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Starch grafted poly(butylene succinate) via conjugating reaction and its role on enhancing the compatibility

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ABSTRACT

A single step process of grafting poly(butylene succinate) (PBS) on starch to obtain starch-*g*-PBS in a heterogeneous system is proposed. Starch-*g*-PBS is accomplished by a conjugating reaction in chloroform at room temperature between hydroxyl groups of starch and carboxylic acid terminal groups of PBS by using *N*-*N*′-dicyclohexylcarbodiimide (DCC) conjugating agent. The grafting of PBS at both primary alcohol and secondary alcohol of starch is as high as 20–30% as confirmed by ^{1}H NMR and HMBC 2D NMR. The grafting of PBS results in a drastic changes of the crystallization as seen from the decrease in size of spherulite. The starch-*g*-PBS is a good compatibilizer between PBS and starch by promoting strong interfacial adhesion of the blend as evidenced from the improvement of modulus (2 times increase) and the miscibility of the blend in SEM images.

1. Introduction

The blending of starch and biodegradable polyester has received much attention (Averous, 2004; Shah, Hasan, Hameed, & Ahmed, 2008) since both polymers are environmental friendly materials. A combination of these two components could possibly solve the limiting properties of each other. The mechanical properties and the processability of starch are gradually improved when it is blended with biodegradable polyester (Averous & Boquillon, 2004; Follain, Dole, & Bliard, 2005). Moreover, the cost of biodegradable polyester can be reduced when using starch as an additive (Gaspar, Benko, Dogossy, Reczey, & Czigany, 2005; Godbole, Gote, Latkar, & Chakrabarti, 2003). Examples of biodegradable polyesters are polylactic acid (PLA) (Chen et al., 2006; Xiong et al., 2013), polycaprolactone (PCL) (Sarazin, Li, Orts, & Favis, 2008), and polybutylene succinate (PBS) (Ohikita & Lee, 2005; Zeng, Jiao, & Li, 2011). PBS has unique properties such as excellent impact strength, high flexibility, good thermal stability and chemical resistance which are similar to those of polyethylene (Ba, Yang, Hao, Liu, & Cao, 2003; Li, Zeng, Wang, Yang, & Wang, 2008).

Starch exhibits hydrophilicity with a strong inter- and intramolecular structure via hydrogen bonds (Nabar, Raquez, Dubois, & Narayan, 2005), while PBS shows hydrophobic properties due to the aliphatic repeat unit on the chain. As a result, PBS and starch are immiscible. The development of PBS and starch blends by adding a compatibilizer such as anhydride-based functional group (Mani & Bhattacharya, 2001), glycerol (Lai, Huang, & Shen, 2005), lysine diisocyanate (LDI) (Ohikita & Lee, 2005), and toluene-2,4-diisocyanate (Zeng et al., 2011) has been reported.

In general, the development of a blend to satisfy the overall physical and chemical behaviors relies on the ability to control the strong interfacial adhesion and dispersed phase size (Nabar et al., 2005). To increase the interfacial adhesion between the starch and the PBS matrix, the functionalization of the starch surface by grafting PBS (starch-*g*-PBS) should create a strong interfacial adhesion of PBS and starch. Previously, the functionalization of biodegradable polyester on a starch surface such as starch-*g*-PLA (Chen, Qiu, et al., 2005) and starch-*g*-PCL (Choi, Kim, & Park, 1999; Chen, Ni, et al., 2005), to act as a compatibilizer, has been previously investigated. Although there are some reports on obtaining a modified starch surface, the points on the functionalization with long chain aliphatic polyester, the multiple steps reaction, the use of catalyst, including unclear structural clarification still require further study.

In principal, there are many types of coupling and conjugating agents that widely used in the carbohydrate polymer field. For example, the thermally reversible

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poly(N-isopropylacrylamide)–dextran derivative conjugate, wassynthesized by conjugating amino-terminated poly(N-isopropylacrylamide) to a dextran via ethyl-3-(3-dimethyl-aminopropyl)-carbodiimide (EDC) or *N*-*N*′-dicyclohexyl carbodiimide (DCC) in the organic solvent (Anastase-Ravion, Ding, Pelle, Hoffman, & Letourneur, 2001). Dextran–methylprednisolone conjugate was prepared using carbonyldiimidazole (CDI) as a coupling agent with succinic acid as a spacer at room temperature (Mehvar, Dann, & Hoganson, 2000). However, it should be noted that CDI and EDC are easily to hydrolyze so this can limit the overall reaction yield (Fangkangwanwong, Akashi, Kida, & Chirachanchai, 2006).

The present work focuses on the grafting of PBS on a starch based on the single step conjugating reaction in a heterogeneous system with detailed structural analysis. The work also studies the effects of the molar ratio of PBS and starch on the degree of substitution and thermal and crystallization behaviors. In addition, the work also extends to the use of starch-*g*-PBS as compatibilizer between PBS and starch.

2. Experimental

2.1. Materials

PBS resin was purchased from Mitsubishi Chemicals Co., Ltd., Japan (M_w = 47,000, M_n = 37,000). Tapioca starch was purchased from ETC International Trading Co., Ltd., Thailand. Chloroform, ethanol, and acetone were analytical grade and bought from RCI Labscan, Thailand. Deuterated chloroform ($CDCl_3$) was purchased from Sigma–Aldrich, USA. *N*-*N*′-dicyclohexylcarbodiimide (DCC) was purchased from Fluka, Germany. PBS was reprecipitated in acetone before use whereas other chemicals were used without purification.

2.2. Methodology

2.2.1. Preparation of starch-g-PBS

PBS (1.75 g, 0.037 mmol) was dissolved in chloroform in a three-necked round-bottom flask (250 ml) with a magnetic stirrer and nitrogen inlet. DCC (1.5 mmol of PBS) and tapioca starch (16 g, 0.1 mol) were added to the solution and stirred for 24 h at room temperature. The product obtained was centrifuged at 10,000 rpm for 10 min to remove the unreacted starch before precipitating in acetone followed by washing thoroughly with ethanol several times to exclude the unreacted DCC and dicyclohexylurea. The purified product was dried at 50 °C for 24 h to obtain starch-*g*-PBS (72% yield). Similarly, other starch-*g*-PBS prepared by using different molar ratios of PBS to starch for 0.63, 1, 1.5, 2.2, 3.5, and 6 mmol with a specific amount of DCC (1.5 equivalent mol of PBS) were carried out (% yield was in Table 1).

2.2.2. Preparation of starch/PBS blends containing starch-g-PBS

Blends of starch/starch-*g*-PBS/PBS were prepared by using a Brabender mixer at a screw speed of 80 rpm. The weight ratios of starch/PBS were varied from 20/80 wt%, 40/60 wt%, 60/40 wt%, to 80/20 wt%. Starch-*g*-PBS was subsequently added to the blends with 5 phr at 130 °C for 10 min.

2.3. Measurements

2.3.1. Structural characterization

Structural characterization was carried out by an Avance 500 Bruker Biospin nuclear magnetic resonance (NMR) at room temperature. The samples were dissolved in deuterated chloroform.

2.3.2. Physico-chemical and thermal properties

Intrinsic viscosity was evaluated by a CANNON Ubbelodhe viscometer (50 B582) with a constant temperature bath CT1000 CANNON. The products obtained were dissolved in chloroform at 0.25 g dl^{-1}. The intrinsic viscosity was calculated by the Solomon–Ciuta equation below:

$$[\eta] = \frac{\sqrt{2((t/t_0) - 1) - 2\ln(t/t_0)}}{c} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity (dl g^{-1}), t is the flow time of the sample (s), t_0 is the flow time of the pure solvent (s), and c is the concentration of the sample (g dl^{-1}).

A non-isothermal temperature profile was carried out using a 200 F3 Netzsch DSC (differential scanning calorimeter) as follow: (i) heating from 25 °C to 130 °C at a heating rate of 10 °C min^{-1} and holding at 130 °C for 5 min, (ii) cooling from 130 °C to −50 °C at a cooling rate of 10 °C min^{-1} and holding at −50 °C for 5 min, and (iii) heating from −50 °C to 130 °C at a heating rate of 10 °C min^{-1}. Melting temperature (T_m), heat of fusion (ΔH_m), and glass transition temperature (T_g) were determined from the second heating under the non-isothermal measurement. The crystallization temperature (T_c) and heat of crystallization (ΔH_c) were obtained from the cooling under non-isothermal measurement.

A pyris diamond Perkin Elmer TGA (thermogravimetric differential analyzer) was used to observe the degradation temperature of the neat PBS and the products obtained. The samples were heated form 30 °C to 600 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

2.3.3. Processing and testing

The blends were obtained with a Brabender mixer using an operating temperature of 130 °C, mixing time of 10 min and screw speed for 80 rpm.

A Wabash compression molding machine was used to compress the products obtained from the mixer. The conditions were: (i) preheating at 130 °C for 10 min, (ii) compressing at 130 °C for 5 min at 10 tons loading and (iii) cooling from 130 °C to 30 °C.

Flexural properties were measured by using an Instron 4206 universal testing instrument with a 5 kN load cell and a rate of crosshead motion of 0.85 mm/min. Rectangular samples (2.5 cm × 10 cm × 0.2 cm) were used with a gauge length of 8 cm. The tests were done in 10 replication and the results were averaged for mean value.

Melt flow index (MFI) was measured according to ASTM D1238 using a Zwick 4105 extrusion plastometer capillary canal melt viscometer. The melting temperature at 190 °C was applied with an applied load of 2.16 kg.

2.3.4. Spherulite formation and compatibility studies

Spherulite formation was observed by a DMRXP Leica polarizing optical microscope. The isothermal temperature profile was carried out by the following steps: (i) heating at 130 °C for 5 min, (ii) quenching from 130 °C to 80 °C. The spherulite formation was observed at 80 °C every 1 s.

Compatibility was characterized by an S-1500 Hitachi ultra-high resolution cold field emission scanning electron microscope (FE-SEM).

3. Results and discussion

Up to the present, the number of grafting polymers on starch has been reported such as starch-*g*-PLA and starch-*g*-PCL. Considering substitution degree of grafting or grafting percentages, we found that most works showed the structural clarification based on qualitative analysis using Fourier transform infrared spectrometer (FTIR). In some case, the quantitative analysis using thermogravimetric differential analyzer (TGA) was done. It should be noted that those characterizations were based on indirect information. Here

Table 1
Thermal and crystallization behavior of the starch-*g*-PBS and neat PBS.

Starch:PBS	Yield (%)	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})	T_g (°C)	T_d onset (°C)	Ash (%)
1:0.37	72	109.2 ± 1.3	67.5 ± 3.6	65.4 ± 1.0	60.0 ± 3.1	-34.20 ± 2.0	372.4 ± 4.0	1.50
1:0.63	68	109.7 ± 1.2	66.6 ± 2.4	66.2 ± 1.0	58.0 ± 3.0	-34.20 ± 3.0	372.3 ± 0.4	1.80
1:1.00	70	110.0 ± 0.6	69.7 ± 2.1	66.7 ± 1.1	58.3 ± 2.0	-33.80 ± 3.3	373.0 ± 0.4	2.37
1:1.50	64	110.1 ± 0.8	65.0 ± 3.2	66.0 ± 0.7	57.0 ± 2.6	-34.20 ± 3.1	370.0 ± 2.8	2.42
1:2.20	60	109.3 ± 0.4	71.4 ± 2.2	66.1 ± 0.7	62.0 ± 3.4	-34.43 ± 3.4	372.5 ± 1.1	2.00
1:3.50	57	109.4 ± 0.3	71.0 ± 3.0	67.0 ± 0.7	62.0 ± 3.3	-34.13 ± 1.6	372.0 ± 0.2	1.41
1:6.00	46	110.1 ± 0.4	70.6 ± 3.3	67.0 ± 0.7	61.3 ± 2.0	-33.13 ± 3.0	373.0 ± 0.5	1.70
Neat PBS	–	110.2 ± 0.7	72.0 ± 2.9	68.3 ± 0.4	62.7 ± 3.3	-34.20 ± 0.1	372.0 ± 3.3	0.00

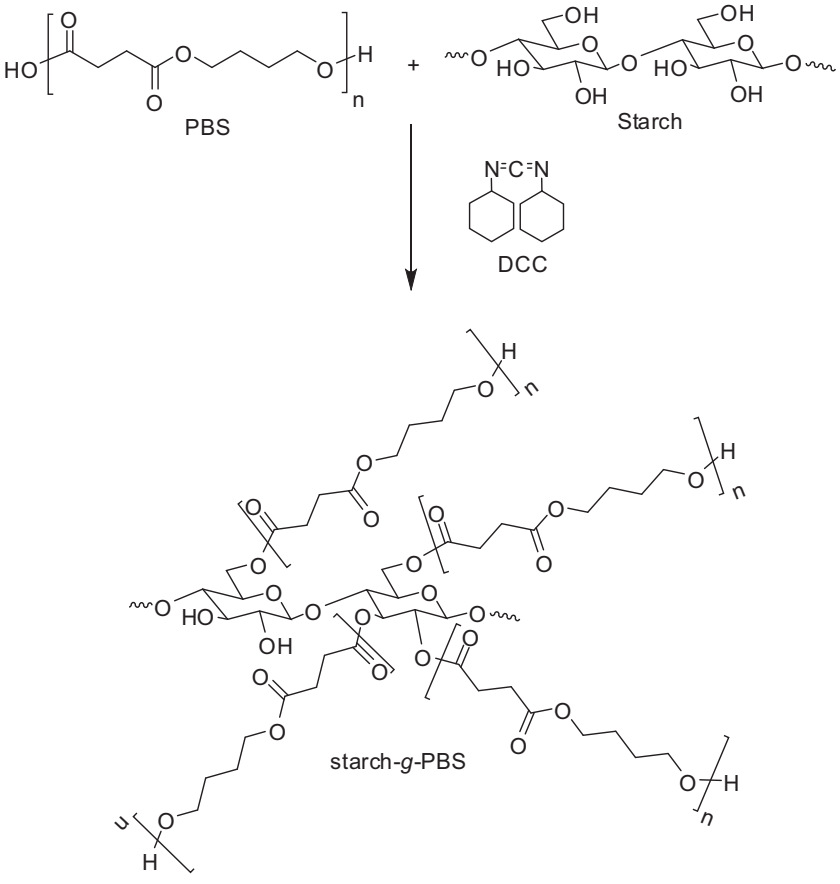
we attempt to quantify the degree of substitution of PBS on starch. It should be noted that, in preparation steps, a careful purification to exclude unreacted starch was carried out. It was found that starch-*g*-PBS obtained was partially soluble in chloroform and this allowed us to clarify the structure using ^{1}H NMR and HMBC 2D NMR.

3.1. Structural characterization

PBS was grafted on the starch backbone under a heterogeneous reaction. Based on the structure, the conjugations of PBS on starch are possible at C_2, C_3, and C_6 to form ester linkages as shown in Scheme 1. The products show chemical shifts at 1.7 ppm (4H, m, —**CH$_2$**—CH$_2$—O—), 2.6 ppm (4H, s, —(C=O)—CH$_2$—**CH$_2$**—(C=O)—), and 4.1 ppm (4H, t, —CH$_2$—**CH$_2$**—O—), which are similar to those of the neat PBS (Fig. 1A). The product also shows new chemical shifts at 3.3–3.8 ppm (1H, m, —O—**CH**—CH) and 5.1 ppm (1H, m, —O—**CH**—), which can be reasonably assigned to H_2 to H_5 and H_1 of the pyranose ring, respectively. This confirmed an existence of starch molecules on starch-*g*-PBS. It should be noted that all products obtained from other PBS and starch molar ratios showed similar patterns of ^{1}H NMR spectra.

To investigate the grafting at each position on the pyranose ring, ^{13}C NMR was applied. Fig. 1B presents a typical ^{13}C NMR spectrum for the product obtained. The three distinct carbonyl ^{13}C signals at 171.8 ppm, 171.6 ppm, and 170.5 ppm correspond to the carbon atoms that belonging to the ester group. The results imply that the carboxylic groups of PBS are conjugated with all three reactive hydroxyl groups of starch.

In order to identify the detailed structure of starch-*g*-PBS, heteronuclear multiple bond correlation (HMBC) technique was used. This technique determines the correlation between the carbon and proton via multiple bonds. For example, if the structure (Scheme 1) is an ester linkage at C_2 and C_3, it should correlate with the proton at H_1 of the pyranose ring because it is the adjacent carbonyl atom of H_1 via two and three bonds, respectively. In the case of an ester linkage at C_6, it should correlate with the proton at H_6 of pyranose ring because it is the neighboring atom of H_6 of the pyranose ring via one bond.



Scheme 1. Preparation of starch-*g*-PBS.

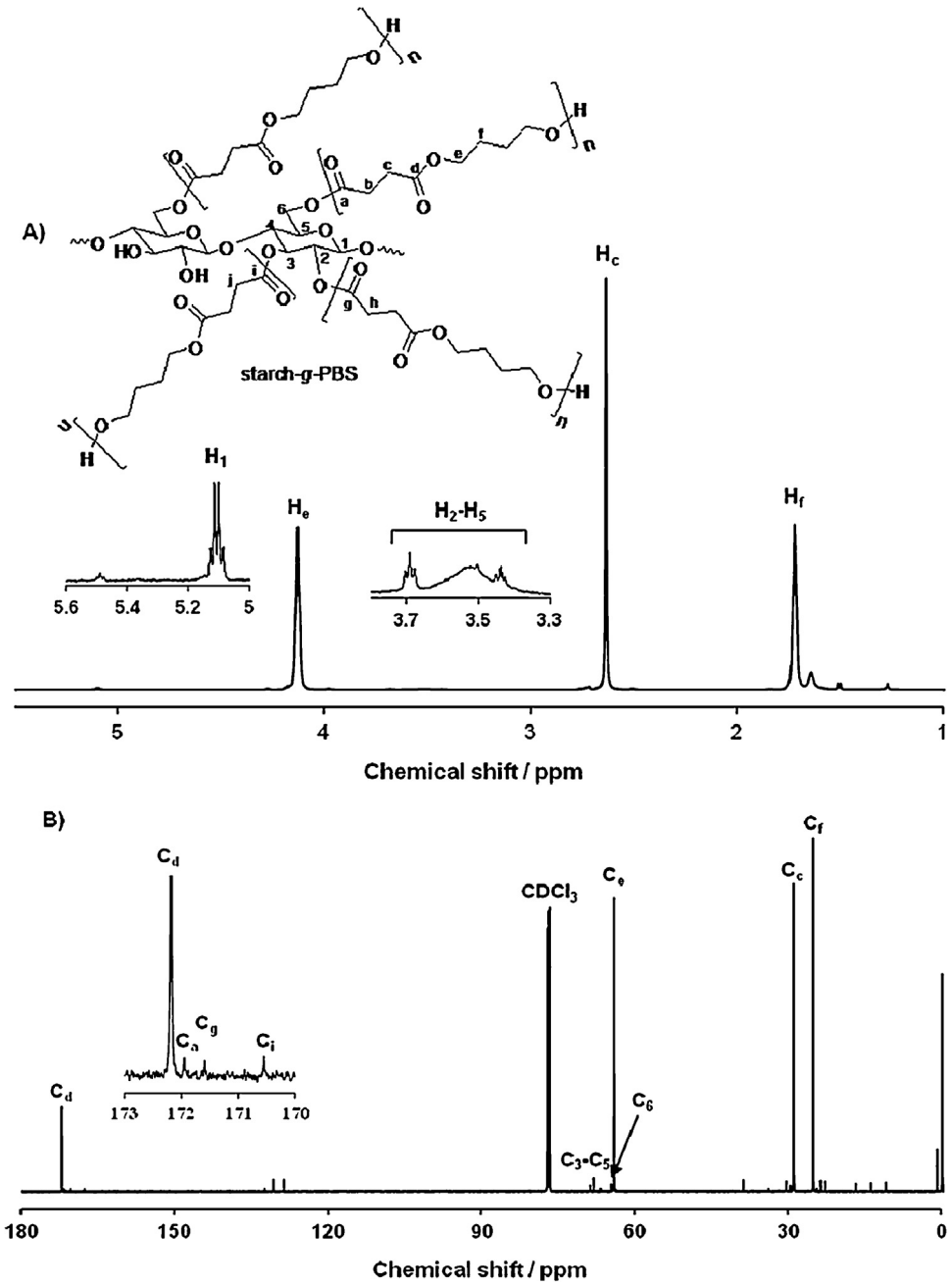


Fig. 1. (A) ^{1}H NMR and (B) ^{13}C NMR of starch-*g*-PBS.

Fig. 2 shows HMBC spectrum of starch-*g*-PBS. The fact that there are three positions, i.e. C_i, C_a, and C_g, that PBS conjugates on starch as indicated in the structure in Fig. 1, the interaction with the proton on the pyranose ring is a good indicator of quali- and quantitative conjugation. The correlations between C_i of the carbonyl (at 170.5 ppm) and the three species of protons, which are H_1 of the pyranose ring (at 5.1 ppm), H_c (at 2.6 ppm), and H_j of the methylene protons (at 2.54 ppm), are identified. For C_g (at 171.6 ppm), the correlation with H_1 of the pyranose ring (at 5.1 ppm), H_c (at 2.6 ppm), and H_h (at 2.7 ppm) of the methylene protons are confirmed. These two results suggest that the grafting of PBS on starch is based on the ester bond at C_3 and C_2 of the pyranose ring, respectively. The correlation between carbonyl group C_a (at 171.8 ppm) and proton species, i.e., H_6 (at 4.16 ppm), H_c (at 2.60 ppm), and H_b (2.63 ppm) is also investigated. This further suggests the PBS conjugation at C_6 of the pyranose ring.

3.2. Degree of PBS grafting

The degree substitution (%DS) of PBS on starch could be identified based on the abovementioned three correlations, which are (i) between carbonyl C_a (at 171.8 ppm) and methylene proton H_b (at 2.63 ppm), (ii) carbonyl C_g (at 171.6 ppm) and methylene proton H_h (at 2.7 ppm), and (iii) carbonyl C_i (at 170.5 ppm) and methylene proton H_j (at 2.54 ppm) (Fig. 2). The chemical shifts of interest are; H_b at 2.63 ppm, H_h at 2.70 ppm, H_j at 2.54 ppm and H_1 of the pyranose ring at 5.1 ppm. Based on Eq. (2), %DS of PBS on starch with a systematic variation of the PBS feeding mole ratio can be calculated. Fig. 3 shows the effect of mole ratio of PBS on %DS. The %DS is the highest

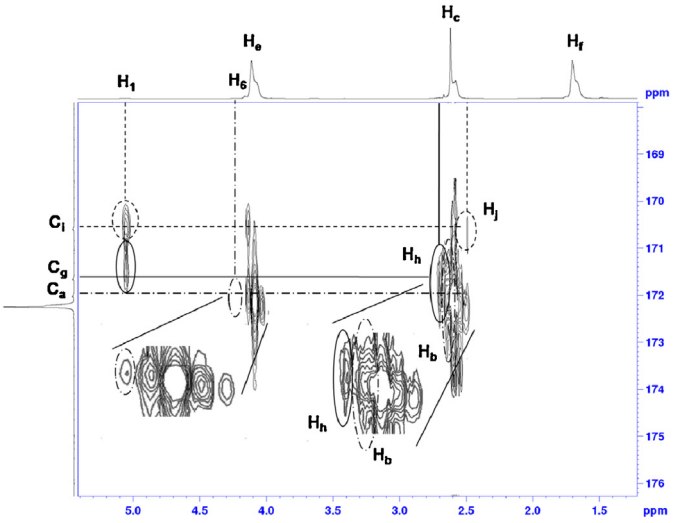


Fig. 2. HMBC 2D NMR spectrum of starch-*g*-PBS.

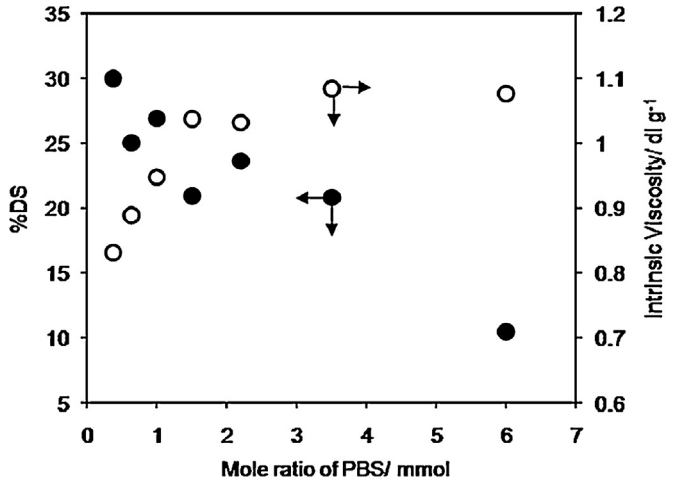


Fig. 3. Degree substitution of PBS on starch evaluated by ^{1}H NMR (●), and intrinsic viscosity of starch-*g*-PBS (○).

(25–30 mol%) when the PBS feed ratio was only 0.5–1.0 mmol. The plots indicate that the substitution decreases with an increase of the mole ratio of PBS. This might occur when the concentration is high, the chain entanglement of PBS chains is significant and consequently reduces its reactivity.

$$\%DS = \frac{\frac{\int H_b}{2} + \frac{\int H_h}{2} + \frac{\int H_j}{2}}{3\int H_1} \times 100 \quad (2)$$

3.3. Intrinsic viscosity

It comes to the question about the molecular weight of starch and starch-*g*-PBS. Gilbert et al. pointed out that the molecular weight of starch-based materials can be measured by light-scattering with a complete dissolution of the sample in the concentrated NaOH for a long time under a careful condition to avoid starch degradation (Gilbert et al., 2010). In our case, the use of NaOH for starch-*g*-PBS might lead to alkaline hydrolysis of PBS. The fact that our starch-*g*-PBS was partially soluble in chloroform, an attempt to clarify the molecular weight of starch-*g*-PBS by using size exclusion chromatography (SEC) was carried out. The chloroform solution was neatly filtrated to obtain the clear solutions. Although the clear solution represented a relatively low molecular weight of the grafted starch, the SEC result insisted the molecular weight of starch-*g*-PBS in chloroform solution to be about 10^5 Da.

Normally, the higher the molecular weight and branches, the lower the viscosity. In general, starch is difficult to dissolve in solvent however, the starch-*g*-PBS could be dissolved in chloroform which allowed clarification of the viscosity. The intrinsic viscosity of the neat PBS was at 1.25 dl g^{-1}. As shown in Fig. 3, the intrinsic viscosity of starch-*g*-PBS is about 0.8–1.0 dl g^{-1} which is increased with increasing mole ratio of PBS, but still lower than that of the neat PBS. It is clear that the higher the %DS of PBS on starch, the lower the viscosity.

3.4. Thermal properties and crystallization behaviors

A differential scanning calorimeter (DSC) was used to study thermal properties and crystallization of starch-*g*-PBS. The results from DSC allowed us to study the packing structure, including chain mobility initiated after the molten state.

The starch does not show T_m, T_c, or T_g during the non-isothermal temperature profile. As shown in Table 1, the products obtained show T_c at 65–67 °C which is caused by the effect of the PBS chain on the starch molecule. It is clear that T_c slightly increases with decreasing %DS. This might be due to a higher %DS, which is bulkier, causing difficulty in chain packing to induce the crystalline phase. This process occurs during the cooling cycle. The starch-*g*-PBS, with higher %DS, requires a higher energy level to align the chains to form the crystalline phase than starch-*g*-PBS with lower %DS. The heat of crystallization (ΔH_c) decreases with increasing %DS. This implies that the grafting of PBS reduces the chain packing of starch. The starch-*g*-PBS shows T_m and T_g at ~110 °C and −34 °C, respectively, which are similar to those of neat PBS. These results were relevant to the work that reported by Lai et al. (2005). This confirms the grafting of PBS on starch results in the polymers with the T_m and T_g which are important information in production.

The thermo-gravimetric analysis of all starch-*g*-PBS samples shows a single degradation, similar to the neat PBS. However, starch-*g*-PBS shows an ash content of ~1.5–2.5%, which can be referred as starch content.

3.5. Spherulite formation

Spherulite formation is important information to evaluate the semi-crystalline structure of a polymer. It is expected that the branching polymer will show faster spherulite formation than that of the linear polymer (Phuphuak & Chirachanchai, 2013). The spherulite formation of starch cannot be investigated due to the character of starch molecules, resulting in blurry picture. Starch-*g*-PBS performs fast spherulite formation and has small spherulite size as compared to the neat PBS (Fig. 4A). Fig. 4B quantifies the spherulite growth rate (G) and the number of spherulite. The measurement of spherulite growth rates was investigated in isothermal conditions by following the growth of a spherulite radius (r) with time (t) according to Eq. (3) (Lorenzo, 2001). The spherulite growth rates of all starch-*g*-PBS samples and the neat PBS are similar to each other at ~0.6 μm s^{-1}. The number of spherulite formation of the neat PBS was at ~600 per mm^2. However, the number of spherulite formation of the starch-*g*-PBS is in the range of 1000–1500 per mm^2, which is much higher than that of neat PBS (2 times). Moreover, the number of spherulite formation increases during an increase of %DS of PBS. This implies that the branches of the polymer crystallized into small spherulite. The polymers with branches have more chain segments which can be active nuclei upon the isothermal crystallization from the melts, the high

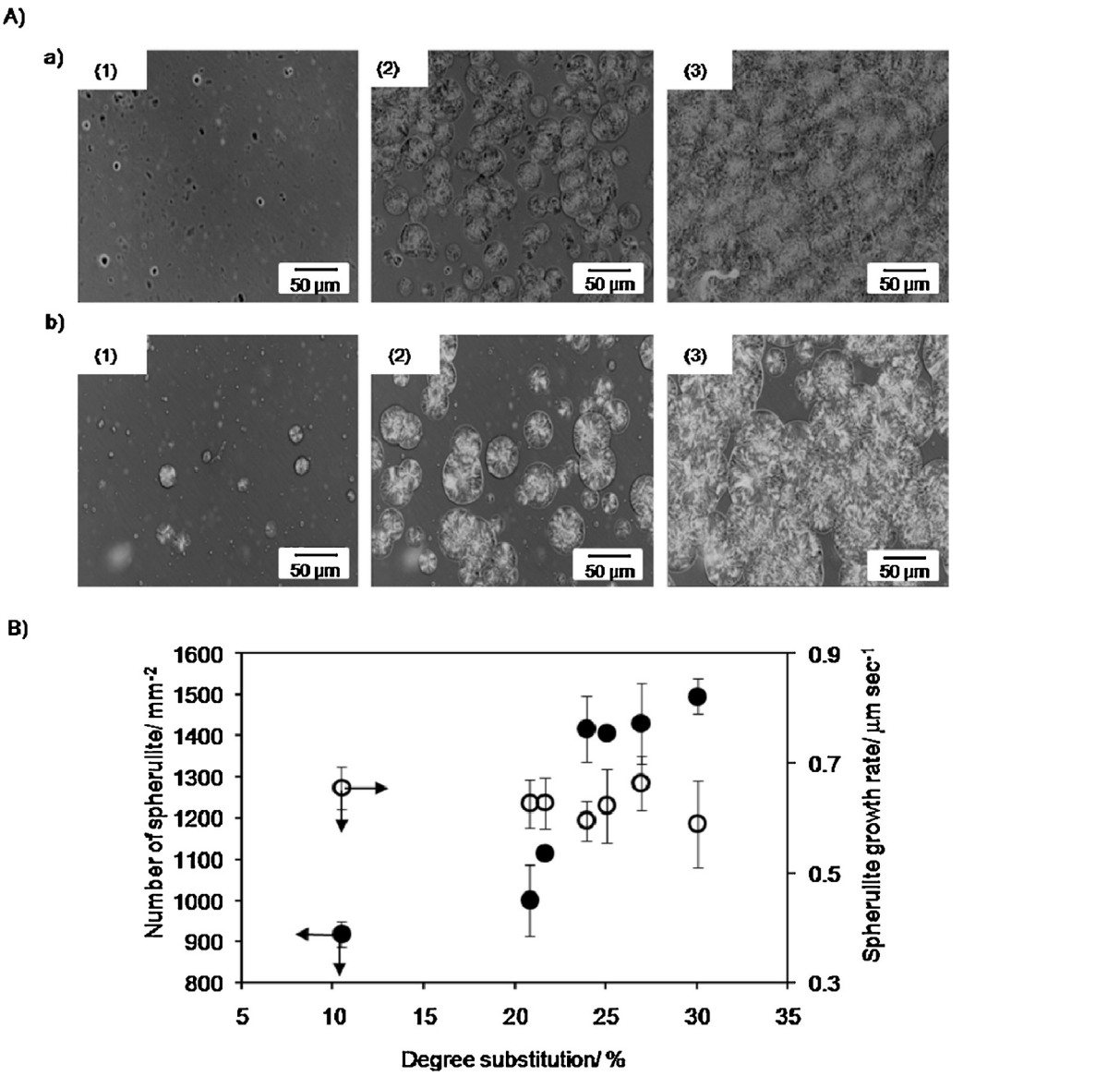


Fig. 4. (A) Spherulite formation images of (a) neat PBS and (b) starch-*g*-PBS (%DS = 30) under isothermal treatment at 80 °C at: (1) 0 s, (2) 60 s, and (3) 120 s and (B) number of spherulite (●) and spherulite growth rate (○) of starch-*g*-PBS with variation of degree substitution.

spherulite formation and small radius of the spherulites can be formed.

$$G = \frac{dr}{dt} \tag{3}$$

3.6. Starch/PBS blends containing starch-g-PBS

The preliminary study for the performance of starch-*g*-PBS as a compatibilizer between starch and PBS blend was investigated and starch-*g*-PBS (%DS = 30) as a compatibilizer for 5 phr was fixed in a series of starch/PBS blends.

The performance of starch-*g*-PBS can indicate from the compatibility of the blend. It was evaluated by the phase separation in terms of the gap between starch and PBS. Fig. 5 reveals the FE-SEM micrographs of the blends. The blends with starch-*g*-PBS show good compatibility as identified by a few gaps between the starch granules and PBS compared with the blend without starch-*g*-PBS. It is clear that starch-*g*-PBS shows good performance as a compatibilizer. However, the starch-*g*-PBS with 5 phr can improve phase separation in the blend containing 20% and 40% starch, as seen in Fig. 5.

The compatibility reflects the mechanical properties of the blend. As shown in Table 2, the blends with starch-*g*-PBS show higher modulus and higher yield strength than those of the blends without starch-*g*-PBS. This might be due to the fact that starch-*g*-PBS provides the interfacial adhesion between PBS and starch resulting in the improvement of the stress transfer between the two component phases. In addition, the modulus of the blend containing starch-*g*-PBS also shows an increase with increasing of the starch content. This indicates the stiffness of the starch.

From overview points, it can be concluded that 5 phr starch-*g*-PBS is suitable as compatibilizer for the blends containing 20% and 40% of starch due to the compatibility and mechanical properties improvement.

The melt viscosity is also a good guideline for processing. The MFI of the blends containing 20% and 40% of starch is ~5–7 g/10 min (Table 2), which is suitable for the production of foam products (Bahari, Mitomo, Enjoji, Yoshii, & Makuuchi, 1998; Matuana, Faruk, & Diaz, 2009).

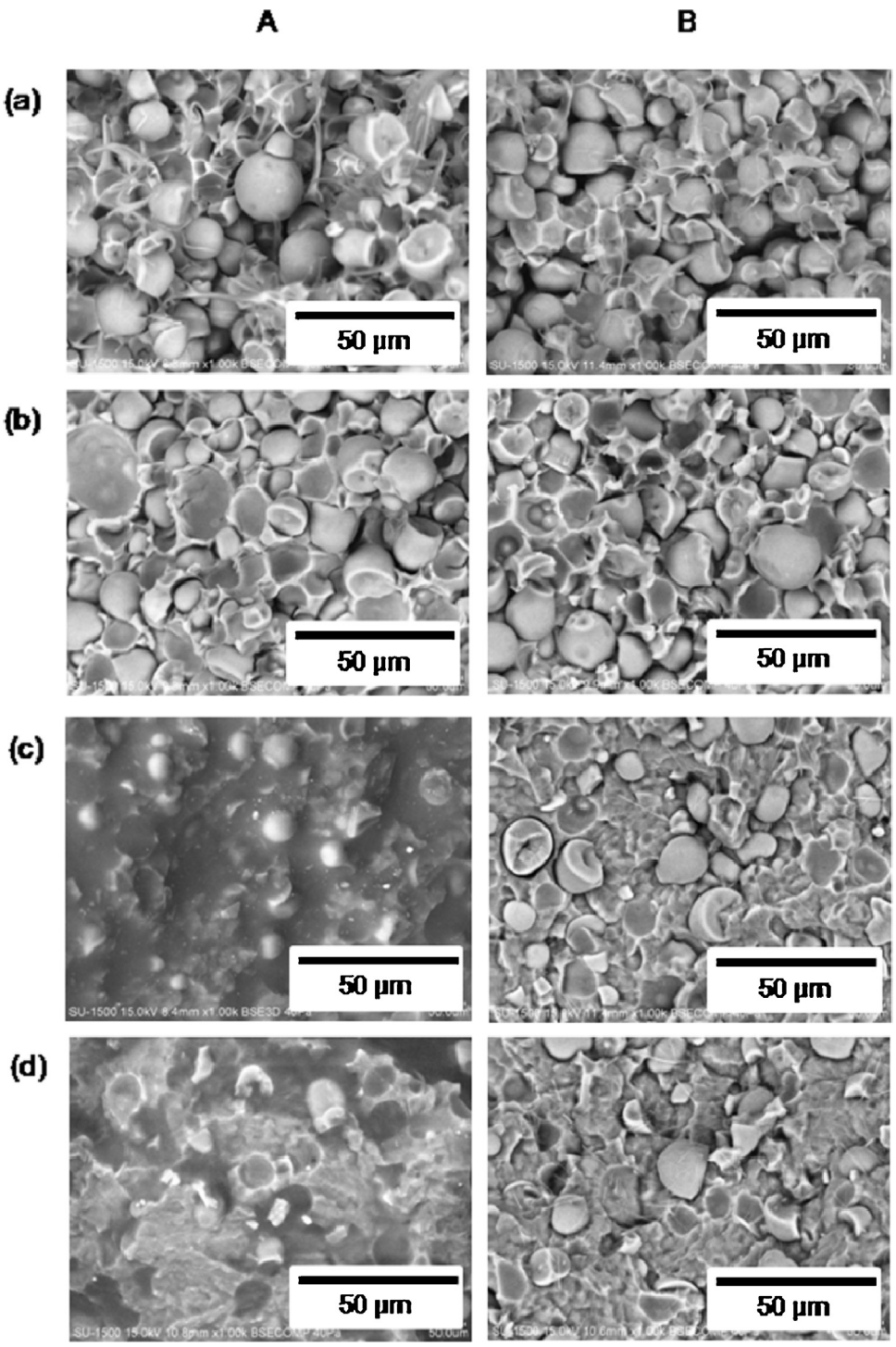


Fig. 5. FE-SEM images of starch/PBS blended (A) with starch-*g*-PBS and (B) without starch-*g*-PBS by various weight ratio of starch/PBS: (a) 80/20, (b) 60/40, (c) 40/60 and (d) 20/80.

Table 2
Yield strength, modulus, and MFI of the blend with and without starch-*g*-PBS.

Feed ratio of the blend/starch:PBS	Without starch-*g*-PBS			With starch-*g*-PBS (5 phr)		
	Yield strength (MPa)	Modulus (MPa)	MFI/g/10 min	Yield strength (MPa)	Modulus (MPa)	MFI/g/10 min
Neat PBS	18 ± 0.4	500 ± 11	14.7	–	–	–
20:80	16 ± 1.1	700 ± 50	4.45 ± 0.5	23 ± 1.4	900 ± 55	6.60 ± 0.6
40:60	14 ± 0.6	1000 ± 75	3.21 ± 1.0	21 ± 0.6	1400 ± 85	5.00 ± 1.0
60:40	13 ± 2.2	1800 ± 270	1.80 ± 0.2	22 ± 1.2	2200 ± 155	2.70 ± 0.5
80:20	n/a[a]	n/a[a]	n/a[b]	n/a[a]	n/a[a]	n/a[b]

[a] The sample could not be prepared due to fracturing during compression.
[b] The sample could not pass through the piston of the tube.

4. Conclusions

The present work succeeded in conjugating PBS on a starch surface to obtain starch-*g*-PBS in one step. It was the first time that the detailed analyses by NMR confirmed ester bonds between PBS and starch at the secondary hydroxyl groups at C_2 and C_3 as well as the primary alcohol at C_6 position. Quantitative analysis indicated the substitution of PBS on starch at 20–30%. As compared to starch, starch-*g*-PBS showed T_m, T_g, and T_c which are important for production. The spherulite formation was faster due to the effect of the branching structure. Starch-*g*-PBS can act as a good compatibilizer of starch/PBS blend. The blend containing starch-*g*-PBS is expected to be used in foam applications. It should be noted here that the systematic variation of starch-*g*-PBS content on the compatibility improvement and the foam processing are ongoing research.

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