

Grafting of Telechelic Poly(lactic-co-glycolic acid) onto O₂ Plasma-Treated Polypropylene Flakes

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ABSTRACT: In this work, we described a facile approach to preparing polypropylene (PP) surface functionalized with telechelic poly(lactic-co-glycolic acid) (HO-PLGA-COOH). The PP flakes were first treated with oxygen plasma and then grafted with different molecular weight PLGA ($M_w = 50, 100,$ and 300 K) in dry dichloromethane solution with the addition of phosphorus pentachloride (PCl₅). The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy measurements were used to characterize the composition of the PP surface. The appearance of 1756 cm^{-1} for carbonyl (C=O) stretching and 1090 cm^{-1} for C—O—C and the morpholo-

gies observations by atomic force microscopy show that PLGA graft covered the surface of PP flake. The IR intensity at 1756 cm^{-1} increases with the decreasing M_w of PLGA, and the molecular weight of PLGA also influence the grafting of PLGA on PP. The contact angle was used to monitor the changes in hydrophilicity of PP flake surface along the treatment procedure. PLGA-grafted PP (PP-g-PLGA) was eventually obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 210–216, 2011

Key words: polypropylene; telechelic poly(lactic-co-glycolic acid); oxygen plasma; grafting

INTRODUCTION

Polypropylene (PP), a very important polymeric material, is used widely in both industrial and medical field because of its good chemical resistance, high-impact strength, and flexibility. Therefore, PP is commonly used in the production of packing materials, textiles, laboratory equipment, automotive components, medical implant materials (like hernia repair mesh), and so on. The wide application of PP has

made postpolymerization modification procedures a great interest very necessary for surface functionality.^{1–3} A typical postpolymerization modification is to increase surface reactivity or hydrophilicity by changing surface chemistry. The improved adhesion, printability, wettability, or biocompatibility is extremely desired in many applications. In the past several decades, numerous methods, like corona discharge, plasma treatment, photoinitiated grafting, and chemical etching, were frequently used to modify the surface of PP or polyethylene.^{4–15}

Hydroxyl-terminated molecules (including polymers) can be used as coiniciators in the polymerization of L-lactide (LA) in bulk or solution polymerization. For instance, LA was polymerized from the hydroxyl ending group of poly(ethylene glycol) to form block copolymers in solution.^{16–18} The solid Au substrates were first immersed into EtOH solution of HS(CH₂)₁₁(CH₂CH₂O)₃OH to obtain hydroxyl-terminated self-assembled monolayers on Au substrate, and then this Au substrates with hydroxyl groups were used as coiniciators to initiate ring-opening polymerization of LA with tin(II) octoate (Sn(Oct)₂) as catalyst, and the thickness of thin film of PLA on Au substrate is less than 100 \AA .¹⁹

Cold plasma or nonthermal plasma is a convenient technique to modify the surface of polymers.^{20,21} One of the major advantages of plasma is the

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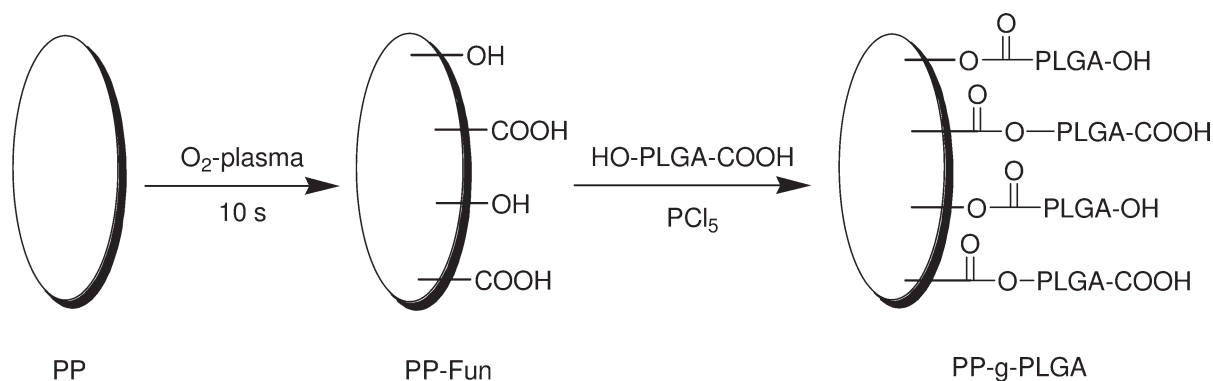
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Scheme 1 Schematic illustration of grafting of PLGA on polypropylene flake surface.

modifications are limited to the outermost layers of several hundreds angstroms while the bulk properties of polymeric material is not altered.²² Some typical gases: Ar, He, O₂, NH₃, and CF₄ were usually used. Generally, O₂-plasma treatment can introduce oxygen-containing functional groups, such as carboxylic acid groups, peroxide groups, and hydroxyl groups to the surface. Some useful monomer can be grafted on the surface of plasma-treated polymer by a postpolymerization, such as glycidyl methacrylate, acrylic acid, α -allyl glycoside, or heparin.^{23–31}

Poly(lactic-*co*-glycolic acid) (PLGA) has been successful as a biodegradable polymer, because it undergoes hydrolysis in the body to produce the original monomers, lactic acid, and glycolic acid, which is useful for sutures and implant.^{32,33} PLGA is synthesized by means of random ring-opening copolymerization of two different monomers, the cyclic dimers (1,4-dioxane-2,5-diones) of glycolic acid and lactic acid.³⁴

Here, we attempted to graft PLGA directly on the PP hydroxyl flake, which can be obtained through treating the PP flakes with O₂ plasma.

EXPERIMENTAL

Materials

Phosphorus pentachloride (PCl₅) and dichloromethane (CH₂Cl₂) were purchased from Wanqing Chemicals. Telechelic PLGA (HO-PLGA-COOH, $M_w = 50, 100, \text{ and } 300 \text{ K}$, LA : GA = 75 : 25), which was abbreviated as PLGA_{50K}, PLGA_{100K}, and PLGA_{300K}, was purchased from Shandong Daigang Company. PP was obtained from C. R. Bard. The dichloromethane was dried carefully by 5 Å molecular sieves before use. The native PP flakes with a thickness of about 0.3 mm were prepared by pressing molten PP sample. PLGA_{50K}, PLGA_{100K}, and PLGA_{300K} film samples were prepared by casting polymer solution in chloroform onto cleaned glass slides. Solvent was allowed to evaporate slowly at room temperature for 24 h, and then the films were dried under vacuum at 40°C.

Oxygen plasma treatment

PP was first washed with CH₂Cl₂ for 2 h to remove any additives, such as antioxidants, wetting agents, and other impurities. After dried under vacuum at 60°C for 2 h, they were flaked when melted. Then, the flake samples were, for the second time, cleaned with CH₂Cl₂ for 2 h. After dried under vacuum, then flakes were treated with oxygen-containing plasma in a plasma chamber (PDC-M, Chengdu Weike Spectrum Apparatus, China) for 10 s. Treatment was done with the oxygen flux of 800 mL min⁻¹ and the power of 40 W. The samples treated with O₂ plasma were functionalized with hydroxyl groups and carboxylic acid groups, which hereafter is denoted PP-Func.

Graft of PLGA on PP flake surface

About 0.5 g HO-PLGA-COOH was dissolved into 20-mL dry dichloromethane, and then excess phosphorus pentachloride was added to form the acid chloride HO-PLGA-COCl. Then, O₂ plasma-treated-PP flakes were put into the PLGA solution in CH₂Cl₂ with stirring for 10 h, then PP flakes were taken out from the solution and washed with dichloromethane for 2 h to remove adsorbed PLGA and finally dried at 60°C. The grafting reaction of HO-PLGA-COOH and PP flake was illustrated in Scheme 1.

Characterizations of PP flake surface

Atomic force microscopy observation

The topography of the PP flake was probed by the atomic force microscopy (AFM, Agilent, PicoPlus).

ATR-FTIR measurement

The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were obtained using a Nicolet 5700 spectrometer (Thermo, USA) with an

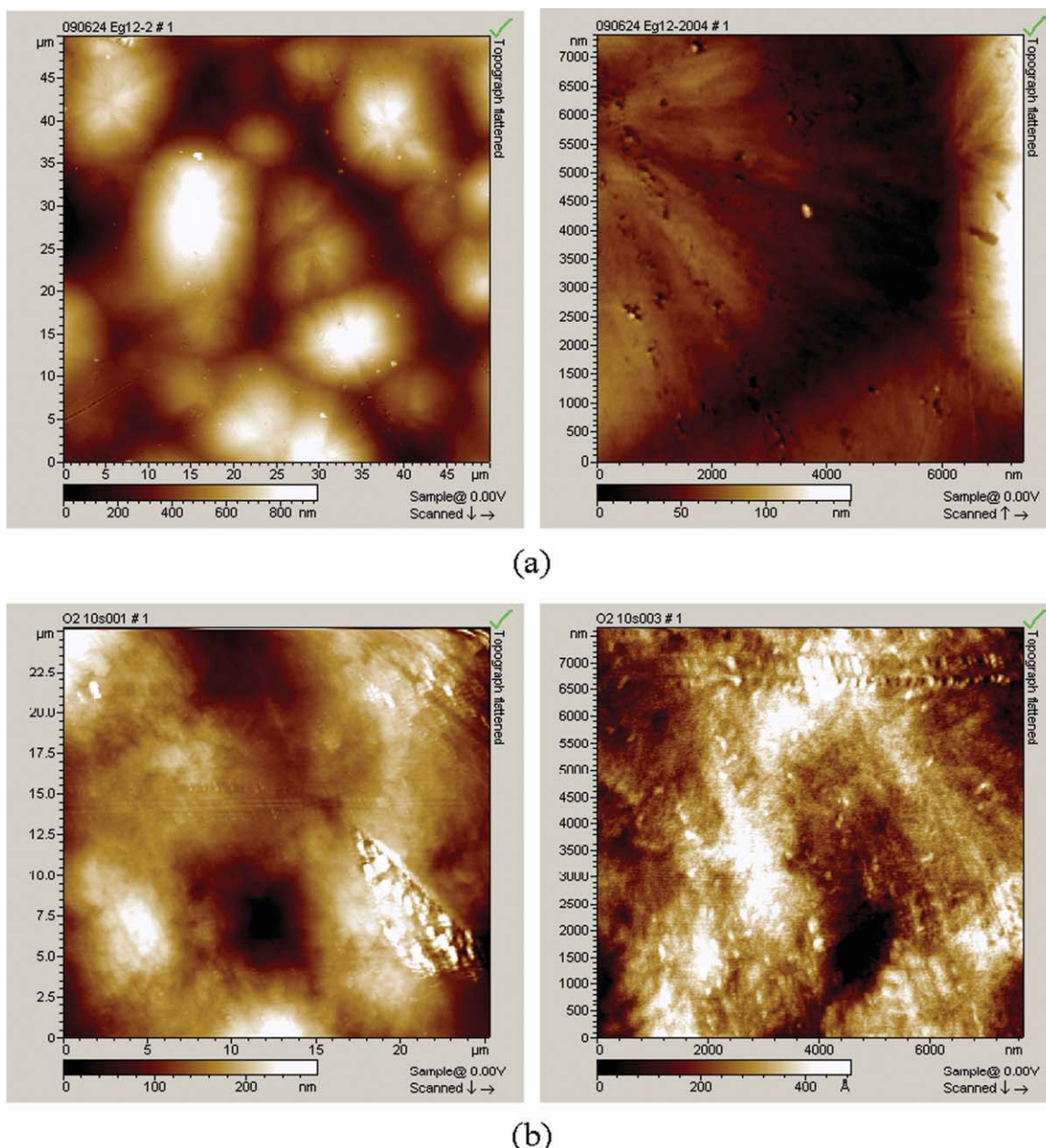


Figure 1 AFM images of original PP flake (a) compared with that of oxygen-containing plasma treated PP flake (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

internal reflection accessory ZnSe crystal at an angle of 45° and a DTGS KBr detector. Spectra were recorded at 4 cm^{-1} resolution between 4000 and 400 cm^{-1} and were the sum of 256 individual scans.

Water contact angle measurement

The sessile drop method was used for contact angle measurements at $20^\circ\text{C} \pm 1.5^\circ\text{C}$ using a commercial contact angle meter (CAM 200, KSV Instruments, Finland). Ultra pure water droplets ($10\ \mu\text{L}$) were placed at six different positions for one sample, and then the average value was obtained.

X-ray photoelectron spectroscopy

XPS (AXIS-ULTRA^{DLD} spectrometer, KRATOS Analytical, UK) was used to determine the surface composition of PP flakes at different process stage. The monochromatic Al $K\alpha$ X-rays source was operated at 1486.7 eV, and the anode X-ray source was operated at 15 kV and 8.9 mA. Survey spectra were acquired from 0 eV to 1200 eV binding energy (BE) with a pass energy of 160 eV, a step size of 1.0 eV, and a dwell time of 50 ms. For high-resolution spectra, a pass energy of 17.9 eV, an energy step of 0.1 eV, and a dwell time of 1.2 s were used with a typical average of 12 scans. The operating pressure of the spectrometer

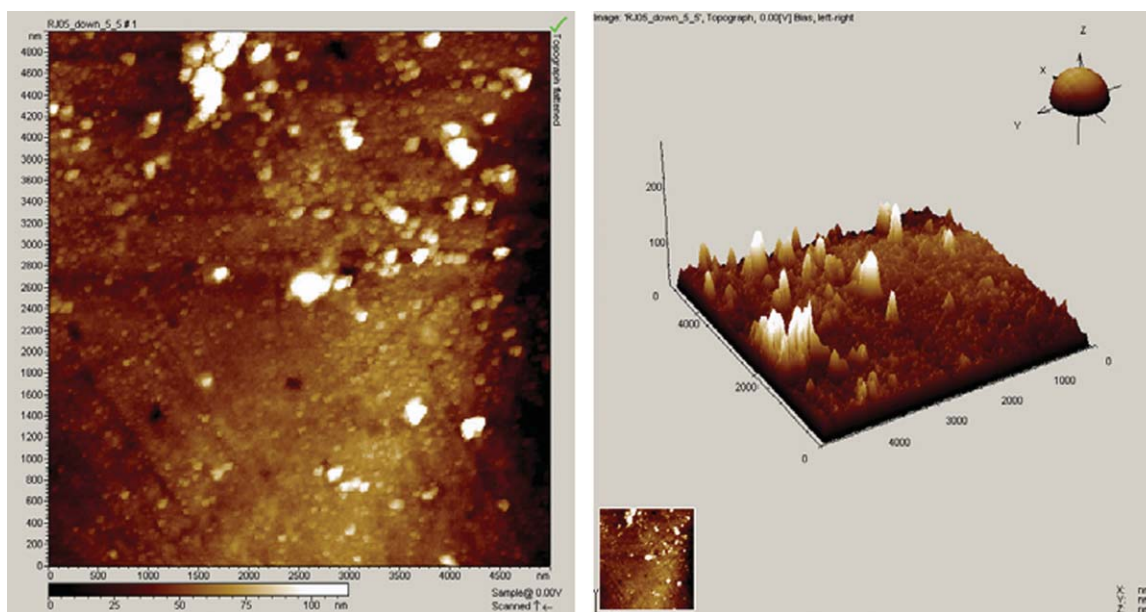


Figure 2 AFM images of the PP-g-PLGA_{50K} flake. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was $\sim 10^{-9}$ mbar. All data were collected and analyzed using software provided by the manufacturer.

RESULTS AND DISCUSSION

The surface of native PP flake is smooth and flat, where some spherulites can be found clearly, because the molten method was used to prepare these PP flakes. The diameter of these visible spherulitic crystallines in AFM micrographs ranges from 5 to 15 μm [Fig. 1(a)].

After the samples treated with O₂ plasma for 10 s, the smooth in flat surface was destroyed although the profile of some spherulites still loomed and became rougher as seen in Figure 1(b).

The HO-PLGA-COCl can be easily attached to the PP surface using the type of coupling reaction as illustrated in Scheme 1. The telechelic polymer PLGA has different ending groups, hydroxyl and carboxylic acid, resulting in two possibilities of coupling reaction, one is that the ending group carboxylic acids of PLGA reacted with hydroxyl groups of PP-Func, and

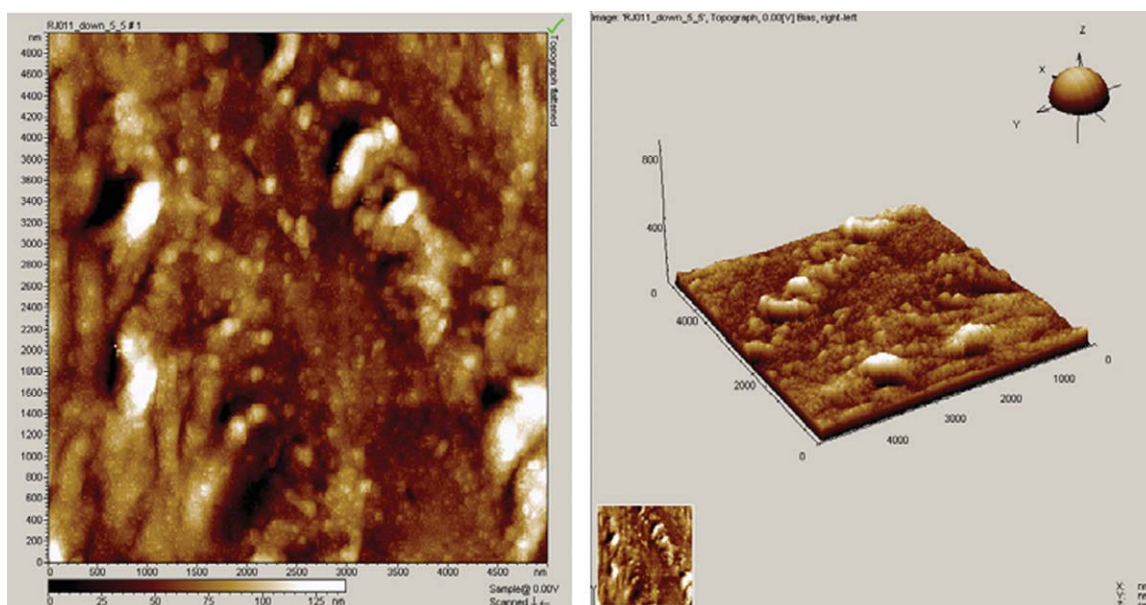


Figure 3 AFM images of the PP-g-PLGA_{100K} flake. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

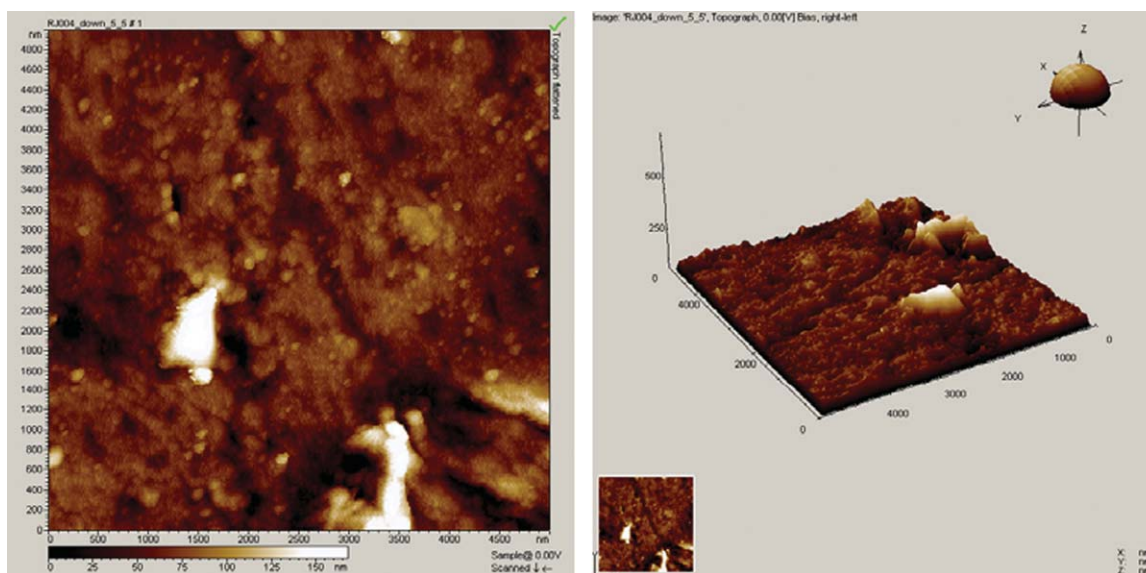


Figure 4 AFM images of the PP-g-PLGA_{300K} flake. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

another is that the ending groups hydroxyls of PLGA reacted with carboxylic acid groups of PP-Func.

The morphologies of PP-g-PLGA change obviously with the different molecular weight of PLGA. When HO-PLGA-COOH with $M_w = 50$ K was used to coupling reaction, a rougher surface with the numerous narrow peaks with maximal height of about 100 nm was formed (Fig. 2).

As expected, when the molecular weight of PLGA increases to 100 or 300 K, only the relatively smooth surface with gently rolling hills was found, which is a little similar to the surface of O₂ plasma-treated PP flake; therefore, the effect of coupling reaction is not very obvious (Figs. 3 and 4).

The ATR-FTIR measurement also illustrated the change of surface composition before and after the coupling reaction (Fig. 5).

The IR spectrum obtained from the surface of O₂ plasma-treated PP flakes did not show a significant difference from that of original PP flake because of the detection limit of ATR-FTIR technology (the lowest detection concentration is ~ 0.1 – 1% , and the depth of information is ~ 0.1 – 3 μm). There was no absorption peak around 1756 cm^{-1} of C=O in the IR spectrum in the surface of the O₂ plasma-treated PP flakes (curve a). The surface of the O₂ plasma-treated PP flake was presumed to be hydroxyl and carboxylic acid functional groups according to reference.^{28,29} After the coupling reaction with PLGA, the stretching peaks of carbonyl (C=O) and C–O–C is about 1756 and 1090 cm^{-1} (curves b, c, and d). The intensity of peaks at 1756 and 1090 cm^{-1} increases with the decreasing molecular weight of PLGA. The coupling reaction of PLGA_{50K} with PP flakes can lead to the highest intensity of the peak at 1756 cm^{-1}

and 1090 cm^{-1} , respectively, (curve d) compared to that of PLGA_{100K} and PLGA_{300K}. These IR measurements indicate that the low-molecular weight PLGA is more easily to couple with PP, which is in accordance with the direct AFM morphologies observations.

At the same time, the IR spectra of PP-g-PLGA are not completely same as that of pure PLGA_{50K} film (Fig. 6), which implies the graft thickness of PLGA on PP flakes is rather thin.

The possible reason is that the higher molecular weight, 100 or 300 K, meaning the longer chain and an bigger steric hindrance, prevents the PLGA-COCl chain from effectively coupling with PP-Func;

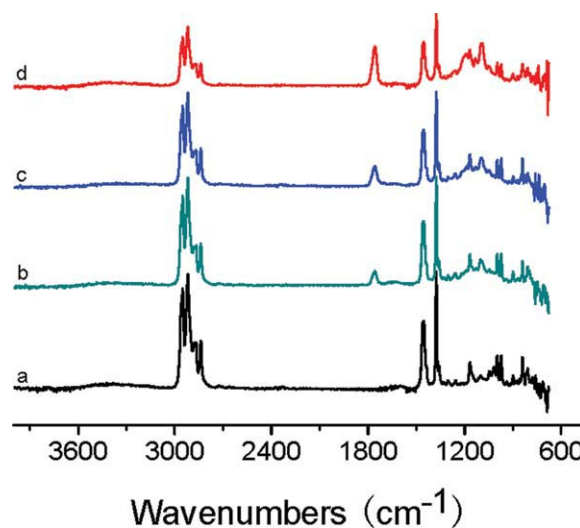


Figure 5 ATR-FTIR spectra of the O₂ plasma treated PP (a), PP-g-PLGA_{300K} (b), PP-g-PLGA_{100K} (c), and PP-g-PLGA_{50K} (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

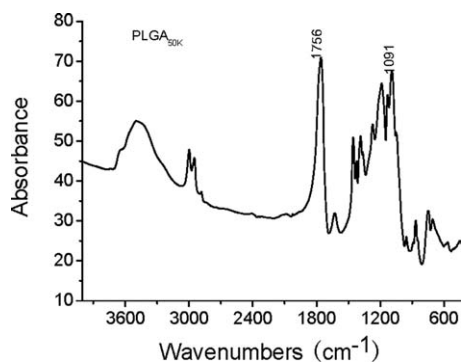


Figure 6 ATR-FTIR spectrum of the pure PLGA_{50K}.

therefore, the graft layer of PLGA_{100K} and PLGA_{300K} is thinner than that of PLGA_{50K}; correspondingly, the intensity of peaks at 1756 cm⁻¹ of PP-g-PLGA_{50K} increased compared to that of PP-g-PLGA_{100K} or PP-g-PLGA_{300K}.

Figure 7 shows the XPS C1s core-level spectrum of the PP-g-PLGA_{50K} flake, which can be curve fitted with two peak components, having BEs at about 284.6 eV and 286.8 eV, attributed to the C—O and O—C=O in PLGA grafts.

Table I shows the change in water contact angle of PP flake at different treatment stage comparison with that of pure PLGA film. For the original PP, the water contact angle is 106°. The contact angle of pure PLGA film ranges from 70.9° to 87.6° with molecular weight, showing slightly hydrophilic. After treatment of O₂ plasma, the contact angle decreased to 77° due to the introduction of oxygen-containing groups, such as —OH, —COOH, and so on. With the coupling reaction of PLGA-COCl with PP flake, and the corresponding formation of a rougher surface, the contact angle increased to about 103°–104°, leading to a slightly hydrophobic surface.

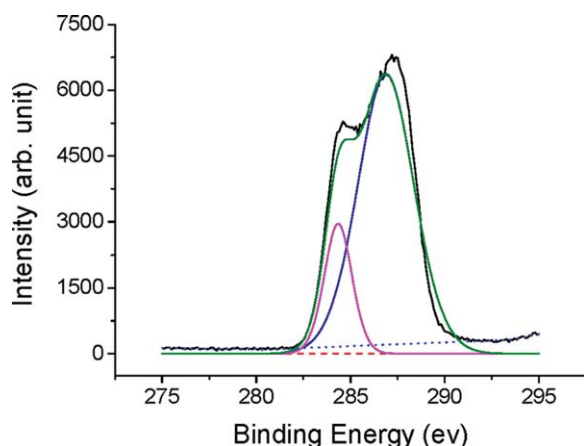


Figure 7 XPS C1s core level spectra of PP-g-PLGA_{50K}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Water contact angle of PP-g-PLGA_{50K}, PP-g-PLGA_{100K}, PP-g-PLGA_{300K}, O₂ plasma-treated PP flakes, and pure PLGA film

Sample	Contact angle
PP-g-PLGA _{50K}	103.8
PP-g-PLGA _{100K}	103.5
PP-g-PLGA _{300K}	104.8
O ₂ -plasma-treated PP	77.2
PLGA _{50K}	70.9
PLGA _{100K}	87.6
PLGA _{300K}	76.4

CONCLUSIONS

The combination of the first O₂ plasma treatment and the subsequent coupling reaction of telechelic HO-PLGA-COOH with the addition of PCl₅ is a facile method to graft PLGA to the PP flakes surface. The ATR-FTIR measurements indicate the change in surface composition, namely, the appearance of carbonyl (C=O) and C—O—C stretching peaks, the XPS measurement confirmed the presence of O—C=O and C—O groups of PLGA grafts on PP flake, and AFM observation further showed the morphology change caused by PLGA grafting. The grafting results of PLGA_{50K}, PLGA_{100K}, and PLGA_{300K} indicate that the lower molecular weight PLGA_{50K} can be easily grafted on the surface of PP flakes than the higher molecular weight PLGA_{100K} and PLGA_{300K}. The further IR spectrum comparison of PP-g-PLGA and pure PLGA film suggests that the graft thickness of graft PLGA on PP flakes is rather thin. The further research, including the quantification of grafting density (or determination of thickness of graft layer) and the relation of topography and contact angle, still needs to be performed.

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