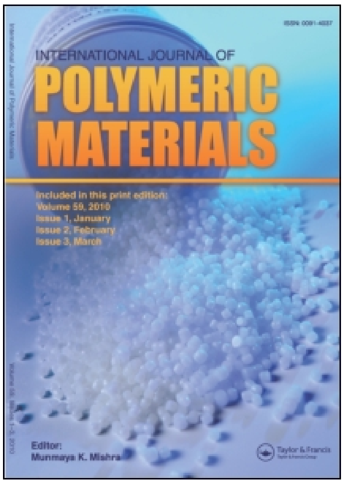

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Synthesis of PLA-co-PGMA Copolymer and its Application in the Surface Modification of Bacterial Cellulose

Zhao Qian Li[a,b]; Xiao Dong Zhou[a]; Chong Hua Pei[c]
[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China [b] School of Chemistry and Molecular Engineer, East China University of Science and Technology, Shanghai, China [c] School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, China

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Zhao Qian Li,[1,2] Xiao Dong Zhou,[1] and Chong Hua Pei[3]

[1]State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China
[2]School of Chemistry and Molecular Engineer, East China University of Science and Technology, Shanghai, China
[3]School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, China

Nature fibers have been developed for the reinforcement of polymers. The main disadvantage of the natural fibers to be used as reinforcement is their hydrophilic nature. In this paper, a novel copolymer of polylactide and glycidyl methacrylate (PLA-co-PGMA) was prepared by free radical polymerization and used to modify the cellulose surface. The characterization of the PLA-co-PGMA copolymers was conducted by Fourier transform infrared (FTIR) and gel permeation chromatography. Modified bacterial cellulose (BC) with the copolymer was characterized by FTIR and contact angle measurements. Interfacial thermodynamic properties were studied. The results suggested that PLA-co-PGMA was efficient in modifying the BC nanofibril surface and in improving the compatibility of PLA/cellulose composites.

Keywords bacterial cellulose, compatibility, glycidyl methacrylate, polylactide, surface modification

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Address correspondence to X. D. Zhou, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: xdzhou@ecust.edu.cn

INTRODUCTION

A biocomposite is a material comprising a matrix and a reinforcement of natural fiber (usually derived from plants). The matrix is a petroleum-derived nonbiodegradable polymer like polypropylene, polythene, and epoxies or a biopolymer like polylactide and polyhydroxyalkanoate. Clearly, biocomposites derived from natural fiber and biopolymer is likely more ecofriendly, and such biocomposites are sometimes termed “green composites.” As one of biocomposites, PLA/cellulose biocomposites have received significant attention due to possessing those characteristics [1,2].

However, the preparation of PLA/cellulose biocomposite is handicapped by the low compatibility between the highly hydrophilic cellulose fibers and hydrophobic PLA matrix. In order to reduce the hydrophilicity of cellulose fibers and to improve their adhesion properties, it is necessary to undertake a modification of the cellulose surface and/or an addition of compatibilizers. Several approaches have been studied, such as surface modification of cellulose (for example esterification of cellulose, graft copolymerization onto cellulose substrates) and the use of some compatibilizers (e.g., maleated polylactide, isocyanate) [3–7]. Nevertheless, only a limited number of studies achieved good results.

In our previous work, bacterial cellulose (BC)-reinforced polylactide was investigated. Bacterial cellulose is a biopolymer that is produced by bacteria strains of *Acetobacter xylinum*. BC is superior to plant cellulose owing to its purity and nanomorphology and consists of weblike networks of ribbon-shaped nanofibers about 3–8 nm thick and 50–80 nm wide [8]. Therefore, BC has potential to reinforce materials in polylactide composites. However, poor interface compatibility of BC and polylactide limited its application.

Glycidyl methacrylate (GMA) is a commercially interesting functional monomer, since it has two reactive functional groups: a very reactive epoxy group and an acrylic group. The acrylic group of glycidyl methacrylate can copolymerize with vinyl monomer and the pendent epoxide groups of the copolymers may enter into a large polynumber of chemical reactions [9]. Therefore, some applications of those copolymers are in blends and composites as compatibilizer [10,11].

To the best of our knowledge, copolymers of GMA with biodegradable polyesters PLA as a compatibililizer have not been reported so far. In this study, we attempt to copolymerize GMA onto polylactide to obtain PLA-co-PGMA copolymers that serve as a compatibilizer for PLA/cellulose composites. The chemical structures of the copolymer were identified by FTIR and GPC. BC was modified with PLA-co-PGMA and the surface properties of modified BC were studied. In addition, the compatibility of cellulose and PLA was analyzed by interfacial thermodynamics.

EXPERIMENTAL

Materials

Commercial PLA (2002D) from NatureWorks was used with number-average and weight-average molecular weight of 70 kDa and 100 kDa, respectively. It was dried at 80°C for a minimum of 24 h under vacuum prior to use. GMA (Shanghai Yuanji Chemical Co., Ltd.) was purified by a neutral aluminum oxide column. 2,2′-azobisisobutyronitrole (AIBN) was recrystallized from methanol. Bacterial cellulose pellicles were obtained from an *Acetobacter xylinum* culture. The gel-like pellicles of BC, about 5 mm, thick, were cut into pieces of 150 mm by 15 mm. KH550 was supplied by Shanghai Yaohua Chemical Plant. All other reagents and solvents were analytical grade, and dried before use.

Synthesis of the Macromonomers (PLA-GMA)

The methacrylate-terminated PLA was prepared according to the literature [12]. 3 g of PLA, 0.1 g of GMA and Zn powder (0.3 wt% of the total amount of the reactants) were added to a 100 mL flask equipped with a magnetic stirrer and 40 mL of xylene was used as solvent. The flask was immersed in an oil bath at 80°C under nitrogen protection for 10 h. Then the reaction system was cooled and the resulting solvent was precipitated into the ethanol with stirring. The PLA-GMA was collected and dried at 50°C under vacuum.

Synthesis of the Copolymers (PLA-co-PGMA)

The PLA macromonomers were completely dissolved in xylene at 70°C under a nitrogen atmosphere. AIBN and GMA in xylene were added to the system, and the reaction continued for 5 h. The resulting copolymers were precipitated in a ten-fold excess of methanol and dried under vacuum for several hours.

Determination of GMA Content

The weight percentage of grafting was determined by titration, the most common procedure used in epoxide analysis. The grafted polymer was refluxed with xylene for 0.5 h, and then HCl-acetone solution was added. The solution was allowed to complete the reaction for 0.5 h. The GMA content of grafted polymer was determined by titration of the residual hydrochloric acid by back-titration with standard sodium hydroxide.

Hydrolytic Degradation

The PLA and PLA-co-PGMA were cast from chloroform solution (5 wt%) and dried overnight to obtain colorless films. After being dried in vacuum, the films (about 20 × 10 × 0.5 mm) were incubated in 0.1 M phosphate buffered saline (pH 7.4) at 60°C for predetermined periods of time. The samples were washed intensively with distilled water to remove residual buffer solution and dried under reduced pressure for at least 2d before being subjected to analyses. Each data point is the mean of three measurements. Mass loss was calculated according to the following equation:

$$\text{Mass loss }\% = \frac{m_i - m_t}{m_i} \times 100$$

where m_i and m_t represent the initial mass and the dry mass at time t.

Surface Modification of BC

We carried out the reaction of hydroxyl group of cellulose and epoxide under various conditions:

1. BC pellicles were immersed in the dioxane solution of PLA-co-PGMA at the concentration of 1 wt% for 24 h. After being dried at room temperature, the products were submitted to a 24 h Soxhlet extraction with THF and labelled as PGBC.
2. The difference from (1) method is that BC was placed in the oven at 105°C for 2 h, after drying at room temperature. Treated BC in this condition was labelled as PGhotBC.
3. The difference from (1) method is that hydrochloric acid was used to catalyze open-ring reaction during the impregnation. Treated BC in this condition was labelled as PGHABC.
4. BC pellicles were immersed in 5 wt% KH550 solution for 24 h, dried at room temperature and then placed in the oven at 120°C for 2 h. Next, it was treated according to (1) method. Treated BC in this condition was labelled as PGKHBC.

Fourier Transform Infrared (FTIR)

FTIR spectra of PLA, GMA, PLA-GMA and PLA-co-PGMA were taken on an FTIR-NICOLET5700 (Shimadzu) spectrometer by a KBr disk. The spectrometer was used in the range of 4000–400 cm^{-1}.

Gel Permeation Chromatography (GPC)

The molecular weight, polydispersity index (PDI) of PLA-GMA, PLA-co-PGMA was determined by a multi-detector GPC equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector, which was produced by Wyatt Technology Corporation. GPC was performed using THF as eluent at a flow rate of 1 mL/min.

Contact Angle Measurements

Contact angle measurements were carried out by depositing calibrated liquids, distilled water and methylene iodide drops, on the samples, and the given value is the average value of 5 measurements. The apparatus used for these measurements was a homemade static instrument equipped with a CCD camera working up to 25 images per second.

RESULTS AND DISCUSSION

Macromonomers PLA terminated with methacrylate function at one of their ends were synthesized by the reaction of the epoxy group of GMA and carboxylic of PLA, and their free radical copolymerization with GMA was further investigated. The polymerization reaction gives rise to the formation of graft copolymers, which have a synthesis route that is represented in Figure 1.

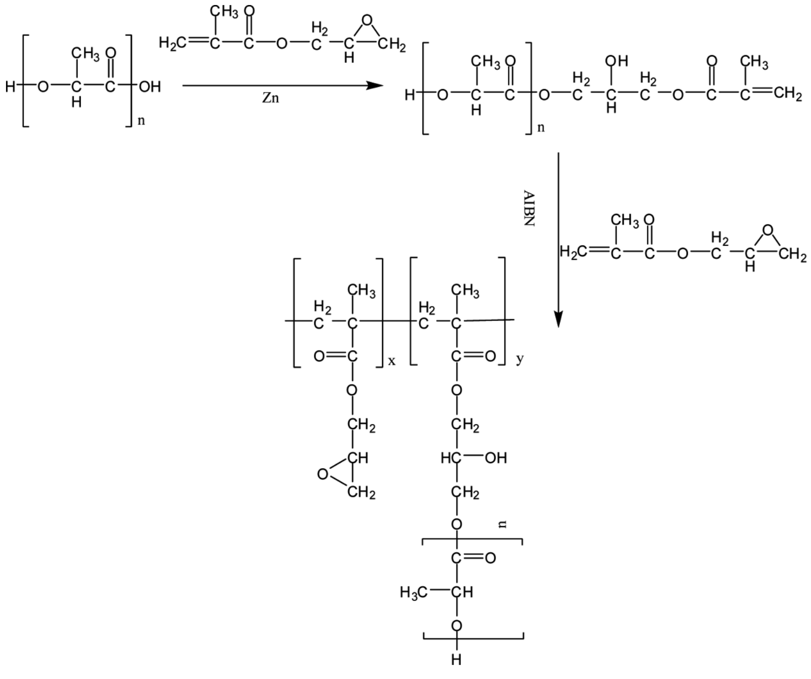

Figure 1: Synthesis route of PLA-co-PGMA copolymers.

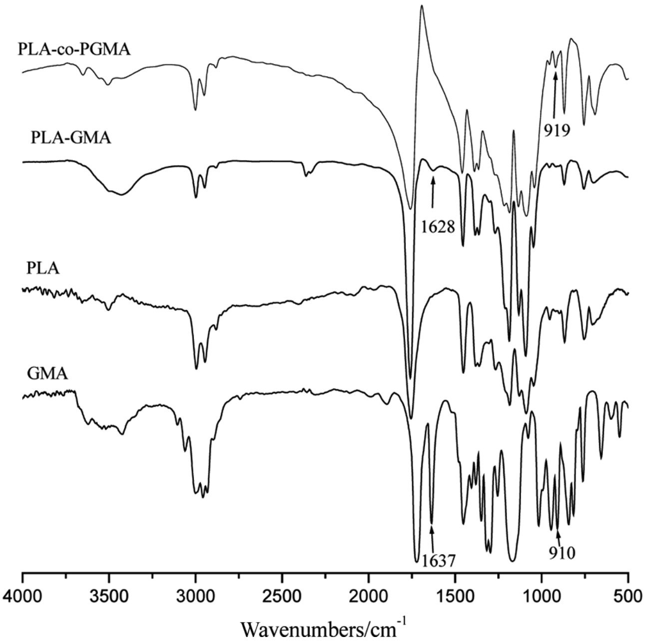

Figure 2: IR spectra of GMA, PLA, PLA-GMA and PLA-co-PGMA.

Molecular weights of PLA-GMA were determined by GPC. The results were with a Mn of 42000 with a polydispersity (PDI) of 1.5. The result was lower than that of PLA because of the degradation of PLA, and this will contribute to form more PLA-GMA macromonomers. PLA-GMA and GMA were expected to copolymerize in solution and GMA has been shown to polymerize well under a variety of solution conditions with typical vinyl and acrylic monomers [13,14].

Figure 2 shows the respective IR spectra of GMA, PLA, PLA-GMA and PLA-co-PGMA. By comparison with PLA, the new peak at 1628 cm^{-1} as can be seen in the spectrum of the PLA-GMA macromonomer is associated with the C=C bonds of the GMA. Meanwhile, the absence of the peak of the epoxy group (910–920 cm^{-1}) indicated the reaction of COOH and epoxy group carried out. Further, we can see that in PLA-co-PGMA, a band attributed to the C=C bonds was not observed around 1628 cm^{-1}, and this meant that the C=C bonds disappeared after polymerization. In addition, a new absorption band at wave numbers of about 919 cm^{-1} was ascribed to the asymmetric stretching of the epoxy group. All these seem to indicate that the PLA-co-PGMA copolymer has been successfully synthesized.

Effect of Initiator Concentration

Table 1 shows the effect of initiator concentration on the content of GMA. First, the graft content increases from 6.23% to 12.08% as the initiator

Table 1: Effect of initiator concentration on content of GMA.

Sample	Monomer molar ratio ($m_{PLA\text{-}GMA}/m_{GMA}$)	Initiator (wt.%)	Content of GMA (wt.%)
1	1:60	1	6.23
2	1:60	1.5	10.75
3	1:60	2	12.08
4	1:60	2.5	4.27

concentration rose from 1% to 2%, and then decreases speedily. This may be ascribed to the increase of macroradicals with increasing the initiator concentration at low concentration of initiator until all of PLA-GMA macromonomer was initiated, then homopolymerization of GMA became in a dominant position, which resulted in the decrease of content of GMA.

Effect of Monomer Molar Ratio

Several polymer compositions were studied, and the results are outlined in Table 2. It can be seen that the contents of GMA are decreased as an increase of $m_{PLA\text{-}GMA}/m_{GMA}$. The molecular weight of the copolymer slightly increases at first and then decreases. Meanwhile, PDI of the copolymer, firstly, becomes narrow and then broad. When $m_{PLA\text{-}GMA}/m_{GMA}$ were over 1:15, the molecular weight of the copolymer was even lower than PLA-GMA. This was different from the result that molecular weights of copolymer increase with macromonomer being the majority monomer [15]. The reason may be explained that the chain of PLA is long and the homopolymerization of PLA-GMA is difficult in our work.

Hydrolytic Degradation

In our work, the copolymer is used as a surface compatibilizer of green composites. Therefore, the degradability of the copolymer becomes important. To evaluate the degradability of the PLA-co-PGMA, its degradation behavior was investigated in 0.1 M phosphate buffered saline (pH 7.4) at 60°C and compared with that of PLA.

Table 2: Effect of monomer molar ratio on content of GMA.

Sample	Monomer molar ratio ($m_{PLA\text{-}GMA}/m_{GMA}$)	Initiator (wt.%)	Content of GMA (wt.%)	Mn (g/mol)	PDI
5	1:50	2	14.20	43680	1.74
6	1:25	2	7.44	45400	1.45
7	1:15	2	5.37	34400	1.69
8	1:10	2	2.89	32670	1.76

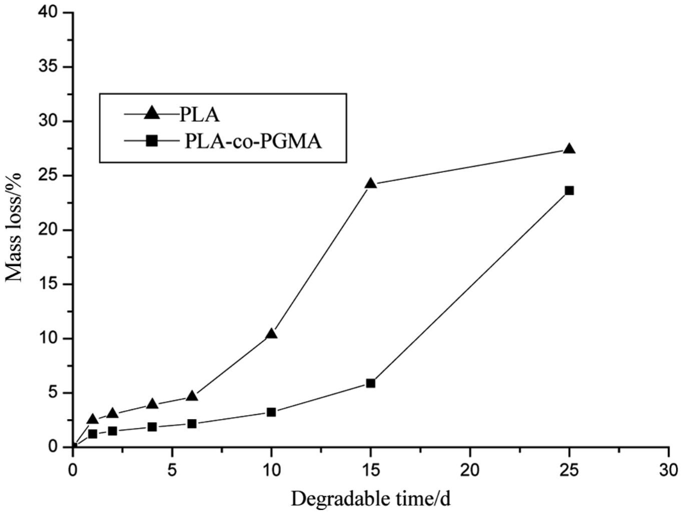

Figure 3: Mass loss of PLA and PLA-co-PGMA with degradable time.

Figure 3 shows the percent mass loss profile for PLA and PLA-co-PGMA as a function of degradation time. According to convention, the incorporation of hydrophilic group should enhance its degradation. However, the degradation rate of PLA-co-PGMA was lower than that of PLA. We speculated that degradation was impeded by the epoxy group because it can react with COOH which was obtained during degradation. Jang thought it was caused by the increase of the crystallization of the polymer because of changes in the structure of the chain [16].

Surface Modification of BC

We want to reduce hydrophilicity and improve the interfacial adhesion between BC and PLA matrix by surface modification of BC with PLA-co-PGMA. One can expect a chemical reaction between the cellulose hydroxyl groups and the PLA-co-PGMA epoxy groups, which is a typical reaction for epoxy groups. Besides the chemical binding, strong physical binding as H bonding is also expected. Sources have it that the reaction of OH of cellulose and epoxy group may be difficult in common condition [17]. In order to improve reactivity of cellulose and PLA-co-PGMA, we have studied the treatment of BC with KH550 before the treatment of PLA-co-PGMA.

Figure 4 shows a spectrum of BC and modified BC and hypothetical reaction was illustrated in Figure 5 [11]. It was noticed that the O–H stretching band does not show marked changes due to the introduction of the epoxide moieties. Because hydroxyl groups of cellulose react with the epoxy groups, the hydroxyl groups formed in the epoxy system would compensate in spectral

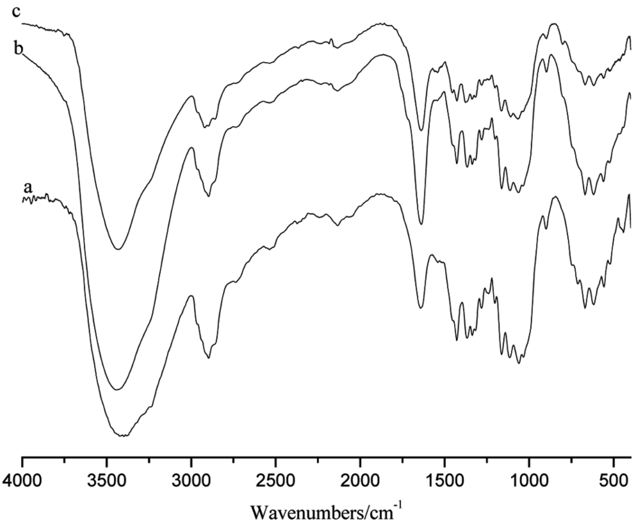

Figure 4: FTIR of BC modified with PLA-co-PGMA: (a) BC, (b) PGBC, (c) PGKHBC.

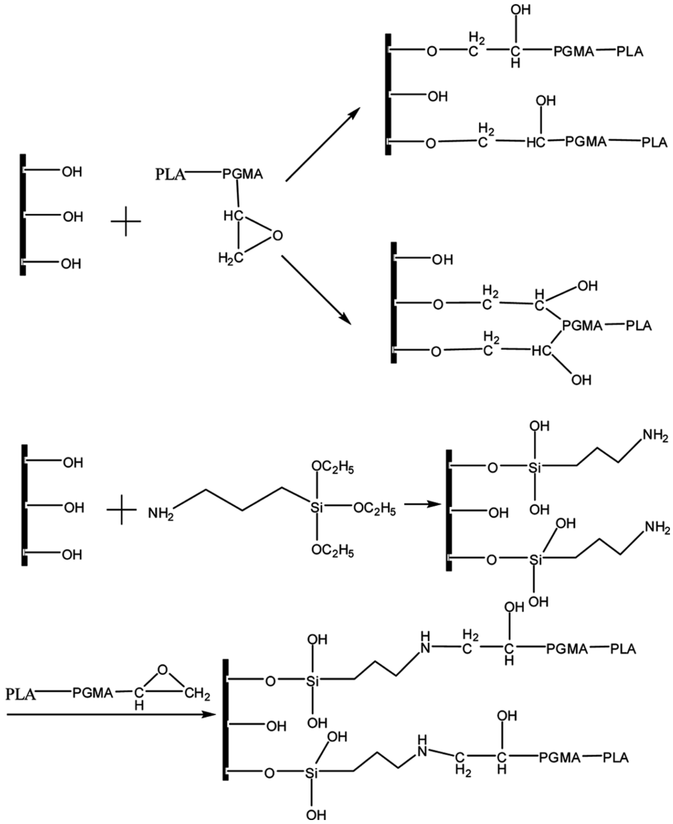

Figure 5: Proposed reaction scheme between PLA-co-PGMA and BC or BC modified with KH550.

Table 3: Surface properties of BC before and after modification at 20°C.

Sample	Water (°)	Methylene iodide (°)	Dispersive component (mJ/m^2)	Polar component (mJ/m^2)	Total surface energy (mJ/m^2)
PLA	78.85	37.73	37.14	4.04	41.18
BC	35.89	27.82	32.48	29.05	61.53
PGBC	50.61	34.96	31.91	20.57	52.47
PGhotBC	58.79	46.71	27.33	17.84	45.17
PGHABC	61.37	57.69	21.48	19.52	41.00
PGKHBC	81.97	44.80	33.83	3.70	37.53

intensity for this loss [18]. On the other hand, it is also possible to see an increment in the band corresponding to $1640\,\text{cm}^{-1}$ that indicates an increase in H–O–H interactions when the copolymer is deposited in the cellulose surface. This is also ascribed to an extra OH group in the epoxide, after the reaction of the GMA with the BC. The shoulders that appear at 1758 and $1730\,\text{cm}^{-1}$ in BC treated with the epoxides are attributed to the presence of PLA and PGMA. The epoxy band (910–$920\,\text{cm}^{-1}$) was absent in b and c spectra, which suggests the reaction of epoxide and hydroxyl groups. All together, the FTIR analyses effectively showed that the PLA-co-PGMA had reacted with cellulose and the BC nanofibril surface was modified.

Table 3 showed the surface properties of BC and modified BC with PLA-co-PGMA in different conditions. As expected, the virgin BC without surface treatment displayed a low water contact angle ($\sim$36°) arising from a high density of hydroxyl groups on the cellulose backbone and the water contact angle increased after surface treatment. Among all modified BC, the increase of the water contact angle of PGKHBC is the most obvious. This contributes to amido (NH_2) is active than the hydroxyl group, and the copolymers are easy to graft to cellulose substrate.

The surface energies were calculated from the contact angle data of two liquids at equilibrium by the Owens and Wendt method, which divides the total surface free energy into two components, the dispersive and the polar components [19].

$$\gamma_s^{total} = \gamma_s^p + \gamma_s^d$$

$$\gamma_{l1}(1+\cos\theta_1) = 2\left(\sqrt{\gamma_s^d \times \gamma_{l1}^d} + \sqrt{\gamma_s^p \times \gamma_{l1}^p}\right)$$

$$\gamma_{l2}(1+\cos\theta_2) = 2\left(\sqrt{\gamma_s^d \times \gamma_{l2}^d} + \sqrt{\gamma_s^p \times \gamma_{l2}^p}\right)$$

where, γ_l is the liquid surface tension, γ_s is the solid surface tension, γ_s^p is the polar component of solid surface tension and γ_s^d is the dispersive component of solid surface energy. From Table 3, total surface energy of PLA and BC was 41.18 and 61.53 mJ/m^2, respectively. These results corresponded well to those reported in the literature [20,21]. The decrease in the surface energy of BC after modification was essentially due to the reduction in its polar component, because of the replacement of the surface hydroxy groups by the nonpolar aliphatic chains. The calculated values in Table 3 indicate that the dispersive part of the cellulose surface energy is larger than the polar contribution. The reduction of the polar component is obvious, while the change of dispersive component is slight when BC was modified. This indicates that surface modification changes the component of the surface energy of BC and makes it more hydrophobic.

Interfacial tension is one of the key parameters that govern the compatibility between the components and the morphology of polymer composites. It is an accessible parameter that describes the thermodynamic state and structure of an interface [22]. In this work, we attempt to investigate the compatibility of the composite by obtaining the interfacial tension of BC/PLA.

Due to experimental difficulty in handling and ensuring equilibrium of highly viscous melts and its degradability of PLA melt, we have measured the surface intension in the solid state and extrapolated to the melt. The surface tension of PLA varied linearly with temperature with $-(d\gamma/dT)$ about 0.05 mN/(m $\cdot$ K) at ordinary temperature far below the critical temperature [23]. The polarity is independent of temperature, i.e., $dx^p/dT = 0$ [24]. Thus, surface tension of PLA melt is as follows: dispersive component ($\gamma^d = 29.86$ mN/m), polar component ($\gamma^p = 3.32$ mN/m). The result of the calculation was approximate to the values of literatures [23].

According to Wu [24], the interfacial tension can be calculated from the surface tensions and their components of the two phases by the harmonic mean equation or the geometric mean equation, and the interfacial tension of cellulose and PLA can thus be calculated:

Geometric mean

$$\gamma_{SL} = \gamma_S + \gamma_L - 2[(\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2}]$$

Harmonic mean

$$\gamma_{SL} = \gamma_S + \gamma_L - \left(\frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \right)$$

where, γ_L represents the surface tension of PLA melt, γ_S represents the surface tension of BC or modified BC, γ_{SL} represents the interfacial tension of BC and PLA, and the superscript (d, p) represents the dispersive component and polar component, respectively.

Table 4 gives the interfacial tension of BC/PLA by calculating. We can notice that the interfacial tension of cellulose/PLA decreased visibly after

Table 4: The interfacial tension of BC/PLA.

Sample	Geometric-mean γ_{SL} (mN/m)	Harmonic-mean γ_{SL} (mN/m)
BC/PLA	12.78	20.56
PGBC/PLA	7.39	12.51
PGhotBC/PLA	5.82	10.08
PGHABC/PLA	7.43	12.86
PGKHBC/PLA	0.13	0.27

modification despite which method was used, especially for PGKHBC/PLA, close to 0 (0.13, 0.27 mN/m). This represents the surface modification has improved the compatibility of BC/PLA and this is an effective approach to optimization of a natural fiber/PLA matrix interface for composite materials containing natural fibers.

CONCLUSIONS

The copolymer of PLA-co-PGMA was successfully synthesized in solution and applied to modify bacterial cellulose. FTIR analysis proved the reactions of BC and PLA-co-PGMA and ensured efficient chemical bonding of them. Contact angle measurements revealed that the hydrophilic character of the cellulose nanofibers can be strongly decreased after the treatment. Surface modification obviously reduced the interfacial tension of BC and PLA, which will improve the compatibility and the dispersability of the fiber in matrix.

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