CA-D Contact Angle Goniometer at ambient humidity and temperature.
3. Dye and color measurement. PP fiber samples were immersed in an aqueous solution of methylene blue. The dye solutions were buffered by adding acetic acid and sodium acetate. The dye solution was heated slowly to boiling and then continued heating for 1 h. Dyed samples were washed thoroughly with hot water and acetone and dried at room temperature. The color measurement of PP fiber sample was performed on a SC-80 Colorimeter.
4. Tensile shear adhesive strength measurement. The polymer sheets of 60-mm length and 10-mm width were cut lengthwise into half. Two parts of the polymer sheet were bonded with a 10×5 mm overlap with the epoxy resin adhesive, and the adhesive was cured for 24 h at room temperature. The adhesive strength was measured at a SHICKCH Tensile Testing Instrument.
5. Photo-oxidation test. The photo-oxidation test was carried out in a Model CS-801 Weather-Ometer supplied by Chongqing Test Equipment Plant. Two 1000W high-pressure mercury lamps were used as the light source and a Pyrex glass filter was used to cut off light with a wavelength shorter than 290 nm. The test temperature was 50°C . The extent of oxidation of the PE film during irradiation was followed by the growth of the carbonyl absorption at 1712 cm^{-1} , expressed in the form A_{1712}/A_{729} , where A_{729} is the IR absor-

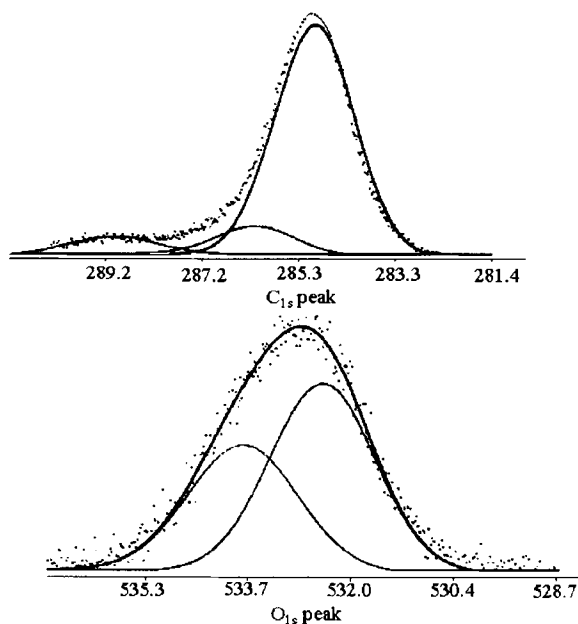


Figure 2 C_{1s} peak and O_{1s} peak of ESCA spectrum of PE sheet after UVO treatment. Irradiation time is 40 min, temperature is 50°C .

bance at 729 cm^{-1} , used as an internal standard.

RESULTS AND DISCUSSION

Surface Oxygenation

As an example, a ESCA spectrum of PE sheet after UVO treatment is shown in Figure 2. The tail on

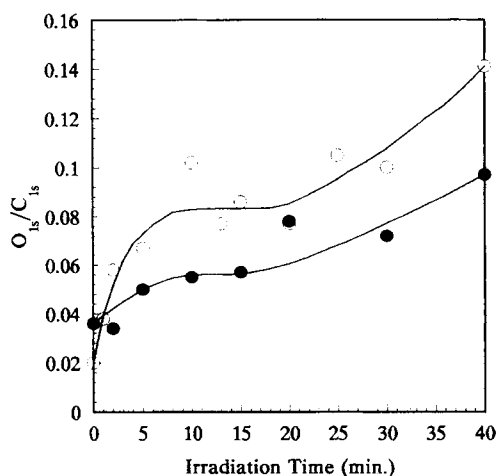


Figure 3 Changes of O_{1s}/C_{1s} measured from ESCA with irradiation time of PE and PP sheets. Treatment conditions: temperature, 40°C ; O_2 flow rate, 3 L/min. ●, PP sheets; ○, PE sheets.

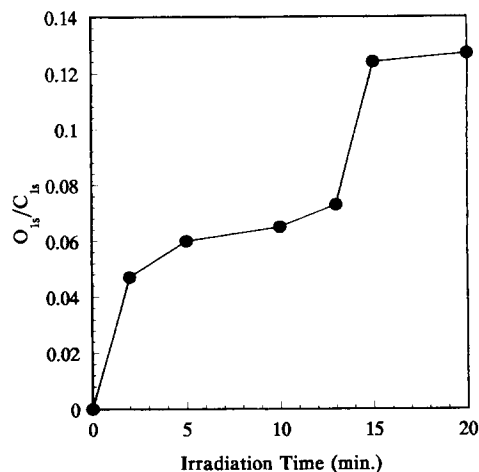


Figure 4 Changes of O_{1s}/C_{1s} measured from ESCA with irradiation time of PE film. Treatment conditions: temperature: 40°C ; O_2 flow rate: 3 L/min.

the high binding energy side of the main C_{1s} peak for PE shows that oxygen incorporation into the polymer surfaces gave rise to a variety of functional groups. This C_{1s} peak can be resolved into component peaks at binding energies of 285, 286.5, 289 eV, corresponding to carbon in $-\underline{\text{C}}-\text{H}-$, $-\underline{\text{C}}-\text{O}-$, and $-\underline{\text{C}}=\text{O}$. The O_{1s} peak can be decomposed into two peaks with binding energies of 532.4 eV and 533.8 eV, respectively. The peaks are assigned as follows: O_{1s} 533.8 eV ($\text{O}=\text{C}-\underline{\text{O}}-\text{H}$ or $\text{O}=\text{C}-\underline{\text{O}}-\text{C}-$) and O_{1s} 532.4 eV ($-\text{C}=\text{O}$ or $-\text{C}-\text{O}-$). From ESCA data, it can be seen that after UVO treatment, there appeared oxygen functional groups such as carbonyl, ether, and car-

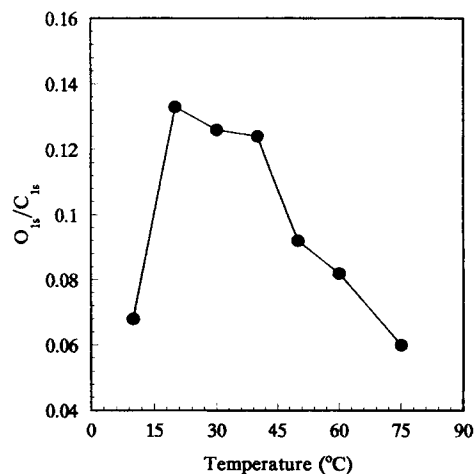


Figure 5 Changes of O_{1s}/C_{1s} measured from ESCA with temperature of PE film. Treatment conditions: irradiation time: 15 min; O_2 flow rate: 3 L/min.

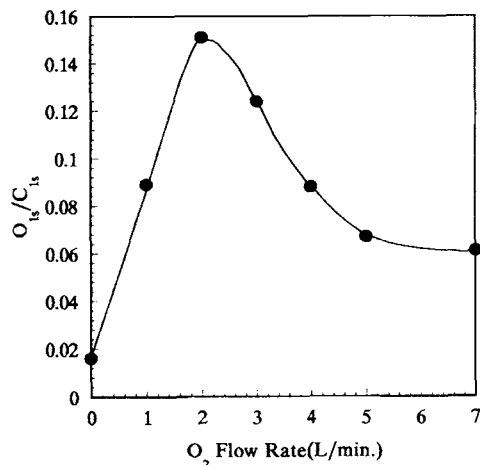


Figure 6 Changes of O_{1s}/C_{1s} measured from ESCA with different O_2 flow rate of PE film. Treatment conditions: irradiation time: 15 min; temperature: 40°C .

boxyl in PE surface. It is in agreement with the earlier studies.⁶ Therefore, we can use the ratio of intensity of O_{1s} to that of C_{1s} (O_{1s}/C_{1s}) as a measure of the surface oxygenation extent. And by means of ESCA measurement, we investigated the dependency of surface oxygenation of PE and PP on different experimental conditions. No matter which exact oxygen-functional group it was, so long as the amount of oxygen-functional groups increased and the surface properties of polymer might be improved.

The increase in the extent of surface oxidation with time of UV/ozonation is shown in Figure 3. The atomic ratio of oxygen to carbon of PE without UVO treatment is lower than that of PP. Probably

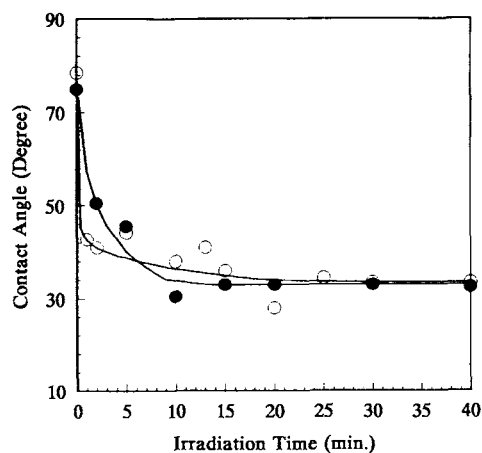


Figure 7 Changes of contact angle with irradiation time of PE and PP sheets. UVO treatment conditions: temperature: 40°C ; O_2 flow rate: 3 L/min. (●): PP sheets; (○): PE sheets.

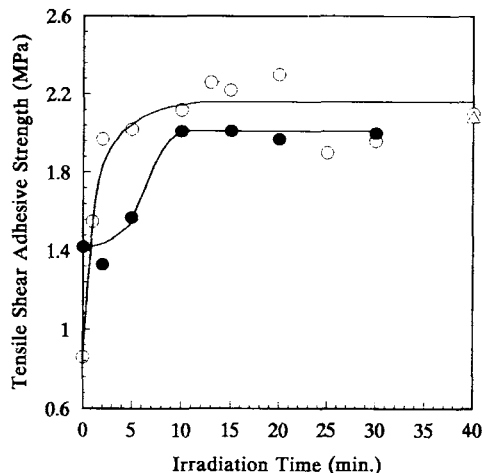


Figure 8 Changes in tensile shear adhesive strength with irradiation time of PE and PP sheets. UVO treatment conditions: temperature: 40°C ; O_2 flow rate: 3 L/min. (●): PP sheets; (○): PE sheets; (Δ): PP sheets broken.

the thermal oxidation in the process procedure of PP was more serious than that of PE. The initially faster oxidation of the PE shows that the ratio of O/C can reach a level which changes the surface composition distinctly in a short time (on the order of one minute). And this point is very important for commercial practice. The situation of PE film is similar to that of PE sheets as displayed in Figure 4. The high oxidation rate of PE film in the beginning of UVO treatment is also useful to practice.

Figures 5 and 6 displayed the changes of O/C measured from the ESCA spectra with the reaction temperature and oxygen gas flow rate, respectively. From these figures, an optimum experimental condition can be found. This is: the reaction temperature lies between 20°C and 30°C and suitable oxygen flow rate is 2–3 L/min.

Improvement of Surface Properties of PE and PP

The surface properties of PE and PP after UVO treatment were measured to examine the efficiency

Table II Color of PP Fiber

UVO Treatment Time (min)	Color Specification		
	L^*	a^*	b^*
0	78.20	1.22	-5.88
5	78.64	15.27	-8.40
10	82.11	14.21	-11.50
15	71.08	12.91	-13.07
20	80.59	15.38	-13.09
30	76.12	22.50	-14.17

Table III Value of A_{1712}/A_{729} of PE Film

Photo-oxidation Time (h)	UVO Treatment Time (min)					
	0	2	5	10	13	20
0	0	0	0.0191	0.0125	0.0182	0.0152
130	0.239	0.244	0.223	0.218	0.245	0.390

of this modification method. The wetting property of the modified PE and PP were estimated on the basis of the contact angle measurement. Figure 7 shows the change of contact angles to water of PE and PP sheets with the UVO treatment time. The contact angle to water of samples reduced with the exposure time. The surface of PE sheet became hydrophilic more rapidly than that of PP, and the reduction of the contact angle is in agreement with the increase of amount of oxygen functional groups showed by the ESCA spectra. These results indicate that surface modification with UVO is effective in enhancing their hydrophilicities.

Figure 8 represents the change of tensile shear adhesive strength with the UVO treatment time. The adhesive strength increased with the treatment time. In the first 10 min of treatment, the adhesive strength increased rapidly. It coincides with the increase of the oxygen functional groups measured from the ESCA spectra. It is worth emphasizing that PP sheets of some adhesive samples broke in the tensile test during elongation instead of separation of two adhesive sheets. This reflects that the strength at which the two modified PP adhesive sheets separated almost reached the same value as the bulk tensile strength of the PP sheet. Furthermore, the bulk tensile strength of modified PE or PP samples was the same or slightly higher than that of pure PE or PP without UVO treatment, although no rigorous mechanical data were attained. The result stated that the bulk property of polymer wasn't influenced by UVO treatment. It can be concluded that UVO treatment can not only improve the tensile shear adhesive strength, but also maintain the bulk property of polyolefine samples.

The colors of different PP fiber samples were measured on the colorimeter in order to investigate the dyeability of PP fiber after UVO treatment. The results are shown in Table II. It can be found that the value of colorimetric parameters L^* , a^* and b^* change with the treatment time. The significant increase of a^* and b^* shows the deepening of color of methylene blue of PP fiber. Therefore the UVO treatment is benefit to improve the dyeability of PP fiber.

The photooxidation test of PE films was carried out in a weather-ometer to show the influence of UVO treatment on the photostability of PE films. Some results are shown in Table III. It can be seen that the difference of values of A_{1712}/A_{729} of PE films after UVO treatment and PE film without UVO treatment after 130 h photo-oxidation is rather small (except PE film after 20 min UVO treatment). It showed that UVO treatment in short time does not have notable effect on the ageing property of PE films.

CONCLUSION

ESCA spectra of PP and PE reveal well the effect of UVO treatment on the polymer surface composition. There appeared oxygen functional groups such as ether, ketone, and carboxyl groups in the polymer surface after UVO treatment. The experimental conditions, such as irradiation time, reaction temperature, and oxygen gas flow rate, influence the degree of surface oxidation. The atomic ratio O_{1s}/C_{1s} of ESCA spectra can be taken as a measure of the degree of surface oxidation in UVO process.

The results of contact angle measurements, adhesive strength, and dyeability measurements show that UVO is an effective method to improve the surface properties of polyolefine. UVO treatment in short time does not have notable effect on the ageing property. Furthermore, from present investigation it can be seen that UVO technology for polyolefine surface modification appears to offer a number of advantages: 1) the equipment is simple and cheap; 2) the equipment can be safely and easily operated; 3) no chemical reagents are required; 4) there are no residual polluting byproducts and tedious after-treatment. Therefore, it is expected that UVO treatment is a promising technology to modify polyolefine surface properties in industry field.

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