Optimization of Superheated Steam Treatment to Improve Surface Modification of Oil Palm Biomass Fiber

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Superheated steam (SHS) pretreatment is an effective method for hemicellulose removal from oil palm biomass (OPB) fiber, which leads to the surface modification of the fiber. However, the current SHS pretreatment is conducted at a high temperature and has a long retention time, which causes the removal of cellulose, which is an important component for biocomposite production. This study was conducted to optimize the SHS treatment temperature and retention time so that hemicellulose but not cellulose was removed. Three types of OPB fibers were used: oil palm mesocarp fiber (OPMF), oil palm empty fruit bunch (OPEFB), and oil palm frond (OPF). The chemical composition data was analyzed using a type of response surface methodology (RSM), *i.e*., central composite design (CCD). The optimal SHS treatment temperature and retention time were 265 °C/5 min, 280 °C/5 min, and 300 °C/9 min for OPMF, OPEFB, and OPF, respectively. The removal of hemicellulose at these temperatures was in the range of 60% to 70%, while the cellulose degradation was maintained below 5%. Statistical analysis showed that the optimal SHS treatment time can be shortened to 5 min to 9 min, which is 18 to 20 times shorter than previously reported methods.

Keywords: Oil Palm Biomass Fiber; Pretreatment; Superheated steam; Surface modification; Optimization

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INTRODUCTION

Recently, the rapidly expanding use of composites has been focused on sustainable and renewable reinforced composites (Akil *et al.* 2011). Natural fiber-reinforced composites are emerging as replacements for those with synthetic fibers, as they are more environmentally friendly and more cost-effective than petroleum-based materials. Natural fibers offer several advantages to the composite industry, such as low density, high toughness, good specific strength properties, good thermal and insulation properties, low cost, non-abrasiveness on the processing equipment, biodegradability, and easy recycling (Acha *et al.* 2007; Bogoeva-Gaceva *et al.* 2007; Raju *et al.* 2008; Spoljaric *et al.* 2009; Akil *et al.* 2011). Therefore, the demands for natural fiber-reinforced composites have increased greatly over the past few years for various commercial applications (Akil *et al.* 2011). In Malaysia and other tropical climate countries, there is a rising interest in making biocomposites with fibers from oil palm biomass (OPB), such as oil palm mesocarp fiber (OPMF), oil palm empty fruit bunch (OPEFB), and oil palm frond (OPF). This is motivated by the fact that huge amount of OPB is generated daily from the palm oil industry. In 2014, it was reported that a total of 80 million tonnes of OPB (dry weight) was generated from the industry in Malaysia (Kheang and May 2015). OPB

generally contains 40 to 60% cellulose, making it an interesting material for biocomposite production. Moreover, unlike the other agricultural waste, which is scattered around the plantation area, OPB is concentrated at the mill, making the collection process easy, and less logistics issues will be faced. Most OPB is currently used for mulching. OPMF on the other hand is burnt in a boiler at the mills for energy supply; however it is done inefficiently due to the abundance amount of the OPMF, making the burning as one of the methods to dispose of the material. It is hence a great idea to use OPMF as reinforce material in biocomposite, in order to make use of the valuable biomass.

Fiber architecture and the fiber-matrix interface are two major elements that influence the performance of biocomposites (Fowler *et al.* 2006). Natural fibers are considered lignocellulosic material, as they are mainly composed of cellulose, hemicellulose, and lignin. Of these components, cellulose and lignin are the most beneficial because they provide a rigid structure to the fibers and can act as a natural compatibilizer between the fiber and the matrix polymer, respectively. Apart from its hydrophilic nature and amorphous structure, hemicellulose has the lowest thermal degradation temperature among all, which is between 220 °C to 315 °C, thus making it the most unfavorable lignocellulosic component within natural fibers. The presence of abundant hydroxyl (OH) groups in natural fiber makes it hydrophilic in nature, whereas the polymer matrix is hydrophobic in nature, which results in non-uniform dispersion within the matrix (Akil *et al.* 2011). Hence such composites may exhibit poor mechanical properties, as stress cannot be transferred properly from the matrix to the fibers (Hosseinaei *et al.* 2012). Natural fiber contains a high moisture content, which is in the range 3% to 13% (Rout *et al.* 2001). The moisture needs to be removed to avoid a breakdown in mechanical properties and from being easily attacked by decay organisms (Akil *et al.* 2011; Bhat *et al.* 2011; Hosseinaei *et al.* 2012). Hence, surface modification of the fiber is necessary in order to enhance the interfacial adhesion between the fiber and the polymer matrix (Bledzki *et al.* 2010).

Surface modification by chemicals such as alkaline treatment, coupling agent, crosslinking, and compatibilizer has been widely used. The use of superheated steam (SHS) for surface modification has been recently reported, and it was shown that SHS treatment altered the properties of OPMF (Nordin *et al.* 2013; Then *et al.* 2014), OPEFB (Bahrin *et al.* 2012), and OPF (Karuppuchamy *et al.* 2015) by selective removal of hemicellulose. Moreover, the treatment resulted in the removal of silica bodies from the surface of fibers and an increase in fiber thermal stability and the removal of moisture. Alteration of the fiber surface can make it more compatible with hydrophobic polymer matrix. SHS treatment is conducted at atmospheric pressure; it is hence safer compared to high pressure steam treatment. As a non-chemical treatment method, SHS treatment would be preferred for the production of green products such as biocomposite, as it is a more environmental friendly process. SHS is widely used in the food industry for drying food products, which makes the process advantageous as it will be easily scaled-up due to availability of large equipment in the market.

Based on Nordin *et al.* (2013), the best SHS temperature and retention time for surface modification of OPMF, in terms of hemicellulose removal, was at 230 °C/120 min, where about 70% of the hemicellulose was removed. However, at these treatment conditions, cellulose started to degrade, as can be seen by a marked reduction in the cellulose composition. Moreover, a long treatment time will not be favorable for large scale purpose, as it will burden the equipment and add to the cost of production. It is expected that a prolonged SHS treatment retention time causes high degradation of cellulose, which eventually reduces the mechanical properties of the fiber because cellulose functions provide the crystalline structure to the fiber. Therefore, this study was conducted to optimize the SHS treatment temperature and retention time aimed at surface modification of oil palm biomass fibers, so that high hemicellulose removal can be achieved with less effect on the cellulosic content.

EXPERIMENTAL

Material

OPMF and OPEFB were obtained from the Seri Ulu Langat Palm Oil Mill, Selangor, Malaysia, while the OPF was obtained from the Taman Pertanian Universiti (TPU), Universiti Putra Malaysia (UPM). The OPF was first shredded and then pressed to remove the juice as described by Abdullah *et al.* (2015). Raw OPMF, OPEFB, and OPF were prepared as described by Nordin *et al.* (2013). The size of each fiber was about 8 cm to 10 cm in length, and there was no further mechanical treatment prior to the SHS treatment.

Superheated Steam Treatment

The OPB fibers were treated using a lab scale superheated steam oven (QF-5200C, Naomoto Corporation, Osaka, Japan) under ambient pressure as described by Nordin *et al.* (2013). The steam flow rate and heater power of the SHS oven were kept constant at maximum values of 4.95 kg/h and 6.6 kW, respectively. Both the temperature and retention time of the SHS oven were varied in the range of 220 °C to 300 °C and 5 min to 30 min, respectively.

Experimental Design and Statistical Analysis

A face-centered central composite design (CCD) with two variables and three levels was chosen to study the response pattern and establish a model (Latip *et al.* 2014; Zzaman *et al.* 2014). The independent variables in this experiment were the temperature (X_1) and retention time (X_2), with three levels selected for each variable, while the hemicellulose and cellulose content were the responses. Preliminary studies were conducted to define the specific range of the independent variables for the experiments (Table 1). Table 2 represents the experimental design, which consists of 14 runs with six center points to reduce the variability in the data collection and verify the accuracy of the model predicted by the software. Design Expert software (Version 7.0, Stat-Ease Inc., Minneapolis, MN, USA) was used for the statistical and mathematical analyses.

Table 1. Range of Independent Variables Used for the Central Composite Design

Independent Variables	Coded Symbols	Levels		
		-1	0	1
Temperature (°C)	X_1	220	260	300
Retention time (min)	X_2	5	17.5	30

Table 2. Actual and Coded Values of the SHS Experimental Design

Run	Temperature (°C, X_1)		Retention Time (min, X_2)	
	Coded	Actual	Coded	Actual
1	0	260	1	30
2	0	260	0	17.5
3	-1	220	1	30
4	0	260	0	17.5
5	0	260	0	17.5
6	1	300	0	17.5
7	0	260	0	17.5
8	1	300	1	30
9	-1	220	0	17.5
10	1	300	-1	5
11	0	260	0	17.5
12	0	260	-1	5
13	-1	220	-1	5
14	0	260	0	17.5

The significance of each variable, as well as the regression coefficients of linear, quadratic, and interaction terms, were evaluated using analysis of variance (ANOVA). Three-dimension (3D) surface plots were used to show the effects of the variables on the responses and to locate the optimal levels. The predicted optimal conditions of the SHS treatment temperature and the retention time were validated by conducting an actual experiment to verify the predicted values for the hemicellulose and cellulose content of OPB fibers obtained from the software. The behavior of the system was explained by the second order polynomial equation (Eq. 1),

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \quad (1)$$

where *Y* is the response, the hemicellulose content and cellulose content; X_1 and X_2 are the input variables of temperature and retention time, ranging from -1 to 1, which influenced the response variable *Y*; β_0 is the constant coefficient; β_1 and β_2 are linear coefficients; β_{11} and β_{22} are quadratic coefficients; and β_{12} is an interaction of coefficients.

Chemical Compositional Analysis

The gravimetric determination of the lignin, cellulose, and hemicellulose in the OPMF, OPEFB, and OPF, was performed according to the method by Iwamoto *et al.* (2008).

RESULTS AND DISCUSSION

The experimental and predicted values of the hemicellulose and cellulose content after the SHS treatment for OPB fibers are shown in Table 3. From the data obtained, a quadratic model was chosen for all types of OPB fibers, as it was found to be the best fit model for both responses on the basis of model probability, lack of fit test probability, and coefficient of determination (R^2). A second order polynomial equation for each response was generated based on the data obtained from experiments, and then analyzed through the analysis of variance (ANOVA) test in order to evaluate the model. A good model should have a significant *p* value, where $p < 0.05$, an insignificant lack of fit test *p* value, where $p > 0.05$, and an R^2 value, which should be closer to 1 or at least 0.80 to fit into the model (Zaibunnisa *et al.* 2009). A summary of the results obtained from the ANOVA test for the OPB fibers in the response surface quadratic model are shown in Table 4.

Effect of SHS Treatment Temperature and Retention Time on Hemicellulose Content of Oil Palm Biomass Fibers

To evaluate the effect of temperature and retention time on hemicellulose content, the design matrix of experimental conditions, with their corresponding hemicellulose content, was subjected to a regression analysis. The mathematical model that relates the hemicellulose content to the independent process variables of temperature and retention time, is given in the quadratic regression as follows:

$$Y_{1a} = 0.11 + 0.02X_1 + 0.08X_2 + 0.023X_1X_2 + 0.005047X_1^2 + 0.07X_2^2 \quad (2)$$

$$Y_{1b} = 0.14 + 0.041X_1 + 0.11X_2 + 0.016X_1X_2 + 0.015X_1^2 + 0.009806X_2^2 \quad (3)$$

$$Y_{1c} = 0.12 + 0.04X_1 + 0.074X_2 + 0.028X_1X_2 + 0.008765X_1^2 + 0.013X_2^2 \quad (4)$$

where Y_{1a}, Y_{1b}, and Y_{1c} represent hemicellulose content (g) in OPMF, OPEFB, and OPF, respectively; and X_1 and X_2 are coded values of independent variables, which represent temperature and retention time, respectively.

Table 3. Experimental and Predicted Values for Hemicellulose and Cellulose Content of SHS-treated OPMF, OPEFB, and OPF

Run	OPMF				OPEFB				OPF			
	Hemicellulose Content (g)		Cellulose Content (g)		Hemicellulose Content (g)		Cellulose Content (g)		Hemicellulose Content (g)		Cellulose Content (g)	
	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted	Exp.	Predicted
1	0.097	0.087	0.38	0.36	0.12	0.11	0.44	0.43	0.11	0.092	0.50	0.47
2	0.11	0.11	0.39	0.39	0.13	0.14	0.46	0.49	0.13	0.12	0.48	0.48
3	0.21	0.21	0.33	0.33	0.22	0.22	0.47	0.51	0.15	0.15	0.46	0.47
4	0.12	0.11	0.38	0.39	0.15	0.14	0.50	0.49	0.12	0.12	0.50	0.48
5	0.10	0.11	0.41	0.39	0.12	0.14	0.59	0.49	0.14	0.12	0.46	0.48
6	0.097	0.10	0.27	0.29	0.059	0.04	0.023	0.16	0.067	0.062	0.43	0.43
7	0.13	0.11	0.38	0.39	0.14	0.14	0.52	0.49	0.16	0.12	0.46	0.48
8	0.093	0.10	0.28	0.28	0.022	0.03	0.47	0.45	0.040	0.059	0.38	0.39
9	0.25	0.26	0.33	0.34	0.26	0.26	0.49	0.39	0.18	0.21	0.46	0.45
10	0.11	0.094	0.33	0.32	0.068	0.079	0.54	0.49	0.096	0.082	0.50	0.49
11	0.12	0.11	0.41	0.39	0.13	0.14	0.46	0.49	0.11	0.12	0.47	0.48
12	0.099	0.13	0.40	0.42	0.21	0.19	0.48	0.60	0.13	0.17	0.48	0.51
13	0.31	0.30	0.37	0.36	0.33	0.33	0.47	0.45	0.32	0.29	0.46	0.45
14	0.10	0.11	0.40	0.39	0.15	0.14	0.42	0.49	0.11	0.12	0.49	0.48

Table 4. ANOVA of the Response Surface Quadratic Model for Hemicellulose and Cellulose Content of Oil Palm Biomass Fibers

	OPMF		OPEFB		OPF	
	Hemicellulose Content	Cellulose Content	Hemicellulose Content	Cellulose Content	Hemicellulose Content	Cellulose Content
Model-Quadratic	< 0.0001*	0.0002*	< 0.0001*	0.0063*	0.0020*	0.0176*
A-Temperature	0.0212*	0.0147*	< 0.0001*	0.0555	0.0101*	0.0435*
B-Retention time	< 0.0001*	0.0038*	< 0.0001*	0.0046*	0.0003*	0.1715
AB	0.0281*	0.7846	0.0412*	0.0358*	0.0881	0.0171*
A^2	0.6281	0.3519	0.0988	0.6259	0.6261	0.5053
B^2	0.0001*	< 0.0001*	0.2556	0.0101*	0.4901	0.0137*
Lack of Fit	0.1035*	0.1720*	0.1553*	0.0665*	0.0811*	0.1272*
R^2	0.9624*	0.9329*	0.9829*	0.8285*	0.8728*	0.7734
Standard deviation	0.017*	0.015*	0.013*	0.092*	0.029*	0.019*
*Statistically significant at $p < 0.05$ for model, statistically insignificant at $p > 0.05$ for lack of fit test						

The ANOVA results showed that *p*-values for the quadratic model of OPMF, OPEFB, and OPF were all lower than 0.05, indicating that the quadratic models for all types of OPB fibers were significant in terms of their hemicellulose content. A significant *p*-value represents a good model.

A lack of fit test measures the failure of the model to represent the data in the experimental domains at points that are not included in the regression (Gomathi and Neogi 2009). If a model has a significant lack of fit, it is not a good predictor of a particular response, and it should not be used. Regarding hemicellulose content, the *p*-values for the lack of fit test of OPMF, OPEFB, and OPF were 0.1035, 0.1553, and 0.0811, respectively. Because the *p*-values were higher than 0.05, the lack of fit test was insignificant. The insignificant lack of fit test is a positive sign because it demonstrates a good fit of the model to the data.

The coefficient of determination, R^2 for OPMF, OPEFB, and OPF in terms of hemicellulose were 0.9624, 0.9829, and 0.8728, respectively. An R^2 value close to 1 means that the dependent variable, the hemicellulose content, was predicted with less error from the independent variables of temperature and retention time. In this case, about 96%, 98%, and 87% proportion of the variance in hemicellulose content was predictable from temperature and retention time of SHS treatment for OPMF, OPEFB, and OPF, respectively. An R^2 value which is close to 1 also indicates a good agreement between the experimental and predicted values. In addition, the adequacy of the model was also investigated by a comparison between the experimental and predicted values for the hemicellulose content in OPMF, OPEFB, and OPF, as shown in Figs. 1(a), 1(c), and 1(e), respectively. The comparison was done by observing the proximity of the points that were scattered along the fitted line. Based on the graph stated above, there is an agreement between the experimental and predicted values, which proved that the models were adequate for predicting the hemicellulose content after SHS treatment.

Figure 2 illustrates the three-dimensional response surfaces based on Eqs. 2, 3, and 4, which showed the effect of the temperature and retention time of a SHS treatment on the hemicellulose content in OPB fibers. In this case, the lowest hemicellulose content is preferred, as it will contribute to better mechanical properties of the fibers for biocomposite purposes. As shown in Fig. 2, the hemicellulose content in OPMF, OPEFB, and OPF was inversely proportional to an increase in temperature and retention time of the SHS treatment. This result reflects that hemicellulose has the lowest thermal degradation temperature compared with the other lignocellulose components, which is in between 220 °C to 315 °C (Nordin *et al.* 2013). A higher temperature and a longer retention time used during the SHS treatment caused the hemicellulose component to degrade drastically (Fig. 3). Based on the three-dimensional response surfaces, the effect of temperature on the hemicellulose content was greater than the effect of retention time. The degradation of hemicellulose was higher when the temperature increased from 220 °C to 300 °C, at a constant minimum point of retention time of 5 min, compared with when the retention time was increased from 5 min to 30 min at a constant minimum point of temperature of 220 °C. This result is in agreement with Nordin *et al.* (2013), which reported that a prolonged retention time of up to 3 h for SHS treatment at 230 °C did not give a significant difference in the hemicellulose content. Upon reaching the maximum temperature of 300 °C, there was no significant change in the hemicellulose degradation even when the retention time increased up to 30 min. Hemicellulose degradation was almost constant at this temperature, which may reflect the composition of recalcitrant hemicellulose. This recalcitrant hemicellulose is closely linked to lignin through a covalent bond, such as ester and ether bonds, which may require more energy to break (Nordin *et al.* 2013); hence, it is difficult to remove.

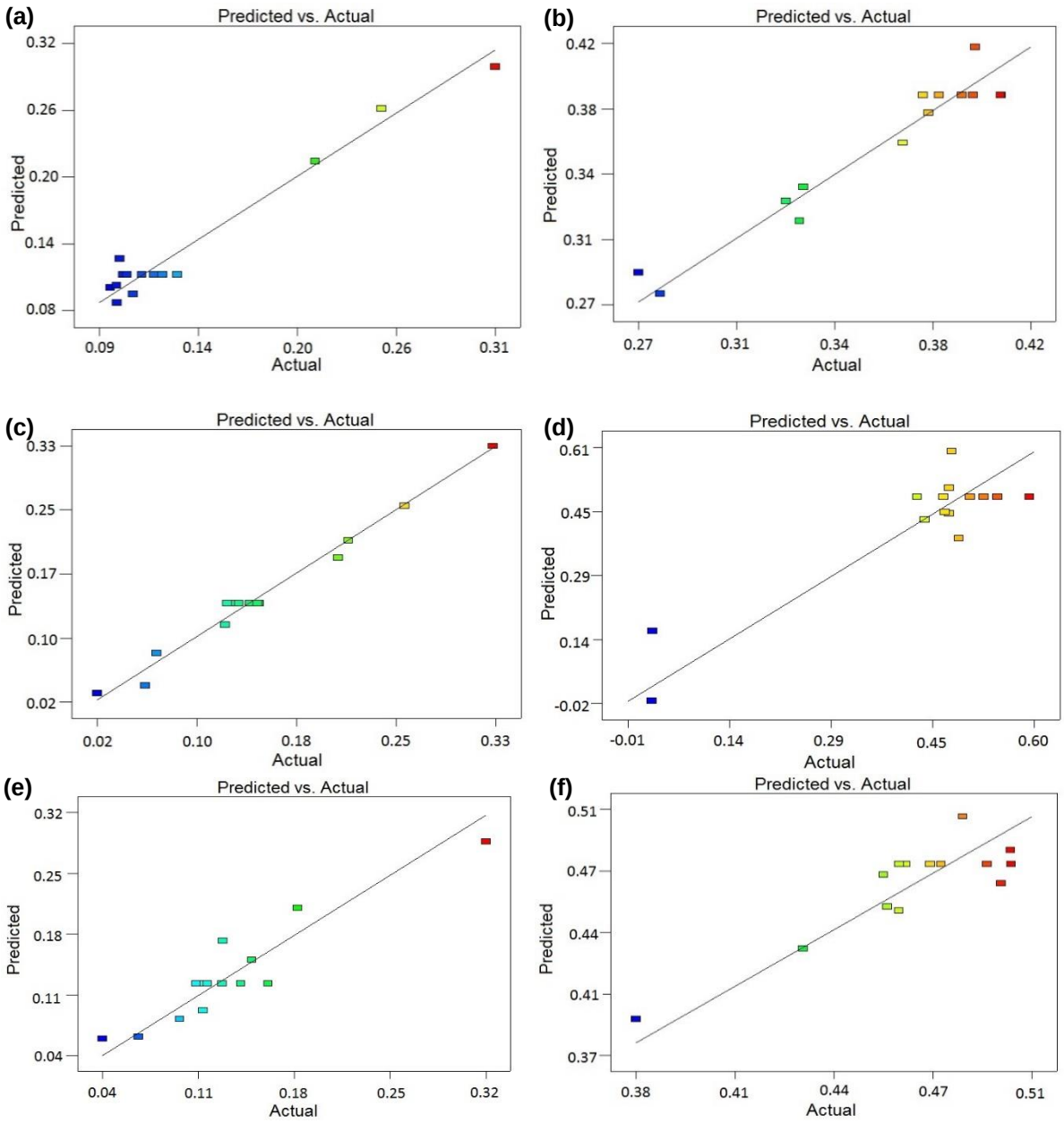

Fig. 1. Experimental and predicted values for (a) hemicellulose content in OPMF, (b) cellulose content in OPMF, (c) hemicellulose content in OPEFB, (d) cellulose content for OPEFB, (e) hemicellulose content in OPF, and (f) cellulose content in OPF

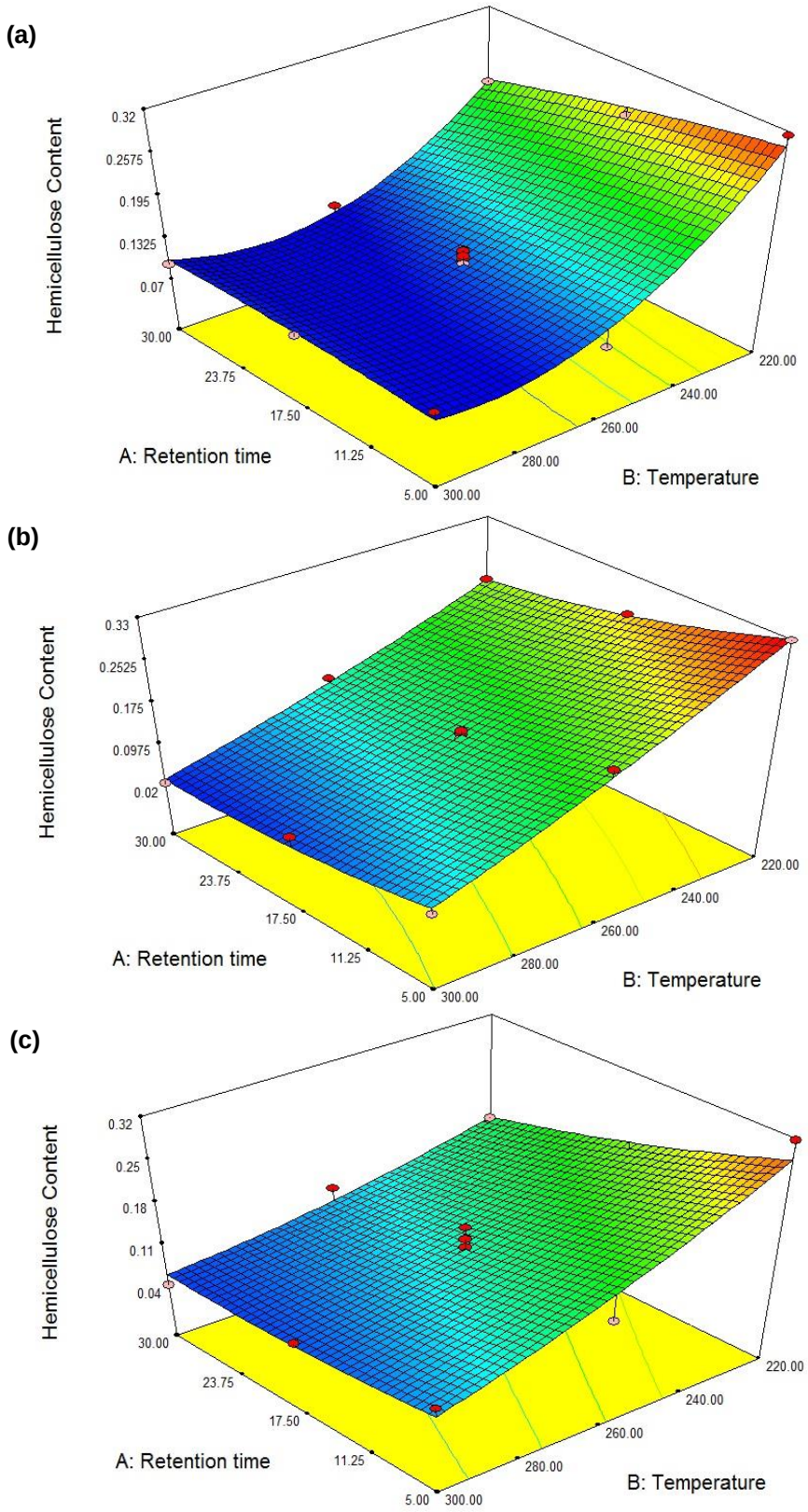

Fig. 2. Three-dimensional response surfaces plotted for temperature and retention time *vs*. cellulose content for (a) OPMF, (b) OPEFB, and (c) OPF

Effects of SHS Temperature and Retention Time on Cellulose Content of OPB

Similarly, to evaluate the effect of the temperature and retention time on the cellulose content, the design matrix of experimental conditions with their corresponding cellulose content was subjected to regression analysis. The mathematical model that relates the cellulose content to the independent process variables of temperature and retention time is given in the quadratic regression as follows,

$$Y_{2a} = 0.39 + 0.019X_1 + 0.024X_2 + 0.0021X_1X_2 + 0.008724X_1^2 + 0.077X_2^2 \quad (5)$$

$$Y_{2b} = 0.49 + 0.084X_1 + 0.15X_2 + 0.12X_1X_2 + 0.0281X_1^2 + 0.18X_2^2 \quad (6)$$

$$Y_{2c} = 0.48 + 0.019X_1 + 0.012X_2 + 0.029X_1X_2 + 0.008053X_1^2 + 0.036X_2^2 \quad (7)$$

where Y_{2a}, Y_{2b}, and Y_{2c} represent the cellulose content (g) in OPMF, OPEFB, and OPF, respectively, and X_1 and X_2 are coded values of the independent variables, which represent temperature and retention time, respectively. The ANOVA test showed that the *p*-value for the quadratic model of OPMF, OPEFB, and OPF were all significant, as they were all less than 0.05. Hence, in terms of cellulose content, all types of OPB possess a good model.

The *p*-values for the lack of fit test of OPMF, OPEFB, and OPF were 0.1720, 0.0665, and 0.1272, respectively. The insignificant *p*-value for the lack of fit test is a good sign which shows the model fit the data well; hence, the model can be used to predict the cellulose content in OPMF, OPEFB, and OPF during the SHS treatment.

The R^2 coefficient of determination for OPMF, OPEFB, and OPF was 0.9329, 0.8285, and 0.7734, respectively. For OPMF and OPEFB, both possess a high R^2 value, or at least more than 0.80 in order to fit into the model, in which 93% and 82% proportion of the variance in the cellulose content, respectively, is predictable from the temperature and retention time of the SHS treatment. However, R^2 for the OPF is slightly lower than 0.80, where about 77% proportion of the variance in the cellulose content can be predicted from the temperature and retention time. Based on Figs. 1(b), 1(d), and 1(f), all points scattered in the graphs were close to the fitted line, which means there is an agreement between the experimental and predicted values. Thus, these models were adequate for predicting the cellulose content of OPMF, OPEFB, and OPF after the SHS treatment.

Figure 4 illustrates the three-dimensional response surfaces based on Eqs. 5, 6, and 7, which show the effect of temperature and retention time of the SHS treatment on the cellulose content in the OPB fibers. In contrast with the hemicellulose content, the cellulose content needs to be retained as much as possible during the SHS treatment because it is important for the crystalline structure to the fibers. Basically, a higher cellulose content leads to higher stiffness, which explains why the cellulose content and the microfibril angle have a major influence on the mechanical properties of composites (Doan *et al.* 2006). As shown in Fig. 3, the cellulose degradation pattern is almost similar with the degradation of the hemicellulose content, whereby the degradation of cellulose was increased proportionally with an increase in the temperature and retention time. However, the reduction pattern of the cellulose content is not as remarkable as the reduction pattern of the hemicellulose content; cellulose possesses a higher thermal degradation temperature compared to hemicellulose, which is between 315 °C and 400 °C (Nordin *et al.* 2013).

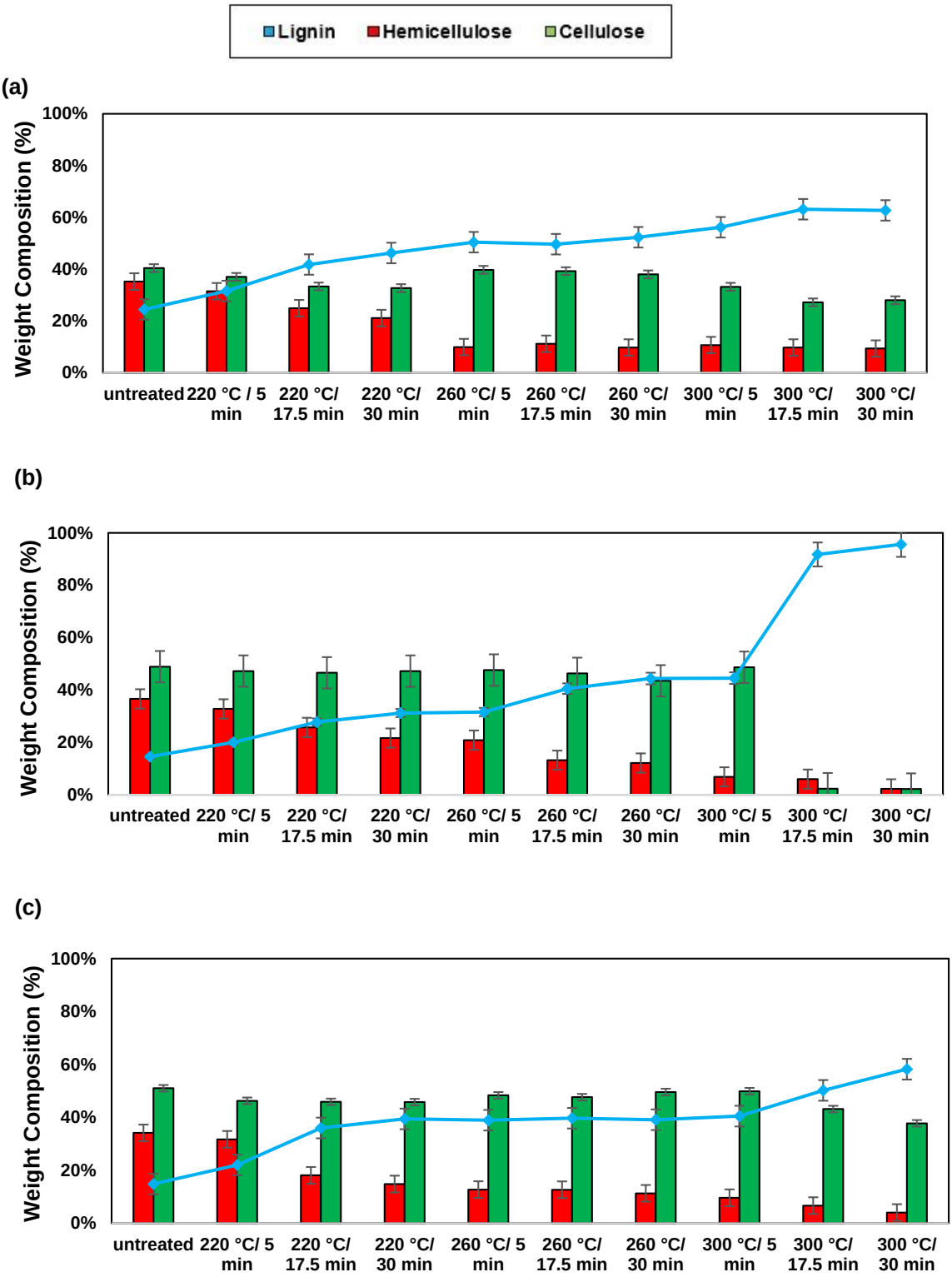

Fig. 3. Chemical composition of untreated and SHS-treated (a) OPMF, (b) OPEFB, and (c) OPF

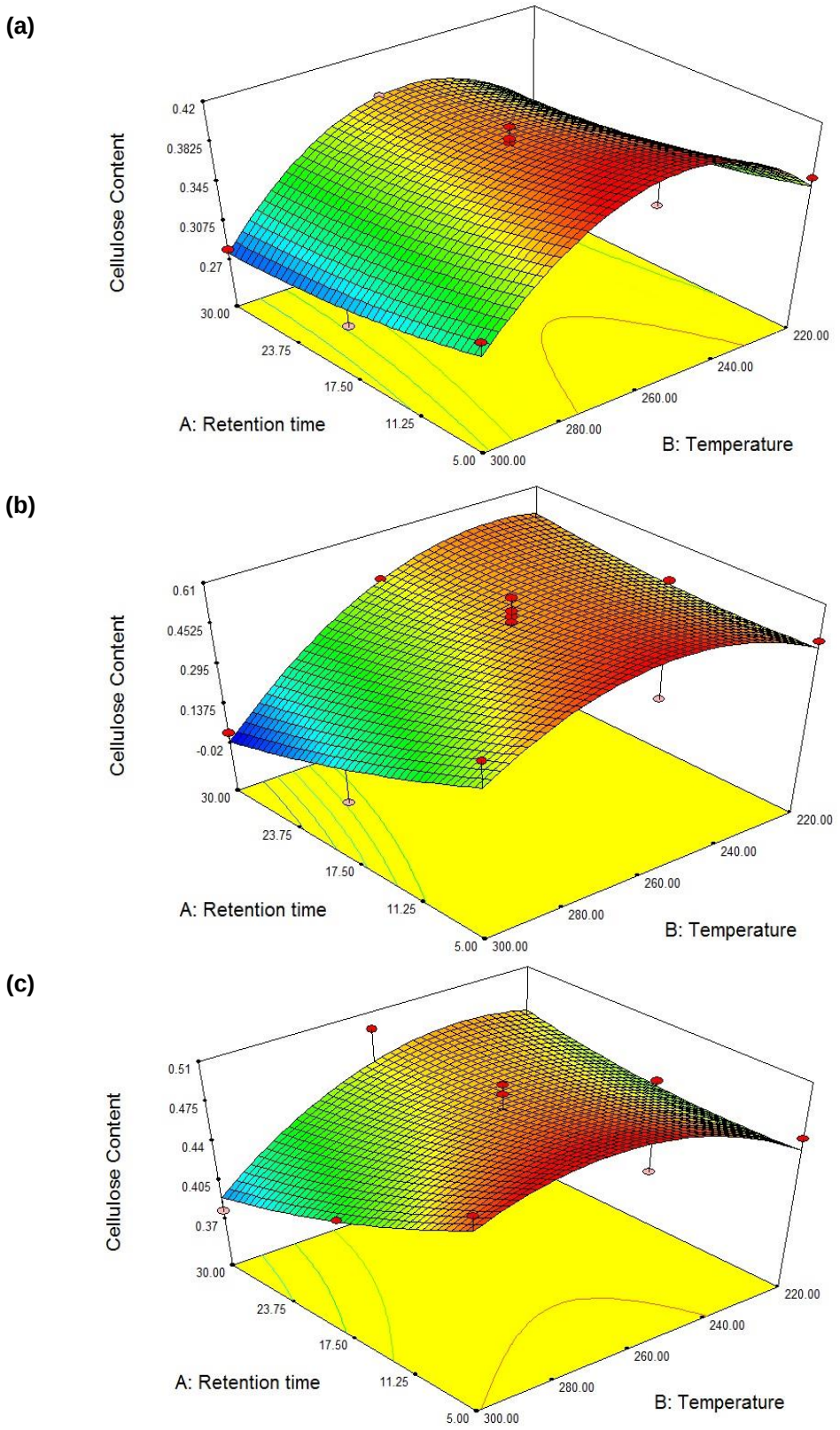

Fig. 4. Three-dimensional response surfaces plotted for the temperature and retention time *vs.* cellulose content for (a) OPMF, (b) OPEFB, and (c) OPF

Based on the three-dimensional response surface, there was not much change in the degradation of the cellulose when treated at the temperature range of 220 °C to 280 °C. However, the degradation of cellulose was more significant at 300 °C (Fig. 4). The effect of retention time was more notable when the fibers are treated at a higher temperature, such as 300 °C, than at a lower temperature, 220 °C, due to higher thermal stability of cellulose compared with hemicellulose. Thus, the interaction between the retention time and the temperature affects cellulose degradation in fibers during the SHS treatment.

Process Optimization

Following the design and analysis of the experimental data obtained, numerical optimization was carried out for the SHS-treated OPB fibers. The criteria for the hemicellulose content was set at minimum value, while for the cellulose content it was set at maximum value in order to get the optimal temperature and retention time of the SHS treatment (Table 5). This is corresponding to the aim of this study, which was to remove the hemicellulose content as much as possible while retaining the cellulose content to the utmost, prior to the preparation of fiber for biocomposite purposes.

Table 5. Constraints Applied for Optimization

Fiber	Name	Goal	Lower Limit	Upper Limit
OPMF	Temperature	In range	5	30
	Retention time	In range	220	300
	Hemicellulose content	Minimum	0.0934	0.3144
	Cellulose content	Maximum	0.2717	0.4066
OPEFB	Temperature	In range	5	30
	Retention time	In range	220	300
	Hemicellulose content	Minimum	0.0222	0.3276
	Cellulose content	Maximum	0.0216	0.5933
OPF	Temperature	In range	5	30
	Retention time	In range	220	300
	Hemicellulose content	Minimum	0.0404	0.3170
	Cellulose content	Maximum	0.3774	0.4991

As shown in Table 6, the optimal temperature and retention times of the SHS treatment for OPMF, OPEFB, and OPF were 265 °C for 5 min, 280 °C for 5 min, and 300 °C for 9 min, respectively. The generated optimal SHS treatment temperature and retention time was based on the maximum hemicellulose removal that can be achieved from the fibers with only minimal removal of the cellulose. The predicted hemicellulose content removal (based on original hemicellulose content in sample) for OPMF, OPEFB, and OPF are 72%, 67%, and 72%, respectively, while the predicted cellulose content removal from the original content for all types of OPB fibers was less than 5%.

Throughout the SHS treatment, the lignin content was less affected. The percentage of lignin in the fiber increased, which is in agreement with Nordin *et al.* (2013) and Bahrin *et al.* (2012). The percentage of the removed hemicellulose and cellulose content was shifted to the total percentage of the lignin content left in the fiber, which explains why the percentage of lignin appeared to increase throughout the SHS treatment. The complexity of the lignin structure makes the fiber difficult to degrade. Lignin in fiber is an advantage in biocomposite production. Lignin affects the compatibility between fibers and a polymer; it acts as a natural coupling agent due to its polar hydroxyl groups and non-polar hydrocarbon and benzene rings (Acha *et al.* 2007).

Table 6. Summary of Optimized SHS Treatment Conditions for Oil Palm Biomass Fibers in Comparison with Other Reports*

Fiber	Temperature (°C)	Retention time (min)	Hemicellulose content (%)	Cellulose content (%)	References
OPMF	230	120	16.8 (33.1)	33.7 (42.8)	Nordin *et al.* (2013)
OPEFB	210	90	NA	NA	Bahrin *et al.* (2012)
OPF	210	180	NA	NA	Karuppuchamy *et al.* (2015)
OPMF	265	5	9.8 (35.2)	39.7 (40.3)	This study
OPEFB	280	5	13.8 (33.4)	49.1 (52.0)	This study
OPF	300	9	9.6 (34.1)	49.8 (51.0)	This study

*Note: Values in ( )'s represent the original content of hemicellulose/cellulose before the SHS treatment,
NA–Not available

A validation experiment was carried out with the parameters as suggested by the model, and the comparison between the predicted and experimental values are summarized in Table 7. Based on the predicted and experimental results, the experimental values were in good agreement with the predicted values proposed by the model. Comparison studies were also made between this study with other previous studies regarding the SHS treatment temperature and retention time (Table 6). A higher temperature range was used in this study, ranging from 265 °C to 300 °C; previous studies were in the range of 210 °C to 230 °C. The highlight of this study is the retention time of the SHS treatment, which was significantly reduced to only 5 min to 9 min, which is 18 to 20 times higher than in previous studies. Interestingly, even though the SHS treatment time was markedly reduced, there was lower hemicellulose content. The high treatment temperature could have affected this result. Based on the statistical analysis, the best combination between the SHS treatment

time and the temperature aimed for hemicellulose removal and cellulose retention. The cellulose content was less affected after the SHS treatment than in previous studies, whereby the cellulose degradation in this study was less than 5%. Thus, this study described an appropriate SHS treatment temperature and retention with high hemicellulose removal and less effect on the cellulose content.

Table 7. Comparison between Predicted and Experimental Values of Hemicellulose and Cellulose Content of Fibers Treated using Optimal Conditions of SHS Treatment

Fiber	Temperature (°C)	Retention time (min)		Hemicellulose content (%)	Cellulose content (%)
OPMF	265	5	Predicted	9.7 (72% removal)	39.7 (1% removal)
			Experimental	9.8 (72% removal)	39.7 (1% removal)
OPEFB	280	5	Predicted	11.9 (67% removal)	50.7 (No significant removal)
			Experimental	13.1 (64% removal)	46.3 (5% removal)
OPF	300	9	Predicted	9.5 (72% removal)	49.5 (3% removal)
			Experimental	9.6 (71% removal)	49.8 (2% removal)

A short SHS treatment time is not only an advantage in retaining cellulose content, but also would give remarkable impact on the processing especially for commercial purpose. Non-alteration of cellulosic component during treatment is important to ensure superior mechanical properties of biocomposite. On the other hand, shorter processing time would be more economical and may cause the overall production cost to be lowered. Detailed cost analysis on the impact of short SHS treatment time could be done in order to evaluate the feasibility of this process for large scale processing.

CONCLUSIONS

1. The optimal SHS treatment temperature and retention time for OPMF, OPEFB, and OPF were 265 °C for 5 min, 280 °C for 5 min, and 300 °C for 9 min, respectively.
2. At optimal conditions, the hemicellulose removal was 72%, 62%, and 71%, while the cellulose removal was 1%, 5%, and 2%, respectively, for OPMF, OPEFB, and OPF.
3. High SHS treatment temperature and lower retention time rapidly removed up to 70% of the hemicellulose but did not affect the cellulose content.
4. The SHS pretreatment time was reduced drastically from 90 min to 180 min down to only 5 min to 9 min. The reduction in the SHS treatment time resulted in higher hemicellulose removal, which provides a better surface for biocomposite production.
5. A reduced retention time for the SHS treatment of natural fiber is advantageous, especially for scaling up the process for commercial applications.

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