Direct Graft Polymerization of L-lactic Acid onto Oxidatively Functionalized Polypropylene Flakes

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A facile approach to prepare surface-functionalized polypropylene (PP) with L-lactic acid (LLA) was described. The polypropylene flakes were first treated with an aqueous chromic acid solution and then grafted with L-lactic acid monomer in the aqueous solution. The ATR-FTIR spectroscopy measurements indicate that the existence of carboxylic acid groups (1757 cm^{-1} for carbonyl; 3350 cm^{-1} and 1041 cm^{-1} for hydroxyl in carboxylic acid groups) and morphologies observations by atomic force microscopy show that poly(L-lactic acid) graft covered the surface of polypropylene flake and water contact angle measurements were carried out to monitor the change in hydrophilicity of polypropylene flake surface along the treatment procedure. The cover percentage of poly(L-lactic acid) graft on polypropylene flake is more than 60 %. Poly(L-lactic acid)-grafted polypropylene (PP) (PP-g-PLLA) was eventually obtained with the loss of mechanical property of polypropylene.

Key Words: Polypropylene, L-lactic acid, Graft polymerization.

INTRODUCTION

As a kind of important polymeric material, polypropylene are used widely in both industrial and medical field because of the high chemical resistance, the high impact strength and the flexibility, such as packing materials, textiles, laboratory equipment, automotive components, medical implant materials (like hernia repair mesh) *etc.* The wide application of polypropylene has made post-polymerization modification procedures very necessary[1-3]. A typical post-polymerization chemistry is the surface modification to increase surface reactivity or hydrophilicity. The improved adhesion, printability, wettability or biocompatibility is extremely desired in many practical instances.

Whitesides *et al.*[4-8] oxidized the polyethylene film with chromic acid/sulfuric acid and obtained polyethylene carboxylic acid (PE-COOH) and investigated the distribution of polar organic functional carboxylic acid and subsequent conversion and provided detailed wettability and ATR-FTIR adsorption information on the composition of a treated polyethylene film surface. Bergbreiter *et al.*[9,10] modified polyethylene and polypropylene by hyperbranched grafting with a poly(acrylic

acid) (PAA) graft, where the used strategy is called the "forgiving graft-on-a-graft". These resulting hyperbranched grafts are stable to repeated treatments with strong aqueous acid or base.

In addition to the above chromic acid oxidation, numerous other methods, like corona discharge, plasma treatment, photo-initiated grafting and chemical etching, were frequently employed to modify the surface of polypropylene or poly-ethylene[11-25].

Poly(lactic acid) (PLA) is a kind of natural polyester with biodegradable, bioabsorbable and biocompatible properties, which currently used in surgery (such as sutures), tissue engineering, drug delivery and packaging applications[26,27]. High molecular weight poly(lactic acid) mainly was synthesized at higher temperature by a ring-opening polymerization of lactide, which is a cyclic diester of lactic acid[28,29].

Hydroxyl-terminated molecules (including polymers) can be used as co-initiators in the polymerization of L-lactide (LA) in bulk or solution polymerization. For instance, L-lactide was polymerized from the hydroxyl end group of poly(ethylene glycol) (PEG) to form block copolymers in solution[30,31]. The solid Au substrates with hydroxyl groups was grafted with

L-lactide (LA) and formed a poly(lactic acid) film of less than 100 Å[32,33].

As the widely used polymeric materials, polypropylene surface needs to be modified to antibacterial properties. However, to our knowledge, the surface modification of polypropylene flakes with graft polymerization of L-lactic acid has not been reported so far[34,35]. Very different from the earlier ring-opening polymerization grafting of L-lactide (LLA) on hydroxyl-terminated substrates, here we attempted to polymerize L-lactic acid directly on the polypropylene carboxylic acid flake, or the carboxylic acid-terminated polypropylene (PP-COOH) flake, which can be obtained through treating the polypropylene flakes with chromic acid. In this polymerization grafting of L-lactide, polypropylene-carboxylic acid can be considered as the "macromonomers".

EXPERIMENTAL

Tin(II) dichloride dihydrate ($SnCl_2 \cdot 2H_2O$), methane dichloride (CH_2Cl_2) and succinic anhydride were purchased from Shanghai Chemical Reagent Inc. and used as received. 88 % L-lactic acid aqueous solution was purchased from Jinan Institute of Medical Instrument and used as received. Polypropylene was obtained from C.R. Bard, Inc. The native polypropylene flakes with a thickness of about 0.3 mm and a diameter of 1 cm were prepared by pressing molten polypropylene.

Oxidation of polypropylene: Polypropylene flake samples were first extracted with CH_2Cl_2 for 24 h to remove the additional antioxidants and other soluble additives. After dried under vacuum, they were treated at 85 ºC for 10 min with an oxidizing solution containing mixture of H_2SO_4, CrO_3 and water (1:1:2 by weight). After this period, the samples were rinsed 4 times first with distilled water and then with acetone and finally allowed to air-dry before being washed with CH_2Cl_2. The sample after oxidation was named polypropylene carboxylic acid, which is denoted PP-COOH.

Graft polymerization of L-Lactic acid on polypropylene flake surface. The PP-COOH flake samples were placed into a two-neck flask filled with 5 mL 85 % L-lactic acid aqueous solution and 0.018 g (0.18 mmol) succinic anhydride and 0.030 g (0.13 mmol) $SnCl_2 \cdot 2H_2O$ as catalyst. The poly-condensation reaction proceeded at 160 ºC for 10 h. The polypropylene flake floated on the solution at the beginning of reaction. In order to have polypropylene flake contacting with aqueous lactic acid fully, the violent stirring was carried out. After this period, the polypropylene flake samples sunk at the bottom of flask and were took out and washed first with distilled water and then with methane dichloride and finally dried at 60 ºC. (**Scheme-I**)
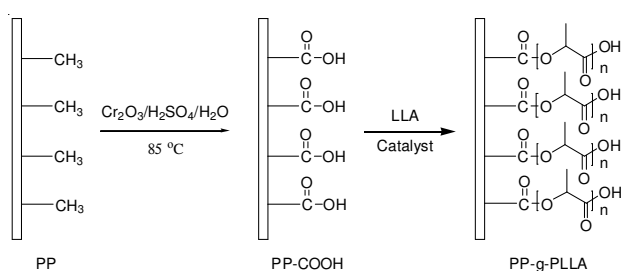
Scheme-I Schematic illustration of polymerization grafting of L-lactic acid on polypropylene carboxylic acid flake surface

Characterizations of polypropylene flake surface: The surfaces of the polypropylene flake were probed by the atomic force microscopy (AFM, Agilent, PicoPlus). The attenuated total reflectance fourier transform infrared (ATR-FTIR) spectra were obtained using a Nicolet 5700 spectrometer (Thermo, U.S.A.) with a Wilks model 10 ATR accessory at an angle of 45º using a KRS-5 crystal.

The sessile drop method was used for contact angle measurements at 20 ± 1.5 ºC using a commercial contact angle meter (Solon Tech. Shanghai, China). The diameter of droplet used for the measurement was *ca.* 2 mm. Ultra pure water droplets were placed at six different positions for one sample. Then the average value was obtained. The experimental error of the measurements was about ± 2º.

RESULTS AND DISCUSSION

For the native polypropylene flake, *i.e.*, the unoxidized flake, its surface is smooth and flat. With the different magnification, atomic force microscopy observations indicate that there are some spherulites in the surface of polypropylene flakes because a molten method was used to prepare these polypropylene flakes. The diameter of these visible spherulitic crystallines in atomic force microscopy micrographs ranges from *ca.* 5 μm to *ca.* 15 μm. (Fig. 1).
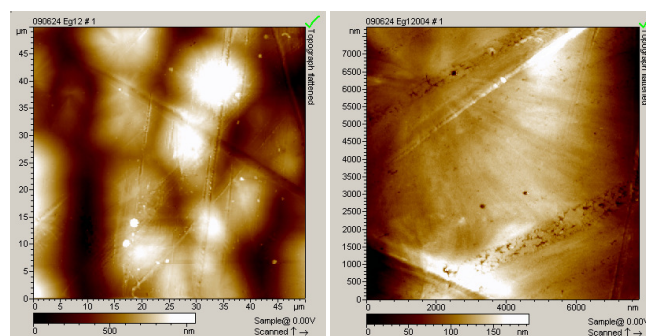
Fig. 1. Atomic force microscopy images of native polypropylene flake with the different magnifications

After the oxidation of chromic acid at 85 ºC for 10 min, as can be seen in the atomic force microscopy images in Fig. 2, no intact spherulites in the surface survived although the profiles of some remained spherulites still loomed, these spherulite structures of polypropylene flake surface were heavily destroyed and therefore the surface of polypropylene flake become rougher (Fig. 2).
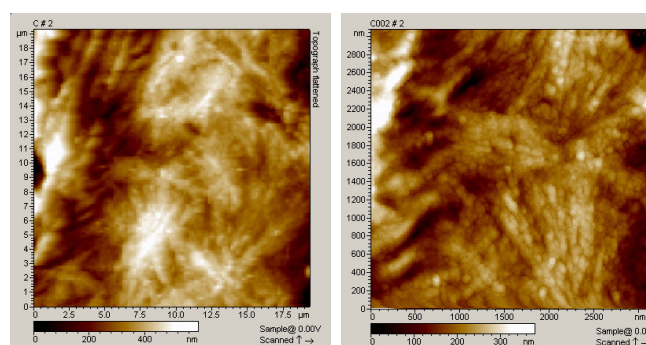
Fig. 2. Atomic force microscopy images of oxidized polypropylene (PP-COOH) flake with the different magnifications

Because ATR-IR spectroscopy can only analyze a relatively thick interface of 1-10 μm and possible lower surface density of carboxylic acid groups in a monolayer, no adsorption peaks of carbonyl (C=O) were observed in IR spectroscopy[24]. Fig. 3 presents the ATR-FTIR spectra of the chromic acid oxidized polypropylene flakes (PP-COOH flake, the below curve) and poly(L-lactic acid) grated polypropylene flakes (PP-g-PLLA flake, the above curve). There was no absorption peak around 1756 cm^{-1} in the spectrum for PP-COOH flakes. The surface of chromic acid oxidized polypropylene flake was presumed to contain carboxylic acid functional groups.
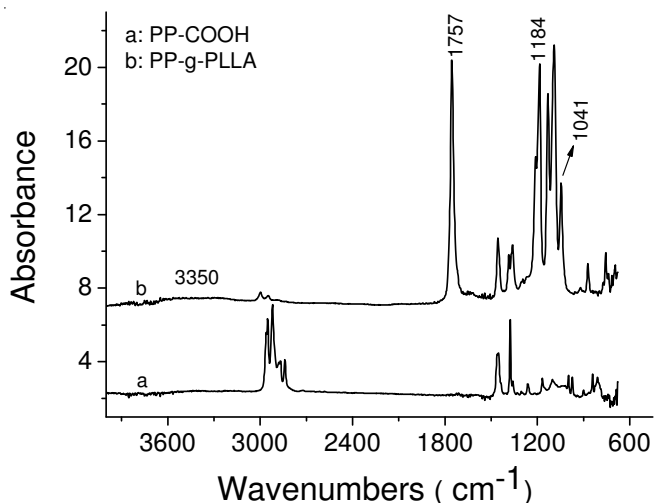

Fig. 3. ART-FTIR spectra of oxidazed polypropylene (PP-COOH) flake and poly(L-lactic acid), grafted polypropylene (PP-g-PLLA) flake

After grafted with poly(L-lactic acid), there are some new absorption peaks in the above IR curve in Fig. 3. The IR absorption peak at 1756 cm^{-1} was assigned for the abundant carbonyl C=O stretching of ester groups in bulk poly(L-lactic acid) graft and peak at 1184 cm^{-1} is for the symmetric stretching of C-O-C. According to **Scheme-I**, poly(L-lactic acid) grafts grew on the polypropylene substrate and finally were theoretically terminated with carboxylic acid groups. One broad absorption band can be seen at 3350 cm^{-1} and another peak was found around 1041 cm^{-1} for the poly(L-lactic acid)-grafted polypropylene flakes, which can be assigned to the hydroxyl groups of the carboxylic acid of poly(L-lactic acid) grafts.

The change in morphologies of poly(L-lactic acid)-grafted polypropylene flake surface is compared with that of both native polypropylene flakes and chromic acid oxidized polypropylene flakes. Atomic force microscopy show that the poly(L-lactic acid) graft was effectively covered on the polypropylene flake surface. However, this poly(L-lactic acid) film cannot completely coat the surface of polypropylene flake, there is still bare polypropylene surface.

Following the treatment procedure, the water contact angle of polypropylene flake changed accordingly. For the native polypropylene flake, the water contact angle measurements is 106º and indicates that the polypropylene surface is hydrophobic. After the oxidation of chromic acid, the formed carboxylic acid groups on the polypropylene surface leads to a slight hydrophilicity with a contact angle of 93º and the further grafting polymerization of L-lactic acid on polypropylene surface
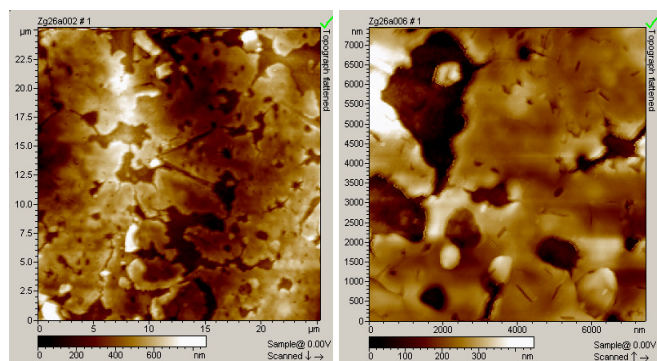

Fig. 4. Atomic force microscopy images of poly(L-lactic acid)-grafted polypropylene (PP-g-PLLA) flake with the different magnifications

recover the water contact angle to 104º (Fig. 5). The surface of poly(L-lactic acid)-grafted polypropylene flake is hydrophobic whereas the water contact angle of the pure poly(L-lactic acid) smooth film is 77º.[36,37] These two measured water contact angles seem paradoxical each other. A theoretical calculation probably can help us to interpret this phenomenon. The relationship between the contact angle of a flat surface θ and that of a suitably rough surface θ$_r$ can be expressed by Eqn. (1)[38,39]:

$$\cos \theta_r = f_1\cos\theta - f_2 \qquad (1)$$

where, f$_1$ and f$_2$ are the fractional interfacial areas of the smooth PLLA film and of the air in the poly(L-lactic acid)-grafted polypropylene flake, respectively and f$_1$ + f$_2$ = 1. From Eqn. (1), f$_1$ can be calculated according to the values of θ$_r$ and θ. Here θ$_r$ = 104º and θ = 77º, so f$_1$ = 0.6. The calculation result indicates that the cover percentage of poly(L-lactic acid) on polypropylene flake is about 60 %. Although the calculated value is obviously lower than the directly atomic microscopy observations, the calculation result of the contact angle and direct atomic force microscopy morphologies observations coincidentally suggest that poly(L-lactic acid) was grafted on polypropylene flake.
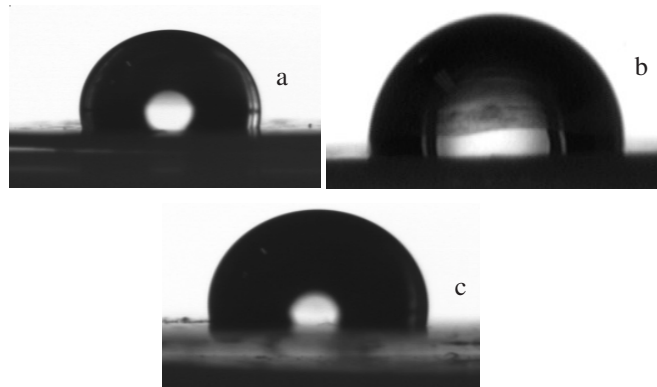

Fig. 5. Water contact angle of native PP, PP-COOH and PLLA-g-PP flakes: a) Native PP flake (105°); b) PP-COOH flake (93°); PP-g-PLLA flake (104º)

It is worth noting that the mechanical properties of polypropylene have lost severely at 160 ºC. Some polypropylene flakes broken into small pieces and mixed with the formed poly(L-lactic acid). The survived polypropylene flake became rather fragile and therefore lost their application value.

Conclusion

The chromic acid oxidized polypropylene (PP-COOH) flakes can be used effectively as co-initiator to undergo a poly-condensation reaction with L-lactic acid momomer in aqueous solution at heating condition. Consequently, poly (L-lactic acid) grew on the surface of PP-COOH flakes, that is to say, L-lactic acid was grafted eventually onto the surface of poly-propylene flakes. ATR-IR spectra measurements together with atomic force microscopy obversations confirmed the changes in chemical and morphological aspect of the poly(L-lactic acid)-grafted polypropylene flakes compared with that of the native polypropylene or PP-COOH flakes surface. The hydrophilicity changes along the chemical etching and the subsequent grafting process were monitored by the static water contact angle measurements. The calculation of water contact angle indicates that the cover percentage of poly(L-lactic acid) on polypropylene flake is more than 60 %. In order to identify the surface composition of poly(L-lactic acid)-grafted polypro-pylene flakes, the further experiment, like X-ray photoelectron spectroscopy (XPS) measurement, has to be carried out. The higher polycondensation temperature needs to be decreased in maintain bulk property of polypropylene for the purpose of practical biomedical application.

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