

Effect of Oxidation Progress of Tributylborane on the Grafting of Polyolefins

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ABSTRACT: Effect of the oxidation progress of tributylborane on the grafting reaction of PMMA onto high-density polyethylene (HDPE) and isotropic polypropylene (iPP) surface with tributylborane as initiator was studied in detail. The oxidation of tributylborane was triggered by the slow diffused oxygen or exposed contact to oxygen, so that the oxidation progress of tributylborane would be different. The grafted polyolefin surfaces were characterized by attenuated total reflection infrared (ATR-IR) spectroscopy, X-ray photoelectron spectroscopic (XPS), scanning electron microscope (SEM) and so on. The results of ATR-

IR spectroscopy and XPS analysis suggested that PMMA could be grafted onto polyolefin surfaces successfully through these two ways, but the grafting degrees were varied due to the different oxidation progresses of tributylborane. The surface morphologies of the polyolefin indicated the different grafting degrees as a result of different oxidation progress of tributylborane. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: tributylborane; oxidation; high-density polyethylene; isotropic polypropylene; graft

INTRODUCTION

Polyolefins such as polyethylene, polypropylene, and their copolymers are inexpensive and lightweight, which can be tailored to achieve a wide range of properties to fabricate objects for different appliances. But the inherent low surface energy of polyolefins is a major drawback in many applications, particularly in closed, dyeability, printability, or compatibility with other polymers. Lots of efforts have been directed toward pretreatment the surface of these low surface energy materials to achieve satisfactory functionality. Such pretreatments include vapor cleaning, acid etching, flame treatment, corona discharge and plasma treatment.^{1–5} Unfortunately, such techniques are often complicated, costly, and environmentally unfriendly. Another attractive method for modification of polyolefin surfaces is grafting, which has many advantages over other methods in several points, including easy and controllable introduction of graft chains with a high density and exact localization of graft chains to the surface with the bulk properties unchanged. Furthermore, covalent attachment of graft chains onto a polymer surface avoids their delamination, and assures the long-

term chemical stability of introduced chains. Many synthetic routes can be employed to introduce graft chains onto the surface of polymeric substrates, such as plasma discharge,^{6–8} UV irradiation,^{9–11} ozone pretreatment,^{12,13} and so on. Recently, Sonnenschein and others have disclosed the adhesion to low surface energy polymers with the polymerization of acrylic monomers initiated by trialkylborane at room temperature without surface pretreatment.^{14–18} The mechanism was elucidated as the formed *n*-butoxy radical generated from the oxidation of tributylborane could abstract hydrogen atom from polyolefin and provide a radical initiation site from which a grafted polymer chain could commence. This would be a method available for the grafting of low surface energy polyolefin. In this study, the grafting reaction of acrylic monomers onto polyolefin surface was promoted by trialkylborane at room temperature without surface pretreatment.

It was expected that the radical chemistry of trialkylborane was closely related to its oxidation progress, so that the grafting degrees of acrylic monomers onto polyolefin surfaces would be varied due to different radical chemistry involved. In this study, we had chosen two extremity of the oxidation process, slow oxidation of tributylborane and immediately oxidation of tributylborane, to study the effect of the oxidation process of tributylborane on the grafting of acrylic monomers onto polyolefin surfaces.

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EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and acetone were from Sinopharm Chemical Reagent (Sinopharm Chemical Reagent Co. Ltd). MMA was washed by sodium hydroxide and treated by anhydrous sodium sulfate, then distilled under vacuum; tributylborane (TBB), 1 mol/L in ethyl ether, was obtained from Aldrich and distilled under vacuum to remove ethyl ether before used. High density polyethylene pellet was purchased from Alfa Aesar and isotropic polypropylene power was from Jingshan Petroleum and Chemical.

Grafting of PMMA onto polyolefin surfaces by exposed treatment

The 0.3 mm thickness isotropic polypropylene (iPP) and high-density polyethylene (HDPE) sheets were prepared by hot-press molding. Then the impurities were extracted by methanol for 72 h. About 1 mL of the mixture of MMA and TBB was dropped and spread on the polyolefin surface (the molar ratio of MMA:TBB was 45 : 1). Trialkylborane was oxidized through immediate contact with plenty of oxygen. After being kept in the oven at 30°C for 12 h, the treated polyolefin sheets were transferred to a Soxhlet apparatus to extract PMMA homopolymer by acetone for 24 h until the weight reached a constant. The above processes were carried on for once, three times, five times, and the obtained samples were named as PES1, PES3, PES5 and PPS1, PPS3, PPS5, respectively.

Grafting of PMMA onto polyolefin surfaces by closed treatment

The mixture of MMA and TBB was sandwiched between two polyolefin sheets, and the thickness of the interlayer was limited at 0.03 mm. This thickness was so thin that tributylborane was oxidized by the slow diffused oxygen through the interspace between two sheets. After being kept at 30°C for 12 h, the samples were transferred to a Soxhlet apparatus and PMMA homopolymer was extracted with acetone for 24 h. The above processes were done for once, three times, five times, and the samples were named as PED1, PED3, PED5 and PPD1, PPD3, PPD5, respectively.

Characterization

Attenuated total reflection infrared (ATR-IR) spectroscopy was performed on EQUINOX 55 FTIR of Bruker at room temperature.

XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer)

with Mg K α radiation ($h\nu = 1253.6$ eV) or Al K α radiation ($h\nu = 1486.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The data analysis was carried out by using the RBD AugerScan 3.21 software provided by RBD Enterprises.

Optical microscope (OM) was performed on Leica DM LP Polarizing Optical Microscope of Leica Microsystems GmbH.

Scanning electron microscope (SEM) test were measured by FEI SIRION 200 (FEI, USA and OXFORD, UK). The samples were treated by gold sputtering for 30 s before characterization.

RESULTS AND DISCUSSIONS

The grafting of PMMA onto polyolefin was resulted from a series of reactions, including the hydrogen atom abstraction by alkoxy radical generated from the initial oxidation of trialkylborane, followed by the polymerization of MMA monomers initiated by polyolefin macro-initiator. Few researches devoted to study effect of the oxidation progress of trialkylborane on the grafting of PMMA onto polyolefin, so we tried to well understand that based on two kinds of experiment programs.

ATR-IR and XPS analyses of polyolefin surfaces

After being treated by the mixture of MMA and TBB through the above two process, the polyolefins surfaces were examined by ATR-IR, and the spectra were shown in Figures 1–4. When tributylborane was oxidized through immediate contact with oxygen, the overoxidation of tributylborane would produce boronate ($\text{BuB}(\text{OBu})_2$) and borate ($\text{B}(\text{OBu})_3$) species which were poor radical initiators at room temperature. Additionally, excess oxygen terminated the radical chain in the same manner as in the ordinary radical process. So it was expected that the exposed treatment was not an effective grafting method. Figures 1 and 2 showed that after three times of exposed treatment, the characteristic peaks of $-\text{C}=\text{O}-$ and $-\text{C}-\text{O}-$ appeared on the ATR-IR spectra of HDPE and iPP surfaces. If oxygen diffused into the mixture of MMA and tributylborane through the gap between two polyolefin substrates, tributylborane was slow oxidized to avoid the overoxidation. The initial oxidation product of tributylborane would produce radicals that are available for hydrogen atom abstraction and initiating polymerization. Additionally, the grafting site on polyolefin tented to initiate the polymerization of MMA monomers instead of being oxidized. So the grafting reaction was more likely to proceed if the oxidation of tributylborane was triggered by slow diffused

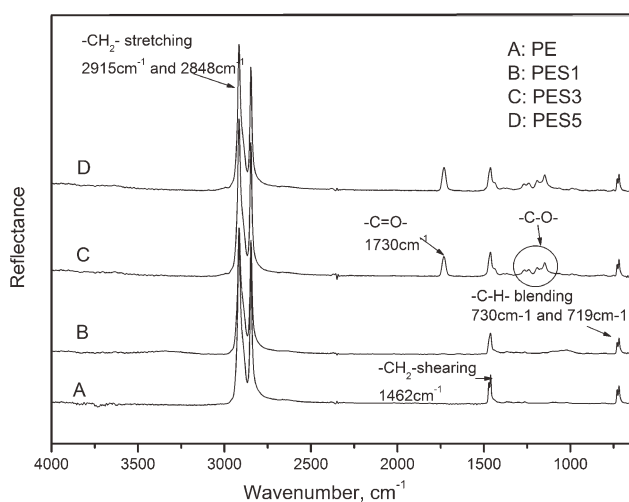


Figure 1 ATR-IR spectra of HDPE sheets after exposed treatment for different times.

oxygen. Figures 3 and 4 suggested that after closed treatment for once, PMMA could be grafted onto both HDPE and iPP sheets.

The proposed grafting mechanism was illustrated in Scheme 1, which involved insertion of oxygen between boron and a butyl group of the tributylborane, followed by homolysis of the peroxide bond to form a reactive *n*-butoxy radical and a stable borinate radical ($\text{O}-\text{BBu}_2$) due to the back-donating of electron density to the empty *p*-orbital of boron. *n*-Butoxy radical may subsequently abstract hydrogen atom from polyolefin surface, thus providing the polyolefin macro-radical as grafting site. Or the peroxyborane ($\text{Bu}-\text{O}-\text{O}-\text{BBu}_2$) was decomposed by the unreacted tributylborane, generating mono-

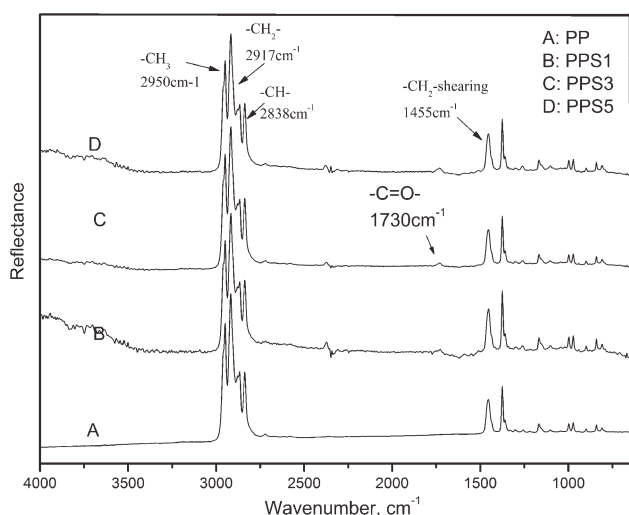


Figure 2 ATR-IR spectra of iPP sheets after exposed treatment for different times.

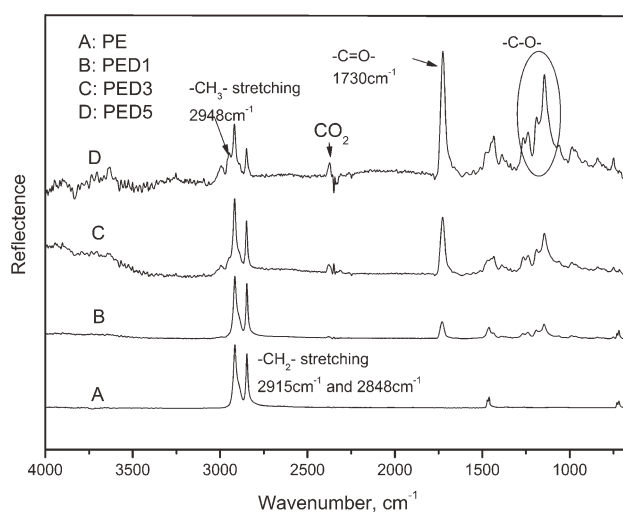


Figure 3 ATR-IR spectra of HDPE sheets after closed treatment for different times.

oxidized tributylborane ($\text{BuO}-\text{BBu}_2$), and *n*-butyl radical.

After the closed treatment, the grafting degrees of PMMA onto HDPE and iPP substrates were calculated according to eq. (1) and showed as Table I.

$$R = \frac{W_i - W_o}{W_o} \times 100\% \quad (1)$$

where *R*, grafting degree; W_i , weight of polyolefin sheets after treatment; W_o , weight of polyolefin sheets before treatment.

The grafting degree of HDPE was higher than iPP. This was mainly attributed to the varied selectivity of *n*-butoxy radicals towards radical attack at different sites of C-H bonds. According to the previous

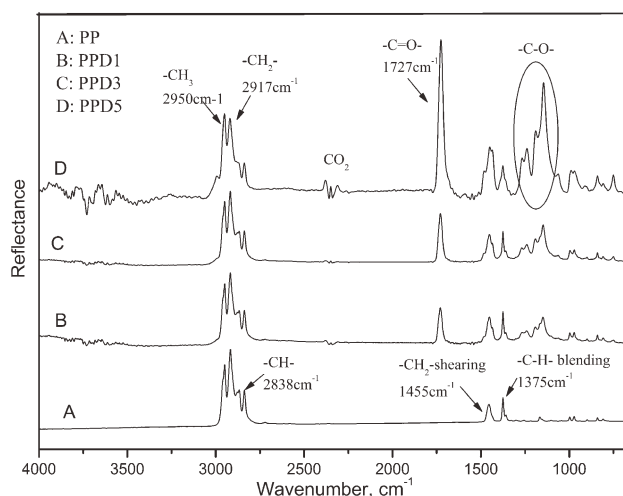
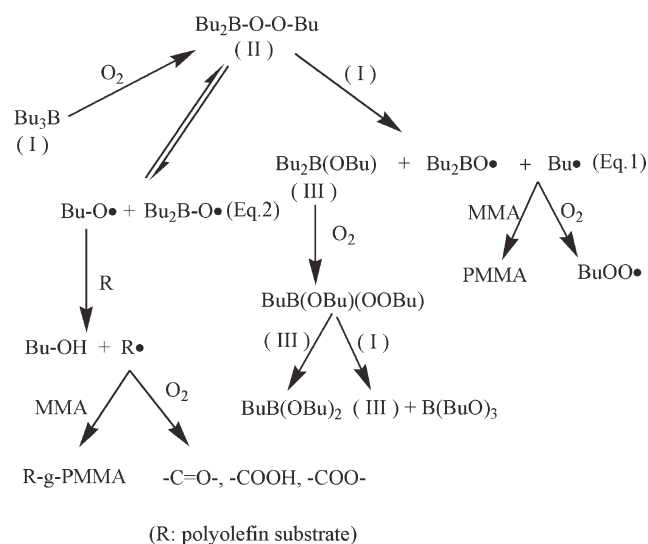


Figure 4 ATR-IR spectra of iPP sheets after closed treatment for different times.



Scheme 1 The grafting mechanism of PMMA onto polyolefin surface.

studying,^{19–22} the varied selectivity of alkoxy radicals towards radical attack at different sites of C–H bonds generally follows the expected order tertiary > secondary > primary, which correlating with the order of decreasing bond strength. Hydrogen atom abstraction occurred principally from the tertiary site of iPP and secondary position of HDPE, and then afforded grafting sites. The tertiary carbon grafting site on polyolefin surface underwent an instant conversion into the corresponding peroxy radical in contact with oxygen, while the secondary carbon radical on polyolefin was of low reactivity with oxygen.²³ The tertiary carbon grafting site, the major component of radicals on iPP surface, is very susceptible to oxygen and scavenged. However, the secondary carbon radical which was the major component of radicals on HDPE surface is much less reactive to oxygen. Moreover, oxygen diffused fast

TABLE I
Grafting Degrees of Polyolefin Sheets After Closed Treatment for Different Times

Treatment time	Substrate	
	iPP	HDPE
Once	0.75	2.30
Three times	1.58	3.26
Five times	1.59	3.87

into the amorphous regions of polymer, while its permeability in the crystalline phase was much slow or even negligible. Therefore, in the amorphous phase, most of the polyolefin macro-radicals on the surfaces decayed by reaction with oxygen to form $-\text{COO}-$, $-\text{C}=\text{O}$, $-\text{COOH}$, $-\text{COH}$, but in the crystalline region, the macro-radical had much longer lifetime to initiate the polymerization of monomers. The much higher crystallinity of HDPE than iPP (the crystallinities of HDPE and iPP were 90 and 67%, respectively, according to density method), led to the higher grafting degree.

Comparing with Figures 1 and 2 and Figures 3 and 4, it could be concluded that the closed treatment was more beneficial than exposed treatment to the grafting reaction. The peak of $-\text{CH}_2-$ bending was chosen as internal reference, and the relative amount of grafting PMMA was calculated from the degree of peak intensity of $\text{C}=\text{O}$ group to CH_2 group on ATR-IR spectra. The figures showed that the grafting PMMA increased with times of treatment.

XPS technique was used to characterize the compositions of polyolefin surfaces before and after closed treatment to obtain more support information for the grafting reaction.

The carbon 1s spectra of polyolefins surface after closed treatment could be seen in Figures 5 and 6.

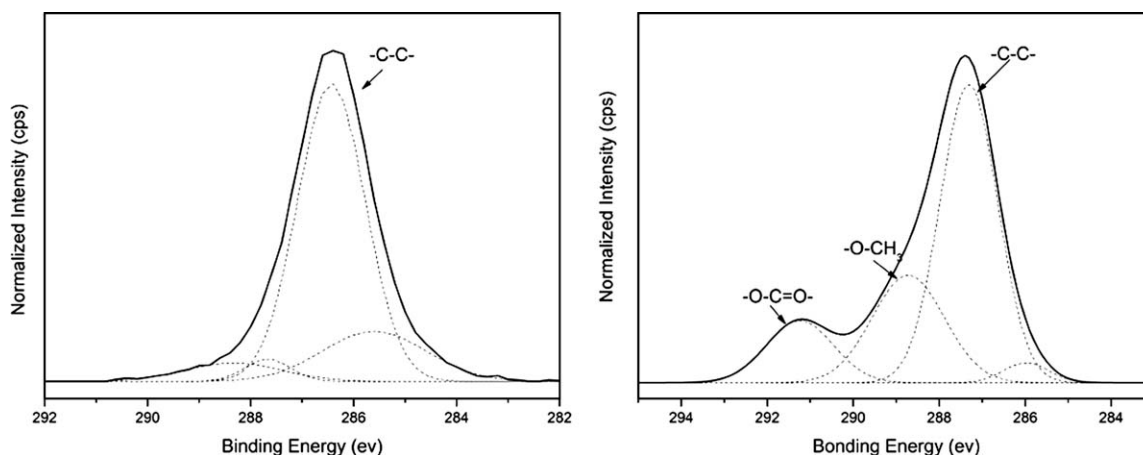


Figure 5 Carbon 1s spectra of HDPE sheets before and after closed treatment.

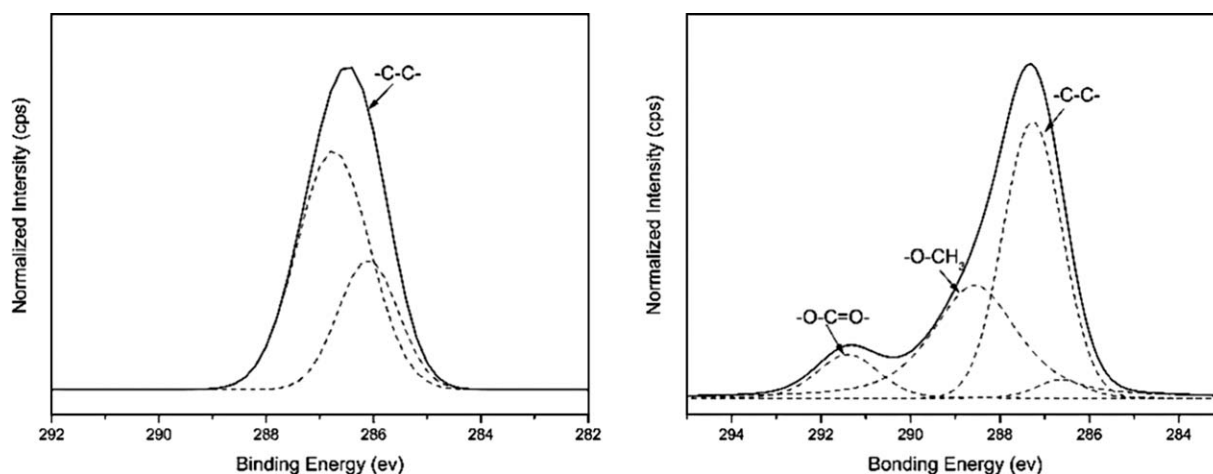


Figure 6 Carbon 1s spectra of iPP sheets before and after closed treatment.

The peaks corresponding to carbon atoms with C—O single bonds (288.8 eV) and C=O double bonds (291.4 eV) appeared on the carbon 1s spectra of polyolefins except aliphatic carbons (C—C). That indicated PMMA was successfully grafted onto polyolefin surface.

Figure 7 showed the oxygen 1s spectra of the polyolefin surface after closed treatment. The oxygen 1s spectrum was separated into two peaks at 534.9 and 536.5 eV which correspond to oxygen atoms with C=O double bonds and C—O single bonds, and their contents were 51 and 49%, respectively. That was consistent with the oxygen 1s spectrum of PMMA,²⁴ so it could be confirmed that the oxidation of tributylborane by slow diffused oxygen would lead to the successfully grafting of PMMA onto polyolefin surfaces.

The polyolefin surface would show different morphology after grafting reaction. Both of macroscopic and microscopic morphologies of the polyolefin

surfaces were observed to directly understand the effect of the oxidation progress of tributylborane on grafting.

The photographs of polyolefin sheets after closed treatment were showed in Figure 8. It could be seen that the treated area on polyolefin surfaces whitened, and the change at the fringe area was more significant than the center area. These photographs suggested that the grafting reaction at the fringe area of polyolefin sheets was more effective than at the center area, namely, PMMA was more likely be grafted onto the fringe area than onto the center area. This phenomenon could be explained by the grafting mechanism showed in Scheme 1.

In deficit amount of oxygen at the center area, the formed peroxyborane $Bu_2B(OOBu)$ rapidly decomposed by unreacted Bu_3B [eq. (1)]. There were few peroxyborane which cleaved to produce *n*-butoxy radical, accordingly, the amount of

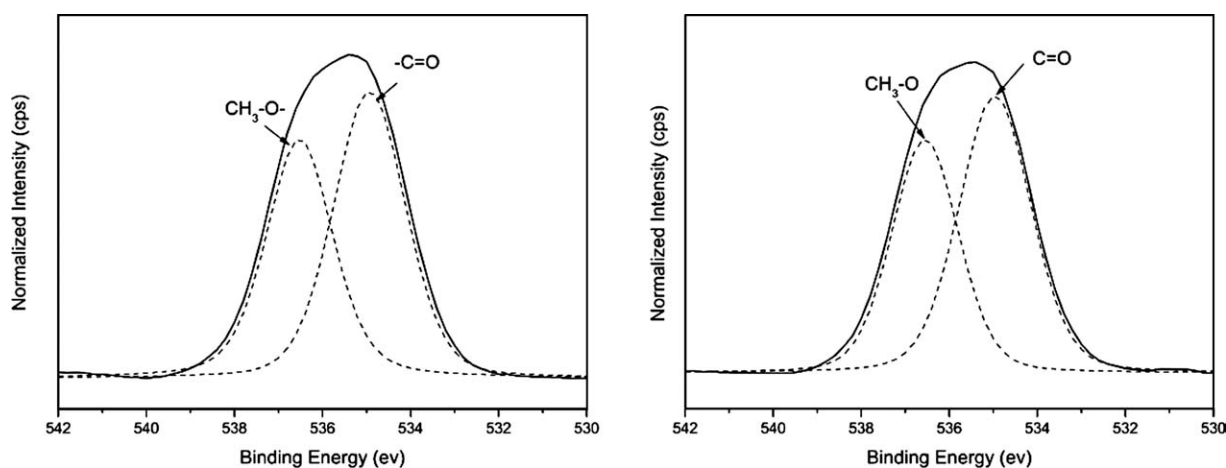


Figure 7 Oxygen 1s spectra of and PED3 (left) and PPD3 (right).

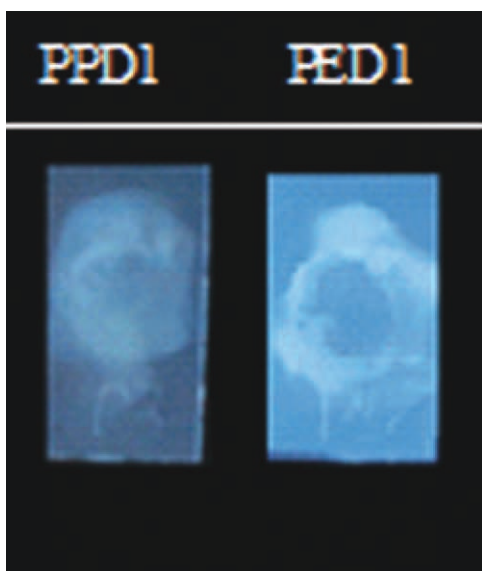


Figure 8 Picture of polyolefin sheets after closed treatment for once. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grafting site on polyolefin surface formed by the attack of *n*-butoxy radical was small. At the fringe area, oxygen was enough for the balance reaction eq. (2) turning to right, therefore more *n*-butoxy radicals were generated, and then produced more grafting sites.

The morphology of polyolefin surfaces

The surfaces of HDPE sheets before and after grafting process were observed by optical microscope, and Figure 9 showed the optical micrographs. The images of PES5 being almost the same as PE indicated that the closed treatment could not change the image of HDPE surface much due to less grafted PMMA. However, after the exposed treatment, the roughness of HDPE surface changed much and increased with the times of treatment because of more grafted PMMA. The images were showed as PED1, PED3, and PED5.

The optical micrographs of the center area of iPP sheet before and after grafting process were showed in Figure 10. The smooth PPS5 surface suggested exposed treatment could not change the image of iPP surface either, even after five times of treatment, but the closed treatment made iPP sheet uneven. Comparing with PED and PPD samples, PED surface changed more significantly than PPD surface due to more grafted PMMA onto PED samples.

The optical micrographs results were consistent with the conclusions drawn from ATR-IR spectra: in the grafting process, the oxidation of tributylborane initiator by slow diffused oxygen was more advantageous than the exposed plenty of oxygen. Moreover, the grafting degree of PMMA onto HDPE surface was higher than onto PP surface.

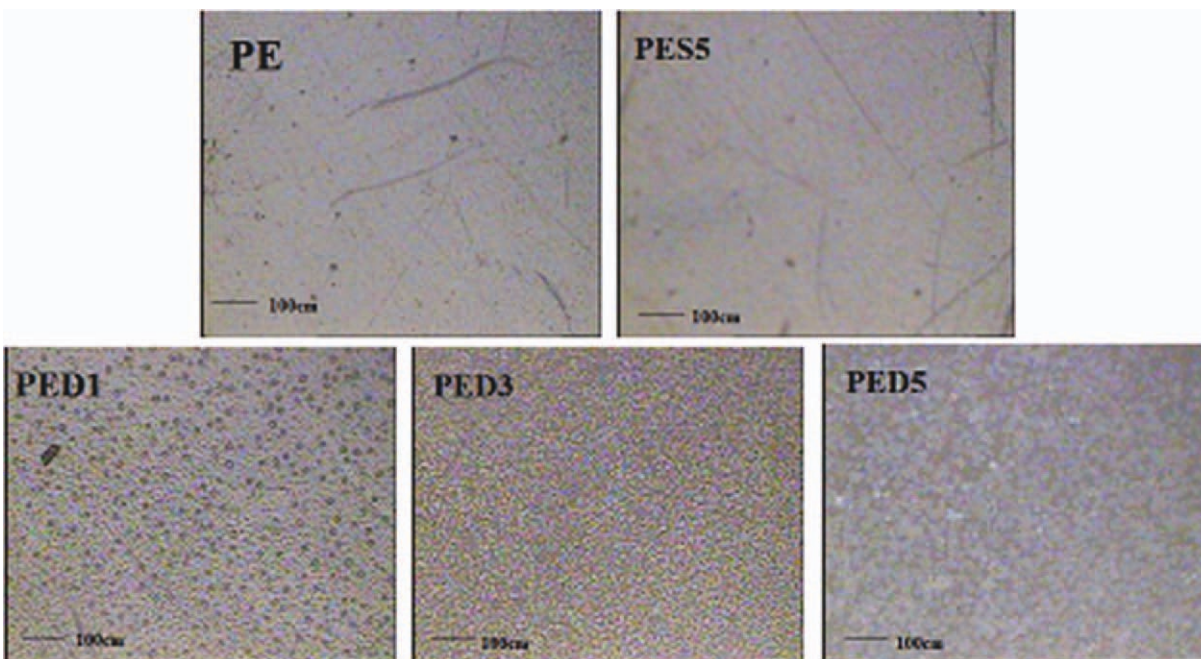


Figure 9 Optical micrographs of HDPE sheets before and after treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

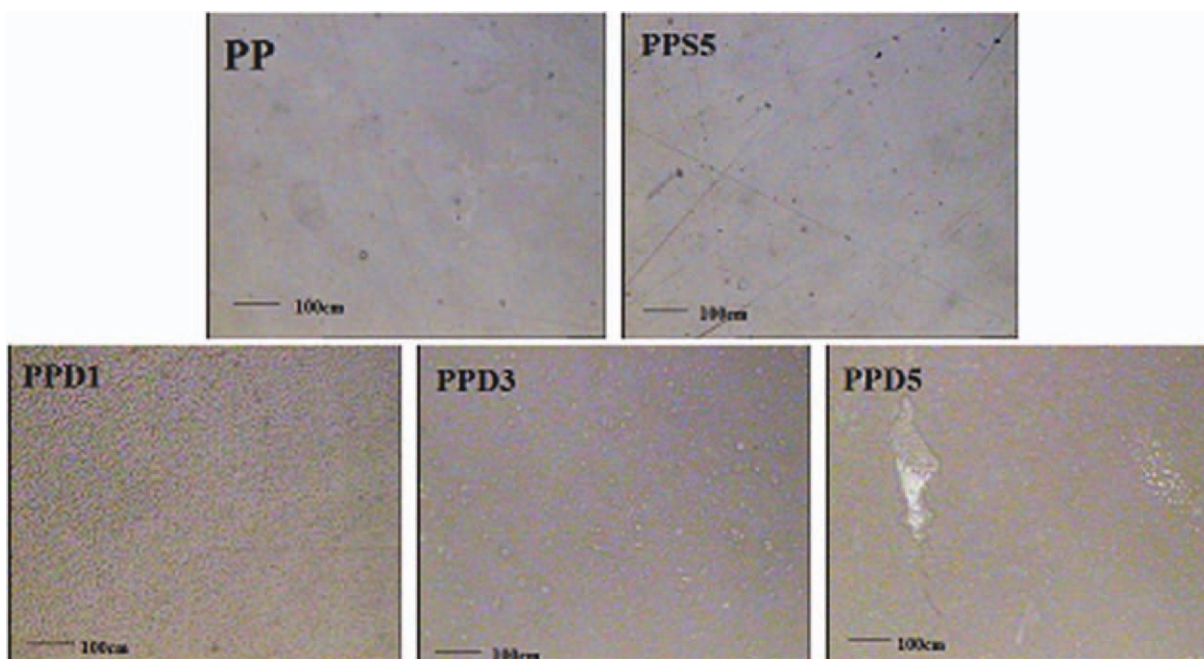


Figure 10 Optical micrographs of iPP sheets before and after treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The microscopic morphologies of the polyolefin surfaces before and after grafting promoted by slow oxidation of tributylborane for different times were observed by SEM, and the images were showed in Figures 11 to 13.

The SEM images of HDPE sheets after the grafting reaction promoted by the immediate oxidation of tributylborane were showed in Figure 12. The HDPE sheet revealed an uneven surface after treatment for once. Many protuberances appeared resulting from grafted PMMA. Then the HDPE surface was covered with gelatinous smooth

PMMA layer after treatment for three times so that PED3 exhibited a flatter surface than PED1 as a result of the swelling of the grafted PMMA layer. Big clusters were seen bulging out from the PMMA layer after treatment for five times, indicating more grafted PMMA.

Figure 13 showed the SEM images of PP surface after closed treatment. There were many tentacles protruding from PPD1 surface, then these tentacles grown bigger and denser on PPD3 surface. After five times of treatment, the surface morphology changed remarkably from a continuous

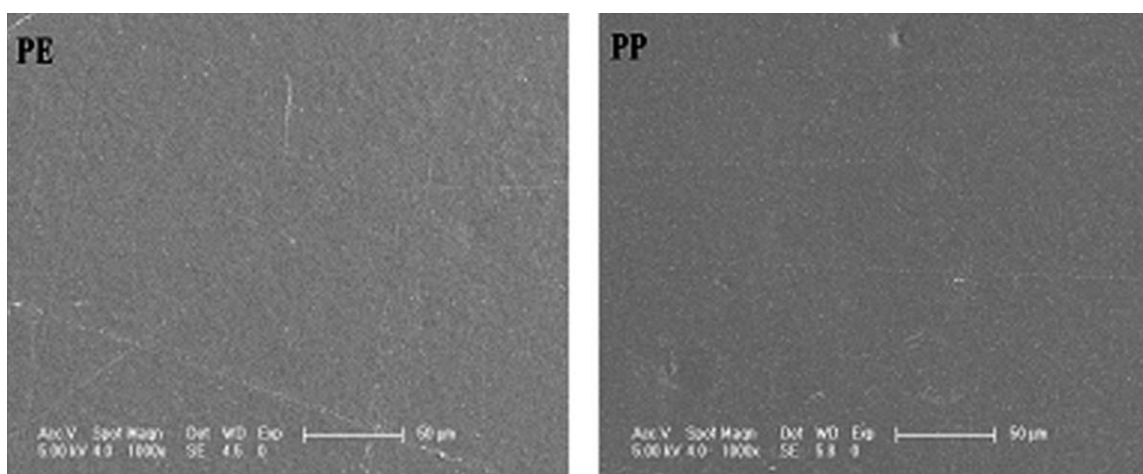


Figure 11 SEM images of the polyolefin sheets before treatments.

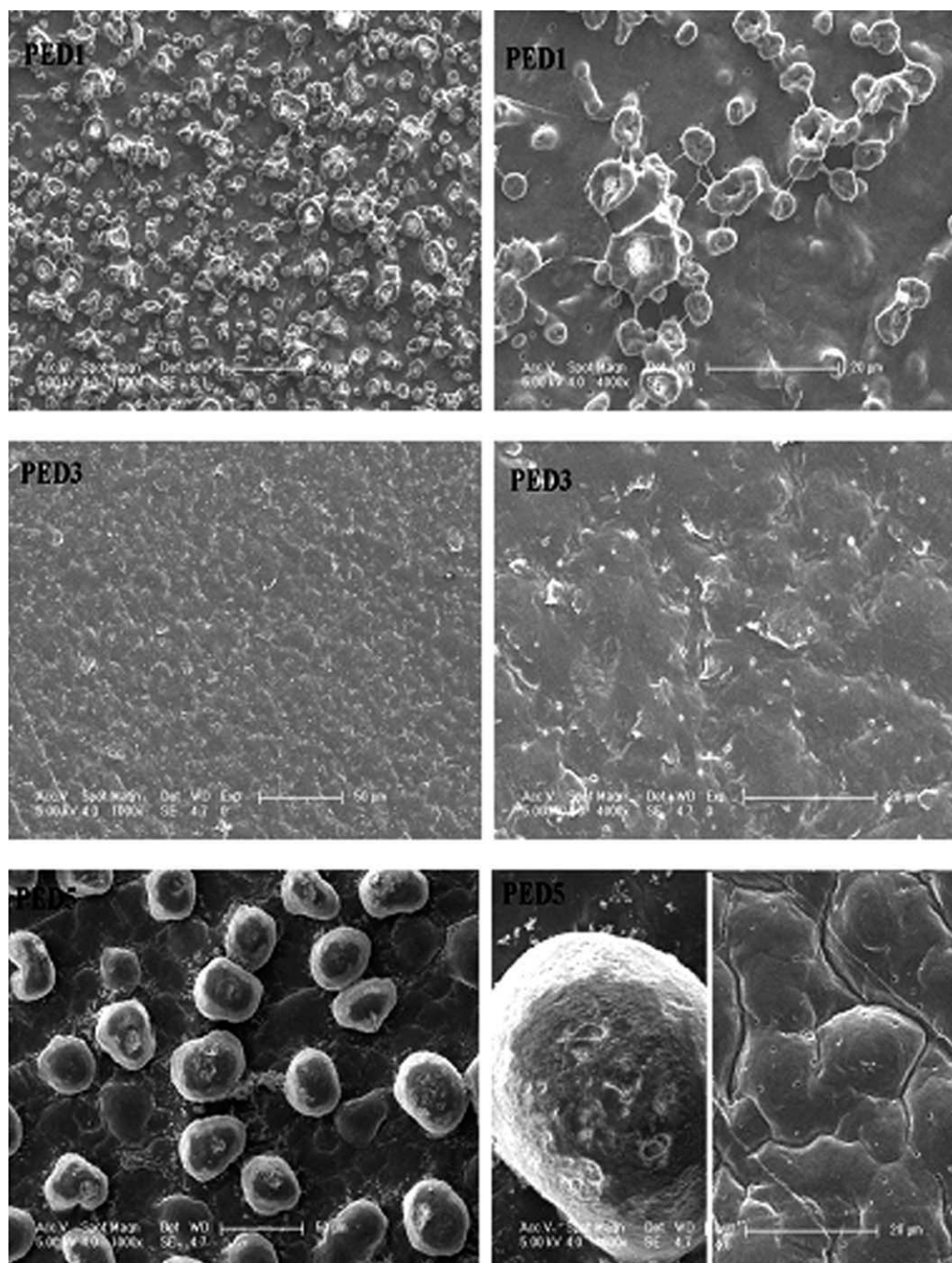


Figure 12 SEM images of the HDPE sheets after closed treatment for different times.

morphology to a disrupted and rugged morphology due to the swelling of grafted PMMA clusters. Figures 12 and 13 suggested that the surface morphologies of iPP sheets were different from HDPE sheets after closed treatment. The PMMA clusters on iPP surface were smaller but denser than that on HDPE surface after once of treatment. After five times of treatment, the iPP surface exhibited a nonuniform morphology, this was very different from that of HDPE surface.

CONCLUSION

In summary, this study for the first time reported the effect of oxidation progress of tributylborane on the grafting of PMMA onto polyolefin surfaces. In the exposed treatment process, tributylborane was oxidized by plenty of oxygen in such a way that it was more likely to be over-oxidized, then the polyolefin macro-radicals formed by the attack of *n*-butoxy radicals would be oxidized. Besides, excess

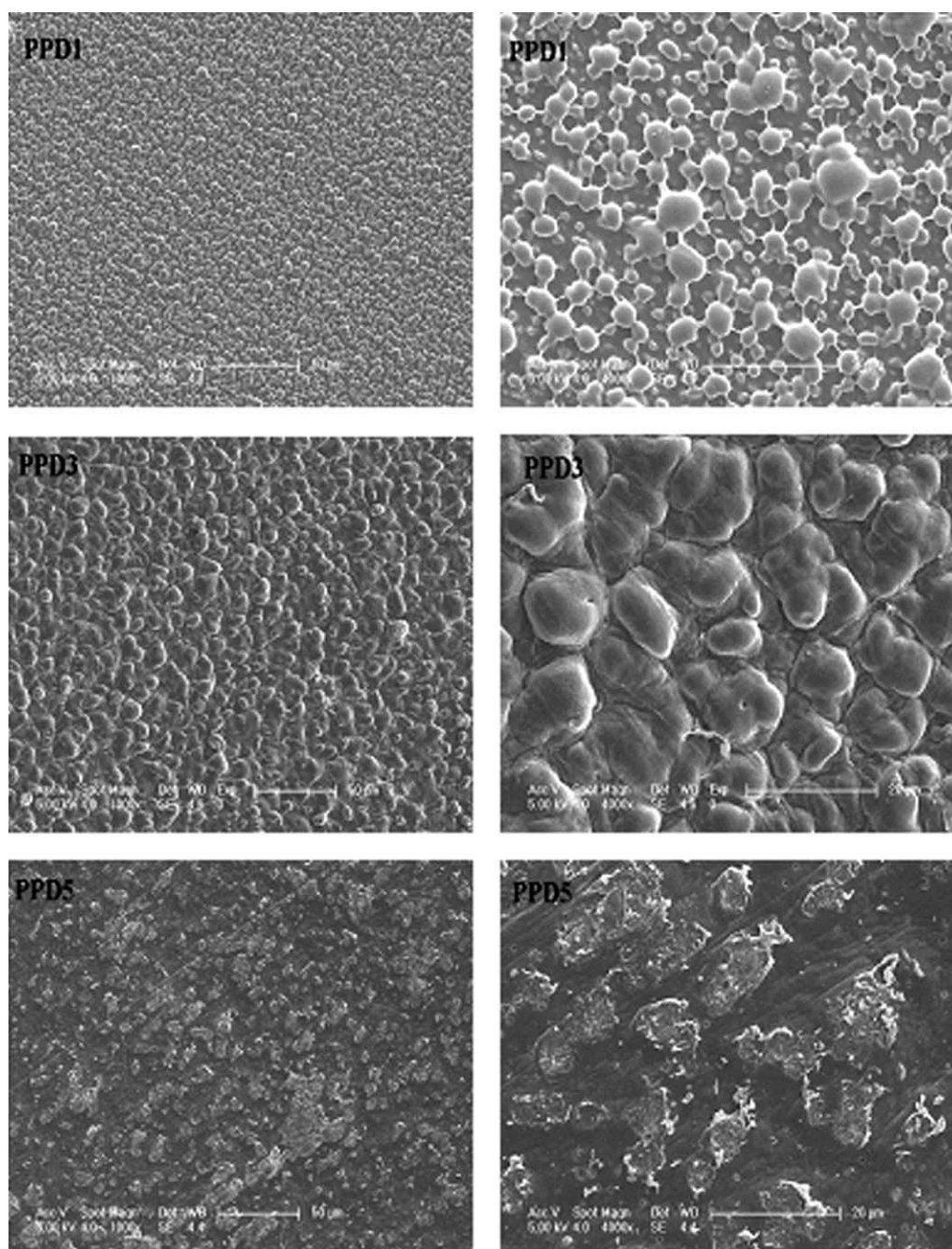


Figure 13 SEM images of iPP sheets after closed treatment for different times.

oxygen would inhibit the polymerization of MMA. As a result of these reasons, the grafting reaction of PMMA onto polyolefin surface was not pronounced. In the closed treatment, the oxidation of tributylborane was promoted by gradually diffused oxygen so as to avoid overoxidation. More alkoxy radicals were generated, followed by the formation of more grafting site on the polyolefin surface. Furthermore, insufficient amount of oxygen would not significant inhibit the polymerization of PMMA. When comparing with these two kinds of grafting program, the

oxidation of tributylborane triggered by gradually diffused oxygen which would give much higher grafting degree.

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