# Supporting Information for

# Solvent-free preparation of propionyl modified pulp fibers for

## high-density polyethylene reinforcement

Shuya Zhang,<sup>a</sup> Yixin Zhao,<sup>a</sup> Mingda Che,<sup>a,c,\*</sup> Renliang Huang,<sup>b,c,\*</sup> Mei Cui,<sup>a</sup> Wei Qi,<sup>a</sup>

Rongxin Su <sup>a,b,c,\*</sup>

<sup>a</sup> State Key Laboratory of Chemical Engineering, School of Chemical Engineering and

Technology, Tianjin University, Tianjin 300072, P.R. China

<sup>b</sup> School of Marine Science and Technology, Tianjin University, Tianjin 300072, P.R. China

<sup>c</sup> Zhejiang Institute of Tianjin University, Ningbo, Zhejiang, 315201, China

<sup>d</sup> Tianjin Sustainable Novel Materials Co. Ltd., Tianjin 300192, China

\* Author to whom correspondence should be addressed:

cmd@tju.edu.cn (M.C), tjuhrl@tju.edu.cn (R.H.), surx@tju.edu.cn (R.S.)

## **Supplementary Figures**



## Fig. S1 SEM images of PAF-0.11.



**Fig. S2** SEM images of fracture surface at high multiples: (a) HDPE; (b) HDPE/SBKP; (c) HDPE/PAF-0.13; (d,) HDPE/PAF-0.40.



Fig. S3 Comparison of surface SEM images of HDPE/SBKP and HDPE/PAF-0.40.



Fig. S4 (a) Cole-Cole plot as functions of temperature for HDPE and HDPE/PAF

composites; (b)  $\mbox{tan}\delta$  curve of HDPE and HDPE/PAF composites.

![](_page_2_Picture_5.jpeg)

Fig. S5 The appearance of PA and IPA after two cycles of recycling.

![](_page_3_Picture_0.jpeg)

Fig. S6 The respective appearances of LDPE, PP, and composites reinforced with PAF-

0.40 are depicted.

![](_page_3_Picture_3.jpeg)

Fig. S7 HDPE/PAF-0.40 composite in kilogram preparation of pre-mix materials,

materials to be extruded, masterbatch of composites.

## **Supplementary Tables**

Sample		Reaction conditions			Crl	WPG
name	D3 (-)	Temperature (°C)	Time (h)	Catalyst	(%)	(%)
SBKP	0	-	-	-	81	
PAF-0.11	0.11	120	4	-	77	<3%
PAF-0.13	0.13	120	1	$K_2CO_3$	74	<3%
PAF-0.40	0.40	120	2	$K_2CO_3$	73	19~21
PAF-0.38	0.38	120	4	$K_2CO_3$	74	23~25

**Table S1** Degree of substitution (DS), reaction conditions, crystallinity index (CrI) andweight percent gain (WPG) of SBKP and PAF

Table S2 The water absorption of HDPE and composites after storage for 10 months

Sample name	Water absorption (%)
HDPE	0.39
HDPE/SBKP	0.45
HDPE/PAF-0.11	0.44
HDPE/PAF-0.13	0.36
HDPE/PAF-0.40	0.35
HDPE/PAF-0.38	0.41

Note: The water absorption test of the sample after 10 months of storage was calculated according

to formula (5) in Text S3.

Table S3 Tensile properties and CTE of HDPE and composites

Sample name	Elongation at break (%)
HDPE	>100
HDPE/SBKP	3.41
HDPE/PAF-0.11	4.56
HDPE/PAF-0.13	4.11
HDPE/PAF-0.40	4.26
HDPE/PAF-0.38	4.36

Raw	Proportion	Modified	Auxiliary methods		Cost	Ref.
material	of fiber (%)	reagent	after modification	wechanical property	(CNY/ton)	
SBKP	30	PA	-	TS: Increased by 141.3%	2.89×10 <sup>5</sup>	This work
SBKP	10	ASA	-	TS: Increased by 143.5%	6.59×10 <sup>5</sup>	1
SBKP	10	ASA	-	TS: Increased by 100.92%	6.70×10 <sup>4</sup>	2
SBKP	10	ASA	High pressure homogenization	TS: Increased by 139.1%	1.10×10 <sup>6</sup>	3
WF	20	Ac	-	IR: Increased by 52.3%	1.05×10 <sup>6</sup>	4
SCB	15	Ac	gamma radiation	TS: Increased by 33.8%	1.64×10 <sup>5</sup>	5

# **Table S4** Comparison of the mechanical properties and cost of anhydridemodification and other methods for HDPE reinforcement

Note:

(a): SBKP: softwood bleached kraft pulp; WF: wood flour; SCB: sugarcane bagasse;

(b): PA: propionic anhydride; ASA: alkenyl succinic anhydride; Ac: acetic anhydride;

(c): TS: tensile strength; IR: impact-resistance.

#### Table S5 Cost comparison of recovery and non-recovery process routes

	HDPE/PAF-0.40		
Materials	Route 1	Route 2	
Total (CNY/ton)	1.11×10 <sup>5</sup>	2.89×10 <sup>5</sup>	

Note: During the process of reinforcing HDPE with PAF, route 1 involves using PA that is not recycled, while route 2 incorporates recycled PA.

## **Supplementary Texts**

#### **Text S1 Materials**

Softwood bleached kraft pulp (SBKP) was supplied by Xiamen C&D Paper & Pulp Group Company (Xiamen, China). Propionic anhydride (PA, 98%) and isopropyl alcohol (IPA, 99.5%) were purchased from Meryer Biochemical Tech Co., Ltd (Tianjin, China). Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99%) and phenolphthalein (PP, 99%) were supplied by Tianjin Heowns Biochemical Tech Co., Ltd (Tianjin, China). Calcium carbonate (CaCO<sub>3</sub>, 99%) was purchased from Tianjin Guangfu Technology Development Co., Ltd (Tianjin, China). Hydrochloric acid standard titration solution (HCl, 0.09963 mol/L) and sodium hydroxide standard titration solution (NaOH, 0.1001 mol/L) were purchased from Guangzhou Hoawei Pharma Tech Co., Ltd (Guangdong, China). Ethanol (EtOH, 75%) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd (Tianjin, China). Maleic anhydride-grafted polypropylene (MAPP, XYJ1210) was purchased from Dongguan Xingyuan Chemical Co., Ltd (Guangdong, China). The amount of maleic anhydride grafted was 0.8 wt%. High-density polyethylene (HDPE, Microthene FA70000, mp: 134 °C, average size: 20 µm) was purchased from LyondellBasell Industries Holdings (Rotterdam, Netherlands). All chemicals were used as received. Deionized water was used for all purposes.

#### **Text S2 Characterization**

#### 1. Scanning electron microscopy (SEM)

The surfaces of PAF and HDPE/PAF composites and cross sections of the latter were observed with field emission scanning electron microscopes (Apreo S LoVac, Hitachi, Tokyo, Japan) at 3.0 kV.

2. Fourier transform infrared (FTIR) spectroscopy

The chemical structures of PAF were characterized by a Fourier transform infrared spectroscopy (iS50 FT-IR, FEI Company, Hillsboro, USA). FTIR spectra were recorded in the range of 400–4000 cm<sup>-1</sup>.

3. X-ray diffraction (XRD) analysis

The crystal structure of PAF was detected by X-ray diffraction (D8-Focus, Bruker AXS, Germany). The samples were scanned at a scanning speed of 5°/min in the range of 5°–40°. The crystallinity index (CrI) was calculated according to the Scherrer equation:

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%$$
(1)

where  $I_{200}$  is the maximum peak intensity at  $2\theta = 22-23^{\circ}$ ,  $I_{am}$  is the minimum intensity at  $2\theta = 18-19^{\circ}$ .

### 4. Determination of the degree of substitution (DS)

The DS of PAF was determined by acid-base titration and all samples were dried in an oven at 60 °C to remove remaining moisture before testing. 100 mg of sample and 40 mL of 75% ethanol were added to a conical flask. The sample was then heated to 50~60 °C for 30 min with stirring in order to better swell the fibers. Then, 10 mL of NaOH (0.1 mol/L) was added to the sample flask and further heated for 15 min. The finished mixture was stirred at room temperature for 72 h to ensure adequate reaction. The unreacted NaOH was then titrated with HCl (0.1 mol/L) using phenolphthalein as a titration indicator. DS of propionyl groups on the fiber surface was determined using a titration method as described in prior literature.<sup>6, 7</sup> The percentage of ester content and DS values for each sample were calculated using the Eqs. (2) and (3) presented below. To ensure reproducibility, each test was repeated three times.

$$Ester Content (\%) = \frac{[[Blank (ml) - Sample (ml)] \times Molarity of HCl]}{Sample Weight (g)} \times 100$$
(2)

$$=\frac{[162 \times Ester Content]}{[4300 - (42 - Ester Content (\%))]} \times 100$$
(3)

#### 5. Water contact angle (WCA) and water absorption $(W_a)$

DS

WCA of the HDPE/PAF composites was measured by a contact angle meter (Theta Lite, Biolin Scientific). The volume of water droplets accurately controlled with a microsyringe was about 2  $\mu$ L at room temperature. The WCA value was recorded immediately when water was dried onto the surface of the composites.

The HDPE/PAF composites were dried and then immersed in water at room temperature. The mass changes were weighed for 60 days. Each sample was measured an average of three times. The water absorption (W<sub>a</sub>) of the samples was calculated using the following equation:

$$W_a = \frac{W_N - W_d}{W_d} \times 100\%$$
(4)

where  $W_d$  is dry weight of samples,  $W_N$  is the weight after absorption, where N is the number of days immersed in water

#### Text S3. Calculation of the Weight Percent Gain (WPG)

The weight percent gain of PAF was calculated by Eq. (5)

$$WPG(\%) = \frac{m_1 - m_0}{m_0} \times 100$$
(5)

where  $m_0$  is the initial mass of SBKP pulp before modification and  $m_1$  is the final mass of the modified PAF.

#### Text S4. The water absorption test of samples after 10 months of storage

$$W = \frac{W_{10} - W_0}{W_0} \times 100\%$$
(6)

where  $W_0$  is the initial dry weight of samples,  $W_{10}$  is the weight after 10 months of storage.

#### Text S5. Calculation crystallinity ratio (X<sub>r</sub>) of composites

The crystallinity ratio (X<sub>r</sub>) of composites was calculated by Eq. (7)

$$X_r(\%) = \frac{\Delta H_m}{(1-x) \times \Delta H_{lit}} \times 100$$
(7)

where  $\Delta H_m$  is specific enthalpy of fusion of the composites, determined by integration of the peak of fusion for the composites, and  $\Delta H_{lit}$  is specific enthalpy of fusion of the perfect crystal (a reference value of from  $\Delta H_{lit} = 281 \text{ J/g was used}^8$ ).

#### REFERENCES

- Y. Igarashi, A. Sato, H. Okumura, F. Nakatsubo and H. Yano, *Chem. Eng. J.*, 2018, 354, 563-568.
- 2. A. Sato, D. Kabusaki, H. Okumura, T. Nakatani, F. Nakatsubo and H. Yano, *Compos. Pt. A-Appl. Sci. Manuf.*, 2016, **83**, 72-79.
- Y. Igarashi, A. Sato, H. Okumura, F. Nakatsubo, T. Kuboki and H. Yano, *Cellulose*, 2022, **29**, 2985-2998.
- O. Bijaisoradat, L. Yue, I. Manas-Zloczower and H. Manuspiya, *J. Appl. Polym. Sci.*, 2020, **138**, 50197.
- 5. M. M. El-Zayat, A. Abdel-Hakim and M. A. Mohamed, *J. Macromol. Sci. Part A-Pure Appl. Chem.*, 2019, **56**, 127-135.
- 6. M. Singh, A. Kaushik and D. Ahuja, *Carbohydr. Polym.*, 2016, **150**, 48-56.
- L.-S. Johansson, T. Tammelin, J. M. Campbell, H. Setala and M. Osterberg, *Soft Matter*, 2011, 7, 10917-10924.
- 8. P. Cebe, D. Thomas, J. Merfeld, B. P. Partlow, D. L. Kaplan, R. G. Alamo, A. Wurm, E. Zhuravlev and C. Schick, *Polymer*, 2017, **126**, 240-247.