Synthesis and Characterization of MPS-g-PLA Copolymer and its Application in Surface Modification of Bacterial Cellulose

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SYNTHESIS AND CHARACTERIZATION OF MPS-G-PLA COPOLYMER AND ITS APPLICATION IN SURFACE MODIFICATION OF BACTERIAL CELLULOSE

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Polylactide-graft-γ-methacryloxypropyltrimethoxysilane (MPS-g-PLA) was prepared by grafting MPS onto PLA. MPS-g-PLA was characterized by Fourier transform-infrared spectroscopy (FT-IR), hydrogen nuclear magnetic resonance (^{1}H-NMR), and gel permeation chromatography. Furthermore, MPS-g-PLA was used to modify bacterial cellulose (BC), and the changes of surface properties of BC resulting from the treatment were followed by FT-IR and contact angle measurements. The results revealed that the modified BC possessed a much more hydrophobic nature than virgin BC. The surface modification of BC with MPS-g-PLA offers a way to increase the compatibility between the components in biocomposites, and thereby to improve the properties of these composites.

INTRODUCTION

Polylactide (PLA), a synthetic aliphatic polyester derived from agricultural products, is an environmentally friendly polymer and has been emerging as an alternative to conventional petroleum-based polymeric materials due to its renewability, biodegradability, and greenhouse gas neutrality.[1,2] PLA is a unique polymer that in many ways behaves like poly (ethylene terephthalate) (PET), but also performs a lot like polypropylene (PP), a polyolefin. Therefore, PLA is today most widely used within the field of packaging (primarily for food), film, and fiber applications, with a great potential to develop into a newly emerging pillar industry; currently, it has just moved into the early stage of industrialization internationally.[3]

Despite PLA's advantages, the improvement of its physical properties, such as the rate of degradation and mechanical and thermal properties, is a matter of concern, especially when used in industrial and commodity applications.[4,5] Numerous efforts such as blending, clay, carbon nanotubes, cellulose nanowhiskers, and hydroxyapatite-based nanocomposite and fiber-reinforced composite fabrication have been made to modify the properties of PLA.[6–13] These have improved the PLA properties to a certain extent; however, one important limitation for these solutions is the poor compatibility between PLA and other components. To solve this problem, compatibilizing agents, such as PLA-PCL-PLA, PLA-g-AA, PLA-g-MA, or lysine-based diisocyanate (LDI), have been utilized to elevate the compatibility of the immiscible phases.[14–18]

γ-Methacryloxypropyltrimethoxysilane (MPS), a well-known commonly used silane coupling agent, consists of methacrylate and sila-functional alkoxy groups. Methacrylate group in MPS shows copolymerization or grafting reaction by a suitable initiator system, while methoxy silane can hydrolyze and bond to hydroxyl group substrates. Therefore, this improves adhesion to inorganic materials, such as carbon white, clay, stearite, mica, and kaolin.

In this study, we attempt to graft MPS onto aliphatic polyester polylactide to obtain MPS-g-PLA copolymers that serve as compatibilizing agents for solid surfaces having hydroxyl group-reinforced PLA-based composites, for example, natural fibers, hydroxyapatite, and starch. The chemical structures of grafted copolymer were identified by FT-IR and ^{1}H-NMR. Factors influencing the reactivity of grafting MPS onto PLA are discussed such as the reaction temperature and the concentrations of initiator and monomer. In order to investigate the efficiency of MPS-g-PLA, bacterial cellulose, a very promising green nano-reinforcement, was treated with MPS-g-PLA for surface modifications, and chemical changes resulting from the treatment were followed by a study of FT-IR and contact angle measurements.

EXPERIMENTAL SECTION

Materials

Commercial PLA from NatureWorks was used with number-average and weight-average molecular weight of 71 kDa and 100 kDa, respectively. It was dried at 80°C for a minimum of 24 h under vacuum prior to use. MPS was industrial product of high purity and was used as received from Wuhan University Silicone New Material Co., Ltd. Benzoyl peroxide (BPO) obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd. was purified by recrystallization. Bacterial cellulose (BC) pellicle was produced by *Acetobacter xylinum*. BC pellicle was grown static in the medium at 30°C for seven days, and the gels of BC (5 mm thickness) formed on the surface of the medium surface were harvested aseptically. BC film was purified by boiling in 0.1 M NaOH at 100°C for 1 h, and thereafter, it was washed in running water for one day. All other reagents and solvents were analytical grade and dried before use.

MPS Grafting Polylactide

The grafting of MPS and PLA was carried out under nitrogen at a desired temperature. A known amount of PLA was dissolved in xylene at 110°C. When the

dissolution was complete, an MPS/BPO mixture in xylene was added to the system, and the grafting reaction went on over 4 h. The reaction mixture was then poured into methanol under vigorous stirring. The precipitated graft copolymer was further washed with fresh methanol several times and then dried under vacuum for 24 h.

Surface Modification of BC

The surface treatment of BC pellicles was carried out by immersing BC pellicles in the dioxane solution of MPS or MPS-g-PLA at the concentration of 1 wt.% or 5 wt.%; acetic acid (Ac) was used to adjust pH. After being dried at room temperature for two days, BC reacted with MPS-g-PLA at 120°C for 2 h. Subsequently, the products were submitted to a 24 h Soxhlet extraction with THF and dried.

Characterization

FT-IR. FT-IR spectra of PLA, MPS-g-PLA, and the treated bacterial cellulose were taken on an FTIR-Nicolet 5700 (Shimadzu) spectrometer by a KBr disk. The spectrometer was used in the range of 4000–400 cm^{-1}.

Gel Permeation Chromatography (GPC). Molecular weight and polydispersity index (PDI) of PLA and MPS-g-PLA were determined by a multi-detector GPC equipped with a Dawn Heleos static laser scattering detector and an Optilab Rex refractive index detector, produced by Wyatt Technology Corporation. GPC was performed using THF as eluent at a flow rate of 1 mL/min.

^{1}H-NMR Spectroscopy. ^{1}H-NMR spectra were recorded using an Avance 500 instrument. The MPS-g-PLA samples were dissolved in CDCl$_3$ for NMR measurements. All the chemical shifts for resonance peaks are reported in parts per million (ppm) using tetramethylsilane (TMS) as a reference.

The content of MPS grafted onto PLA was calculated from the relative peak area of the methine proton of PLA and the protons of methoxy group of MPS using the following equation:

$$G\% = \frac{\frac{S_{3.55}}{9} \times 248.4}{(S_{5.15} + S_{3.55}/9) \times 72.06} \times 100\%$$

Contact Angle Measurements. Contact angle measurements were carried out by depositing calibrated liquid drops on the sample, and the value given is the average value of 10 measurements. The apparatus used for these measurements was a homemade static instrument equipped with a CCD camera working up to 25 images per second. Distilled water was used as contact liquid.

RESULTS AND DISCUSSION

The methacryloxy group of MPS is very interesting because it can be copolymerized with alkenyl-based matrices, commonly used in composite materials. In this work, the grafting of MPS onto PLA introduces functional groups to improve the

interfacial adhesion of PLA-based composites. The proposed reaction mechanism is shown in Figure 1.[17,19] The grafted copolymer obtained is completely soluble in THF, indicating that no cross-linking reaction occurs during the grafting procedure.

FT-IR Spectroscopy

The structural features of PLA, MPS, and the grafted copolymer were evaluated by FT-IR analysis and are shown in Figure 2. For MPS, the strong peak at $1719 \, cm^{-1}$ was the carbonyl C=O stretching mode. The bands at 1167, 1191, 1296, and $1321 \, cm^{-1}$ were associated with the ester functionality, while the bands at 1089 and $818 \, cm^{-1}$ resulted from Si–O–CH$_3$ asymmetric and symmetric stretching vibrations, respectively. The peaks at 1638 and $941 \, cm^{-1}$ originated from the vinyl C=C stretching and vibration mode, respectively. PLA showed a characteristic ester C=O band at $1755 \, cm^{-1}$. In the case of MPS-g-PLA, many peaks were in accord with PLA, while the relative absorption intensity of 1755 to $1089 \, cm^{-1}$ became smaller than that of pure PLA because of Si–O–CH$_3$. After hydrolysis of MPS-g-PLA, broad bands at $3497 \, cm^{-1}$ were obvious, assigned to the hydroxyl group in the Si–OH groups derived from hydrolysis of the Si–O–CH$_3$ groups. Altogether, the FT-IR analyses effectively showed that the monomers have been covalently attached to PLA.

^{1}H-NMR Spectroscopy

To further confirm the grafting of MPS onto PLA, ^{1}H-NMR spectra were used to characterize the structure; they are shown in Figure 3. The signal at 5.15 ppm could be assigned to the methine proton of PLA and that at about 1.57 ppm attributed to methyl protons of PLA, while 4.08 ppm and 3.55 ppm could be attributed
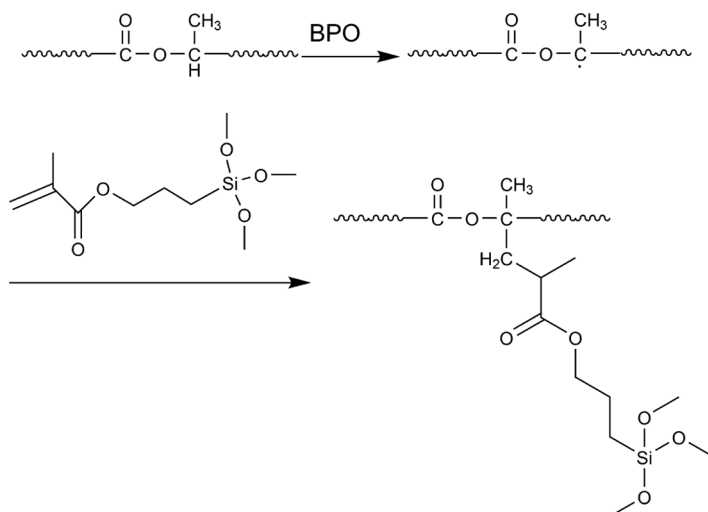
Figure 1. Schematic for proposed reaction mechanism of MPS with PLA.
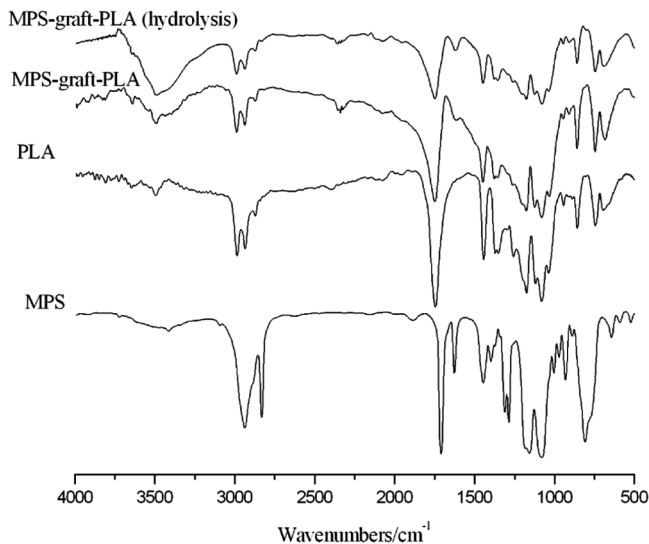
Figure 2. FT-IR of MPS, PLA, and MPS-g-PLA before and after hydrolysis.

to methylene and methyl protons of MPS respectively. The appearance of the methyl proton peak at 3.55 ppm and the disappearance of the peaks of hydrogen of alkenyl group in MPS monomer could be considered as evidence of successful grafting.
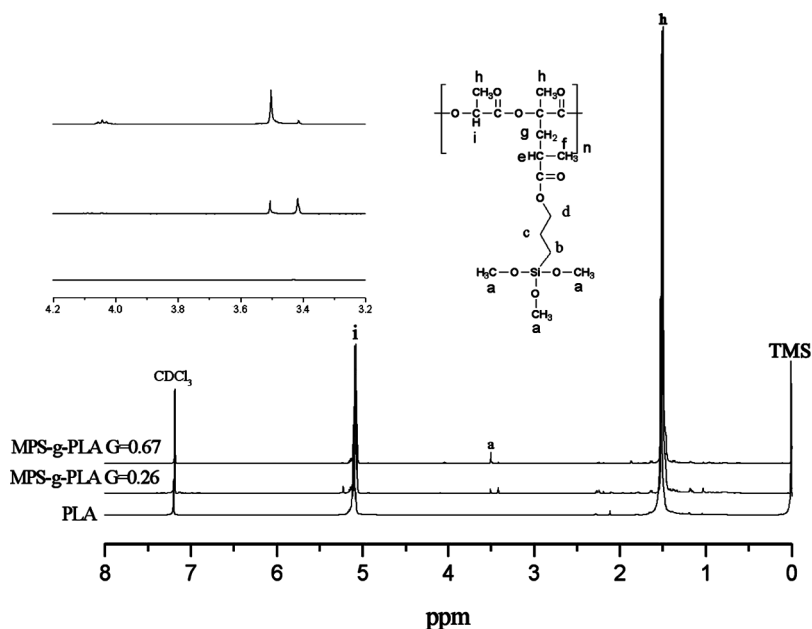

Figure 3. ^{1}H-NMR spectra of PLA and MPS-g-PLA copolymer.

Effect of Reaction Temperature

The free radical grafting reaction starts with thermal decomposition of peroxide initiator into free radicals, which are capable of abstracting hydrogen atoms from the PLA molecules. The polymerizations were carried out at different temperatures, and the results are shown in Table I. Increasing the reaction temperature from 80° to 140°C, while keeping other variables such as monomer and initiator concentration constant, about doubled the percentage of MPS obtained. An increase in temperature causes the complete decomposition of the initiator and hence produces more radicals simultaneously and results in higher graft content. Meanwhile, these radicals can recombine with other radicals, eliminating grafting sites and thus adversely affecting the grafting efficiency. An increase in temperature reduces the viscosity of the medium and enhances the diffusion. Therefore, a higher temperature helped achieve higher grafting. However, at higher temperatures, the recombination reaction is also prominent and this will reduce the graft degree. This is the reason that the grafting content at 140°C is not higher than that at 110°C.

Meanwhile, molecular weight values obtained after the grafting reaction were slightly lower than that of pure PLA, and the polydispersity index (Mw/Mn) became broader with the temperature increase. This may be attributed to the degradation and chain scission of PLA, which become stronger with increasing temperature. Previous studies suggested that the PLA macroradical could undergo quick chain scission.[20]

Effect of MPS Concentration

From Table II, it was observed that the grafting content increased with increased MPS monomer concentration from 10 to 80% w/w (with respect to PLA) at 110°C with constant initiator concentration (1.0%). At low concentrations of MPS, collision probability of the free radicals formed from PLA and MPS is low. As the concentration increased, it becomes high and a chain propagation reaction takes place, therefore the graft content further increases. These results correspond well to those reported in the literature.[21]

Molecular weight and the polydispersity of graft copolymers were also studied. From the results, we could observe that the degradation of PLA became obvious when MPS content increased. In Mani's research of maleic anhydride grafting PLA, similar change of intrinsic viscosity was reported.[21] This was due to more chain scission at a higher concentration of MPS.

Table I. Effect of reaction temperature on graft content and molecular weight

Sample	Temperature (°C)	Graft content (%)	Mn (g/mol)	Mw/Mn
1	80	0.72	69730	1.52
2	110	1.37	65910	1.56
3	140	1.34	43130	1.91

Table II. Effect of concentration of monomer on graft content and molecular weight

Sample	PLA (g)	MPS (g)	Graft content (%)	Mn (g/mol)	Mw/Mn
4	2.00	0.20	0.20	68980	1.48
5	2.00	0.40	0.67	64630	1.55
6	2.00	0.80	0.64	57890	1.63
7	2.00	1.60	1.37	65910	1.56

Effect of Initiator Concentration

To elucidate the effect of the initiator concentration, graft copolymerization was studied at various BPO concentrations by keeping other reaction conditions constant. As shown in Table III, the graft content increases with increasing initiator concentration, which may be ascribed to the increase of radicals. More BPO attacking the tertiary carbon atom of PLA will generate more macroradicals, and more active sites of PLA can react with MPS; when BPO dosage is 0.020 g, the grafting content reaches a maximum value.

Molecular weight and the polydispersity of graft copolymers are shown in Table III. Molecular weight of graft copolymers decreased in the first instance and then increased with an increase of initiator concentration. This is due to the higher initiator concentration, which can cause partial cross-linking of PLA.[22]

Surface Modification of BC

In order to confirm the chemical reaction between the MPS-g-PLA and BC, BC modified with MPS-g-PLA before and after reaction at 120°C was analyzed by FT-IR spectroscopy. In Figure 4, spectrum a, the bands at 1755, 1091, and 1013 cm^{-1} were associated, respectively, with the stretching of the C=O, Si−OCH$_3$, and Si−OH bond. After reaction and extraction (Figure 4, spectrum b), the bands around 1162 and 1114 cm^{-1} were related to the −Si−O−Si− linkage and −Si−O-cellulose bonds. It could be seen that the band at 1013 cm^{-1} disappeared and was replaced by the Si−O−Si band at 1035 cm^{-1}. The shoulder peaks near 813 cm^{-1} are related to residual unhydrolyzed Si–OCH$_3$ groups. This indicated the reaction between Si−OH of MPS-g-PLA and −OH of cellulose took place, as schematically and hypothetically illustrated in Figure 5.[23] These peak assignments are in agreement with those reported in other studies dealing with natural fibers treated with the coupling agents.[23]

Table III. Effect of initiator concentration on graft content and molecular weight

Sample	PLA (g)	MPS (g)	BPO (g)	Graft content (%)	Mn (g/mol)	Mw/Mn
8	2.00	0.40	0.010	0.26	59370	1.64
9	2.00	0.40	0.015	0.45	56080	1.54
10	2.00	0.40	0.020	0.67	64630	1.55
11	2.00	0.40	0.025	0.67	79600	1.40
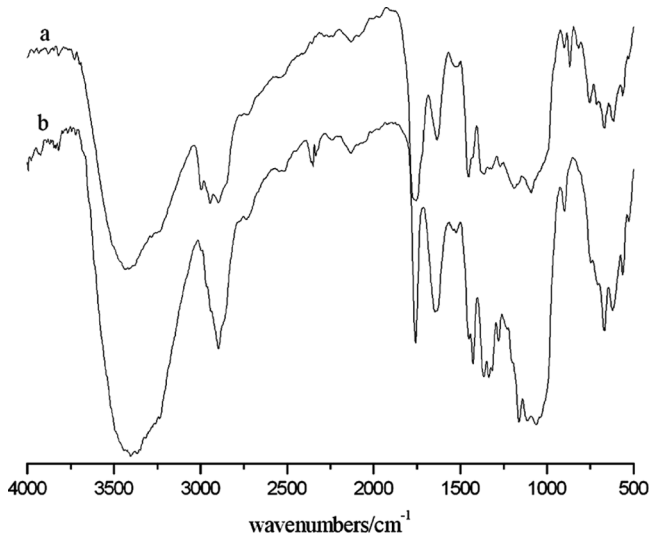
Figure 4. FT-IR of BC modified with MPS-g-PLA (a) before and (b) after reaction at 120°C.

Contact Angle Measurements

Table IV shows the contact angle values of BC and modified BC by MPS or MPS-g-PLA after reaction at 120°C and extraction. As expected, the virgin BC without surface treatment displayed a low contact angle ($\sim36°$) arising from a high
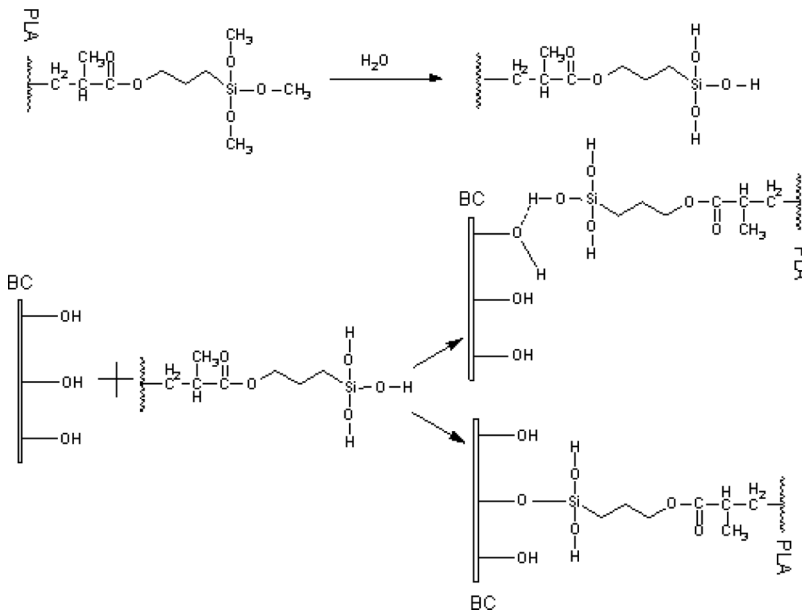

Figure 5. Schematic illustration of reaction of MPS-g-PLA on BC sheets' surface.

Table IV. Surface properties of BC sheets with and without MPS-g-PLA modification

Sample	Contact angle (°)	Surface energy (mJ/m^2)	Work of adhesion (mJ/m^2)
BC	35.89	61.50	131.61
MPS1%-Ac	45.98	45.27	126.98
MPS-g-PLA1%	77.87	37.59	89.20
MPS-g-PLA1%-Ac	86.53	31.41	77.18
MPS-g-PLA5%-Ac	100.29	22.95	59.94

density of hydroxyl groups on cellulose backbone. The contact angle significantly increased after surface treatment and varied according to the following trend: MPS-g-PLA5%-Ac > MPS-g-PLA1%-Ac > MPS-g-PLA1% > MPS1%-Ac.

The surface energy and the work of adhesion (W_a) were also calculated according to the equations:

$$1 + \cos\theta = 2\sqrt{\gamma_{sg}/\gamma_{lg}} \bullet \exp[-\beta(\gamma_{lg} - \gamma_{sg})]$$
$$W_a = \gamma_{lg}(1 + \cos\theta)$$

where θ stands for measured contact angle, γ_{lg} stands for liquid surface tensions, γ_{sg} stands for solid surface tensions, and constant β is known.[24] Thus, the solid surface tensions could be determined from experimental (Young) contact angles and liquid surface tensions. Table IV gives the surface energies and the work of adhesion of distilled water on the unmodified and modified BC sheets. Unmodified BC exhibited the well-known high polar behavior. Just following the modification with MPS, BC showed a slight decrease in the surface energy and the work of adhesion. Modified with MPS-g-PLA, the surface energy and the work of adhesion further decreased. This is attributed to the consumption of hydroxyl group of BC by the reaction of BC and MPS-g-PLA since the PLA chain is hydrophobic. Therefore, the hydrophilic character of BC can be strongly decreased. This represents an effective approach to optimize fiber/PLA matrix interface for composite materials containing natural fibers.

CONCLUSIONS

FT-IR and ^{1}H-NMR spectra confirmed the grafting of MPS onto a polylactide polymer, which was achieved via free radical polymerization. However, the degradation of PLA was evident due to the free radical initiator. Temperature and monomer and initiator concentrations affect the graft content. When amount of PLA is 2.0 g, BPO is 0.02 g, and MPS is 1.6 g at 110°C, the desired graft content with slight degradation could be obtained. Because of the chemical reaction between MPS-g-PLA and BC, surface modification of BC with MPS-g-PLA increases its contact angle and decreases the surface energy and the work of adhesion, which indicates that the hydrophilic character of BC strongly decreases. This investigation provides a novel approach to modify the surface of reinforcements having hydroxyl groups, which is expected to improve the compatibility between reinforcements and PLA matrix.

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