In-line Plasma-induced Graft-copolymerization of Pentaerythritol Triacrylate onto Polypropylene

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Abstract Pentaerythritol triacrylate (PETA) was successfully grafted onto the plasma-treated isotactic polypropylene (*i*PP) *via* the *in situ* melt processing. The X-ray photoelectron spectroscopy (XPS) results showed that the hydroxyl and carbonyl groups, and peroxides could be generated *via* plasma treatment. The content of free radical in plasma-treated *i*PP (P*i*PP) was measured by 2,2-diphenyl-1-picrylhydrazyl (DPPH). It was found that the resulting peroxides induced the grafting copolymerization of PETA onto *i*PP, and the grafted PETA promoted the formation of *β*-crystal in P*i*PP, which was evidenced by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) measurements, respectively.

Keywords Plasma treatment; Melt processing; Graft copolymerization; Pentaerythritol triacrylate

INTRODUCTION

Various types of grafting techniques have been developed in recent decades, including ion radiation-induced graft reaction, photo-induced graft reaction, chemical initiator, plasma-induced graft polymerization, *etc*[1]. Among these techniques, the plasma method is very useful because of the uniform and extensive creation of active radical sites on the existing polymer substrate[2], where catalyst or initiator is not required.

Polypropylene (PP) shows multi-advantages such as light weight, lower price and excellent mechanical properties. The PP-based materials are qualified for a broad range of applications, *e.g.*, toolbox, automobile parts and pipes. To meet the rapid growth of application, high performance and functionality of PP materials are required. For instance, the foaming process needs sufficient melt strength and dip dye expects the modified to have polar groups. Thereinto, the preparation and investigation on high melt strength and surface functionalization of PP are very active in the past decade[3−12]. Simultaneously, many researchers have reported the plasma-induced grafting reaction of monomer onto PP[13−20], which was carried out *via* treating the solid polymer surface with plasma to induce the grafting reaction. Although the fusion grafting of long chain acrylate onto PP has been studied by chemical method for a long time, Wang *et al*.[10] explored the possibility of producing branched polypropylene (PP) by a reactive extrusion (REX) process, where isotactic PP was reacted with a polyfunctional monomer, pentaerythritol triacrylate (PETA), in the presence of 2,5-dimethyl-2,5(*t*-butylperoxy)hexane peroxide. Yu *et al*.[11] studied linear PP modified by melt grafting reaction in the presence of 2,5-dimethyl-2,5(*tert*-butylperoxy)hexane peroxide and PETA in mixer and the rheological characterization of long chain branching polypropylene. Wang *et al*.[12] discussed the grafted reaction of a polyfunctional reactive monomer, trimethylolpropane triacrylate (TMPTA), onto PP during extrusion by benzoyl peroxide. But no reports have referred to in-line plasma-induced graft reaction of monomers onto polymer chains through a melt bulk processing.

In our laboratory, a novel combined system of plasma nozzle (plasma generator) with internal mixer has been built in order to investigate the feasibility of the plasma modification of polymer melt during molten and mixing in line. In present work, it is hoped that the plasma modification of melt PP will be realized in line and the grafting reaction of monomer onto melt PP will be induced *in situ*. The monomer was chosen to have a larger molecular weight, as pentaerythritol triacrylate (PETA), which also has multiple functional groups. The in-line plasma-induced grafting reaction of PETA onto isotactic polypropylene (*i*PP) melt bulk was studied. The structures and properties of the grafted copolymers *i*PP-*g*-PETA were analyzed in detail.

EXPERIMENTAL

Materials

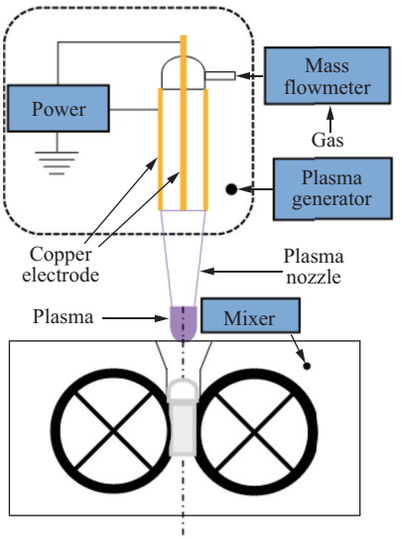
The material used in the present work was an intermediate

product of commercialized isotactic polypropylene powder (*i*PP, T30s) provided from the Zhenhai Petrochemical Ltd (China). The *i*PP had molecular weight $M_w = 3.2 \times 10^5$ g/mol, melting temperature T_m = 167 °C, and melt flow rate 3 g/10min. The antioxidants were externally added during our experiments because of no antioxidant in the PP intermediate products. The antioxidant B225 was a mixed compound of 1010 and 168 with the weight ratio of 1:1, which was provided by Yingkou Fengguang Chemical Engineering Ltd. Pentaerythritol triacrylate (PETA, Molecular weight: 298.29, CP) was purchased from Tianjin Kemao Chemical Reagent Co., China. Carbon dioxide (CO_2, AR) was obtained from Tianjin Liu Fang Gas Co. 2,2-Diphenyl-1-picrylhydrazyl (DPPH, AR) was supplied by A. Johnson Matthey Co. The added concentration of antioxidant B225 was 0.2 wt%.

Test System and Experiments

The combined test system of in-line plasma generator (system) with internal mixer (combined test system) is shown in Scheme 1. The plasma generator was self-designed, which used here was dielectric barrier discharges (DBD) plasma apparatus. The plasma generator (plasma nozzle) was quartz tube with an external diameter of 15 mm between two internal and external electrodes. The plasma excitation power supply was provided by a high-voltage power supply (CTP-2000K, Nanjing Suman Electron Co. Ltd., China) with a variable discharge voltage (from 0 V to 150 V) and an invariable frequency (10 kHz). The plasma generator system could be used alone, and also could be used in conjunction with internal mixer (see Scheme 1) to make up the system of the in-line atmospheric plasma treatment during a continuous melt compounding process using a mixer. The mixing system was a rotating rheological mixer (XXS-30 mixer, Shanghai Kechuang Rubber Machinery Equipment Co. Ltd, China).

The *i*PP was firstly heated to 180 °C and was completely melted at the rotation speed of 36 r/min. Next, the *i*PP melt was treated by CO_2 plasma with a fixed CO_2 flow rate of 150 mL/min, where the treating voltage and duration could be varied. Five discharge voltages of 30, 35, 40, 45 and 50 V and five plasma treatment durations of 5, 10, 15, 20 and 25 min were employed. Then, PETA was added into the plasma treated *i*PP (P*i*PP) melt and further mixed for 20 min to carry out *in situ* grafting reaction. During the treatment process, temperature and rotation speed were kept at 180 °C and 36 r/min. The grafted polymer is named as *i*PP-*g*-PETA.



Scheme 1 Schematic of the in-line atmospheric plasma treatment during a continuous melt compounding process using a mixer

Specimen Preparation

After above plasma treatment and melt mixing, the reacted samples were dissolved in hot xylene at 140 °C, and then the solution was transferred into acetone at room temperature. This operation was repeated for three times to remove the unreacted PETA monomer and soluble PETA homopolymer. The obtained products of *i*PP and *i*PP-*g*-PETA were dried at 60 °C under vacuum for 24 h. Then they were press-molded at 180 °C into films (20 μm thick) and sheets (1 mm thick) for further characterizations.

Free Radical Measurements

1,1-Diphenyl-2-picrylhydrazyl (DPPH) is a stable free radical that is often used to determine the quantity and the decomposition rate constant of macro initiators. DPPH reacts with free radicals to generate inactive products. Thereby, the quantity of free radical can be determined[21, 22]. A certain amount of P*i*PP was taken from the mixer, cooled down and soon put into a 1.0×10^{-4} mol/L deaerated benzene solution of DPPH, then it was kept at 70 °C for 40 h to decompose the peroxides formed on the sample surface and near the sample surface. The amount of consumed DPPH was determined by the transmittance difference at 520 nm between the pristine and plasma-treated samples. The absorption coefficient of DPPH at 520 nm was 8.108×10^4 L/(mol·cm).

Characterization

The data of the chemical composition of *i*PP and P*i*PP surfaces were collected by the XPS spectrograph, using Pekin-Elemer PHI1600ESCA X-ray photoelectron spectroscopy (XPS, USA) with sample thickness equal to 1 mm.

The infrared spectrum of *i*PP-*g*-PETA was recorded by a Perkin Elemer spectrum 100 Fourier transform infrared spectrometer (FTIR, USA) with sample thickness equal to 20 μm.

The wide-angle X-ray diffraction (WAXD) patterns for the samples were analyzed on the Beijing Synchrotron Radiation Facility (China), at beam line 1W2A with detector Mar165 (Mar, USA), and sample thickness was 1 mm.

A differential scanning calorimeter, TA Instruments (Q2000, USA), was used for thermal analysis. The sample weight was about 10 mg, scanning rate was 20 °C/min and the range of scanning temperature was from room temperature to 200 °C under nitrogen.

RESULTS AND DISCUSSION

Plasma Modification of *i*PP Melt

The modification of *i*PP by plasma was firstly examined using XPS method. The high-resolution C1s and O1s XPS spectra of *i*PP and P*i*PP modified by different plasma discharge voltages are summarized in Fig. 1. From Fig. 1(a),

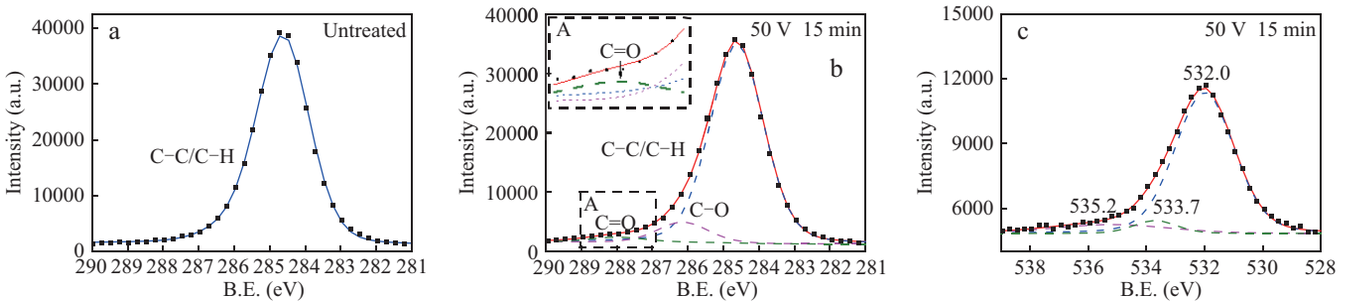


Fig. 1 XPS C1s and O1s spectra of *i*PP and PiPP treated for different durations with different voltages: (a) C1s spectra of *i*PP untreated, (b) C1s spectra of P*i*PP treated for 15 min with 50 V voltage, (c) O1s spectra of P*i*PP treated for 15 min with 50 V voltage

it can be seen that the sole peak located at 284.6 eV corresponds to the hydrocarbon structure of the untreated *i*PP, *i.e.* C—C and C—H bonds. After treated by CO_2 plasma, new peaks appear in the spectrum as shown in Fig. 1(b). The new peaks at 286.4 and 288.1 eV demonstrate the formation of functional groups containing C—O and C=O bonds, respectively.

Fig. 1(c) shows O1s spectra of plasma treated polypropylene, P*i*PP. The peak at 535.2 eV demonstrates the presence of C=O, which corresponds to oxygen in carbonyl group. The peak at 532 eV is attributed to C—O bond. The peak at 533.7 eV may belong to oxygen in peroxides. Based on the XPS results, Table 1 summarizes the relative content of elements varied with plasma treatment time. It can be seen that in P*i*PP, the oxygen content and O/C ratio both increase with increasing plasma treatment time. These active groups can form peroxides radical under atmosphere[15].

Table 1 Relative content of elements varied with plasma treatment time

Plasma treatment		Atomic concentration ratio (%)			Component ratio (%)	
Voltage (V)	Time (min)	C	O	N	O/C	N/C
0	0	97.8	2.2	0.0	2.2	0
50	5	94.6	5.4	0.0	5.7	0
50	10	94.0	5.7	0.3	6.1	0.3
50	15	90.4	9.3	0.3	10.3	0.3
50	20	89.6	10.1	0.3	11.3	0.3
50	25	84.8	14.3	0.9	16.9	1.1

The content of free radical in P*i*PP was determined with DPPH. The results are shown in Table 2. It can be seen that when the CO_2 flow rate is 150 mL/min and melt temperature is 180 °C, a high free radical content of 7.02×10^{-6} mol/g is obtained with the plasma treatment time of 15 min at a discharge voltage of 50 V, and a rotator speed of 36 r/min.

Graft Polymerization of PETA onto *i*PP

FTIR spectra of the purified samples are shown in Fig. 2. For all the *i*PP-*g*-PETA samples, the band observed at 1735 cm^{-1} is related to the stretching vibration of ester carbonyl group in the PETA molecule[11, 12], indicating the grafting of PETA onto the *i*PP chains. From the FTIR spectra, the absorbance ratio R_{CI} was calculated by the following Eq. (1):

$$R_{CI} = \frac{A_{1735}}{A_{841}} \tag{1}$$

where A_{1735} is the absorbance at 1735 cm^{-1}, characteristic of carbonyl groups of ester in the PETA molecule, and A_{841} is the absorbance at 841 cm^{-1}, characteristic of CH_3 groups in the *i*PP backbone. To assess the grafting ratio (Gr), a calibration curve is obtained by preparing the blends of *i*PP with assigned quantities of PETA. The determined Gr values are listed in Table 3. It can be seen that Gr increases with increasing PETA content. Higher fraction of PETA favors the macro-radical recombination and thus facilitates the grafting reaction.

Table 2 Free radical concentrations of P*i*PP under different plasma treatment condition

Mixer rotation speed (r/min)	Discharge voltage (V)	Radical concentrations at different treatment time × 10^{-6} (mol/g)				
		5 min	10 min	15 min	20 min	25 min
36	30	3.74	3.07	5.92	5.19	4.79
	35	4.24	4.15	6.39	3.43	4.96
	40	4.58	5.63	4.85	3.17	4.34
	45	3.19	2.77	4.08	3.03	3.32
	50	4.91	4.27	7.02	3.51	5.15
48	30	1.80	2.57	3.32	2.53	1.55
	35	2.41	3.37	3.39	1.38	0.94
	40	2.94	3.13	3.59	2.13	1.79
	45	1.93	1.97	2.11	2.47	1.69
	50	1.96	1.73	1.99	1.55	2.24
60	30	1.50	2.46	2.15	2.52	2.41
	35	1.68	2.35	1.61	2.13	2.56
	40	2.25	3.21	2.52	2.55	2.81
	45	1.95	2.17	2.11	2.38	1.67
	50	2.06	3.35	2.91	2.35	2.14

Table 3 FTIR parameters of grafted samples

Sample	*i*PP content (wt%)	PETA content (wt%)	I_{1735}	I_{841}	A_{1735}	A_{841}	A_{1735}/A_{841}	Gr (%)
*i*PP	100	0	–					–
P*i*PP	100	0	–					–
F1	99	1	–	–	–	–	–	–
F2	98	2	0.96	0.45	0.02	0.34	0.05	0.15
F3	97	3	0.41	0.15	0.39	0.82	0.47	1.08
F4	96	4	0.25	0.10	0.60	0.98	0.61	1.37
F5	95	5	0.24	0.13	0.61	0.90	0.68	1.54

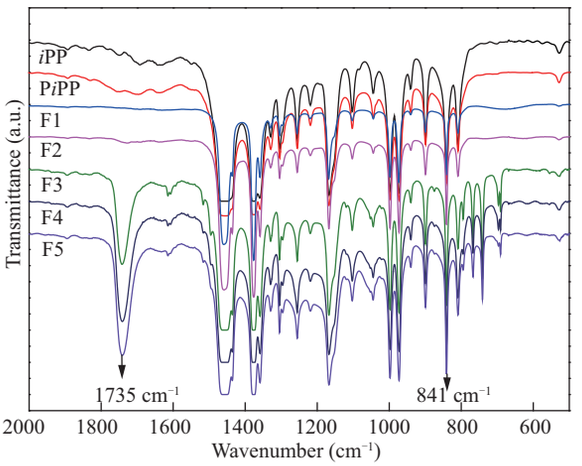


Fig. 2 FTIR spectra of *i*PP, P*i*PP and *i*PP-*g*-PETA (F1 to F5 see Table 3)

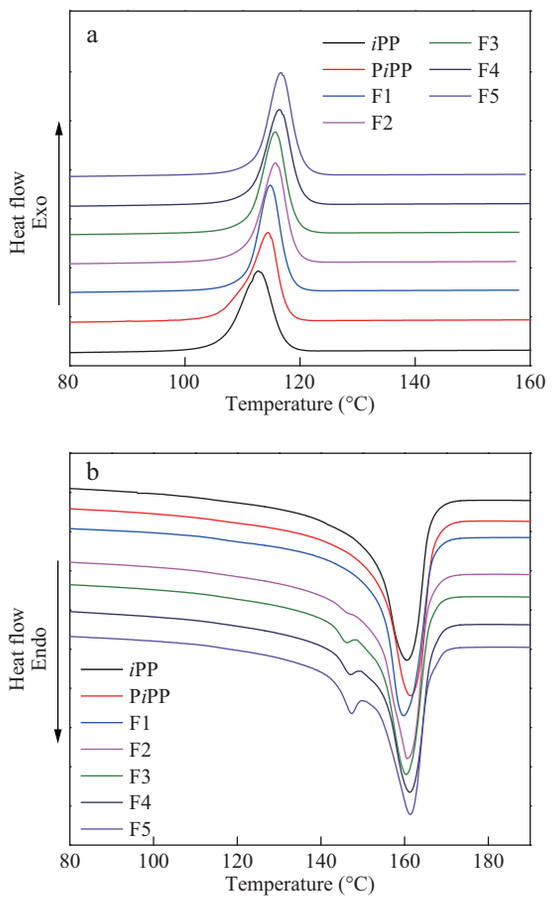


Fig. 3 DSC thermograms of (a) cooling scan and (b) heating scan for *i*PP, P*i*PP and *i*PP-*g*-PETA samples at 20 °C/min

The DSC curves of *i*PP, P*i*PP and *i*PP-*g*-PETA are shown in Fig. 3. It can be seen that the temperature of cooling crystallization increases with increasing PETA concentration, which is consistent with the behavior of PETA branched PP. This is interpreted by the possible reason that the PETA long chains enhance the heterogeneous nucleation to accelerate crystallization process. As shown in Fig. 3(b), a melting peak appears at 147.4 °C for samples F3, F4 and F5, which can be attributed to *i*PP β-crystal[18]. On the other hand, as increasing the PETA concentration, the resulting variation of crystallization temperature and appearance of β-crystal in turn demonstrate that the PETA chains are indeed efficiently grafted on the PP molecules.

Fig. 4 shows the WAXD results of the *i*PP, P*i*PP, *i*PP-*g*-PETA samples. As can be seen from Fig. 4, WAXD results of *i*PP and *i*PP-*g*-PETA with low Gr of PETA (F1 and F2) show characteristic peaks of only α-crystal. WAXD results of *i*PP-*g*-PETA with high Gr of PETA (F3, F4, and F5) show the additional diffraction peak at $2\theta = 16.08°$, indicating the formation of β-crystal in *i*PP-*g*-PETA. The content of β-crystal seems to depend on the Gr of PETA, which is consistent with the DSC results.

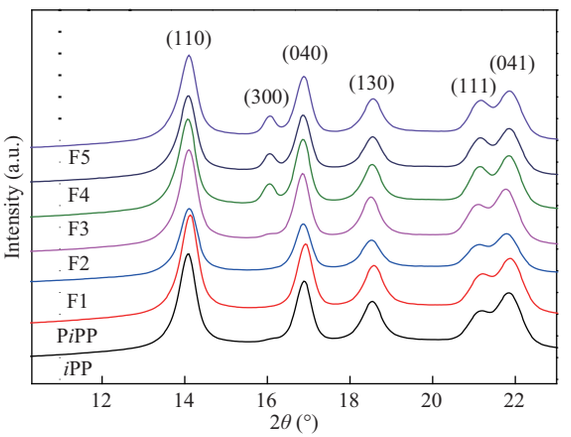


Fig. 4 One dimension WAXD patterns of the *i*PP, P*i*PP, and *i*PP-*g*-PETA samples

CONCLUSIONS

Through melt mixing of the CO_2-plasma treated *i*PP melt, PETA was successfully *in situ* grafted onto *i*PP chains. The XPS results confirm the existence of the hydroxyl group and aldehyde group (or ketone) in P*i*PP, and are used to determine the oxygen contents. The O/C ratio in P*i*PP relates to the increase of plasma time. The analysis of DPPH indicates that the peroxide radical exists in P*i*PP, and the

content of the peroxide radical depends on plasma treatment time, discharge voltage and mixer rotation speed. FTIR results prove the successful grafting copolymerization of PETA onto *i*PP chains. The WAXD and DSC analyses indicate that the grafting of PETA induce the formation of *β*-crystal in *i*PP-*g*-PETA. So this reseach indicates that the in-line plasma-induced grafting reaction of PETA onto *i*PP melt bulk *in situ* is feasible, which results in the fusion grafting reaction of monomer onto *i*PP .

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