Synergistic Effects of Oxygen Radicals and Ozone on Surface Treatment of Polypropylene Measured by Newly Developed VUV Photodissociation Method

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Abstract: In order to understand the role of O radicals on polymer surface treatments using plasma, O and other reactive species (O_3, $O_2(a)$, $O_2(b)$, etc.) with known densities are supplied to polypropylene surface using our newly developed method of "vacuum ultraviolet photodissociation reactive species supply" (VUV PRS). Water contact angle is used to characterize the surface modification. The experimental results demonstrate the role of O radicals as the primary reactants involved in the initial reactions. Meanwhile, synergistic effects of O radicals and ozone is observed. Ozone promotes the surface modification only in the presence of O radicals.

Keywords: oxygen radical, ozone, synergistic effect, water contact angle, polypropylene.

1. Introduction

The treatment by atmospheric-pressure plasma is a widespread processing to customize the adhesion, wettability and surface energy of polymer in modern industry. However, the absence of basic understanding to the interaction between plasma and polymer surface makes the finding of optimized treating condition a time-consuming and trial-and-error process [1]. Our group aims to understand the role of each type of reactive species in the plasma-polymer surface treatment. Reactive species (*e.g.* OH, O) are considered as main roles during the atmospheric-pressure plasma-polymer treatment [2]. To measure the effects of those reactive species on polymer surface treatments quantitatively, we proposed a method to supply reactive species using vacuum ultraviolet (VUV) photodissociation of H_2O and O_2 molecules instead of using plasma [hereafter, VUV photodissociation reactive species supply (VUV PRS) method]. The VUV PRS utilizes photodissociation of Ar/H_2O or Ar/O_2 mixture flowing in a quartz tube by VUV light [3]. The densities of produced reactive species densities can be determined using simulation. The difference between the measured and simulated densities is typically 10-50%, showing a high accuracy of the simulation [4]. By using the H_2O-VUV PRS, the effect of OH radicals on polypropylene (PP) surface treatment was quantitatively measured in our previous research [5].

The present research is based on the O_2-VUV method, trying to figure out the roles of O radicals in the polymer surface treatment. Considering the solid and extensive research foundation [2, 6-8], the PP was chosen as an example of treated target. To characterize the surface modification, we measured the water contact angle (WCA) before and after the treatment. The results showed that the O radicals and the co-produced ozone are the main roles determining the WCA decreasing process under the present experimental conditions.

2. Experiment method

Reactive species are produced by photodissociation of O_2 molecules in the Ar/O_2 mixture flowing in the quartz tube. As the mixture contains H_2O impurity, OH and H are also produced by photodissociation of H_2O. The resulting reactive species cause further chemical reactions to produce OH, H, H_2O_2, HO_2, O, O_3, $O_2(a)$ and $O_2(b)$. The densities of these species supplied to the PP surface under different experimental conditions are determined using simulations by solving a set of rate equations containing photodissociation reactions, chemical reactions, and wall reactions.

The PP sample type is Toyobo P2002. The thickness of PP sample is 40 μm, which is cut to 50×50 mm squares before experiment. The PP film is previously cleaned by an ultrasonic cleaning machine with 1:1 mixture of pure water and ethanol for 10 minutes. The distance between the quartz tube end and PP surface is 1 mm. The treatment area is assumed to be a circle with a 2-mm diameter (the same as the inner diameter of the quartz tube). WCA is measured by dropping 1 μl pure water at the centre of the treatment area. The ambient temperature during treatment is ~17 °C.

In order to change the reactive species densities supplied to the PP surface, the O_2 density and gas flow rate (F) of Ar/O_2 mixture are varied among different experimental conditions using mass flow controllers (Kofloc). The O_2 density is measured by a zirconia oxygen analyzer (OX400, Yokogawa). H_2O is a trace impurity in the Ar/O_2 mixture. Its density is measured by a dew point meter (TK-100, Tekhne) and controlled less than 15 ppm among different experimental conditions.

3. Results

(1) Experiment 1: The effect of ozone with very few O radicals.

Photodissociation of O_2 produces O radicals as: $O_2 + hv$ (172 nm) $\rightarrow$ $O(^1D) + O$. If the quartz tube length in the downstream part of the VUV light-irradiated (L_d) area is sufficiently elongated, the O radicals are mostly converted to O_2 and O_3 by wall reactions and $O + O_2 + M \rightarrow O_3 + M$ reaction. The effect of only ozone on PP surface can be checked by increasing L_d. The experimental conditions and reactive species densities to PP surface are present in Table 1. As shown in Table 1, the density of O radicals is quite low, while the ozone density is relatively high. Table 2 shows the results for different treatment times. The WCA

Table 1. Radical density on PP surface.

Radicals	Density	Radicals	Density
OH	5.58×10^{-12}	O	2.11×10^{-07}
H	0.00	O_3	2.17×10^{0}
H_2O_2	1.53×10^{-02}	O_2(a)	8.91×10^{-04}
HO_2	3.02×10^{-11}	O_2(b)	4.12×10^{-14}

Unit: ppm, 1 ppm = 2.45 $\times10^{13}$ molecules/cm^3
Experiment 1 setting: F = 0.2 L/min, [O_2] = 0.3%, [H_2O] = 15 ppm, L_d = 120 cm.

Table 2. Water contact angle variations.

Treatment Time [s]	Water contact angle [×1°]
0	105
300	104
600	103
900	105
1200	106

of untreated PP surface is about 105°. From Table 2, we can observe that the WCA does not change if only O_3 is supplied to the surface, at least 2 ppm O_3 is supplied for 1200 s. It indicates that ozone cannot initiate the surface reaction, as well known.

(2) Experiment 2: The synergistic effect of O radicals and ozone.

We designed and conducted Experiment 2 to study the synergistic effect of O radicals and ozone on the decrease of WCA. The value of L_d is set as short as possible to increase the O density supplied to the PP surface. The densities of reactive species are controlled by varying O_2 density in the Ar/O_2 mixture. The detailed experiment settings and simulated radical densities are shown in Table 3. The only difference in the three experiments is the O_2 density. As we can see from Table 3, when the O_2 density increases, the O radical density decreases while the ozone density increases. Figure 1 shows the WCA variations as a function of the treatment time in the three experiments. The slope of the curve in Figure 1 is the decreasing rate of WCA. The slope in the early phase is almost the same under the three experiment conditions. In polymer surface treatments using oxygen containing plasma, it is often assumed that O radicals are the primary radicals which determine the surface modification rate [2, 9]. However, our result disagrees with the assumption. The O radical density under the O_2 = 0.5% is almost ten times less than those under the O_2 = 0.065%. But the WCA decreasing rate is almost the same. This result indicates that there are other factors promoting the WCA decreasing process in addition to O radicals. Considering the increasing ozone density with increasing O_2 density, we assume it is ozone that promotes the WCA decreasing process in addition to O radicals in the experiment. If ozone indeed worked as we assumed, it should be effective only when O atoms coexist, affecting the whole treatment process by involving in the subsequent reactions process of the initial reactions, because we already proved in experiment 1 that ozone would not work when only ozone exists without O atoms. It was shown that ozone reacts with alkyl radicals, which is produced from hydrogen abstraction reactions [2]. This may explain the synergistic effect observed in this experiment.

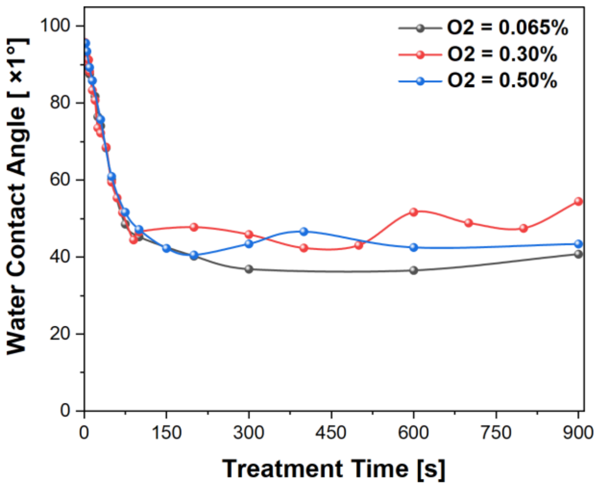

Figure 1. WCA decreasing rate under different O_2 concentrations.

In order to verify the presumption, we plotted the WCA variations as the function of [O]t in Figure 2, where [O] means the density of O radicals supplied to the PP surface and t is the treatment time. Because O radicals are considered as the primary radicals involved in the initial reactions and the initial reactions can be assumed as surface reaction-rate-limited [2, 5], the parameter [O]t can approximately represent the quantity of products after the initial reactions induced by O radicals, such as hydrogen abstracted active sites on PP surface. If the subsequent reactions process after the initial reactions are caused by ozone, the slope of WCA-[O]t would be related to ozone density. Figure 2 shows that the slope of WCA-[O]t curve increases with ozone density. This suggests that there may be synergistic effects between O radicals and ozone. This result agrees with the surface reaction model developed in

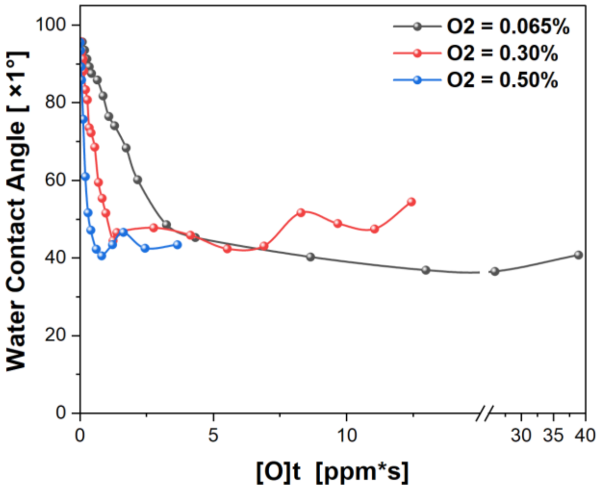

Figure 2. The WCA variation as a function of [O]t. F = 0.5 L/min.

Table 3. Radical density for verifying the synergistic effect of O radical and ozone.

	O_2	OH	H	H_2O_2	HO_2	O	O_3	$O_2(a)$	$O_2(b)$	Treatment time [s]
F = 0.5 L/min $[H_2O]$=15 ppm *Ld* = 0.6 cm Unit: ppm	**0.065%**	9.40E-03	5.03E-05	1.43E-03	6.66E-03	4.32E-02	1.21E-01	3.88E-03	2.38E-12	2, 4, …, 10, 15, 50, …, 100, 200, …, 600, 900.
	0.30%	1.14E-02	4.18E-06	1.72E-03	7.06E-03	1.38E-02	8.79E-01	6.80E-02	2.71E-10	
	0.50%	1.25E-02	8.06E-07	1.88E-03	7.37E-03	4.06E-03	1.52E+0	1.63E-01	1.44E-09	

Table 4. Radical density for confirming the synergistic effect of O radical and ozone.

	O_2	OH	H	H_2O_2	HO_2	O	O_3	$O_2(a)$	$O_2(b)$	Treatment time [s]
F = 0.3 L/min $[H_2O]$=15 ppm *Ld* = 0.6 cm Unit: ppm	**0.025%**	1.15E-02	1.08E-04	3.35E-03	8.20E-03	2.90E-02	5.12E-02	9.70E-04	5.59E-14	2, 4, …, 10, 15, 50, …, 100, 200, …, 600, 900.
	0.20%	1.36E-02	5.09E-06	3.98E-03	8.36E-03	9.43E-03	9.41E-01	5.28E-02	1.56E-10	
	0.30%	1.43E-02	1.57E-06	4.14E-03	8.61E-03	4.10E-03	1.45E+00	1.07E-01	6.27E-10	

[2], which indicates that ozone can react with active site on PP surface produced by hydrogen abstraction by O radicals.

(3) Experiment 3: Confirmation of ozone effect with excluding O_2 effect.

Experiment 2 cannot prove that the different slope of WCA-[O]*t* is caused by only ozone, because O_2 density also increases when the slope of WCA-[O]*t* increases. In order to confirm the ozone effect and exclude the O_2 effect, we designed Experiment 3. The experiment conditions and reactive species densities are shown in Table 4. Experiment 3 adopts similar ozone densities with Experiment 2. Meanwhile, a set of the same O_2 density (O_2=0.3%) is also included to study the O_2 effect. Figure 3 shows the results of both Experiments 2 and 3. By combining Table 3, Table 4, and Figure 3, it is shown that the O_3 density rather than O_2 density affects the slope of WCA-[O]*t* curves. The results indicate that there are synergistic effects of O radicals and ozone. Ozone promoted the WCA decreasing process after the initial reactions induced by O radicals.

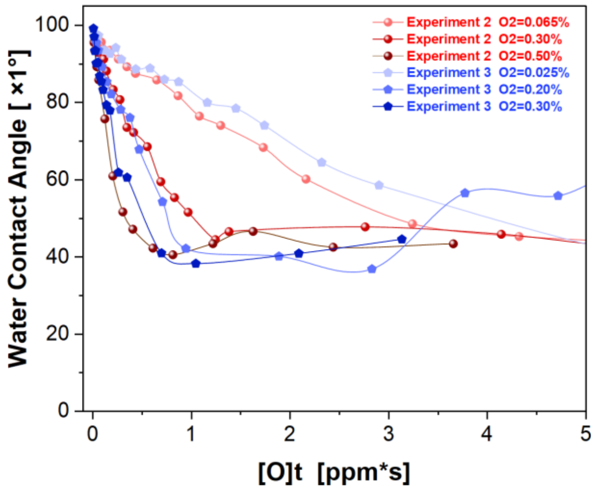

Figure 3. The WCA variation as a function of [O]*t*.
F = 0.5 L/min and 0.3 L/min.

4. Conclusion

The synergistic effects of O radicals and ozone on PP surface modification were revealed using O_2-VUV PRS method. With the results of Experiments 1, 2, and 3, we concluded that O radicals worked as the main reactants involved in the initial reactions. The PP surface was not modified if there were no enough O radicals even if a large amount of ozone was supplied to the surface. There was synergistic effects of O radicals and ozone in the PP surface treatment. Ozone can promote the WCA decreasing process when O radicals coexist. It indicates that properly elevated ozone density may accelerate the plasma-polymer surface treatment.

5. References

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