

Preparation and Characterisation of Linear Low-Density Polyethylene / Thermoplastic Starch Blends Filled with Banana Fibre

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Abstract. In this study, the influence of banana fibre (BF) loading using sodium hydroxide (NaOH) pre-treated and succinic anhydride-treated (SA) BF on the mechanical properties of linear low-density polyethylene (LLDPE)/thermoplastic starch (TPS) matrix is investigated. LLDPE/TPS/BF composites were developed under different BF conditions, with and without chemical modifications with the BF content ranging from 5% to 30% based on the total composite. The tensile strength showed an increase with an increase of fibre content up to 10%, thereby decreasing gradually beyond this level. NaOH pre-treated and SA treated BF added with LLDPE/TPS composite displays a higher tensile strength as compared to untreated BF in LLDPE/TPS composites. Thermal behaviour of the BF incorporated in LLDPE/TPS composite was characterised using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). This showed that SA treated BF exhibits better thermal stability, compared to other composites. This is because of the improvement in interfacial adhesion existing between both the fibre and matrix. In addition, a morphology study confirmed that pre-treated and treated BF had excellent interfacial adhesion with LLDPE/TPS matrix, leading to better mechanical properties of resultant composites.

1. Introduction

Given the current environmental issues resulting from petroleum-based plastics, many research studies have been conducted to investigate how to reduce the amount of plastic waste. Partial replacement of industrial plastics with biodegradable polymer is an effective means to solve the problem of plastic waste. It is usually produced by blending non-biodegradable plastics with biodegradable components as a dispersing filler such as a polysaccharide (cellulose and starch). The polymer combines the high-quality properties of conventional plastics and abundantly available polysaccharides as a biodegradation agent. Incorporating a high-content of a polysaccharide as a filler within the binary and ternary system is limited due to its rigid characteristics and low processing capability. In this study, starch is converted to thermoplastic to optimise the starch content in the resultant composite. The molecular structure of starch granules is destroyed and blended together with targeting polymer. This is undertaken by heating the starch under a condition of significant stress in the presence of a plasticiser, such as glycerol [1]. Although incorporating starch can accelerate the biodegradation of polymer materials, several drawbacks were observed (e.g. one drawback being lower mechanical properties). To enhance the mechanical properties of the resultant blend, BF was used as a reinforcing filler. The combination of using starch in thermoplastic form and cellulosic fibre as a reinforcing filler



could potentially be used to optimise the biodegradation agent in the synthetic polymer matrix, with acceptance mechanical properties. In addition to the increase in interface adhesion between the fibre and matrix, several surface modifications such as mercerisation, acetylation, etherification and graft copolymerization are required. This could potentially reduce the hydrophilicity of natural fibre and the tendency of the fibre to absorb moisture [2]. In this study, the blends of LLDPE/TPS filled with BF will be performed. Chemical modifications of BF are obtained by treating with sodium hydroxide (NaOH) and followed by succinic anhydride.

2. Materials and methods

LLDPE with a density of 0.92 g/cm^3 was supplied by Lotte Chemical Titan, Malaysia. Cassava starch was used in the preparation of thermoplastic starch (TPS) in the presence of glycerol as a plasticiser. Food grade cassava starch was supplied from Thye Huat Chan Sdn. Bhd, glycerol supplied from TTD Chemical, and the reagent grade succinic anhydride supplied from Sigma Aldrich.

2.1. Surface modifications

BF was dried at room temperature for three days before post-dried in an oven for 24 hours where it was then ground and sieved to $75 \mu\text{m}$ in size. The next step was to soak the BF in sodium hydroxide (NaOH) for 4 hours at 30°C to remove any lignin and hemicellulose [3]. The banana mercerised fibre was then soaked in 5% SA solution mixed with sulphuric acid (H_2SO_4) acting as a catalyst. The mixture was then heated at 80°C for 1 hour where the treated BF was washed with distilled water and dried in a heated oven at 80°C for 12 hours [4].

2.2. TPS/LLDPE filled with banana fiber preparation

The preparation of TPS was undertaken by using a heated two roll mill in the presence of 35 wt% glycerol, followed by blending with LLDPE at a temperature of 135°C for a further 10 minutes. The final stage of the process then involved the BF being charged and processed until the mixture was homogeneous. Refer table 1, showing the formulation of TPS/LLDPE filled with BF. A series (consisting of three types) was prepared to represent; untreated BF/LLDPE/TPS, pre-treated BF/LLDPE/TPS and SA treated BF/LLDPE/TPS composites with a variation of 5% to 30% BF loading.

Table 1. Formulation of the TPS/LLDPE filled with banana fiber.

Samples	LLDPE/TPS (70:30) (%)	Banana trunk fiber (%)	Pretreatment (NaOH) (%)	Treatment (SA)(%)
Untreated	100	0	-	-
banana trunk fiber in LLDPE/TPS blends	95	5	-	-
	90	10	-	-
	80	20	-	-
	70	30	-	-
NaOH	100	0	-	-
pretreated banana trunk fiber in LLDPE/TPS blends	95	5	*5	-
	90	10	*5	-
	80	20	*5	-
	70	30	*5	-
SA treated	100	0	-	-
banana trunk fiber in LLDPE/TPS blends	95	5	*5	*5
	90	10	*5	*5
	80	20	*5	*5
	70	30	*5	*5

^abased on the % weight of BF fiber.

2.3. Testing

Tensile testing was conducted using an Instron machine based on ASTM D638. Tensile strength, Young's modulus and elongation at break data were collected from an average of five samples, for each compound. Structural analysis of the composites was determined using a Fourier Transform Spectroscopy (FTIR) with a total of 32 scans performed, at the wavelength ranging from 700 cm^{-1} to 4000 cm^{-1} . The morphology study of TPS/LLDPE filled banana fibre was conducted using a Scanning Electron Microscopic (SEM) at a magnification of 150X and 300X. The specimens were mounted on aluminium stubs and coated with palladium to avoid the possibility of any electrostatic charging occurring during the testing. Thermal analysis was conducted by utilising Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). DSC was carried out using the ambient room temperature to 180°C at a scan rate of 10°C/min. The sample was then cooled to ambient room temperature, allowing the formation of crystals to occur. The amount of crystal structure (X_c) is calculated by using the following equation:

$$\frac{\Delta H^0}{\Delta H_f^0} \times 100\% \quad (1)$$

where: ΔH^0 = Enthalpy of fusion;

ΔH_f^0 = Enthalpy of crystallinity of a sample at 100% crystallinity.

TGA was calculated using ambient room temperature to 600°C at a scan rate of 10°C/min to assess the thermal stability and thermal degradation of LLDPE/TPS/BF composites.

3. Results and discussions

A series of BF incorporated in LLDPE/TPS blends was characterized using a Fourier Transformation Infrared Spectroscopy (FTIR). The spectra for LLDPE/TPS blends filled with 10% untreated, pre-treated and treated BF are shown in figure 1.

A small peak was observed at 3395 cm^{-1} corresponding to -OH stretching, characterizing the TPS and BF functional group. There were two sharp peaks identified at 2917 cm^{-1} and 2849 cm^{-1} respectively, representing -CH stretching of the alkanes group of LLDPE. Compared to the untreated and pre-treated composites, a new peak was observed at 1743 cm^{-1} for treated LLDPE/TPS/BF composites, caused by -C=O stretching vibration occurring from the ester bond. This could possibly represent the esterification reaction occurring between BF and SA. Hence, the presence of SA in the sample was removed before FTIR testing by using a Soxhlet extraction technique.

Thus, the influence of -C=O vibrations occurring from the SA was eliminated. The possible esterification reaction between BF and SA is shown in figure 2. SA can act as a bridge between hydrophobic LDPE matrix and hydrophilic BF and the firm interaction between BF and SA leading to a much higher performance in the mechanical properties of the resultant composites.

The influence of BF reinforced LLDPE/TPS matrix on tensile strength is shown in figure 3. At initial BF loading, the tensile strength value for untreated composite is 4.4 MPa, being lower than in LLDPE/TPS matrix. This indicated that the incorporation of BF interfered with the alignment of LLDPE and TPS chains, therefore influencing the final properties of the composite.

The tensile strength was increased to 6.3 MPa at 10% BF loading, showing the optimum level of untreated BF loading. As the BF content increases above 10%, the tensile strength starts to decrease, attributed to the agglomeration of BF due to strong hydrogen bonding holding the fibres together [5]. The agglomeration of BF within LLDPE/TPS matrix promoted the micro-crack formation appearing when an external force was applied to the samples.

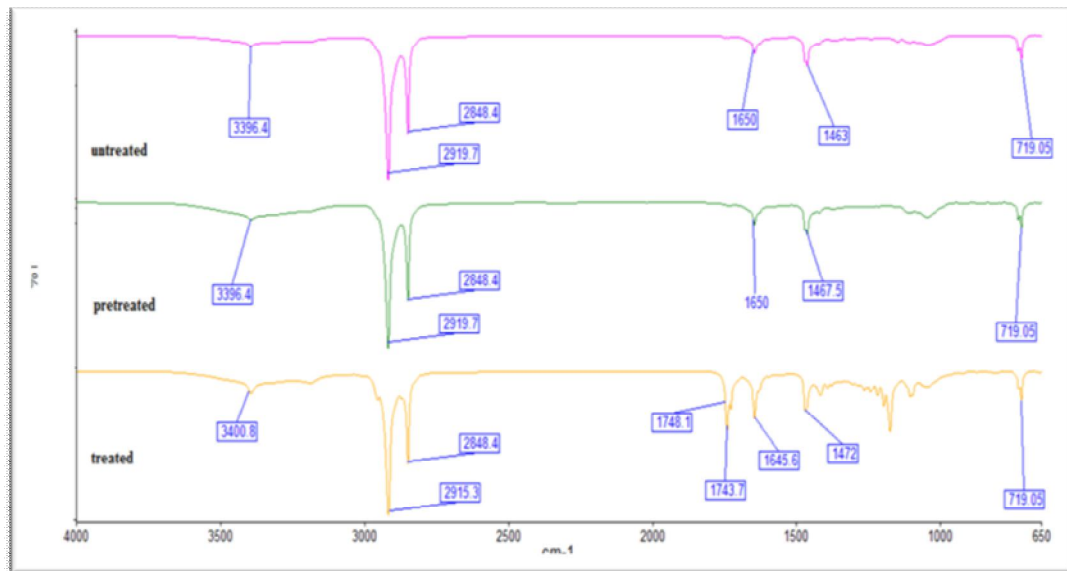


Figure 1. FTIR spectra of untreated, pretreated and treated 10% BF loading in LLDPE/TPS matrix.

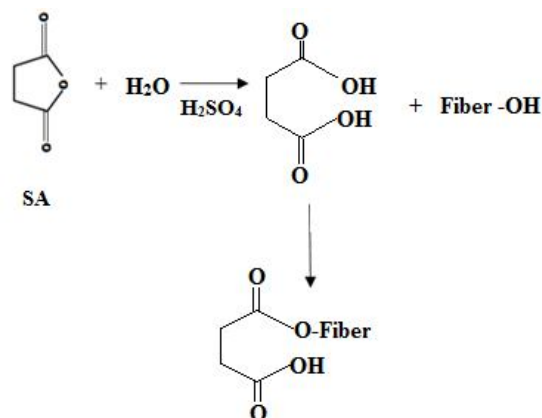


Figure 2. Mechanism of SA treated fiber.

Likewise, when comparing to other composite series, untreated BF shows an inferior value for all samples tested, whereas, the NaOH treated BF/LLDPE/TPS blends show a much higher tensile strength than untreated BF/LLDPE/TPS composite counterparts. The treatment with NaOH physically removes the non-cellulose material and lignin, leaving gaps on the surface of the BF for interacting physically with LLDPE/TPS matrix. Furthermore, NaOH treatment can also cause fibrillation due to the breaking down of the fibre bundle into smaller fibre giving a higher contact area for improved fibre-matrix interaction. In the case of SA-treated BF based composite, tensile strength is marginally lower at initial BF loading, as compared to LLDPE/TPS matrix. This is because the amount may not be adequate for proper load distributions applied to the matrix [6]. However, unlike the untreated NaOH and treated BF, SA treated BF based composites at 10% BF loading and greater; found that the tensile strength was always more than LLDPE/TPS matrix. SA treatment was found to improve the adhesion and compatibility between BF and LLDPE/TPS matrix, leading towards a significant increase in the tensile strength value. Improved interaction at the interphase level implies that the

external force applied to LLDPE/TPS matrix was efficiently transferred throughout the composite system.

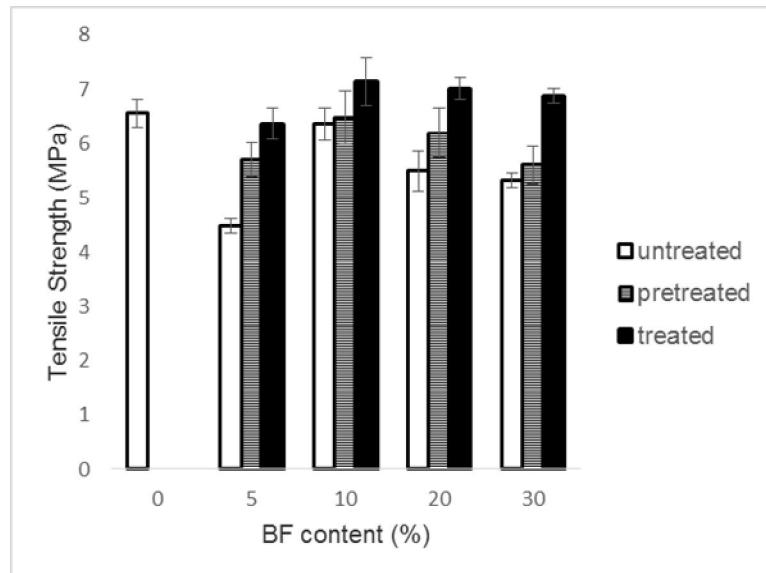


Figure 3. Tensile strength of untreated, pretreated and treated banana fiber reinforced LLDPE/TPS blends at different fiber content.

SEM micrographs of untreated and NaOH treated BF are shown in figures 4(a) and (b). Untreated BF displays a smoother surface with several impurities attached to the fibre. Upon NaOH treatment, the BF exhibited a much rougher surface due to the partial dissolution of lignin and hemicellulose and the removal of impurities on the fibre's surface. The cleaner and more irregular surface could, therefore, provide a higher contact surface area for any mechanical interaction between the BF and the polymer matrix.

The morphology of the tensile fracture surface of untreated BF, NaOH-treated BF, and SA treated BF reinforces LLDPE/TPS matrix, are illustrated in figures 5(a), (b) and (c). Yet, it is commonly known and acknowledged that synthetic polymer, LLDPE is incompatible with cellulosic fibre due to the hygroscopic nature of BF. As illustrated in figure 5(a), significant gaps between fibre and LLDPE matrix are evident, representing the higher level of interfacial tension existing between hydrophobic LLDPE matrix and hydrophilic BF. The fibre tends to agglomerate rather than disperse in LLDPE matrix.

Furthermore, various fibre pullout and voids appear in the micrograph possibly representing a lack of interfacial adhesion occurring between the fibre and LLDPE matrix. Figure 5(b) shows the SEM micrograph of the tensile fracture surface of the NaOH treated BF reinforced LLDPE/TPS blends. When compared to the untreated BF system, NaOH-treated BF showed a better level of dispersion in LLDPE/TPS matrix, leading to enhanced tensile strength of the composite. After BF undergoes NaOH treatment, fibrillation occurred by breaking down the bundle of fibre into smaller fibrils. Smaller sized BF provides a much greater contact area for mechanical interaction between fibre and LLDPE/TPS matrix. SEM micrograph of the tensile fracture surface of SA-treated BF reinforced LLDPE/TPS matrix is shown in figure 5(c).

Contrary to an untreated BF based system, the fibre was well embedded into LLDPE/TPS matrix due to the improved interfacial interaction at the interphase. The formation of ester linkages, following the surface modification, was lowering the hydrophilicity of BF and therefore, increasing its wettability and dispersion within LLDPE/TPS matrix. The matrix polymer uniformly coated the BF

resulting in gaps between the fibre-matrix being significantly reduced. The crack fracture highlights that BF was pull out together with the matrix polymer during tensile testing which implies the cohesive bond existing between SA treated BF and LLDPE matrix.

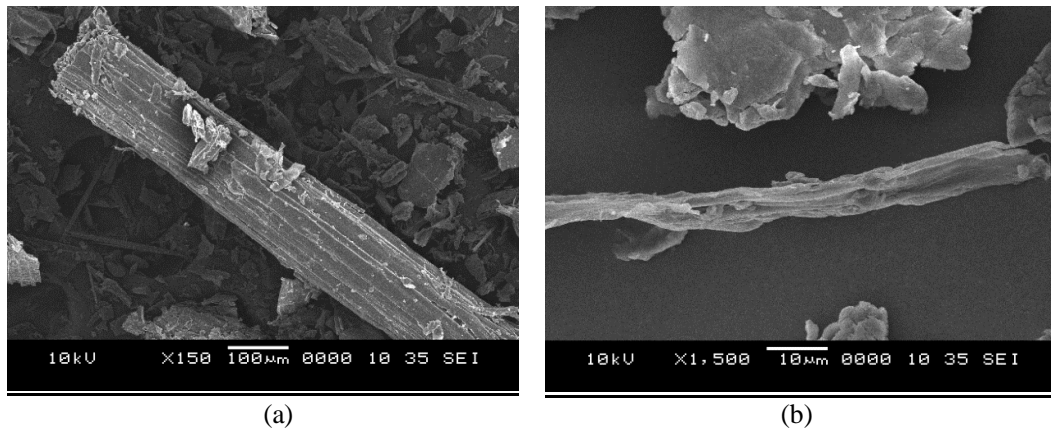


Figure 4. SEM micrographs of (a) an untreated BF and (b) an alkali treated BF.

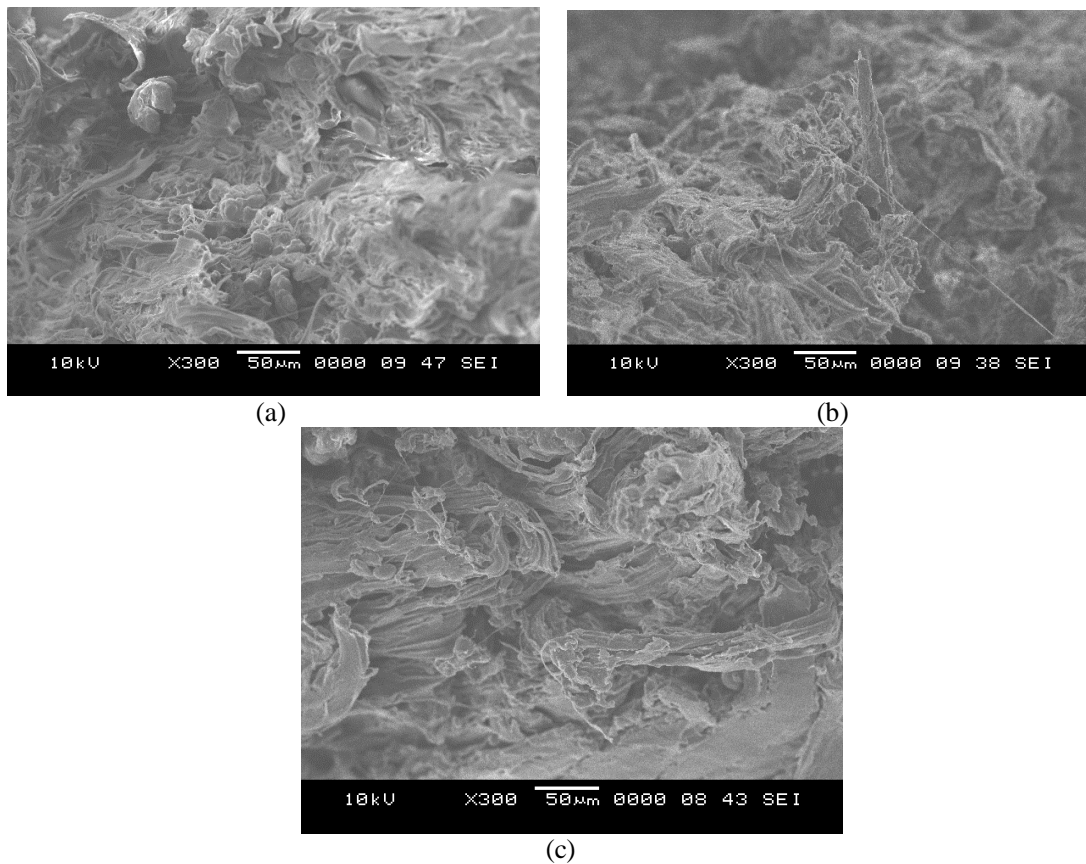


Figure 5. SEM micrograph of tensile fracture surface of (a) the untreated 10% BF, (b) pretreated BF, and (c) SA treated BF reinforced LLDPE/TPS matrix.

TGA curves of LLDPE/TPS matrix filled with 10% and 30% of BF are illustrated in figures 6(a) and (b). The TGA curves highlight three significant slopes for all composite samples. The initial degradation was observed between 120°C to 180°C due to the volatilisation of glycerol used in the preparation of TPS. The second slope starts at 260°C and is correlated to the degradation of polysaccharide, (i.e. starch and cellulose) with the highest degradation recorded at a temperature of 380°C. The degradation of LLDPE occurred at 420°C, with near complete degradation observed at 500°C. The data collected from the first to the third significant degradation was then tabulated in table 2, for further analysis. The value for Td1, Td2 and Td3 was determined from the peak differential thermogravimetric (DTG). Referring to table 2, it shows that the untreated, NaOH-treated and SA treated 10% BF has a higher degradation temperature than the degradation temperature at 30% BF of composite counterparts. In comparing the untreated BF reinforced LLDPE/TPS composite, the Td1 was 123.9°C and 120.9°C for 10% and 30% BF, respectively. Similarly, all 10% BF based composites were recorded as having better thermal stability than the 30% BF based composites. On the other hand, the curves for pre-treated BF reinforced LLDPE/TPS matrix moved to a much greater temperature when compared to the untreated BF composite, indicating higher thermal stability. The weight loss at 200°C, 300°C and 400°C of the pre-treated BF reinforced LLDPE/TPS matrix was lower than the untreated BF reinforced LLDPE/TPS matrix. This indicated that the pre-treated BF reinforced LLDPE/TPS matrix had better thermal stability as compared to the untreated composite.

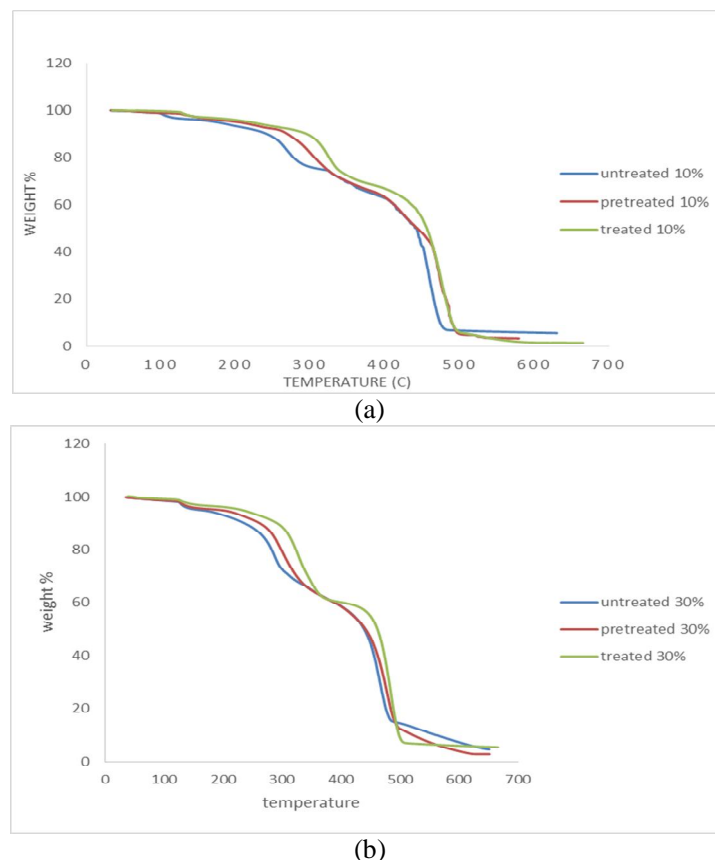


Figure 6. (a) Thermal Gravimetric Analysis (TGA) curve of 10% untreated, pretreated and treated BF in LLDPE/TPS blends; (b) Thermal Gravimetric Analysis (TGA) curve of 30% untreated, pretreated and treated BF in LLDPE/TPS blends.

Alternatively, as shown in table 2, the treated BF reinforced LLDPE/TPS matrix had the highest temperature and maximum degradation when compared to untreated and pre-treated BF counterparts, reflecting better thermal stability.

Table 2. TGA data of LLDPE/TPS matrix filled with 10% and 30% of untreated, pretreated and treated BF.

LLDPE/TPS filled with banana fiber composite		T _{dmax1} (°C)	T _{dmax2} (°C)	T _{dmax3} (°C)	Weight loss (%)		
					200°C	300°C	400°C
10% of banana fiber content	untreated	123.9	271.9	452.9	6.68	24.16	37.34
	NaOH treated	139.9	303.9	462.8	4.80	18.23	37.01
	SA treated	141.8	323.0	465.9	3.99	10.91	33.34
30% of banana fiber content	untreated	120.9	269.0	451.9	6.76	27.55	41.44
	NaOH treated	130.9	293.0	458.9	4.95	20.86	41.53
	SA treated	140.0	321.0	471.0	4.05	11.46	39.95

DSC examined the thermal characteristics that influenced the physical properties of LLDPE/TPS/BF composites. The melting temperature of LLDPE crystal fraction, the heat of fusion and the percentage of crystallinity (X_c), including data for 10% and 30% BF reinforced LLDPE/TPS matrix, are shown in table 3. In table 3, the melting temperature for both 10 % and 30 % BF loading, increased after the fibre was treated with NaOH and SA. The temperature position for melting peak shifted from 115.6°C to 122.8°C, and 123.0°C for untreated, NaOH-treated and SA treated LLDPE/TPS/BF composites, respectively. A similar trend was observed for the 30% BF filled LLDPE/TPS system. The increase in the melting peak position indicates that the SA-treated BF, favoured the formation of larger crystal lamella, thereby restricting the mobility of LLDPE chains. Furthermore, as shown in table 3, the increase of filler loading also decreased the X_c of LLDPE/TPS/BF composite. LLDPE/TPS filled with 10% untreated BF had a heat of fusion value of 72.89 J/g, which corresponds to 24.9% of X_c based on the theoretical value of 293 J/g for 100% crystalline linear polyethylene [7]. This illustrates a much higher value than LLDPE/TPS filled with 30% untreated BF, which is 18.1%. The presence of excessive fibre between LLDPE chains could prevent them from being aligned closely and interfere with the crystal formation of LLDPE phase. Whereas, the pre-treated BF reinforced LLDPE/TPS matrix exhibited higher X_c than the untreated BF reinforced LLDPE/TPS blended composite. Furthermore, the 10% treated BF in LLDPE/TPS blends provided the highest X_c of the entire series. The smaller size of BF after surface modifications can act as nucleation seeds for crystal formation. It was concordance to the higher melting temperature which reflected, a greater fusion of energy required to melt the thicker crystal lamellae.

Table 3. Thermal properties of LLDPE/TPS/BF composites at different BF loadings.

Composition			Melting temperature, T_m (°C)	Heat of fusion, (J/g)	Percentage of crystallinity, X_c (%)
10% BF reinforced LLDPE/TPS matrix		untreated	115.59	72.89	24.88
		pretreated	122.78	84.19	28.73
		treated	123.03	92.69	31.63
30% BF reinforced LLDPE/TPS matrix		untreated	123.78	52.93	18.06
		pretreated	124.51	56.81	19.39
		treated	124.85	73.33	25.03

4. Conclusions

In this study, different modified BF was used as a reinforcing agent in LLDPE/TPS matrix. Based on the tensile strength results, LLDPE/TPS with pre-treated BF showed a better tensile value as compared to untreated BF composites. This is due to the improvement in interfacial adhesion between BF and LLDPE/TPS matrix. SEM morphological confirmed that the surface roughness of BF after NaOH treatment enhanced the physical adhesion at the interphase of BF and LLDPE/TPS matrix. Further modification of BF with SA exhibited the highest tensile strength of the series studied. The chemical reaction between BF and SA has led to better interphase interactions occurring, and subsequently, increased tensile properties. SEM morphology of tensile fracture surface also showed that the proper mixing of LLDPE/TPS with treated BF exhibited less fibre pull-out. Better thermal stability and a higher degree of crystallinity also resulted from the improved interaction between SA treated BF composites as compared to other series.

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