SHORT COMMUNICATION

SURFACE MODIFICATION OF POLYPROPYLENE IN AN IMPULSE CORONA DISCHARGE

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Abstract—The impulse corona discharge was applied to modify surface of polypropylene films. The modified surface was analyzed by contact angle measurements and ESCA. The results were compared to those treated with AC corona discharge. The impulse corona treatment provided a similar contact angle and a similar [O]/[C] ratio on the polymer surface to those in AC corona treatment. On the other hand, [N]/[C] in impulse discharge was much lower than that in AC pulse discharge. The total power input in the impulse corona discharge, however, was lower than that in AC corona discharge to achieve a similar level of surface modification. It was also observed that the lower repetition frequency, the lower contact angle, and the higher [O]/[C].

Key words: Surface Treatment, Impulse Corona Discharge, Contact Angle & ESCA, Plasma Chemical Processing, Biaxially-oriented Polypropylene

INTRODUCTION

Corona discharge is the most commonly used method of modifying polypropylene and polyethylene surfaces to improve coatability, wetting properties, and adhesion. In a typical commercial process, polymer films are treated in a high voltage AC corona field generated between a set of powered and ground electrodes.

Surface modification with a corona discharge plasma features the double effects of UV radiation and chemically active species, while not affecting the bulk polymer properties [Hollahan and Bell, 1974]. In the normal atmospheric environment typically employed in corona treatment systems, polymer radicals generated on the surface react rapidly with oxygenic species in the gas phase. Therefore, the polymeric surface is affected by cross linking, oxygen substitution, or polymer scission. Scission, in particular, can lead to the formation of low-molecular-weight oxidized material on the surface. It was also indicated that a number of oxidized functional groups is present on the surface of corona treated polymers [Brewis et al., 1981]. The nature and number of these functional groups determine the adhesion and wetting characteristics of the final polymer surfaces.

Traditionally, an AC corona discharge has been the principal method of promoting chemical reactions in an electric field for surface treatment applications. However, the use of very short (nanosecond) pulses of DC pulse (impulse) discharge has been gaining interest as a means of corona and plasma treatment. The strong non-equilibrium plasma produced by the impulse corona discharge not only improves the power efficiency, but also initiates chemical reactions more effectively [Milde, 1982]. Recently, chemical reactions in impulse corona discharge have been successfully applied to such processes as O_3 synthesis [Moon et al., 1986], NO/NO_2 synthesis [Hill et al., 1988], NO_x/SO_2 reduction from flue gases [Masuda and Nakao, 1986; Mizuno et al., 1986; Dinelli et al., 1988], production of fine powder [Yamamoto and Masuda, 1992], hazardous gas control [Masuda, 1988], plasma polymerization [Donohoe and Wydeven, 1979], and reduction of the greenhouse gases [Eliasson et al., 1992; Oda et al., 1991].
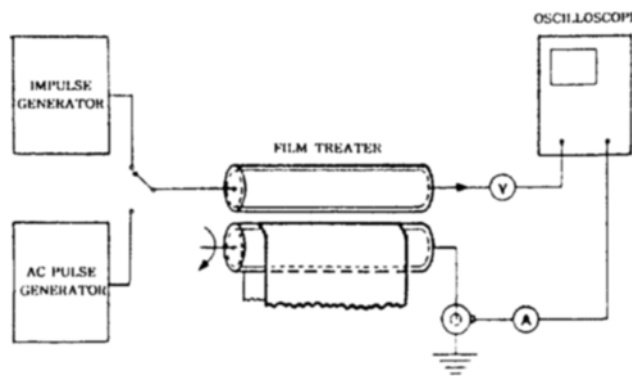

Fig. 1. **Experimental arrangement for surface treatment of polymeric films by impulse and AC pulse corona discharges.**

This letter provides the first experimental observation of surface modification of biaxially oriented polypropylene (BOPP) films with a low-frequency impulse voltage source. These results were also compared with those treated with the recent commercially available high-frequency AC voltage source.

EXPERIMENTAL

An experimental arrangement for impulse and AC pulse corona treatments of polymer surfaces consisted of both DC and AC pulse generators, a cylinder-type surface treater, and an oscilloscope connected to a high-voltage probe and a current transformer (Fig. 1). These experiments were carried out at room temperature and an atmospheric pressure. The corona-treated films (samples) were analyzed by water-contact angle measurement and ESCA.

The applied voltage shapes were a unidirectional saw-tooth for impulse and a sine-wave for AC pulse. The discharge was created between two rolling cylindrical electrodes through which the polymer film was passed.

1. Materials

The polymer samples to be treated were biaxially oriented and high molecular weigh (1.8×10^5) polypropylene (PP). They with a thickness of 0.05 mm and a density of 0.908 g/cm^3 were thermally extruded. The washed corona-treated samples were rinsed in a bath of the distilled and deionized water.

2. Film Treater

The film treatment system consisted of a pair of metal rollers of 10 cm outer diameter and 20 cm long which was covered with a dielectric layer (silicone rubber). The gap distance between the two rollers was adjusted to be 1.7 mm. The electrically grounded roller was rotated with a speed of 20 rpm. The width of samples treated was measured as 1.5 cm for both impulse and AC pulse discharge.

3. AC Pulse Source

A high-frequency power supply (Plasmaloc 1) equipped with a matching transformer (Colomaloc 1) as a feed-back circuit was used. The net power dissipated in the corona discharge was measured with a directional power meter on the supply. In these studies, the polymer surfaces were treated with an output power of 50 W at a frequency of 55 KHz. The discharge area on the dielectric roll was 1.7 cm$\times$16.5 cm.

4. Impulse Source

The impulse generator was built using a 30 KV/5 mA DC power supply connected to a series of capacitors (5 nF), high-voltage resistance ($\sim$100 MΩ), and a spark-gap switch, which rotates to produce impulse with a high peak voltage and a fast rising times. The output voltages were controlled by adjusting the gap distance of the spark-gap switch and the input voltage amplitude. The shape and intensity of impulse could be varied by controlling the circuit inductance and resistance connected in series to the films treater [Glasoe and Lebacoz, 1949]. The output current was also varied by controlling the pulse width and pulse amplitude.

The output peak voltages were about two-times higher than the input voltages (10-15 KV) and the output peak currents were less than 30 A. The measured rising time and pulse width of the current were less than 40 nsec and than 200 nsec respectively. A pulse repetition frequency of 55 Hz was used.

The dissipated power and energy in the film treater were estimated from the measured current and voltage. They were determined using a current transformer (Pearson, #4100) and a high-voltage probe (Tektronix, #6065), respectively. Both current and voltage were observed simultaneously via a 350 MHz digital oscilloscope (Tektronix, #2465A). The time averaged power consumption was estimated at less than 1.0 W with peak power (during the pulse) approaching 1.0 MW.

5. Contact Angle Measurement

Both advancing and receding contact angles were measured using the sessile-drop method with a Rame'-Hart Goniometer. The water used was distilled, deionized, and filtered. Contact angle measurement errors were approximately $\pm$ 5%.

6. ESCA

ESCA spectra were obtained with a spectrometer (HP, #5950 B) using a monochromatic Al K_α photon source. These were taken at an electron take-off angle of 38° with respect to the film surfaces. The ratios of oxygen [O] and nitrogen [N] to carbon [C] were calculated with reference to a carbon [C] 1s level of 282.7 eV. The measured errors were $\pm$ 10%.

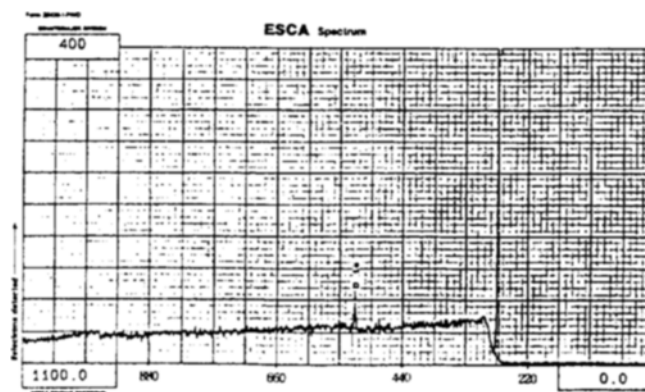## EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 2. A typical ESCA spectrum for BOPP film treated under impulse corona discharge (110 Hz, 2 mm gap, and 10 min).
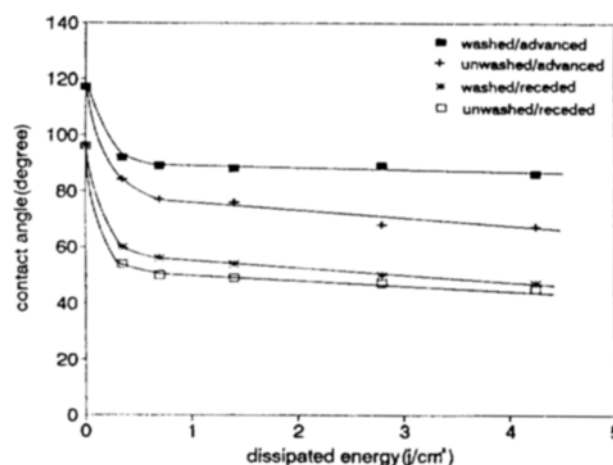

Fig. 3. Contact (advancing) angles measured from impulse and AC corona-treated samples as a function of dissipated energy.

Fig. 2 is a typical ESCA spectrum for BOPP film treated by an impulse corona discharge under atmospheric environment. In most ESCA spectra, were detected [C] 1s (282.7 eV), [O] 1s (531.0 eV), and [N] 1s (409.84 eV). It was observed that [N] in impulse discharge is much lower than that in AC pulse one. No [O] or [N] was detected for untreated films.

Fig. 3 shows the water-contact angles measured from impulse corona-treated samples in terms of the treated time (total dissipated energy). Within 15 seconds (0.355 j/cm^2), the water contact angle decreased rapidly with treatment time at a rate of 2.2°/sec for the advancing angles and of 2.7°/sec for the receding ones. The rapid decrease in contact angles with increasing time of treatment was known to result from formation of low-molecular-weight oxidized materials which are produced in the free-radical oxidation process [Strobel et al., 1989].

An Experimental result showed that water-contact angles strongly depend on whether or not the polymer films have been previously washed [Strobel et al., 1989]. They found that the washed corona-treated samples usually exhibit a lower contract angle than the unwashed corona-treated samples. In these studies, was also examined the effect of washing on the final contact angle measurement. The contact angles measured for the unwashed and the washed samples were identical for the first 15 seconds (while
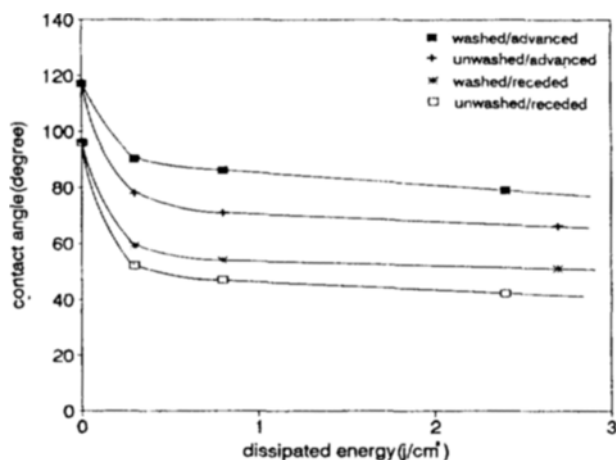
Fig. 4. Contact (receding) angles measured from impulse and AC corona-treated samples as a function of dissipated energy.

Fig. 6. Contact angles and [Oxygen/Carbon] measured from impulse corona discharge as a function of pulse repetition frequency.
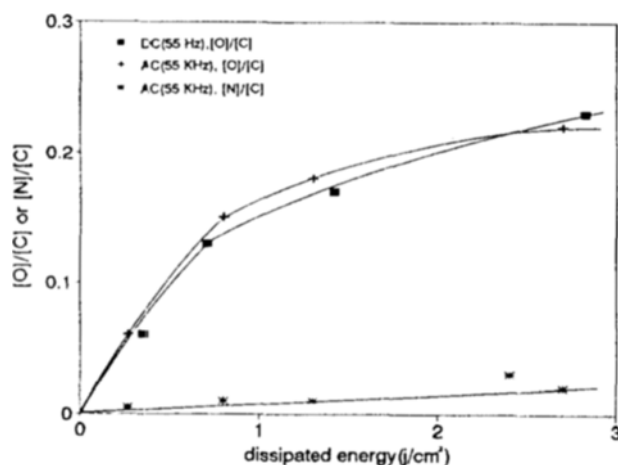

Fig. 5. [Oxygen/Carbon] and [Nitrogen/Carbon] for corona-treated samples as a function of dissipated energy.

the water drop was initially spreading). However, as an equilibrium was approached, the rate of change for the contact angles was slow considerably, i.e., 4°/min for the advancing angles and 2°/min for the receding ones. A difference between the washed and unwashed films was much larger for the advancing contact angles (-20°) than for the receding contact angles (-5°).

The results from the impulse-treated samples (Fig. 3) have been compared with those from AC pulse-treated samples (Fig. 4). The advancing contact angles for the AC pulse-treated samples were slightly lower than those obtained in the impulse discharge. However, the same results of the receding contact angles were observed in both the AC and impulse treated samples.

Fig. 5 is [O]/[C] and [N]/[C] ratios determined from ESCA spectra as a function of the dissipated energy in both the AC pulse (50 W/55 KHz) and impulse (1 W/55 Hz) corona discharge. Since the surface oxidation rates generally increase with increasing power input, it is understandable that surface oxidation should occur faster initially for the AC pulse systems. Based upon dissipated energy, the oxidation occurring in the impulse system was nearly the same as that in the AC pulse system. On the other hand, [O]/[C] of 0.23 at the same energy dissipated of 2.75 j/cm^2 was obtained from 3 min/1 W treatment by impulse (55 Hz) co-
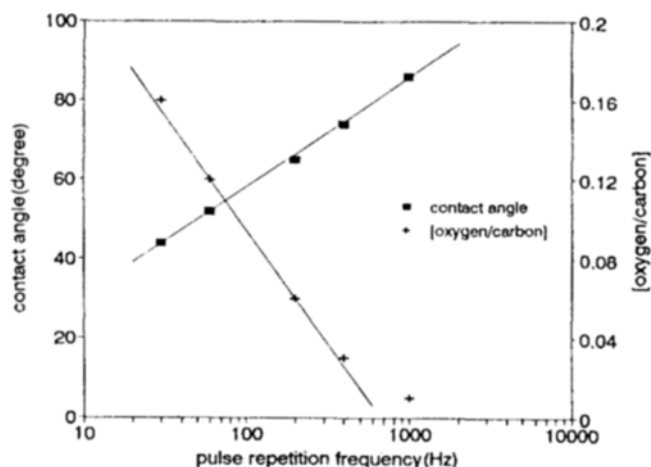
rona discharge and from 30 sec/50 W treatment by AC (55 KHz) corona discharge. The results showed that the oxidation occurring for higher dissipated energies tends to decrease for AC pulse system relative to the impulse system.

The nitration of the surface increased linearly with increasing dissipated energy in both impulse and AC pulse systems. The nitrogen to carbon ratio, [N]/[C], was found to be an order of magnitude smaller than the oxygen to carbon ratio, [O]/[C]. A nitrogen to carbon ratio of 0.03 was observed for a dissipated energy of 2.4 J/cm^2 in AC pulse and for 21 J/cm^2 in impulse corona discharge. Apparently, the input energy of impulse corona discharge was large enough for dissociation of O_2 (5.1 eV) but not for that of N_2 (9.8 eV). Overall, these observations indicated that, for similar dissipated energies, degree of surface derivitization in the impulse corona system is similar to that in the AC corona system.

One of the interesting observations for these impulse corona experiments was the correlation between frequency (pulse width) and contact angle. It was shown that the lower frequency, the lower contact angle, and then the higher [O]/[C] (Fig. 6), which is a strong correlation between surface oxidation ([O]/[C]) and wettability (contact angle). Obviously, oxygen derivitization of the surface is beneficial in increasing the surfaces energy of the polymer film. This, in turn leads to increase wettability and ultimately to increase adhesion and coatability of the polymer surface. Therefore, the high-power and high-frequency AC operation which is exclusively applied in surface-treatment industry to date may be not needed, even though further studies are required.

CONCLUSIONS

This preliminary observation indicated that surface modification of polypropylene (PP) films with a simple and low-power impulse voltage source achieves the same results as those obtained with a AC pulse generator. The average power employed in impulse treatment system was an order of magnitude smaller than that in the AC pulse treatment one. The conclusions of this study may be summarized as follows:

1. Impulse corona discharge can also effectively modify polypropylene film surfaces. For energy densities (0.1-0.3 j/cm^2) similar to those used in the AC pulse corona treatment, an impulse

corona discharge provides a similar contact angle for water and a similar [oxygen]/[carbon] ratio on the polymeric film surface.

2. The degree of modification achieved by the impulse corona discharge seems to be directly related to the peak voltages obtained during the pulse and the pulse frequency. The lower, pulse repetition, the better treatment.

3. The total power input in the impulse system is lower than that in the AC pulse system to achieve a similar level of surface modification.

It is believed that the impulse corona surface treatment for polymeric films may represent a significant advancement of the art. A better understanding of plasma chemistry in an impulse corona discharge and the plasma interaction with polymeric film surfaces (surface chemistry) is required for mechanism for surface modification and for system development.

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