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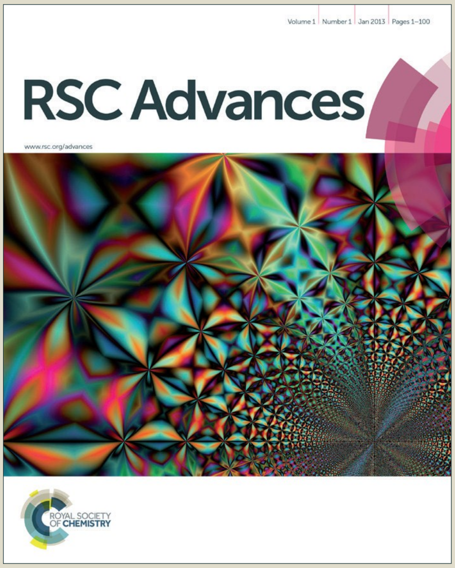

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Preparation and Application of Novel Biodegradable Polyurethane Copolymer

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ABSTRACT

Polyurethanes and polylactides were widely used for excellent mechanical properties, biocompatibility, flexible construction options and degradable, hydrolyzable and biocompatible characteristics, respectively. Herien, a novel polyurethane copolymer poly($_{\mathrm{L}}$-lactide)-b-(4,4'-diphenylmethane diisocyanate)-functionalized graphene (PLLA-b-PU-*f*-G) was prepared by ring-opening polymerization (ROP) of LLA using phenol-functionalized graphene (G-*f*-OH) and tin octoate as initiator and catalyst respectively, followed by condensation polymerization of OH-terminated poly($_{\mathrm{L}}$-lactide)-functionalized graphene (G-g-PLLA) and 4,4'-diphenylmethane diisocyanate (MDI). The compositional analysis and structural characterization of resulting materials were done by FTIR, ^{1}H NMR, TG, DSC. FTIR and^{1}H NMR results clearly showed that graphene can be covaletly functionalized with polyurethane and polylactides by the proposed approach. DSC analysis indicated that with increase of graphene content, the value of Tg of G-g-PLLA polymer tends to increase mildly. Simulative ocean hanging plate experiment indicated that the copolymer material has better antifouling performance than the general polyurethane. Static hydrolysis experiment showed that the incorporation of graphene increased polyurethane hydrolysis ability, which indicated that the functionalized PU can be expected to serve as a marine antifouling coating by confering a smooth surface.

1. Introduction

Biodegradable polyurethanes (PUs) have been extensively used to various field due to its excellent mechanical properties, biocompatibility and flexible construction options[1-2]. The application areas can be expanded via functional modification, PUs with degradable performance are attractive for application such as biomedical-engineering scaffolds[3], drug delivery carrier[4], marine antifouling coatings[5-6]. Recently, the nontoxic, safe and reliable performance of polyurethane has stimulated tremendous interest in the development of nonbiocidal antifouling coatings. Jielin Ma et al. [7] combined thiol-ene click reaction with condensation reaction to prepare a biodegradable polyurethane with N-(2,4,6-trichlorophenyl)maleimide pendant groups, they demonstrated the degradation can lead to a self-renewal surface to reduce the accumulations of biofouling. On the other hand, Kaibin Li [8] succeed in the synthesis of castor oil/pentaerythritol triacrylate-based UV curable waterborne polyurethane acrylate, compositional and performance test demonstrated that water resistance, glass transition temperature and thermal performance was improved.

It is known that polylactides(PLAs) possess the performance of degradation, hydrolyzation as well as biocompatibility[9], which provide us an opportunity to further develop its application, such as thermoplastic plastics and films as well as fiber[10-12]. A kind of renewable, biodegradable and environmentally friendly polylactides composite material can be formed by means of block, graft and co-polymerization. Marc A. and co-workers [13] fabricate PLA-PM-PLA triblock copolymer materials via atom transfer radical polymerization (ATRP), they found this kind of polymer possess a low transmission temperature and a increased degradation rate. Graphene with a two-dimentional carbon nano-construction have showed significant scientific and economic application prospects in the field of chemistry, physics, materials and electronics[14,15]. Especially, the performance of high mechanical strength and antibacterial function make it become an ideal nanofiller. Recently, a number of studies indicated that graphene added to composite materials can enhance the antibacterial performance of system. Tengfei Tian et al. [16] obtained GO-IONP-AgNPs composite nano-materials by growing both iron oxide nanoparticles (IONPs) and silver nanoparticles (AgNPs) on the surface of graphene oxide (GO), which showed much higher antibacterial efficiency. Graphene/Graphene derivatives/L-lysine composite material was prepared by the electrostatic interactions and covalent bonding which can provide potent antibacterial activity with a noncytotoxic effect on environment[17]. Francois Perreault et al.[18] described the design of thin-film composite polyamide membranes containing biocidal graphene oxide nanosheets exhibits excellent antibacterial activity.

Recently, numerous synthetic pathways have been proposed to prepare biodegradable polyurethane materials. However, polycaprolactone (PCL), poly lactic acid (PLA) etc. as common biodegradable polyurethane materials usually exist problems such as high crystallization, slow hydrolysis rate and poor adhesion to the matrix.While considerable progress has been made in the design of biodegradable polyurethane materials, ongoing research in this area should result in the development of even better biodegradable materials in the future. In the present work, the novel polyurethane hybrid materials have been prepared, in which degradation rate is controllable via adjusting the mass ratios of graphene (G) and $_{\mathrm{L}}$-lactide (LLA). A series of degradable polyurethanes were designed and synthesized using OH-terminated poly(L-lactide)-functionalized graphene as initiator, which can react with 4,4'-diphenylmethane diisocyanate (MDI). Chemical covalent incorporation of graphene into a biodegradable polymer chain is expected to improve the antibacterial performance of polymer composite materials. On the other hand, covalent chemical functionalization of graphene is favorable to prolong service life of polyurethane materials due to its strong coordinate bond with inorganic and organic surfaces. In addition, the incorporation of graphene into polyurethane is used to make the product more biodegradable. Thus, a novel degradable polyurethane composite materials containing graphene composition was successfully produced, which have a high potential application for biodegradable coatings.

2. Experimental

2.1. Materials

Natural flake graphite with an average particle size of 300 meshand a purity of >99% was supplied by Qingdao Haida GraphiteCo.,Ltd,China. Dimethylformamide (DMF, 99%, ShanghaiChemical Industrial Co., Ltd., China) was purified by stirringover KOH for 48 h and then distilled under reduced pressure. L-Lactide (LLA), obtained from Aldrich, was recrystalized twice from anhydrous ethyl acetate and stored under dry nitrogen prior to use. 1,4-Butane diol (1,4-BDO) from Aldrich was dried under reduced pressure for 2h prior to use. Toluene, obtained from Aldrich, mixed with small pieces of sodium metal, zeolite and indicator diphenyl ketone, was reluxed untill the solution turns blue, and then distilled under atmospheric pressure prior to use. 3,4-Dihydroxybenzaldehyde, N-methylglycine, 4,4'-diphenylmethane diisocyanate (MDI), stannous 2-ethylhexanoate ($Sn(oct)_2$), were purchased from Aldrich and used without further purification. All other reagents and solvents were purchased from commercial suppliers and used as received.

2.2. Physical measurements

Fourier Transform Infrared (FTIR) spectra were measured with a PE Spectrum One B instrument, The spectra were collected at 64 scans with a spectral resolution of 4 cm^{-1} by KBr disk method. Differential Scanning Calorimetry (DSC) was performed on a DSC 200F3 Netzsch Co., Germany under a nitrogen flow of 50 mL/min. After the sample was heated to 230^{o}C at a rate of 50 °C/min and equilibrated at the temperature for 5 min to remove thermal history, it was cooled to 30 °C at a rate of 10 °C/min. Then, it was heated to 230 °C at a rate of 10 °C/min. Thermagravimetric analysis (TG) on a NETZSCH TG 209F1 instrument was performed under nitrogen atmosphere at a heating rate of 5 °C/min in the range room temperature to 800 °C. Static hydrolysis experiment: a solution of 20% (w/v) polyurethane in refined tetrahydrofuran was dripped onto a epoxy resin panel (25 mm × 25mm in size). The panels coated with PU-Gx were kept at room temperature for 5 days to make THF volatilized completely. Then, the weight (m_o) of each dried coating together with its panel was measured before dipping into natural seawater that was renewed once two weeks. After 10 days, the panel was taken out, rinsed with deionized water , and dried at 60°C in a vacuum oven for 24 h, and the weight (m_s) of the panel was measured again. The mass loss was designated as (m_s-m_o). Simulative ocean hanging plate experiment: we used the natural seawater. Different types of resin are dissolved in tetrahydrofuran and then applied to the epoxy plate thickness of 0.5 mm，it was put into the sea water to soak for 30 days after it is dried

2.3 Preparation of graphite oxide and graphene

Graphite to Graphite oxide: graphite oxide, a pseudo-two-dimensional solid in bulk form, was prepared from natural graphite powder by oxidation with $KMnO_4$ in concentrated H_2SO_4 according to Hummers' method[19]. Concentrated H_2SO_4 (46 mL) was poured into the 250 mL three neck flask and stirred in an ice bath until the temperature dropped to 0~3 ^oC. Natural graphite (2.0 g) and $NaNO_3$(1.0 g) were added and stirred uniformly. $KMnO_4$ (6.0 g) was gradually added with stirring and cooling in order to keep the temperature below 20 °C. The solution was heated to 35±3 °C and maintained for 30 min. Then, distilled water was slowly added, and the temperature was kept lower than 100 °C. After 15 min, this reaction was terminated by addition of a large amount of distilled water and 30% H_2O_2 solution (5 mL). The mixture was filtered and washed with 5% HCl aqueous solution and water. The sample of graphite oxide was obtained after drying. Graphite oxide to Graphene oxide: 100 mg graphite oxide was dispersed in 100 mL of water to create a yellow-brown dispersion,and the exfoliation of graphite oxide to graphene oxide was achieved by sonication with a cylindrical tip for 30 min. Graphene oxide to Graphene: the resulting homogeneous solution was mixed with 80 mL of hydrazine solution as a reducing agent, and 350 mL of ammonia solution was added to adjust pH to around 10. After stirring for a few minutes, the mixed solution was heated at about 95 °C for 1 h. The reduced product was isolated by filtration through polytetrafluoroethylene membrane (0.22 mm), washed with water and methanol, and dried for 24 h in vacuum oven. Then graphene, that is, the reduced graphene oxide, was obtained.

2.4 Functionalization of graphene with phenol (graphene-f-OH)

Graphene to Graphene hydroxide: 20 mg of graphene, 200 mg of 3,4-dihydroxybenzaldehyde and 200 mg of N-methylglycine were suspended in 50 mL of DMF and heated at 120 °C for 5 days. The mixture was then filtered through Millipore filters (0.45 mm) and washed thoroughly with DMF. The filtrate was sonicated in DMF for 1h and then removed; the resulting suspension was filtered again through Millipore filters (0.45 mm). This procedure was repeated three additional times with sonication in (1) DMF, (2) 1 : 1 (v/v) $C_2H_5OH/CHCl_3$, and (3) diethylether. The remaining black solid was dried under vacuum (10^{-2} bar) for 3 days.

2.5 Synthesis of Poly(L-lactic acid) grafted graphene polymer materials (G-g-PLLA)

Poly(L-lactic acid) grafted graphene macroinitiators were synthesized as shown in Scheme 1, using a procedure similar to those described previously for ring-opening polymerization of LLA to give PLLA-OH[20]. The polymerization took place in anhydrous toluene solution at 120 °C using graphene-f-OH as initiator and tin octoate as catalyst. Specifically, 2 g of LLA were charged into the prepared flask and three vacuum-nitrogen cycles were carried out. Calculated amounts of freshly prepared solutions of tin octoate (1 mL) and graphene-*f*-OH (0.04 g), followed by 50 mL of dry toluene, were then added through a septum via a syringe under nitrogen flow. Finally, the system was closed under positive nitrogen pressure, and polymerization proceeded under stirring at 120 °C for 24 h. After reaction, the mixture was stopped by cooling to room temperature. The solidified reaction mixture was dispersed in 30 mL of methanol, then poured into 80 mL of methanol containing 1mL of concentrated HCl to remove the Sn residue. The black solid was collected by filtration, washed with methanol, dried, redissolved in 10 mL of dry dichloromethane or chloroform, and precipitated dropwise into 100 mL of methanol containing 1 mL of concentrated HCl. The precipitate was collected by filtration, washed with methanol and dried in vacuo at 30 °C for 72 h.

2.6 Synthesis of the novel polyurethane copolymer

polyurethane copolymer was synthesized via a condensation reaction in anhydrous toluene solution under a nitrogen atmosphere as shown in Scheme 2. Firstly, the reaction of 1,4-BDO(1.0g, 0.011mol) and 4,4'-MDI(4.0g, 0.015mol) was conducted at 80 ^{o}C for 2h to yield a prepolymer. Subsequently, G-g-PLLA was introduced, and the reaction was conducted at 90 ^{o}C for another 10 h. The resulting polyurethane was precipitated into excess n-hexane and dried under vacuum at 50 ^{o}C for 12 h.

3. Result and Discussion

Our method to prepare novel degradation polyurethane copolymer (G-g-PLLA-b-PU) consisted of three key steps, which are illustrated in Fig. 1, Fig. 2 and Fig. 3, respectively.

FTIR spectrum of (a) Grapnene and (b) functionalization of grapheme with phenol (G-g-OH) is shown in Fig.4. As illustrated in Fig., the FTIR spectrum of graphene-f-OH shows C–H stretch features at 2950, 2922 and 2852cm-1 that do not appear in the spectrum of pristine grapheme (curve a in Fig.4). In addition, apparent C–C stretch bands and a weak aromatic C–H band are observed at 1100–1700 and 618 and 3040 cm-1, respectively. The C–O stretch band was observed at 1120 cm-1 and the O–H stretch band was observed at 3600–3700 cm-1, both of which are characteristic of phenols. The FTIR spectral analysis provides support for successful functionalization of grapnene with phenol

The FTIR spectrum of functionalization of grapheme with phenol (G-g-OH) and PLLA/g-graphene (G-g-PLLA) is shown in Fig. 5. The appearance of peaks at 1040 and

3440 cm^{-1} can be assigned to the stretching vibrations of C-O and –OH, respectively, which appear in the spectrum of PLLA/g-graphene. The new bands at 1440 cm^{-1} is attributed to the bending vibration of $–CH_3$, and the new bands at 1670 cm-1 is associated with the coupling of v_{as} (C-O-C) and δ(CH) vibration modes[21]. These results clearly confrmed that the L-lactide acid molecules were covalently linked to graphene, suggesting successful surface functionalization of the graphene with an OH-terminated group.

The FTIR spectrum of PLLA/g-graphene (curve a) and deradable polyurethane hybrid composite (G-g-PLLA-b-PU)(curve b) are shown in Fig. 6. The band at 3320 cm^{-1} is attributable to the N–H stretching mode and the peaks at 816 cm^{-1} can be assigned to the bending vibration of aromatic C-H. In addition, the 1710 cm^{-1} band is associated with the stretching vibration of the carbonyl C=O in −NH−COO−, which indicated the successful chemical reaction between the OH-terminated poly(L-lactide)-functionalized graphene with the NCO-terminated polyurethane prepolymer[22], and the new bands at 1540 cm^{-1} is attributed to the characteristic absorption peak of –NHCOO-. All these results indicated that the degradable polyurethane hybrid composite was successfully prepared via a combination of ring-opening polymerization and condesation polymerization.

Solusion ^{1}H NMR spectroscopy was used to further testified the success graft of LAA into graphene, Fig. 7 shows the typical ^{1}H NMR spectrum of G-g-PLLA in $CDCl_3$. As shown in Fig. 7, the chemical shifts at 5.16 ppm and 1.53 ppm are resonably assiged to the methylidyne proton(-CH) and methylic proton(-CH_3) in the PLLA chains, respectively. The chemical shift of end group hydroxy proton(-OH) at site c[23], –CH protons at site a. All of these results clearly indicated that the degradable PLLA was successfully grafted into graphene surface via the ring-opening polymerization.

TG thermograms of G-OH, G-g-PLLA and G-g-PLLA-b-PU polymers are shown in Fig. 8. As shown in curves, all the materials show a little mass loss around 100°C due to the deintercalation of H_2O. The obtained G-OH sample shows about 24.6% mass loss, which is resulted from the decomposition of the grafted hydroxyl groups, It can also be observed from Fig. 8b that G-g-PLLA degrads in one step from 180 °C, and there is a mass loss of 43.9% from 45 °C to 600 °C, which is attributed the decomposition of the grafted $_L$-lactide, compared with G-OH, a mass loss of 18.3% can be observed for G-g-PLLA polymer from 45 °C to 600 °C. However, as shown in Fig.8c, G-g-PLLA-b-PU hybrid composites degrades in two step, the first in the 80 °C to 160 °C region, and the second in the 180 °C to 350 °C region. there is a mass loss of 83.9% from 45 °C to 600 °C, which is resonably attributed the decomposition of the grafted $_L$-lactide and polyurethane, compared with G-g-PLLA, a mass loss of 26% can be observed for G-g-PLLA-b-PU copolymer composites from 45 °C to 600 °C.

DSC thermograms of G-g-PLLA polymers are illustrated in Fig.9. we observed that no crystallization peak was detected in the process of cooling scans for scans speeds at 10 °C. From the curves of DSC, we found that the glass transition terperature (Tg) increased from 53.7 °C to 55.2 °C with higher content of graphene, in contrast to PLLA homopolymer, which is ascribed to the incorporation of graphene imposes constraint over the mobility of PLLA chains. The similar phenomenon that the incorporation of inorganic nanoparticles increased the Tg of polymers has shown in previous paper[24].

Fig.10 shows the mass loss of PU-Gx in natural seawater at room temperature. As can be seen from the curve, compared with PU-G_0, other PU-Gx panels loss their weight more quickly, indicating that with the increase of graphene content in polyurethane, a higher hydrolysis rate of polyurethane is presented. However, when graphene content up to 8%, the hydrolysis rate of polyurethane get slowly. This phenomenon is ascribed to the introduction of graphene disrupted the crystallization of PLLA, which resulted in the increase of polyurethane hydrolysis ability. Another reason may be that too much graphene limit the motion of the polymer chain, which resulted in the increase slightly of polyurethane hydrolysis ability.

Fig.11 and Fig.12 shows the initial simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU and simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU for 30 days, respectively. During the 30 days of seawater immersion, the two resins are in the same environment, but the amount of pollutants attached is significantly different. There are many kinds of different pollutants on the surface of ordinary resin (Fig. c of Fig. 12) and its surface has a small amount of degradation, By contrast, the G-g-PLLA-b-PU (Fig. d) surface has a small amount of contaminants attached, at the same time, through the comparison with Fig. b of Fig .11, a lot of resin degradation are degraded. As a result, we know that the copolymer material has better antifouling perform.

4. Conclusions

A novel synthetic method for the preparation of degradable polyurethane containing graphene composition was successfully produced via combination of ring-opening reaction and condensation reaction. FTIR and ^{1}H NMR analysis indicated that PLLA can be successfully grafted onto graphene surface. with increase of graphene content, the value of Tg of G-g-PLLA polymer tends to increase mildly duo to the incorporation of graphene imposes constraint over the mobility of PLLA chains. Static hydrolysis experiment indicated that the incorporation of graphene increase polyurethane hydrolysis ability. The G-g-PLLA-b-PU copolymer material confer a smooth surface through degradation in seawater and the simulated ocean hanging plate experiment proved that the G-g-PLLA-b-PU copolymer material has the better antifouling performance than the ordinary polyurethanes, which indicated that the functionalized PU can be expected to serve as a marine antifouling coating.

Acknowledgements

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Figure captions

Fig. 1 Synthesis of graphene grafted PLLA (G-g-PLLA).

Fig. 2 Synthesis of polyurethane prepolymer.

Fig. 3 Synthesis of degradable polyurethane copolymer materials.

Fig. 4 FTIR spectrum of (a) Grapnene and (b) Grapnene-f-OH

Fig. 5 FTIR spectrum of (a) G-g-OH and (b) G-g-PLLA

Fig. 6 FTIR spectrum of (a) G-g-PLLA and (b) G-g-PLLA-b-PU.

Fig .7 1H NMR spectrum of G-g-PLLA in CDCl3.

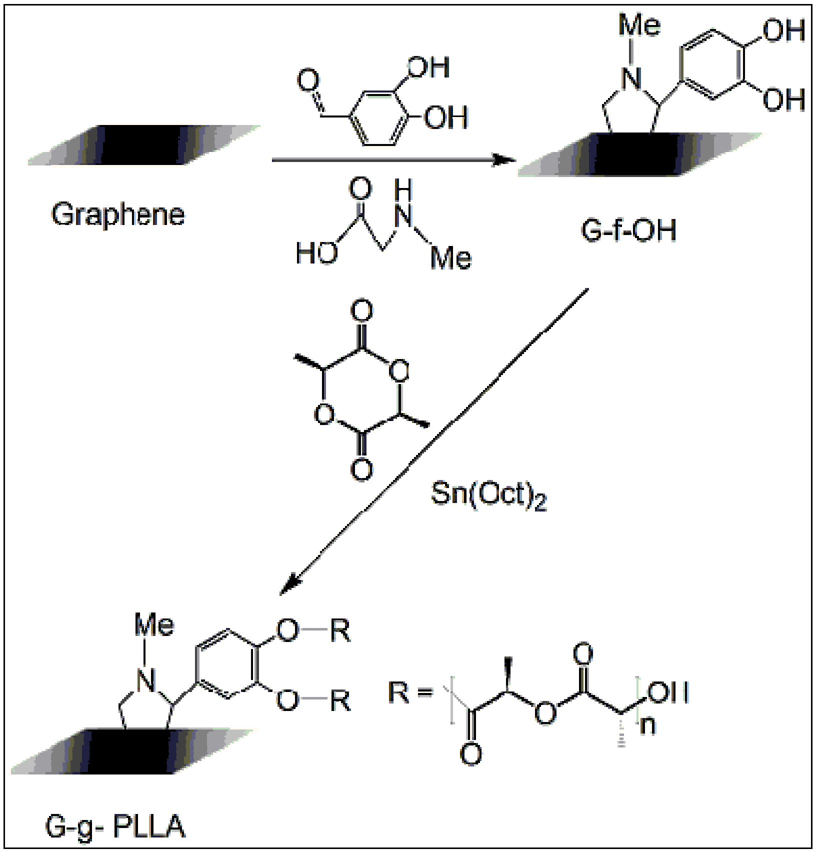
Fig. 8 TG thermograms of G-OH(a), G-g-PLLA (b) and G-g-PLLA-b-PU(c).

Fig. 9 DSC curves of PU-Gx.

Fig. 10 the mass loss of PU-Gx in natural seawater

Fig.11 The initial simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU

Fig.12. simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU for 30 days



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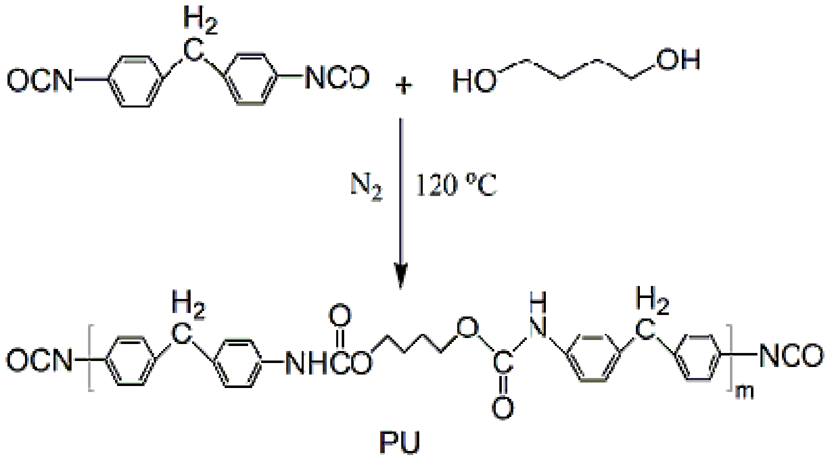

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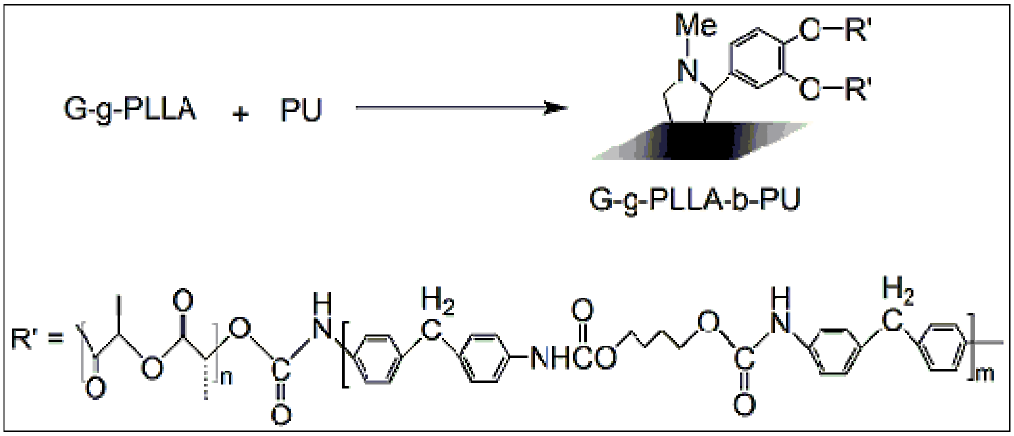

Fig. 3 Synthesis of degradable polyurethane copolymer materials.

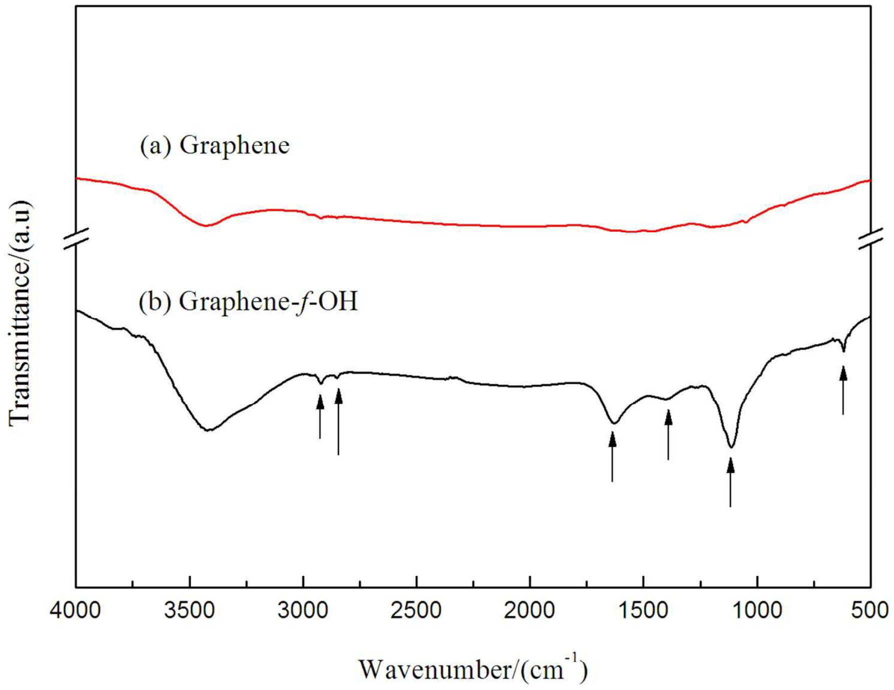

Fig. 4 FTIR spectrum of (a) Grapnene and (b) Grapnene-f-OH

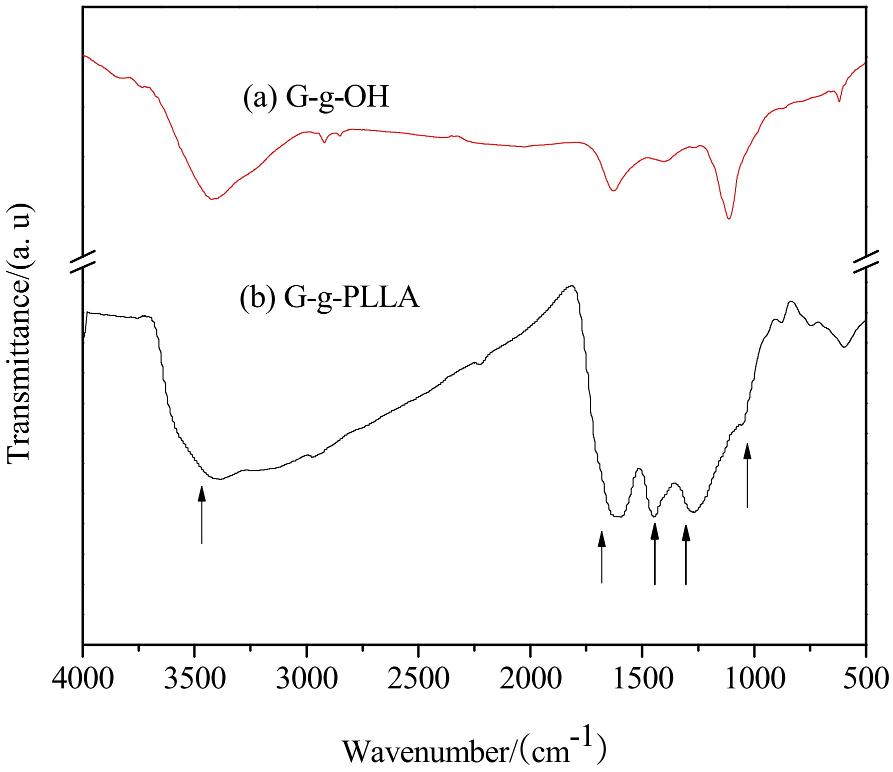

Fig. 5 FTIR spectrum of (a) G-g-OH and (b) G-g-PLLA

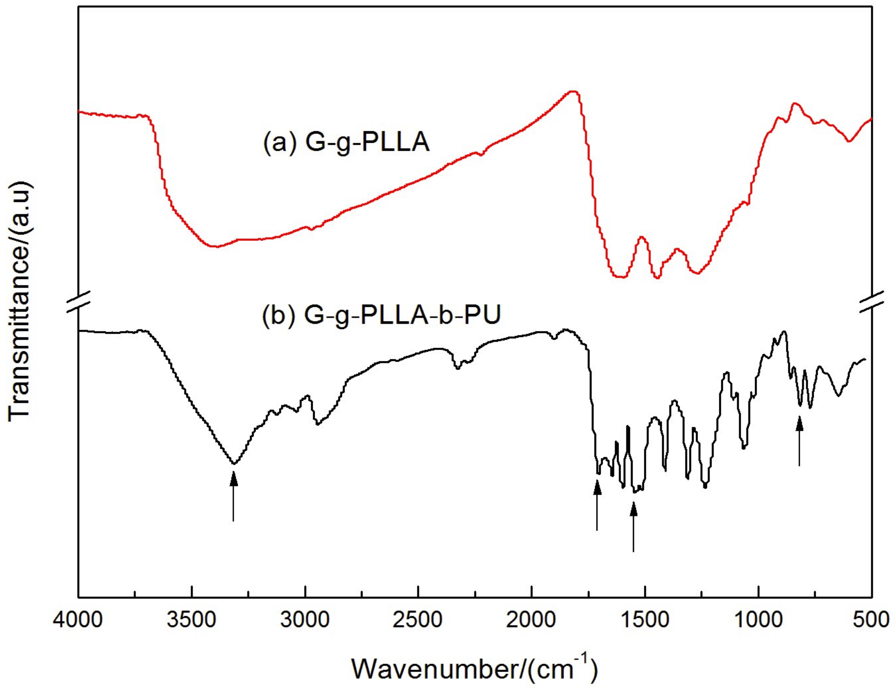

Fig. 6 FTIR spectrum of (a) G-g-PLLA and (b) G-g-PLLA-b-PU.

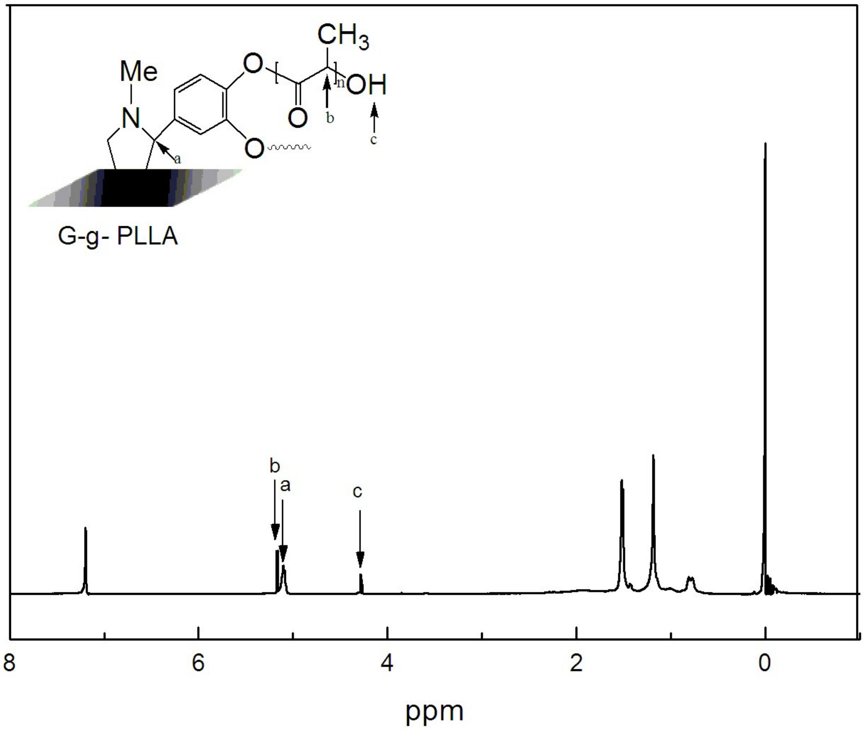

Fig . 7 ^{1}H NMR spectrum of G-g-PLLA in $CDCl_3$.

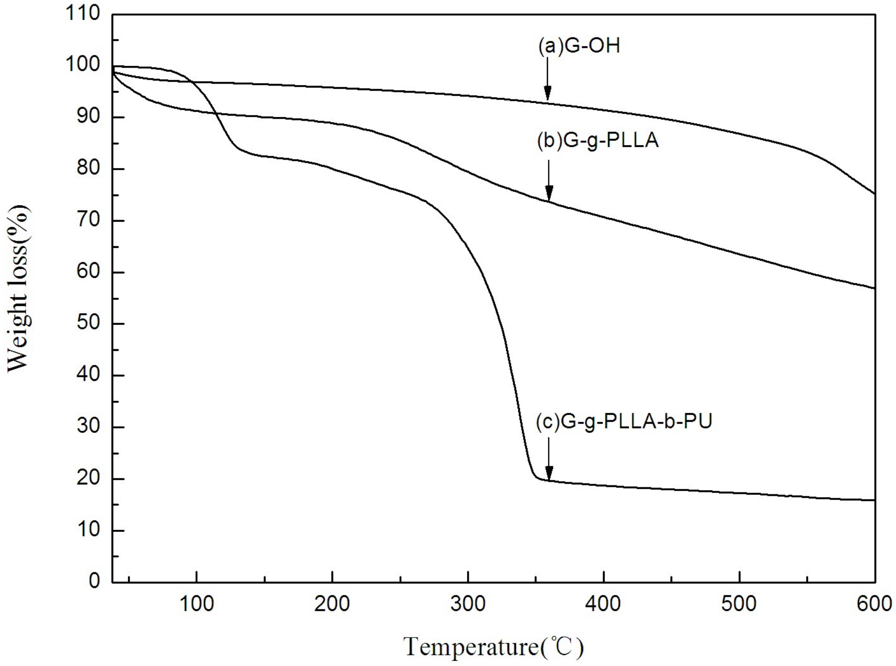

Fig. 8 TG thermograms of G-OH(a), G-g-PLLA (b) and G-g-PLLA-b-PU(c).

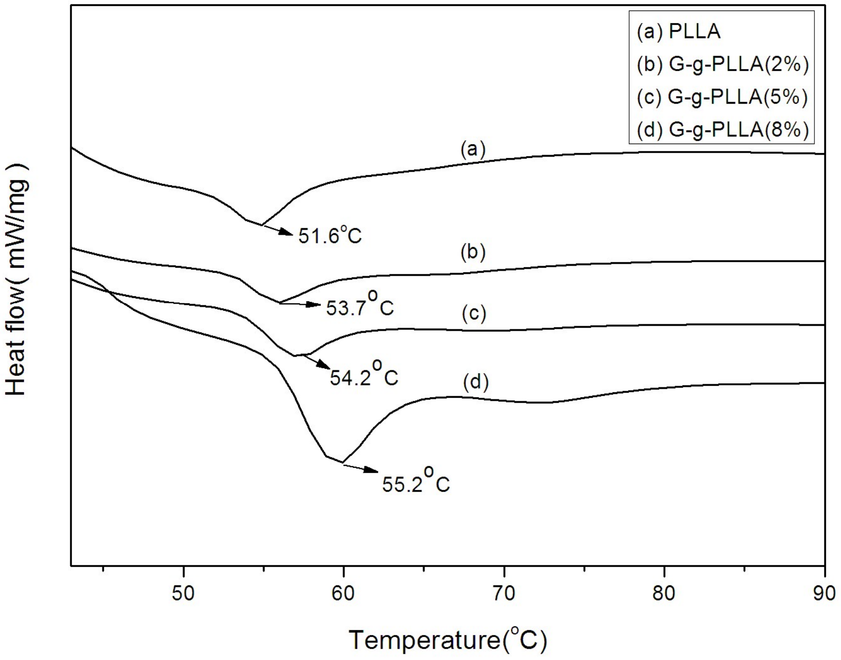

Fig 9. DSC curves of PU-G_x.

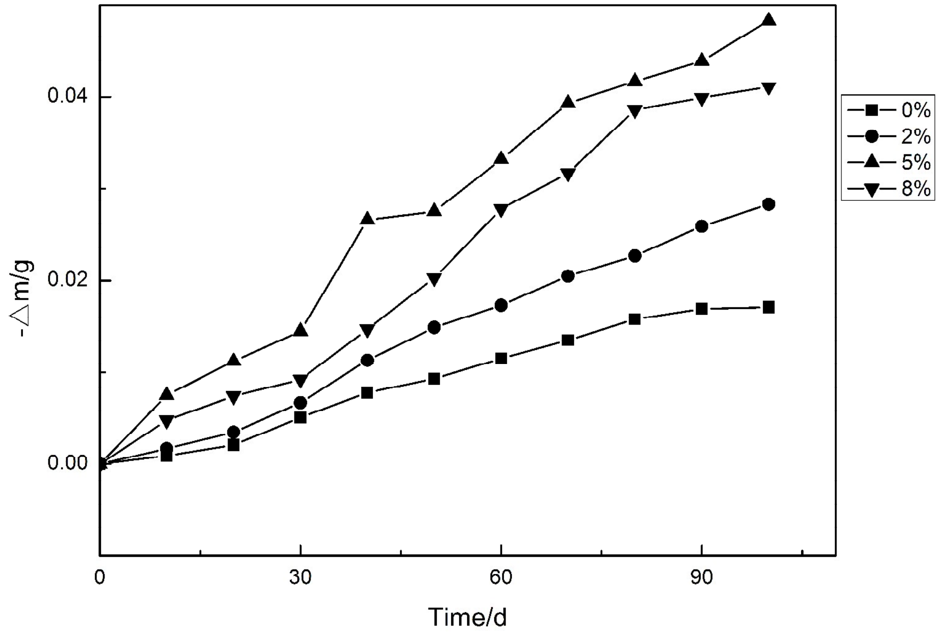

Fig. 10 the mass loss of PU-Gx in natural seawater


(a) PU （b）G-g-PLLA-b-PU

Fig.11. The initial simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU

（c）PU （d）G-g-PLLA-b-PU

Fig.12. simulated ocean hanging plate experiment of PU and G-g-PLLA-b-PU for 30 days