

Rapid Communications

Surface Modification of Polypropylene by Ethylene Plasma and Its Induced β -Form in Polypropylene*

Gui-qiu Ma**, Ya-peng Liu, Shu-xian Wei and Jing Sheng

School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials,
Tianjin University, Tianjin 300072, China

Abstract This study aims to investigate the chemical structure and morphology of plasmapolymers produced by deposition of ethylene on the surface of polypropylene. The deposition films (sediments) of ethylene plasma on the surface of polypropylene are nonuniform, and the characterization results indicate the existence of hydroxyl groups and aldehyde (or ketone) groups in the sediments. The sediment of ethylene plasma on the polypropylene surface could induce the growth of β -form crystals in the surface layer of polypropylene.

Keywords: Plasma polymerization; Plasma modification of polypropylene; β -Form polypropylene.

INTRODUCTION

Plasma contains several activated species such as electrons, ions, free radicals, molecules in excited state and some neutral species. It can be classified into high temperature plasma and low temperature plasma based on the temperature of the plasma gas^[1], and the latter is widely used in plasma chemistry. The temperature of ion species is usually less than 1000 K, while the temperature of other neutral species is not higher than 100–300 °C, but the temperature of electrons can attain 1000 K. These activated species in the plasma can react with each other, as well as with neutral molecules or the surface of a substrate. Depending on the nature of the molecules and the processing conditions, this may result in the deposition of a thin film.

The most attractive objective of surface modification of polymers is to significantly modify the surface properties without altering their bulk properties. Plasma has been successfully employed to improve the surface properties and structure of polymers, either by activating chemically inert polymer surfaces or by coating the substrate with a thin functionalized plasma polymerized layer^[2]. The modification of chemically inert polymer surfaces by plasma treatment can bring in chemical reactive groups and thus lead to the functionalization of polymer surfaces^[3–5]. Ethylene can be polymerized under its plasma state (*i.e.* plasma polymerization of ethylene^[6–8]). While the polymer is treated using ethylene plasma, ethylene plasma can be deposited on the polymer surface to form a thin film.

In this paper, the isotactic polypropylene (*i*PP) surface is treated using the ethylene plasma with a dielectric barrier discharge (DBD) plasma apparatus under atmospheric pressure. The structure of the ethylene plasma sediment (polymerisate) on *i*PP surface and the phenomenon that it induces β -form crystals in *i*PP are mainly studied.

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51033004 and 51473113) and the Natural Science Foundation of Tianjin (No. 12JCYBJC11900).

** Corresponding author: Gui-qiu Ma (马桂秋), E-mail: magq@tju.edu.cn

Received December 26, 2014; Revised January 27, 2015; Accepted January 31, 2015

doi: 10.1007/s10118-015-1631-1

EXPERIMENTAL

Materials and Plasma Equipments

Isotactic polypropylene (*i*PP, 1701, $M_w = 4 \times 10^5$) was obtained from Beijing Yanshan Petrochemical Co.; ethylene (99.5%) was supplied by Dalian DT Co.

The DBD plasma apparatus was self-designed, and the ethylene plasma was obtained between the internal and external electrodes with an external diameter of 15 mm. The plasma generator (CTP-2000K) with a variable discharge voltage (from 0 to 40 kV) and an invariable frequency (13.56 MHz) was purchased from Nanjing Suman Electron Co. Ltd.

Specimen Preparation

*i*PP pellets were washed with distilled water and then dried under 100 °C for 30 min before use. The *i*PP was compression-molded to get slabs of 1 mm thickness and films of 20 μm thickness, respectively, at 190 °C with a residence time of 5 min under a common heating pressure of 24.5 MPa.

Plasma Surface Modification and Blending

The surface of *i*PP slabs was treated by ethylene plasma under atmospheric pressure and room temperature with a ethylene gas flow rate of 30 sccm and a discharge voltage of 35, 38, 41 and 44 V, respectively, for 600 s. The *i*PP sample after surface modification by ethylene plasma was denoted as SM*i*PP-Eth.

*i*PP and the treated *i*PP were blended respectively with a mixing apparatus (XXS-30 mixer, Shanghai, China) at a temperature of 190 °C and a rotation speed of 32 r/min.

Characterization

The chemical structure of *i*PP and SM*i*PP-Eth surface was analyzed on a Perkin Elmer spectrum 100 FTIR spectrometer (sample thickness: 20 μm) and a Pekin-Elmer PHI1600ESCA X-ray photoelectron spectroscopy (XPS) (sample thickness: 1 mm). The surface morphology of *i*PP and SM*i*PP-Eth was observed on a Hitachi Japansu1510 scanning electron microscope (SEM) (sample thickness: 1 mm). The wide-angle X-ray diffraction (WAXD) patterns for the samples were analyzed on a Bruker Germany D8 Advanced X-ray diffractometer operating at 40 kV and 40 mA, CuKα.

RESULTS AND DISCUSSION

Modification of *i*PP Surface

The uniform and flat surface of pure *i*PP is shown in the SEM image of Fig. 1(a). Compared with that of pure *i*PP, the SM*i*PP-Eth surface is nonuniform with the sediment of ethylene plasma as shown in Fig. 1(b). The diameter of the sediment areas was 20–40 μm. In addition, some smaller particles were also observed on the *i*PP substrate. The results indicate that the *i*PP surface was successfully modified by ethylene plasma, which could influence the original surface properties.

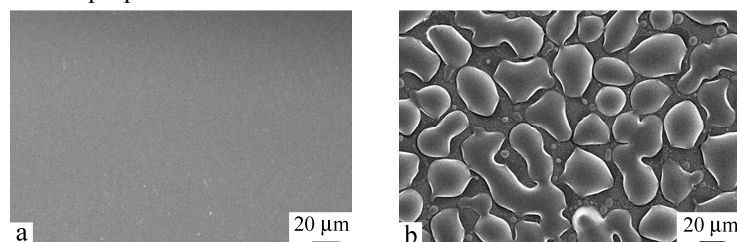


Fig. 1 SEM images of *i*PP surface (a) and SM*i*PP-Eth surface (b) at discharge voltage: 41 V, plasma treating time: 600 s and ethylene flow rate: 30 sccm

Analyses of *i*PP Surface

Typical FTIR spectra of *i*PP and SM*i*PP-Eth obtained in this work are given in Fig. 2. For comparison, the spectra of pristine *i*PP (curve a) and SM*i*PP-Eth (curve b) are included in the same figure. It is noted that the characteristic peaks at around 3200 cm⁻¹ and 1713 cm⁻¹ appear in curve b which could be attributed to the

stretching vibration of the surface hydroxyl and ester (or aldehyde) groups, respectively indicating the existence of hydroxyl groups and aldehyde (or ketone) groups on the surface of SMiPP-Eth. Furthermore, the spectrum of SMiPP-Eth exhibits no other discernible difference from that of the pristine *i*PP.

XPS analysis has been carried out to determine the relative amount of oxygen and carbon at the surface of SMiPP-Eth. The results correlate well with those obtained by FTIR spectroscopy (see Fig. 3 and Table 1).

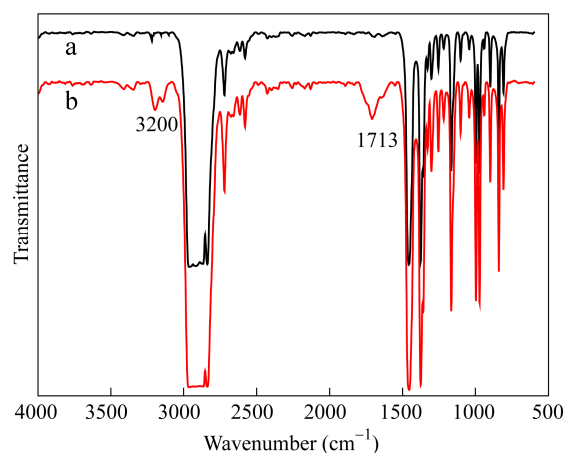


Fig. 2 FTIR spectra of the pristine *i*PP (a) and SMiPP-Eth (b) at discharge voltage: 41 V; plasma treating time: 600 s, and ethylene flow rate: 30 sccm

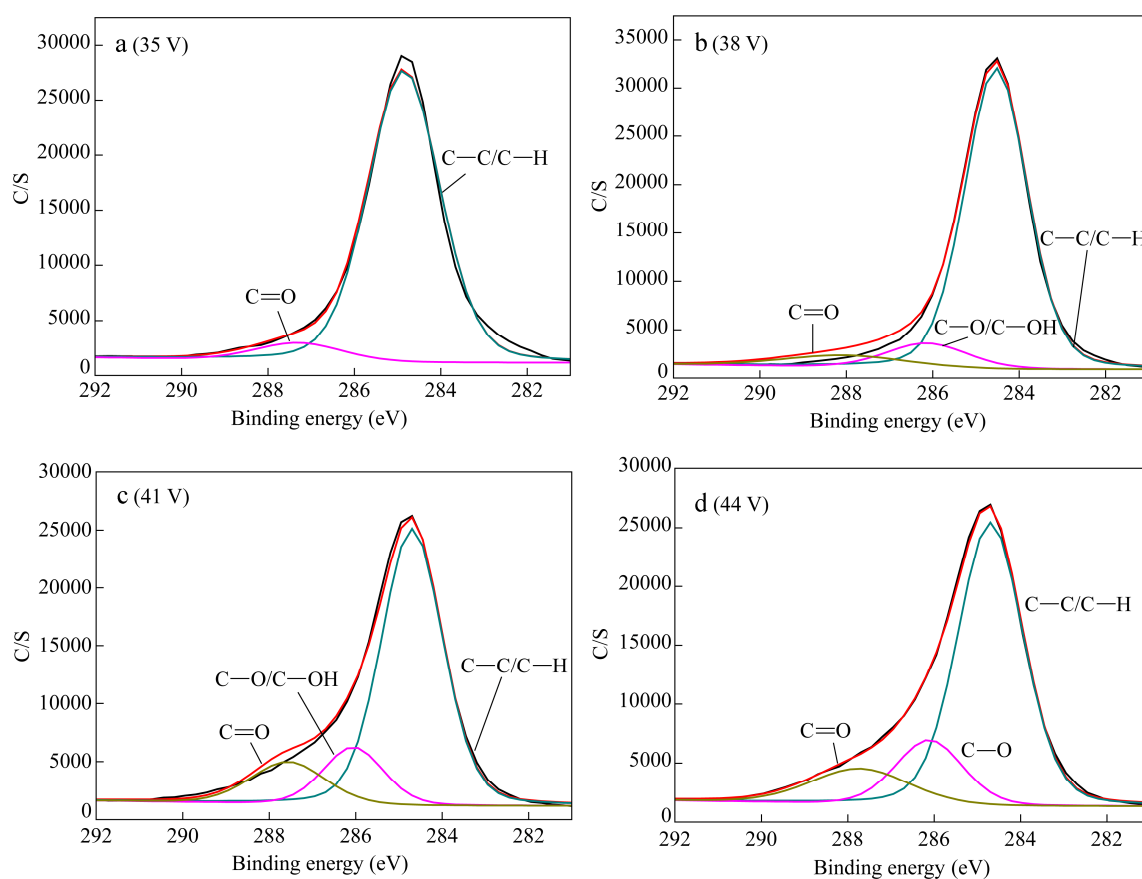


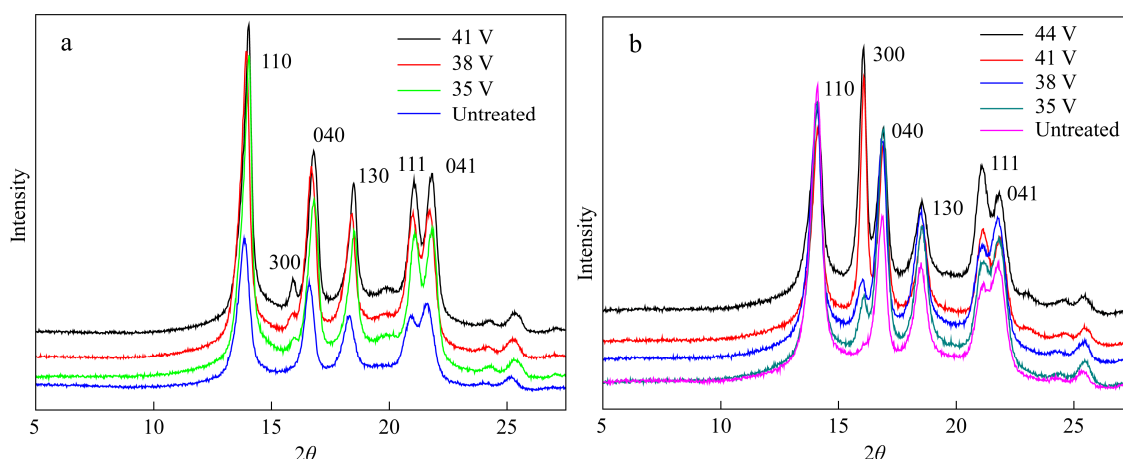
Fig. 3 XPS spectra of SMiPP-Eth surface under different discharge voltages at plasma treating time: 600 s, and ethylene flow rate: 30 sccm

Table 1. XPS results of SMiPP-Eth surface at different discharge voltages in ethylene plasma at plasma treating time: 600 s, and ethylene flow rate: 30 sccm

Position (eV)	Assignment	35 V	38 V	41 V	44 V
284.7	C—C/C—H(%)	92.99	84.28	71.79	70.07
286.1	C—O/C—OH(%)	0.00	9.20	14.81	16.62
287.7	C=O(%)	7.01	6.52	13.40	13.32

Induced β -Form Crystals in Polypropylene

The crystalline structures of the untreated *i*PP and SMiPP-Eth were observed with WAXD (Fig. 4). It is noteworthy that compared to the pristine *i*PP, the WAXD pattern of SMiPP-Eth presents the diffraction peak at 2θ of 16.08° , indicating the formation of β crystals of *i*PP during the plasma treatment. As widely known, the electrons and ions in the plasma have higher energy and temperature, which could activate and etch the surface of *i*PP through the bombardment effect, leading to the compact adherence (or fusion) of the ethylene plasma sediments onto *i*PP. These sediments of ethylene plasma on *i*PP surface could induce β -form crystallization in the surface layer of *i*PP during the process of ethylene plasma treatment, demonstrating the ethylene plasma modification of *i*PP surface could affect the structure of *i*PP bulk.

**Fig. 4** WAXD patterns of SMiPP-Eth (a) and blended SMiPP-Eth (b) under different discharge voltages at plasma treating time: 600 s and ethylene flow rate: 30 sccm

After the SMiPP-Eth samples were blended under molten state and mixed in a mixer, the sediment of ethylene plasma on *i*PP surface could interfuse into the bulk of *i*PP. WAXD patterns of the blended SMiPP-Eth exhibited similar peaks at 16.08° with the original SMiPP-Eth but with much stronger intensity, indicating that the content of β -form crystal greatly increased after blending. The function of the sediment of ethylene plasma in *i*PP was to be an accelerating agent or nucleating agent of β crystals when a number of the sediments interfused into the bulk of *i*PP.

The content of β crystal in SMiPP-Eth (K_β) can be calculated by Turner-Jones equation^[9] as following:

$$K_\beta = \frac{H_{300}}{H_{300} + H_{110} + H_{040} + H_{130}} \quad (1)$$

where H_{300} is the height of the (300) peak for β -*i*PP and H_{110} , H_{040} , and H_{130} are the heights of the (110), (040), and (130) peaks for the α -form *i*PP. The β -*i*PP content (K_β value) calculated by Eq. (1) (the height of each reflection used is obtained separately from the corresponding WAXD pattern) is given against the discharge voltage of plasma in Table 2, indicating K_β bears a relationship to the discharge voltage of plasma. K_β increases with an increase in discharge voltage of plasma. Table 1 could show that the sediments of ethylene plasma increase with an increase in discharge voltage. Thereby, K_β value (β -*i*PP content) depends on amount of the sediments of ethylene plasma on *i*PP surface.

Table 2. The relationship of K_β with discharge voltage at plasma treating time: 600 s, and ethylene flow rate: 30 sccm

Discharge voltage (V)	35	38	41	44
K_β of SMiPP-Eth (%)	6.09	7.07	8.33	–
K_β of blended SMiPP-Eth (%)	11.36	11.43	33.55	35.01

CONCLUSIONS

The SEM image of SMiPP-Eth surface indicates that the nonuniform film of ethylene plasma sediment can be formed on the surface of *i*PP. The results of FTIR and XPS analyses confirm the existence of hydroxyl groups and aldehyde (or ketone) groups in the sediment and the content of the hydroxyl group and aldehyde group bears a relationship to discharge voltage of plasma. The WAXD results show that the sediment of ethylene plasma on *i*PP can induce β -form crystallization in the bulk of *i*PP. The sediment of ethylene plasma in *i*PP exhibits the function of the accelerating agent or nucleating agent of β crystals.

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