

Study on Short Glass Fiber-Reinforced Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) Composites

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ABSTRACT: Biobased non-fossil polyester poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB) containing 4.0 mol % 4-hydroxybutyrate (4HB) was melt-mixed with short glass fibers (SGF) via a co-rotating twin-screw extruder. The compositing conditions, average glass fiber length and distribution, thermal, crystallization, and mechanical properties of the P3/4HB/SGF composites were investigated. Calcium stearate, two kinds of paraffin wax and modified ethylene bis-stearamide (TAF) were investigated as lubricants for the P3/4HB/SGF composites. It revealed that TAF is the most efficient lubricant of the P3/4HB/SGF composites. Coupling agents 2,2'-(1,3-phenylene)bis-2-oxazoline (1,3-PBO) and

pyromellitic dianhydride (PMDA) were used as end-group crosslinkers to reduce the degradation of P3/4HB and increase the mechanical properties of the P3/4HB/SGF composites. It showed that 1,3-PBO is the efficient coupling agent. The optimum condition of the P3/4HB/SGF composites is 1.5 phr TAF, 1.0 phr 1,3-PBO, and 30 wt % glass fiber content. And the maximum of tensile strength, tensile modulus, and impact strength of the composites is 3.7, 6.6, 1.8 times of the neat P3/4HB polymer, respectively. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: blends; compounding; biodegradable

INTRODUCTION

Biobased microbial polyesters or polyhydroxyalkanoates (PHA) have attracted more attention due to their resources renewable, biodegradable properties, and potential applications as environmental friendly polymers for agricultural, marine, and medical applications.¹ Among them, poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB) was produced by *Ralstonia eutropha*, *Alcaligenes latus*, and *Comamonas acidovorans*.^{2,3} The physical property of P3/4HB is from semi-crystallization plastics (e.g., 5% 4HB content) to amorphous elastomers (e.g., 30% 4HB content) depending on the 4-hydroxybutyrate (4HB) ratio.⁴ As plastics, P3/4HB possesses fairly good processing property, but its high cost and limited mechanical properties hinder its applications. Several modifications have been proposed to improve its mechanical properties, such as chemical modification and physical blending,⁵ in which physical blending is preferred because of the low-cost, easy,

and fast working techniques.^{6–9} In recent years, organic-inorganic composites, have received much attention because these materials exhibit unexpected properties. Various fillers, including glass fiber,^{10–12} montmorillonite,¹³ silica,¹⁴ calcium carbonate (CaCO₃),^{15,16} and aluminum oxide¹⁷ are the common fillers to enhance the mechanical and thermal properties of polymer materials, such as the toughness, stiffness, heat resistance, and reduce the cost also. Since organic-inorganic hybrid composites have both the flexibility of an organic component and the hardness of an inorganic component, these organic-inorganic composite materials have been applied in many fields such as in commodity plastics, electronic, cosmetic, adhesive, surface coating materials.^{18–20}

Glass fiber is the common used reinforced filler for plastics with its low cost and high performance. Glass fiber reinforced plastic (GRP) composites possess excellent properties such as high strength, high modulus, easy mouldability, good insulating property, resistant to corrosion, and fatigue damage and so on. GRP composites have been widely used in aviation, electronics, automobile, and other industries.^{21,22} But GRP composites also have some problems. It is known that GRP composites do not achieve their maximum possible stiffness, strength, and toughness properties. One reason is the fiber length within the composites as usually the glass fiber is cut down during processing.²³ Exposure of glass fiber, rough surface, attrition of processing

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equipment are other problems. Fortunately suitable lubricants could improve smooth finish and prevent exposure of glass fiber.^{24,25}

In this study, we intend to use short glass fiber (SGF) to enforce novel nonfossil, biobased P3/4HB materials to improve its strength, modulus, impact strength, thermal stability. Four different lubricants, i.e., calcium stearate, paraffin wax A, paraffin wax B, and TAF were used to improve exposure of the glass fiber. Two different coupling agents 2,2'-(1,3-phenylene)bis-2-oxazoline(1,3-PBO) and pyromellitic dianhydride (PMDA) were studied to reduce the degradation and improve properties of composites. Finally an optimum condition for the P3/4HB/SGF composites was established.

EXPERIMENTAL

Materials

P3/4HB ($M_n = 438,000$, $M_w/M_n = 1.23$, with 4.0 wt % 4HB content, estimated by GPC and NMR, respectively) was provided by Tianjin Bioscience Materials. (Tianjin, China). Short glass fiber (SGF, ECS 303A) was provided by Chongqing Polycomp International. (Chongqing, China), with average length and diameter 3 mm and 13 μm , respectively. Calcium stearate was provided by Hunan Shaoyang Tiantang Auxiliaries Chemical (Hunan, China). Paraffin wax A (S3001 58–60) was provided by Shanghai Specimen and Model Factory (Shanghai, China). Paraffin wax B (58#) was supplied by Sinopec Corp. (Beijing, China). Lubricant ethylene bis-stearamide (TAF) was supplied by SGG Chemical Additives. (Suzhou, China). End group coupling agents 2,2'-(1,3-Phenylene)bis-2-oxazoline(1,3-PBO) was supplied by Dalian Research and Design Institute of Chemical Industry (Dalian, China). Pyromellitic dianhydride (PMDA) was provided by Sinopharm Chemical Reagent. (Shanghai, China). All the chemical agents were used as received without further purification.

Sample preparation

Both P3/4HB powder and chemical agents in various compositional ratios were premixed in a mixer at a speed of 5000 rpm for 10 min. The premixed compounds and SGF were dried in an oven at 80°C for 14 h. Then the premixed compounds and SGF were melt-mixed in a co-rotating selfwiping twin-screw extruder (TSE-20, Ruiya Machinery, Nanjing China) with a screw diameter 22.4 mm, the distance between screw axes is 18.4 mm, and the length to the diameter ratio $L/D = 42$, operating at a screw speed of 60 rpm, and the eight heating zones were set to 70, 120, 150, 160, 170, 170, 170, and 175°C from the hopper to the strand die. The compounded

extrudates were immediately quenched in water bath and cooled in air till ambient temperature and cut into long rod form by a sharp clippers for subsequent tests.

Fiber length measurement

SGF were isolated from P3/4HB/SGF composites using a solvent extraction method using chloroform to remove the P3/4HB matrix and additives. The remained glass fiber was coated on a glass slide for observation. The fiber length measurement was carried out with a converted fluorescence microscope (Nikon, model ECLIPSE TE2000-U) and computer aided image analysis (Nikon ACT-2U). The fiber length distribution was determined by a minimum of 500 fibers.

Melt mass-flow rate

The measurement of melt mass-flow rate or melt flow index (MFR) was performed in accordance with ISO 1133 : 1997, using a melt flow indexer (MTS model ZRZL 402, SANS, Shenzhen, China) at 190°C, and 2.16 kg load. Extruded sample was used for the MFR test.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q50 instrument (New Castle, MA) calibrated with indium. The temperature was ramped at a heating rate of 10°C/min under nitrogen atmosphere from room temperature to a temperature well above the degradation temperature of P3/4HB at 600°C.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed on a TA-Q100 DSC analyzer (Texas Instruments) equipped with a mechanical cooler system under a nitrogen atmosphere and calibrated by indium. Nonisothermal crystallization was employed to study the crystallization behaviors of P3/4HB/SGF composites. The samples were heated from -80°C to 180°C at a heating rate of 10°C/min, held at 180°C for 3 min to destroy the thermal history. After quenched to -80°C at a cooling rate 10°C/min under dynamic nitrogen atmosphere, the tested sample was reheated to 180°C at a heating rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m) and apparent melting enthalpy (ΔH_m) were determined from DSC endothermal peaks at the second heat run. The lasting or cold crystallization temperature (T_{cc}) was determined from the DSC corresponding exothermal peaks at

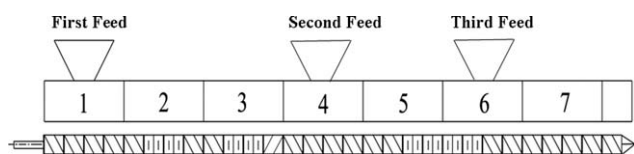


Figure 1 The configuration of twin-screw.

the second heat run. The crystallization onset temperature (T_0) and crystallization peak temperature (T_c) were obtained from the cool scan.

Mechanical properties

Long rod-shaped samples of P3/4HB/SGF composites (gauge length 50 mm, diameter about 3.5 mm) were used for mechanical tests. The tensile strength, elastic modulus, and elongation at break were determined using a universal testing machine (MTS model CMT 4204, SANS, Shenzhen, China) and extension rate of 5 mm/min at room temperature. The unnotched Charpy impact strength was evaluated with an Impact Testing Machine (Ming Yu Electron Tech Information, Dongguan, China).

RESULTS AND DISCUSSION

Average fiber length and distribution

It is known that the length of glass fiber is an important factor to affect the property of GRP composites.²³ The twin-screw configuration is given in Figure 1 and the extruded SGF length is summarized in Table I. For improving the fiber length, the effect of glass fiber feeding place was studied. From Table I, it is noted that the fiber length increases with feeding place move toward to extruding die due to the less shear force to breaking the SGF, as shorter time remains in the extruder. The third feed place gives the maximum fiber length as the shortest time in the extruder. From Table I(c and d), it is also noted that the fiber length increases with the extruding temperature due the less viscous melt resulted. The glass fiber length and distribution in the P3/4HB/SGF composites is shown in Figure 2. Through this optimizing, the average fiber length increased 4.7 times from 180 μm to 850 μm in the P3/4HB/SGF composites.

TABLE I
The Details of Experiment Conditions

Experiments	Fiber feed place	Maximum temperature ($^{\circ}\text{C}$)	Screw speed (rpm)	Mean fiber length (μm)
a	First feed	155	60	180
b	Second feed	155	60	232
c	Third feed	155	60	461
d	Third feed	175	60	850

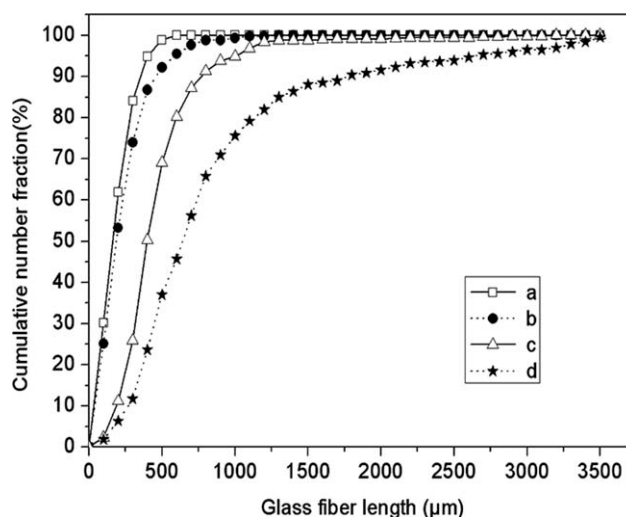


Figure 2 Length distribution of glass fiber in the P3/4HB/SGF composites in different experiment conditions: (a) first feed, 155 $^{\circ}\text{C}$, (b) second feed, 155 $^{\circ}\text{C}$, (c) third feed, 155 $^{\circ}\text{C}$, (d) third feed, 175 $^{\circ}\text{C}$.

Processability of the P3/4HB/SGF composites

In order to reduce the exposure of glass fiber, four different lubricants, i.e. calcium stearate, paraffin wax A, Paraffin wax B and TAF were investigated for improving the processability. A group of the photos of the extruded rods is given in Figure 3. Amount 2 phr lubricant was used in the P3/4HB/SGF composites. It was found that paraffin wax and TAF made better performance [Fig 3(c–e)]. Calcium stearate had, however, little effect, and lots of glass fibers still expose on surface. Among them, TAF gave the best performance in the balanced properties. Thus, TAF was selected for the further study.

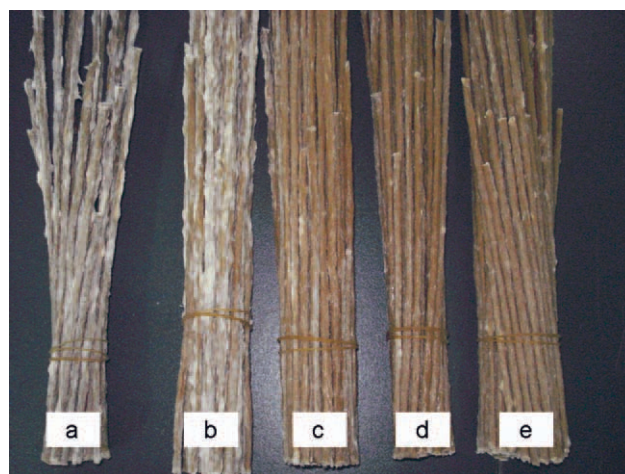


Figure 3 The photos of the P3/4HB/SGF composite extruded rods at 30 wt % SGF and 1.5 phr lubricants: (a) no lubricant, (b) calcium stearate, (c) paraffin wax A, (d) paraffin wax B, and (e) TAF. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE II
Melt Mass-Flow Rate of the P3/4HB/SGF Composites

Glass fiber content (wt %)	Lubricant	Lubricant content (phr)	Coupling agent	Coupling agent content (phr)	Melting index (10 g/min)
0	Non		non		8.6
30	Non		non		6.3
30	Calcium stearate	2.0	non		33.8
30	Paraffin wax A	2.0	non		3.8
30	Paraffin wax B	2.0	non		3.1
30	TAF	2.0	non		8.8
30	TAF	1.5	non		4.4
30	TAF	1.5	PMDA	1.0	1.4
30	TAF	1.5	1,3-PBO	1.0	5.2
5	TAF	1.5	1,3-PBO	1.0	7.1
10	TAF	1.5	1,3-PBO	1.0	5.8
20	TAF	1.5	1,3-PBO	1.0	6.9
30	TAF	1.5	1,3-PBO	1.0	5.2
35	TAF	1.5	1,3-PBO	1.0	4.1
40	TAF	1.5	1,3-PBO	1.0	1.8

TAF, ethylene bis-stearamide; 1,3-PBO, 2,2'-(1,3-Phenylene)bis-2-oxazoline(1,3-PBO); PMDA, pyromellitic dianhydride.

As lubricant, TAF can decrease the frictions between the materials and the equipment and also among the resin particles. It also reduces the viscosity of the melt and thus decreases the exposure of glass fiber.^{26,27} We changed the amount of TAF from 0 phr to 5.0 phr and found that the best amount of TAF was 1.5 phr. This gives the smooth surface and removes the exposure of glass fiber in the P3/4HB/SGF composites.

Melt index and thermal stability

The melt mass-flow rate (MFR, melt flow index) of the P3/4HB/SGF composites was investigated by a melt flow indexer. The results are summarized in Table II. The effect of different lubricants on MFR of the P3/4HB/SGF composites was investigated. At 30% weight fiber content, the MFR increases over five times by calcium stearate (up to 33.8). The too high MFR gives the negative effect to composites. This would be the reason that calcium stearate has the worst performance on controlling exposure of glass fiber. The P3/4HB matrix turns too soft by calcium stearate to bind the rigid glass fiber. The MFR drops to under 4 g/10min by the two paraffins, and it is not a suitable value for processing due to high energy consumption. The MFR locates at 8.8 g/10 min by lubricant TAF. And this is a suitable value for processing. This also reveals that TAF is the appropriate lubricant for the P3/4HB/SGF composites. The extra high MFR from calcium stearate would be induced from the decomposition of P3/4HB matrix. From Table II, it is noted that calcium stearate gives the lowest decomposition temperature. The possible reason might be the basic character of calcium stearate which

would enhance the thermal decomposition of P3/4HB matrix during the heating process.

We also tried to improve properties of the P3/4HB/SGF composites by using two different coupling agent PMDA and 1,3-PBO to reduce the degradation of P3/4HB during extruding. The content of the two coupling agent is 1.0 phr to the P3/4HB/SGF composites. The results are summarized in Table II. The MFR value decreases when the coupling agents are used. The MFR changes from 4.4 to 1.4 and 5.2 g/10 min by PMDA and 1,3-PBO, respectively. One reason of the different performance of the two crosslinkers is the number of the reactive functional group. PMDA has four reactive functional groups, but 1,3-PBO has only two as shown below. Therefore PMDA has stronger coupling effect than 1,3-PBO to crosslink the P3/4HB end groups. The melt flow ability of the composites is lower by PMDA than by 1,3-PBO. The MFI 1.4 g/10min is too low for common processing, but 5.2 g/10 min is reasonable. Thus 1.0 phr 1,3-PBO coupling agent would be the appropriate amount. The glass fiber also affects the MFI deeply. The MFI value of the P3/4HB/SGF composites with 1.5 phr TAF, 1.0 phr 1,3-PBO was reduced sharply with increasing glass fiber content. When fiber content reached to 40%, the MFR dropped to less than 2 g/10 min.

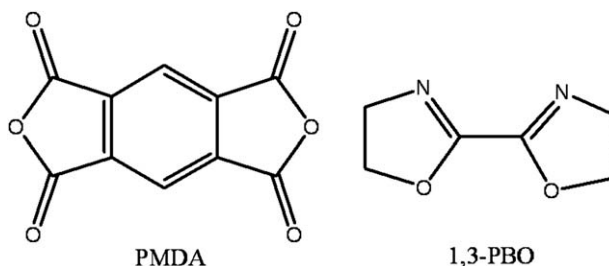


TABLE III
Thermal Stability of the P3/4HB/SGF Composites

Sample No.	SGF content (wt %)	Lubricant		Coupling agent		Weight loss temperature (°C)	
		Class	Content (phr)	Class	Content (phr)	5%	50%
1	0	Non		non		249.4	275.5
2	30	Non		non		247.0	278.4
3	30	Calcium stearate	2	non		236.7	268.2
4	30	Paraffin wax A	2	non		249.2	284.4
5	30	Paraffin wax B	2	non		251.6	286.0
6	30	TAF	2	non		254.8	287.4
7	30	TAF	1.5	1,3-PBO	1.0	241.1	277.2
8	30	TAF	1.5	PMDA	1.0	277.8	298.4
9	5	TAF	1.5	1,3-PBO	1.0	246.6	276.8
10	10	TAF	1.5	1,3-PBO	1.0	244.9	275.6
11	20	TAF	1.5	1,3-PBO	1.0	244.7	278.3
12	25	TAF	1.5	1,3-PBO	1.0	247.4	279.1
13	30	TAF	1.5	1,3-PBO	1.0	244.0	277.1
14	35	TAF	1.5	1,3-PBO	1.0	241.1	277.2
15	40	TAF	1.5	1,3-PBO	1.0	243.9	295.6

Thermal stability

The thermal stability of the P3/4HB/SGF composites was investigated by TGA. The results are summarized in Table III and shown in Figure 4. Glass fibers have no obvious influence on the thermal stability of the P3/4HB/SGF composites, but the lubricants impose different effects on the thermal stability. The weight loss temperature reduced over 10°C by adding calcium stearate, but increased by other lubricants. This would be the reason why the P3/4HB/SGF composites with calcium stearate have maximal MFR. However, TAF enhances the thermal stability of the P3/4HB/SGF composites. This result further supports TAF as the suitable lubricant. The coupling agents increases the thermal stability of the P3/4HB/SGF composites. The thermal decomposition temperature increases 20–30°C by adding PMDA, but no obvious change by adding 1,3-PBO. This also proves that the more functional group PMDA is better to prevent the thermal degradation of P3/4HB. However 1,3-PBO gives better performance in MFR and mechanical properties of P3/4HB/SGF composites.

When adding TAF and 1,3-PBO at low glass fiber content, the 50% weight loss temperature of the P3/4HB/SGF composites increases slightly. However, when glass fiber is more than 35%, the weight loss temperature increases sharply (Table III). But the 5% weight loss temperature of the P3/4HB/SGF composites have no obvious change. This would be due to the thermal stability difference of P3/4HB matrix and SGF fillers. From Figure 4, it is also noted that the composites have no improvement on the thermal stability of P3/4HB matrix. The increase of the 50% weight loss temperature is mainly from the SGF residues. Therefore, the glass fiber does not enhance the thermal stability of the P3/4HB matrix in the composites.

Nonisothermal crystallization of P3/4HB/SGF composites

The thermal transition and the crystallization behaviors of the P3/4HB/SGF composites were investigated by the DSC determination both heat and cool scans (Fig. 5 and Table IV). The nonisothermal parameters are also given out. It is noted that both the glass transition temperature (T_g) and the melting temperature (T_m) of the composites have no obvious change compared with pure P3/4HB matrix, except for the lubricant calcium stearate which would stimulate the matrix decomposition and reduce the T_g and T_m accordingly. The melting enthalpy (ΔH_m) and crystallization degree (X_c) are reduced by adding lubricants and however increased by coupling agents. The crystallization onset temperature (T_0)

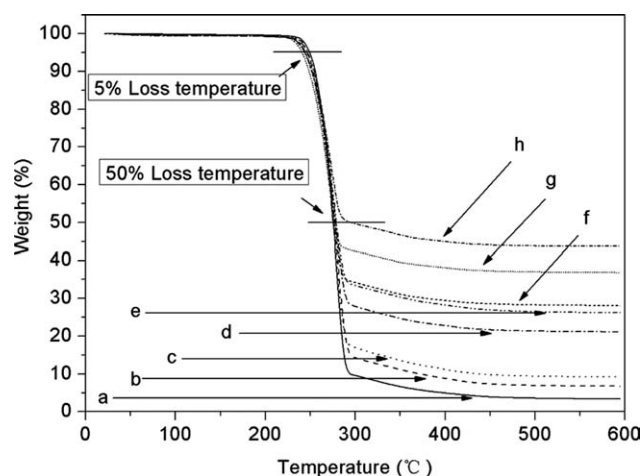


Figure 4 Weight loss temperature of P3/4HB/SGF composites under 1.5 phr TAF and 1.0 phr 1,3-PBO versus different fiber content: (a) 0%, (b) 5%, (c) 10%, (d) 20%, (e) 25%, (f) 30%, (g) 35%, (h) 40% (Table III, Nos. 8–15).

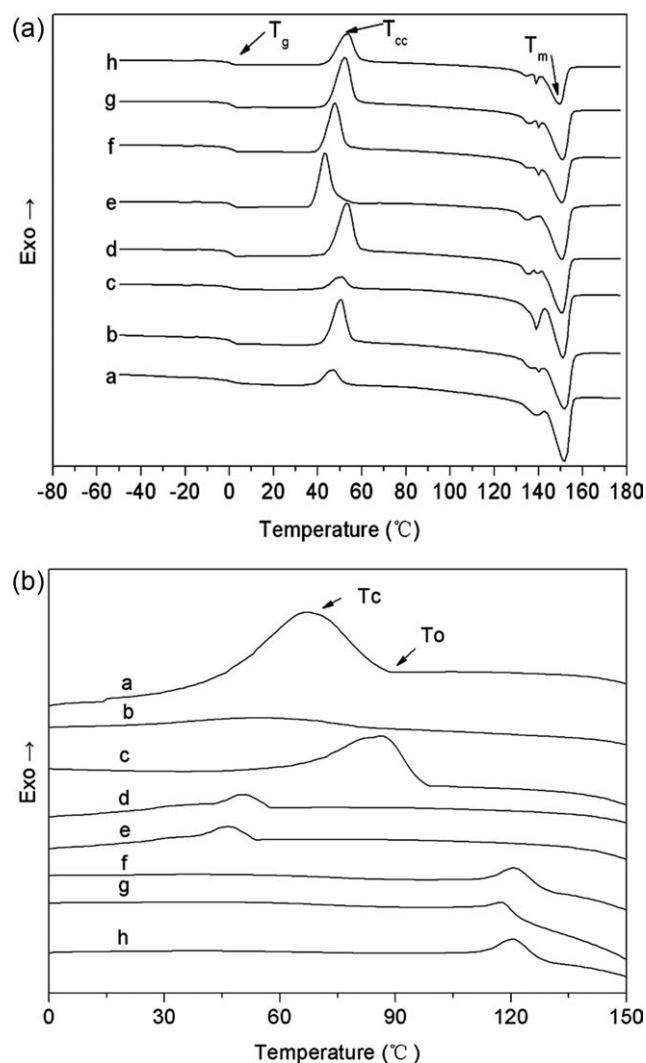


Figure 5 DSC thermograms of P3/4HB/SGF composites with 30 wt % SGF, lubricant 1.5 phr, coupling agent 1.0 phr; (a) heat scan, (b) cool scan at 10°C/min rate: (a) neat P3/4HB, (b) P3/4HB + glass fiber, (c) P3/4HB + glass fiber + calcium stearate, (d) P3/4HB + glass fiber + paraffin wax A, (e) P3/4HB + glass fiber + paraffin wax B, (f) P3/4HB + glass fiber + TAF, (g) P3/4HB + glass fiber + TAF + PMDA, (h) P3/4HB + glass fiber + TAF + 1,3-PBO (Table IV).

and crystallization peak temperature (T_c) were obtained from the cool scans. The value of $(T_0 - T_c)$ was used to evaluate the nonisothermal crystallization rate, namely, at the same cooling rate, the lower value of $(T_0 - T_c)$ means the faster of crystallization rate.²⁸ And the higher T_0 indicates that the polymer could crystallize more easily at a relatively lower under-cooling temperature. From Figure 5(b), it is noted that very slow crystallization rate was observed from no additive P3/4HB/SGF composite (Curve b). This would be explained that glass fiber restricts intermolecular movement of the P3/4HB matrix which hinders the crystallization. The change of the crystallization enthalpy (ΔH_c) also supported

this result. The P3/4HB/SGF composites with no additives have the crystallization enthalpy of 5.5 J/g, which is much lower than that of neat P3/4HB (24.8 J/g) and means the much lower crystallization degree. On the other hand, the additives such as lubricants would enhance the mobility of the polymer chains and increase the crystallization rate. Comparing Figure 5(b–f), it is noted that the values of $(T_0 - T_c)$ are lower than the value of $(T_0 - T_c)$ of neat P3/4HB matrix. This means that all the four lubricants increase the crystallization rate of the P3/4HB/SGF composites. And TAF has the lowest $(T_0 - T_c)$ value 5.0°C, i.e., the highest crystallization rate. But the T_0 values are different in the four lubricants. Composites with calcium stearate and TAF have higher T_0 values than paraffin wax A and paraffin wax B have. This hints that the crystallization trend of the P3/4HB/SGF composites is enhanced by calcium stearate and TAF, however decreased by paraffin wax A and paraffin wax B. The P3/4HB/SGF composites with TAF have the highest T_0 at 128.0°C. However, all the crystallization enthalpy (ΔH_c) value is lower than that of P3/4HB matrix, indicating that the composites possess higher crystallization rate and lower crystallization degree. TAF increases the crystallization rate more efficiently. The $(T_0 - T_c)$ values of P3/4HB/SGF composites were increased by the two coupling agents. It indicates that the P3/4HB/SGF composites with coupling agents have lower crystallization rate. However, the higher crystallization enthalpy (ΔH_c) values means that the coupling agents increase the crystallization degree. For example, coupling agent 1,3-PBO increases the ΔH_c value about two times from 1.6 to 3.1 J/g. This trend is also confirmed from the DSC heat scan [Fig. 5(a) and Table IV]. The opposite trend of crystallization rate and crystallization degree was also observed in the P3/4HB/CaCO₃ composite systems.¹⁶

Mechanical properties of P3/4HB/SGF composites

The mechanical properties of the P3/4HB/SGF composites are summarized in Table V. Tensile strength of the P3/4HB/SGF composites gives an almost parabola trend. At 0–30% glass fiber contents, tensile strength of the P3/4HB/SGF composites increased with glass fiber content. However, when glass fiber is more than 30%, the tensile strength decreases with glass fiber content. The 30% glass fiber composite gives the maximum tensile strength. And it is 3.7 times of neat P3/4HB from 19.6 MPa to 72.7 MPa. When the glass fiber content is further higher, it is difficult to disperse in the P3/4HB matrix. This would induce fault in the composites and thus reduces the tensile strength. The elastic modulus of the P3/4HB/SGF composites increases almost linearly with increase of glass fiber content. And the

TABLE IV
Thermal Transition and Nonisothermal Crystallization Parameters of P3/4HB and P3/4HB/SGF Composites

SGF content (wt %)	Lubricant	Lubricant content (phr)	Coupling agent	Coupling agent content (phr)	T_g^a (°C)	T_m^b (°C)	T_{cc} (°C)	ΔH_m^d (J/g)	X_c^e (%)	T_0^f (°C)	T_c^g (°C)	T_0-T_c (°C)	ΔH_c^h (J/g)
0	Non		Non		1.9	151.9	47.1	56.6	38.8	88.5	66.1	22.4	24.8
30	Non		Non		2.4	156.4	47.2	34.7	33.9	80.7	54.6	26.0	5.5
30	Calcium stearate	1.5	Non		-0.5	148.9	43.4	36.5	35.7	99.7	86.1	13.6	15.2
30	Paraffin wax A	1.5	Non		1.9	152.3	44.1	31.5	30.8	55.3	47.8	7.6	2.3
30	Paraffin wax B	1.5	Non		1.3	151.5	43.6	38.7	37.9	53.3	46.6	6.8	3.1
30	TAF	1.5	Non		2.0	151.5	51.3	23.1	22.6	128.0	123.0	5.0	1.6
30	TAF	1.5	PMDA	1.0	1.6	151.0	48.0	39.9	39.0	127.8	117.4	10.3	2.0
30	TAF	1.5	1,3-PBO	1.0	1.5	151.0	48.0	39.4	38.6	132.8	120.7	12.1	3.1

^a T_g from the second heat scan of DSC.

^b T_m from DSC heat scan.

^c T_{cc} cold crystallization temperature from DSC heat scan.

^d Apparent melting enthalpy ΔH_m determined by calculation of the intensities of the endothermal peaks of P3/4HB in the second heating scan of DSC.

^e X_c crystallization degree estimated according to the following equation: $X_c\% = 100 \times \Delta H_m / w_i \Delta H_m^0$, ΔH_m is the melting enthalpy of P3/4HB in the blends, ΔH_m^0 is the melting enthalpy of 100% crystalline PHB (146 J/g), w_i is the weight fraction of P3/4HB in the blends.

^f T_0 , crystallization onset temperature obtained from the cooling scan of DSC.

^g T_c , crystallization peak temperature obtained from the cooling scan of DSC.

^h ΔH_c , crystallization enthalpy determined by calculation of the intensities of the exothermal peaks of P3/4HB in the cooling scan of DSC.

maximum elastic modulus is 6.6 times from neat P3/4HB matrix 2.3 GPa to 14.8 GPa. This shows that the high modulus glass fiber makes the composite more rigid.

The elongation at break of the P3/4HB/SGF composites also shows a similar trend. At 0–15% glass fiber content, the elongation at break increases with glass fiber content. When the glass fiber content is more than 15%, the elongation at break reduces. When glass fiber is more than 40%, the composites become quite brittle. This demonstrates that the glass fiber would increase the rigidity of the P3/4HB matrix.

At the same glass fiber content, the effect of coupling agent 1,3-PBO on mechanical properties is more obvious than that of PMDA. Tensile strength

of the composites with 1,3-PBO was 38% higher than that of PMDA. The elastic modulus of the composites with 1,3-PBO was 64% higher than that of PMDA. Impact strength of the composites with 1,3-PBO was also 28% higher than with PMDA. The better performance on mechanical properties from coupling agent 1,3-PBO would be due to the higher crystallization degree as discussed above (Table IV).

From Table V, it is noted that the unnotched Charpy impact strength of the P3/4HB/SGF composites gives similar parabola change. At 0–30% glass fiber contents, impact strength increases with increasing of fiber content. But when the glass fiber is more than 30%, impact strength decreases with glass fiber content. There is the maximum impact

TABLE V
The Mechanical Properties of the P3/4HB/SGF Composites

SGF content (wt %)	Lubricant	Lubricant content (phr)	Coupling agent	Crosslinker content (phr)	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation at break (%)	Impact strength (KJ/m ²)
0	non		non		19.6 ± 1.6	2.2 ± 0.1	1.0 ± 0.1	15.2 ± 0.8
5	TAF	1.5	1,3-PBO	1.0	31.0 ± 2.1	3.2 ± 0.3	1.2 ± 0.2	9.1 ± 1.4
10	TAF	1.5	1,3-PBO	1.0	40.5 ± 1.9	4.4 ± 0.5	1.3 ± 0.1	16.1 ± 2.1
20	TAF	1.5	1,3-PBO	1.0	63.9 ± 3.4	7.6 ± 1.0	1.1 ± 0.1	25.7 ± 1.7
30	TAF	1.5	1,3-PBO	1.0	72.7 ± 6.0	12.0 ± 1.4	0.8 ± 0.1	27.6 ± 2.8
35	TAF	1.5	1,3-PBO	1.0	64.6 ± 7.4	10.2 ± 1.4	0.8 ± 0.0	19.4 ± 0.5
40	TAF	1.5	1,3-PBO	1.0	42.9 ± 2.3	14.8 ± 0.8	0.4 ± 0.0	13.0 ± 1.8
30	TAF	1.5	non		56.7 ± 3.1	8.2 ± 1.8	0.8 ± 0.2	26.2 ± 3.9
30	TAF	1.5	PMDA	1.0	52.6 ± 5.2	7.3 ± 1.5	0.8 ± 0.1	21.5 ± 1.1
30	TAF	1.5	1,3-PBO	1.0	72.7 ± 6.0	12.0 ± 1.4	0.8 ± 0.1	27.6 ± 2.8

strength 27.6 KJ/m² around 30% glass fiber content. And it is 1.8 times of the neat P3/4HB matrix 15.2 KJ/m². This means that the glass fiber would reinforce the biodegradable polymer P3/4HB matrix.

CONCLUSIONS

Biobased biodegradable P3/4HB polymer with 4% 4HB content was composited with short glass fiber. The average glass fiber length increased 4.7 times from 180 μm to 850 μm by shortening the route of glass fiber in the extruder and raising the process temperature. TAF is the most efficient lubricant to reduce glass fiber exposure and increase smooth finish of the P3/4HB/SGF composites among lubricants calcium stearate, paraffin wax A, paraffin wax B, and TAF. Coupling agents 1,3-PBO and PMDA were investigated as end-group crosslinker to increase mechanical properties of the P3/4HB/SGF composites and reduce the degradation of P3/4HB. It showed that 1,3-PBO is an efficient crosslinker. The composites have lower crystallization degree than P3/4HB matrix. SGF and coupling agents reduce the crystallization rate, but all the lubricants increase the crystallization rate. The optimum condition for the P3/4HB/SGF composites is 1.5 phr TAF, 1.0 phr 1,3-PBO and about 30 wt % glass fiber content. And the maximum tensile strength, elastic modulus and impact strength are 3.7, 6.6, 1.8 times of neat P3/4HB.

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