

Chemical Modification of *Nypa fruticans* Filled Polylactic Acid/Recycled Low-density Polyethylene Biocomposites

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Nypa fruticans (NF) is a lignocellulosic material belonging to the family Palmae or Arecaceae. Effects of NF content and chemical modification using methyl methacrylate (MMA) on tensile, thermal, and morphological properties of biocomposites were investigated. The results showed that the addition of NF decreased the tensile strength, elongation at break, and crystallinity, but increased the Young's modulus, of biocomposites. Moreover, the addition of NF increased the thermal stability. Meanwhile, the tensile strength and Young's modulus of the biocomposites treated with MMA were higher than the untreated biocomposites. The treated biocomposites exhibited higher thermal degradation temperature and crystallinity compared to the untreated biocomposites. The morphology study of the tensile-fractured surfaces of biocomposites indicated that chemical modification with MMA enhanced the interfacial interaction between NF and the PLA/rLDPE matrix.

Keywords: *Nypa fruticans*; Polylactic acid; Recycled low density polyethylene; Chemical treatment; Biocomposites

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INTRODUCTION

Tailoring new composites within a perspective of sustainable development or eco-design is a philosophy that is being applied to more and more materials. Ecological concerns have resulted in a renewed interest in natural renewable resources-based and compostable materials, and therefore issues such as materials elimination and environmental safety are becoming important. For these reasons, material components such as natural fibers and biodegradable polymers can be considered as interesting and environmentally safe alternatives for the development of new biodegradable biocomposites (Averous and Le Digabel 2006; Kaith and Kaur 2011; Pavlović *et al.* 2011; Yeng *et al.* 2013).

Among the biodegradable polymers, poly(lactic acid) (PLA) in particular is of increasing commercial interest (Dorgan *et al.* 2001; Lee and Wang 2006). PLA has received the most attention because its raw material can be efficiently produced by fermentation from renewable resources such as corn materials. Moreover, it has good properties such as a high melting point, a high degree of transparency, and ease of fabrication. However, the brittleness and the high price of PLA currently limit its applications, spurring considerable efforts to improve the drawbacks of the polymer (Wu 2005; Wu and Wu 2006).

Blending of PLA with another suitable polymer which has comparably better properties will modify the properties, and also contribute toward lower overall material cost (Bhatia *et al.* 2007). Blends of PLA with various polymers such as polycaprolactone, thermoplastic starch, polystyrene, polypropylene, polyethylene terephthalate, and poly(vinyl acetate-co-vinyl alcohol) have been reported (Biresaw and Carriere 2004; Choudhary *et al.* 2011; Razavi *et al.* 2012; Sarazin *et al.* 2008).

LDPE is mainly used in agriculture for greenhouse covering, mulching, and packaging. Therefore, farms get rid of a large amount of LDPE-film wastes, which present an important weight percentage of the plastic waste found in agricultural waste streams (Zhao *et al.* 2013). From the ecological and economical points of view, reprocessing of LDPE is a promising solution to reduce discarded materials and to produce useful, or potentially useful products. In the actual production process, in order to meet the requirements of high-value applications, recycled LDPE has been widely used with virgin polymers to improve their mechanical performance and processability (Al-Salem *et al.* 2009). Therefore, recycled LDPE was blended with PLA, aiming at enhancing its mechanical and thermal properties.

Nypa fruticans belongs to the family Palmae or Arecaceae. *Nypa* grows abundantly in Malaysia and can be found throughout the year. *Nypa*, consisting of frond, shell, husk, and leaf, was chemically characterised for cellulose, hemicellulose, lignin, starch, protein, extractives, and inorganic constituents for its each part. The total chemical composition showed that the cellulose and hemicellulose contents were in the range of 28.9 to 45.6 wt% and 21.8 to 26.4 wt%, respectively. The lignin content was 19.4 to 33.8 wt%, with the highest lignin content found in the leaf.

The incorporation of plant fibers into biodegradable polymers not only can enhance thermal and mechanical properties, but may also reduce the cost of the materials while forming a totally natural green composite (Masirek *et al.* 2007; Plackett *et al.* 2003; Shibata *et al.* 2003). The utilisation of natural filler filled PLA composites has been reported by several researchers (Bajpai *et al.* 2012; Chun *et al.* 2013a; Islam *et al.* 2010; Jiang *et al.* 2012; Ndazi and Karlsson 2011; Yussuf *et al.* 2010).

The main disadvantage encountered during the incorporation of natural fiber materials into polymers is the lack of good interfacial adhesion between the two components, which results in poor properties in the final material (Sreekala *et al.* 1997). Furthermore, the incorporation of natural fibers in polymers is often associated with agglomeration as a result of insufficient dispersion, caused by the tendency of the fillers to form hydrogen bonds with each other during processing (Joshi *et al.* 2004). Therefore, to develop such biocomposites with good properties, it is necessary to decrease the hydrophilicity of the natural fibers by chemical modification (Tserki *et al.* 2006). Many researchers in their study found that using MMA for chemical modification led to promising results which improved the mechanical properties and interfacial adhesion between the matrix and fibers (Debnath *et al.* 2005; Faisal *et al.* 2013a; Kaith and Kalia 2007; Lu *et al.* 2000; Xie *et al.* 2001).

In this research, the goal is to study the effect of NF content and chemical modification on the tensile, morphological, and thermal properties of PLA/rLDPE/NF biocomposites. The effects of methyl methacrylate used as chemical modification to improve the properties of PLA/rLDPE/NF biocomposites were also investigated.

EXPERIMENTAL

Materials

Poly(lactic acid) (PLA) was supplied by TT Biotechnologies Sdn. Bhd., Penang, and recycled low density polyethylene (rLDPE) with an MFI value of 0.6 g/10 min at 230 °C was obtained from STL Plastic Sdn. Bhd., Penang. Methyl methacrylate (MMA) was supplied by Aldrich Chemical Inc. The *Nypa fruticans* (NF) filler was obtained from a plantation at Simpang Empat, Perlis. The NF husk was cleaned and ground to a powder. The NF was vacuum dried at 80 °C for 24 h. The average particle size of NF was 31 µm, determined using a Malvern particle size analyser. The chemical composition of NF, as obtained by incineration (ash), extraction with acetone (extractive), analytical methods (cellulose, hemicelluloses and lignin), colorimetric methods (starch), and SuperKjel 1400 (protein), is presented in Table 1.

Table 1. Chemical Composition of *Nypa fruticans* (Tamunaidu and Saka 2011)

Content	Weight Percentage (%)
Cellulose	36.5
Hemicellulose	21.8
Lignin	28.8
Starch	0.1
Protein	1.9
Extractive	0.8
Ash	8.1
Total	98.0

NF Treatment

In the chemical modification, MMA was dissolved in 3% (v/v) ethanol solution at room temperature. The NF was slowly transferred into the MMA solution and stirred for 1 h. The NF was filtered and dried at 80 °C for 24 h.

Preparation of Biocomposites

Biocomposites were prepared using a Brabender EC Plus at 180 °C and a rotor speed of 50 rpm. First, PLA and rLDPE were charged to the mixing chamber for 2 min until completely melted. After 2 min of mixing, NF was added, and mixing continued for another 6 min. The total mixing time was 8 min. Then, the biocomposites were compressed using a compression moulding machine, model GT 7014A. The compression was done at 180 °C with 1 min of preheating, 4 min of compression, and subsequent cooling for 4 min. A similar procedure was done for treated PLA/rLDPE/NF biocomposites. Table 2 shows the formulation of untreated and treated PLA/rLDPE/NF biocomposites.

Table 2. Formulation of Untreated and Treated PLA/rLDPE/NF Biocomposites

Material	Biocomposites	
	Untreated	Treated
PLA (php)	70	70
rLDPE (php)	30	30
NF (php)	0, 10, 20, 30, 40	10, 20, 30, 40
MMA (%) ^a	-	3

php = parts per hundred of total polymer; ^a 3% from weight of NF

As indicated in Table 2, the ratio of the blend PLA/rLDPE for both untreated and treated biocomposites was fixed at 70/30 (70 php PLA and 30 php rLDPE). Both untreated and treated were incorporated with 10, 20, 30, and 40 php. The difference is that the treated biocomposite was treated with 3% of MMA based on the weight of NF.

Tensile Testing

Tensile tests were carried out according to ASTM D638 using an Instron 5569. The crosshead speed for the biocomposites testing was 20 mm/min. An average of five samples for each formulation was tested. Tensile strength, elongation at break and Young's modulus were recorded and calculated by the instrument software.

FTIR Spectroscopy

FTIR was used to characterise the presence of functional groups in PLA/rLDPE/NF biocomposites. The FTIR analysis was carried out using an FTIR spectrometer, Perkin Elmer, Model L1280044. The attenuated total reflectance (ATR) method was used. The sample was recorded with 4 scans in the frequency range 4000 to 650 cm^{-1} , with a resolution of 4 cm^{-1} .

Morphological Study

The morphological study of the tensile fractured surfaces of the biocomposites was carried out using a scanning electron microscope (SEM), model JSM 6260 LE JOEL. The fractured ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

Differential Scanning Calorimetry (DSC) Analysis

DSC analysis with a Q10 DSC (TA Instrument) was used to determine the glass transition temperature (T_g), crystallisation temperature (T_c), melting temperature (T_m), and the degree of crystallinity (X_c) of each biocomposite. The specimens were heated from 30 to 200 °C at a heating rate of 20 °C/min under a nitrogen atmosphere, and the nitrogen gas flow rate was 50 mL/min. The degree of crystallinity of the biocomposites (X_c) was then evaluated from the DSC data using the following equation:

$$X_c = (\Delta H_f / \Delta H_f^\circ) \times 100 \quad (1)$$

where ΔH_f is the heat of fusion of the biocomposites and ΔH_f° is the heat of fusion for 100% crystalline. For PLA, $\Delta H_{100} = 93.7$ J/g, and ΔH_{100} for rLDPE = 293 J/g.

Thermogravimetric Analysis (TGA)

Thermal analysis was carried out using a Pyris Diamond TGA from Perkin Elmer. The sample (weight 7 ± 2 mg) underwent thermal scanning from 30 to 600 °C using a nitrogen air flow of 50 mL/min and a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Tensile Properties

The tensile strengths of untreated and treated PLA/rLDPE/NF biocomposites are illustrated in Fig. 1. The untreated PLA/rLDPE/NF biocomposites show a decreasing trend of tensile strength as the NF content increases. The decrease of tensile strength of

the untreated biocomposites is due to the poor interfacial bonding between the hydrophobic PLA/rLDPE and hydrophilic NF. This is consistent with the research results obtained from typical natural fiber composites (Chun and Salmah 2013b; Chun *et al.* 2012). However, the tensile strength of treated PLA/rLDPE/NF biocomposites with MMA was higher than untreated PLA/rLDPE/NF biocomposites. The higher tensile strength of the treated PLA/rLDPE/NF biocomposites with the presence of MMA was attributed to the better dispersion and interfacial adhesion of NF in the PLA/rLDPE matrix. The better filler matrix interaction is due to the formation of ester linkage between the hydroxyl group of NF and the ester group of MMA. The effect of NF content on the elongation at break of untreated and treated PLA/rLDPE/NF biocomposites is shown in Fig. 2.

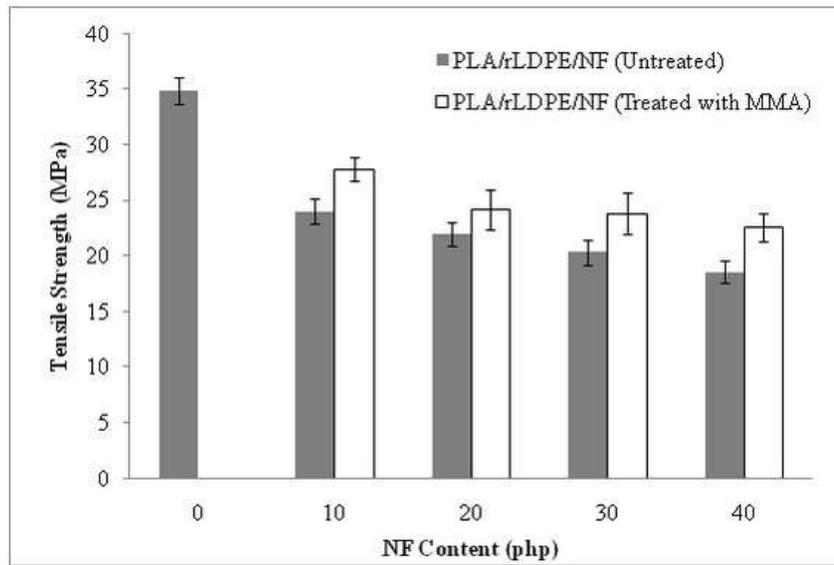


Fig. 1. Effect of NF content on tensile strength of untreated and treated PLA/rLDPE/NF biocomposites

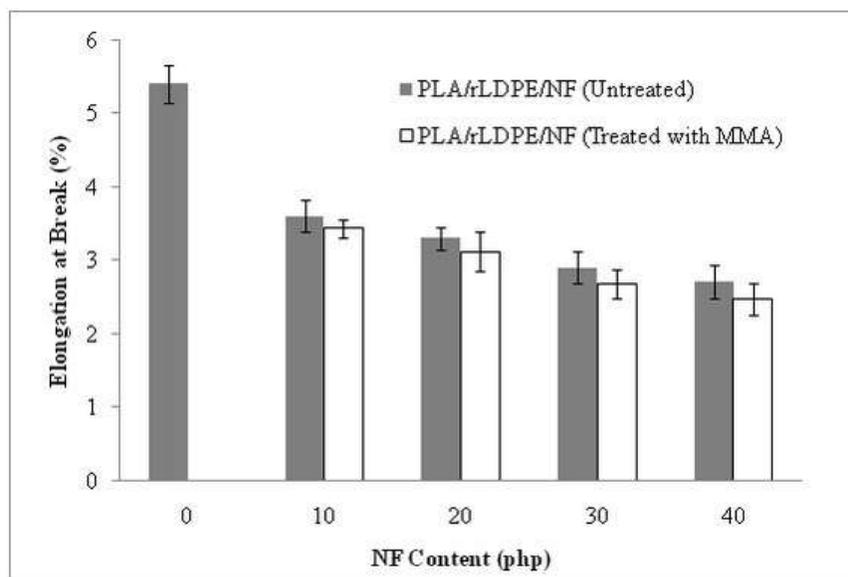


Fig. 2. Effect of NF content on elongation at break of untreated and treated PLA/rLDPE/NF biocomposites

The elongation at break of both untreated and treated biocomposites decreased steadily with the increasing of NF content. The figure shows that the elongation at break of untreated biocomposites decreased with increasing NF content. This can be attributed to the decreasing deformation on stiffness matrix surface between filler and matrix. At higher NF content, the interaction between filler-filler is more dominant than matrix-filler interaction. It can be seen that the treated PLA/rLDPE/NF biocomposites with MMA exhibited lower elongation at break than untreated PLA/rLDPE/NF biocomposites. This is due to enhanced interaction between NF and PLA/rLDPE after chemical modification with MMA.

Figure 3 illustrates the effect of NF content on Young's modulus of untreated and treated PLA/rLDPE/NF biocomposites. The Young's modulus of untreated biocomposites increased with increasing NF content. Young's modulus indicates the stiffness properties of composites materials and depends on the filler loading (Sain *et al.* 2005). The increment of Young's modulus of untreated biocomposites with increasing NF content is expected, since the addition of NF increases the stiffness of the biocomposites. Similar results were also reported by Faisal *et al.* (2013b), who reported that incorporating chitosan in polyethylene increased the Young's modulus of the composites. As observed at similar NF content, the treated PLA/rLDPE/NF biocomposites with MMA showed higher Young's modulus compared to untreated PLA/rLDPE/NF biocomposites. The chemical modification of NF with MMA was used to overcome the dispersion problem and enhanced the Young's modulus of biocomposites by improving adhesion across the interface.

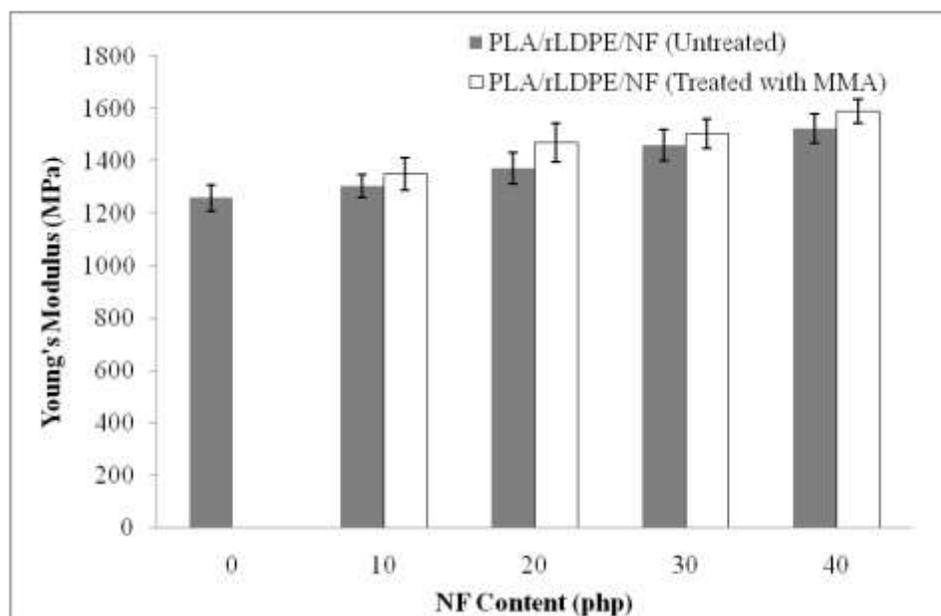


Fig. 3. Effect of NF content on Young's modulus of untreated and treated PLA/rLDPE/NF biocomposites

The compositional dependence of the tensile yield stress and tensile strength of particulate filled composites using a simple model was developed by Pukánszky (1990). This model expresses the effect of filler loading on tensile strength of the composites. This model takes into account the effect of decreasing load bearing cross-section of the

polymer as an effect of filling, while changing interaction is expressed by Eq. 2 (Dányádi *et al.* 2007; Renner *et al.* 2010),

$$\sigma_T = \sigma_{T0} \lambda^n \frac{1-\phi}{1+2.5\phi} \exp(B\phi) \quad (2)$$

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$ and $\lambda = L/L_0$) of the composite and the matrix, respectively, n is a parameter expressing the strain hardening tendency of the matrix, ϕ is the volume fraction of filler in the composite, and B is related to the relative load-bearing capacity of the filler, which depends on interfacial interaction. The correlation of B to the size of the interface and the properties of the interphase are shown by Eq. 3,

$$B = (1 - A_f \rho_f \ell) \ln \frac{\sigma_{Ti}}{\sigma_{T0}} \quad (3)$$

where A_f and ρ_f are the specific surface area and density of the filler, while ℓ and σ_{Ti} are the thickness and strength of the interphase. Equation (2) is then written in linear form:

$$\ln \sigma_{Tred} = \ln \frac{\sigma_T(1+2.5\phi)}{\lambda^n(1-\phi)} = \ln \sigma_{T0} + B\phi \quad (4)$$

Plotting the natural logarithm of reduced tensile strength versus filler content should result in a linear correlation, the slope of which is proportional to the effect of filler content.

Figure 4 shows the reduced tensile strength of untreated and treated PLA/rLDPE/NF biocomposites as a function of NF content. The correlations were reasonably linear with a few points showing deviations at larger NF content. The deviations indicated that structural effects, aggregation, or changing orientation may be the main reasons. The presence of MMA in NF changed the slope of the lines. The parameter B obtained for the untreated and treated PLA/rLDPE/NF biocomposites was 2.65 or 4.05, which indicates that the B value of for treated biocomposites was almost twice higher than that of the untreated biocomposites. This finding confirm that the tensile strength increases both with filler content and chemical modification.

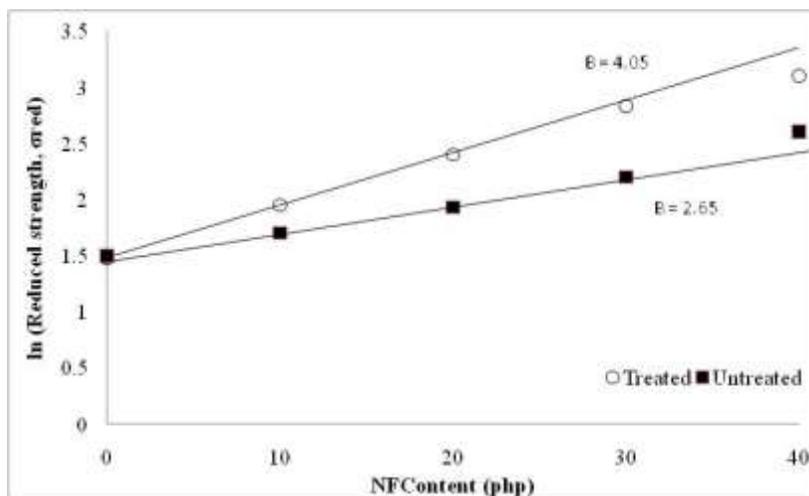


Fig. 4. Reduced tensile strength of untreated and treated PLA/rLDPE/NF biocomposites plotted in linear form (using equation 4)

The statistical analysis for the analysis of variance (ANOVA) was carried out by using computer software MINITAB 16 in order to obtain a better understanding of the effect of NF content and chemical modification. The analysis of variance (ANOVA) was done on the data of tensile strength and Young's modulus for the level of significance of 5%, *i.e.* for a level of confidence of 95%. From the analysis, it is apparent that NF content and chemical modification had statistically significant effect on the tensile strength and Young's modulus of the biocomposites. This was especially the case for the filler content, with a percentage of contribution (P) of 77.4% and 89.4% for tensile strength and Young's modulus, respectively.

Morphology Study

A scanning electron microscope (SEM) was used to examine the tensile fracture surface of PLA/rLDPE/NF biocomposites. Figure 5 shows the micrograph SEM of NF at a magnification of 100X. The material was shown to consist of irregular shapes such as particulates and fibers. Furthermore, the micrographs of the tensile fracture surfaces of untreated PLA/rLDPE/NF biocomposites with NF contents of 20 and 40 php are shown in Figs. 6 and 7, respectively. The micrographs show poor interfacial adhesion and dispersion of NF in the PLA/rLDPE matrix. The micrograph of untreated biocomposites exhibits NF detachment and pull out from matrix. Higher NF content increased the tendency of filler-filler interaction to form agglomerates, as indicated in Fig. 7. This result showed a higher level of de-wetting of filler in the matrix. Meanwhile, Figs. 8 and 9 show SEM micrographs of the tensile fracture surfaces of treated PLA/rLDPE/NF biocomposites at 20 and 40 php NF content. The good interfacial bonding between the matrix and filler was evident from the micrograph of treated biocomposites. The morphology of treated biocomposites exhibits less NF detachment and pull out from PLA/rLDPE matrix. It was apparent that the presence of MMA led to better interfacial interaction between NF and PLA/rLDPE matrix.

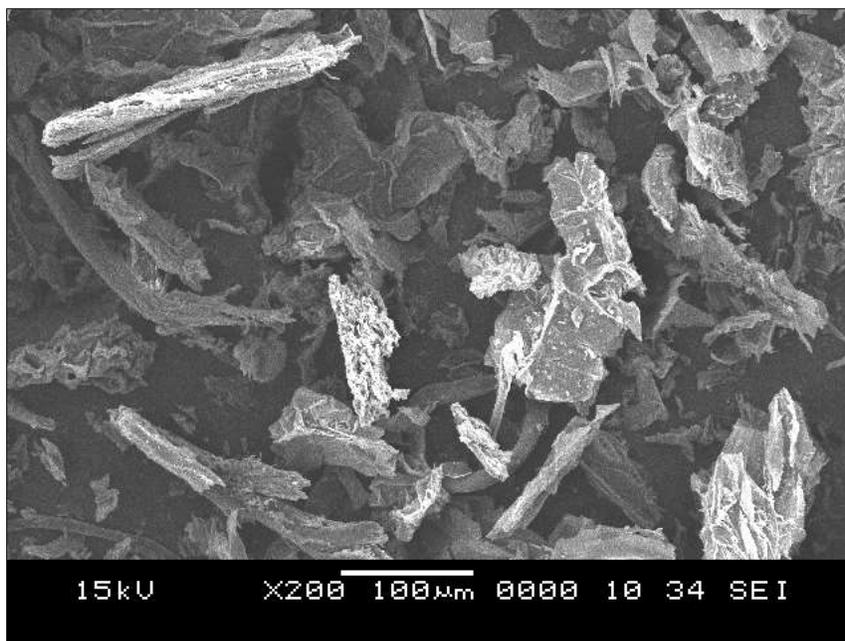


Fig. 5. SEM micrograph of untreated NF

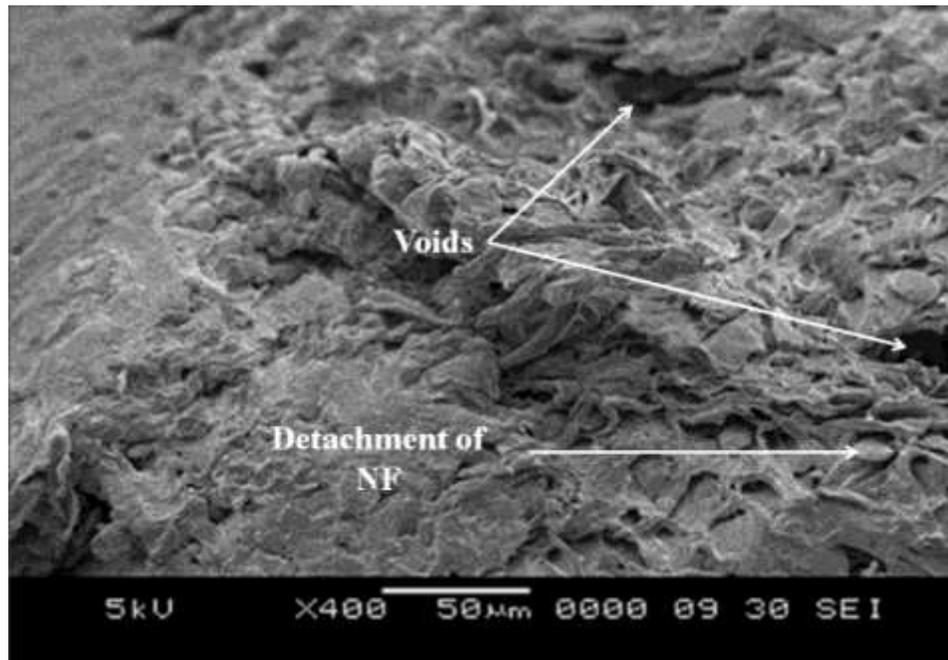


Fig. 6. SEM micrograph of untreated PLA/rLDPE/NF biocomposite (20 phr NF)

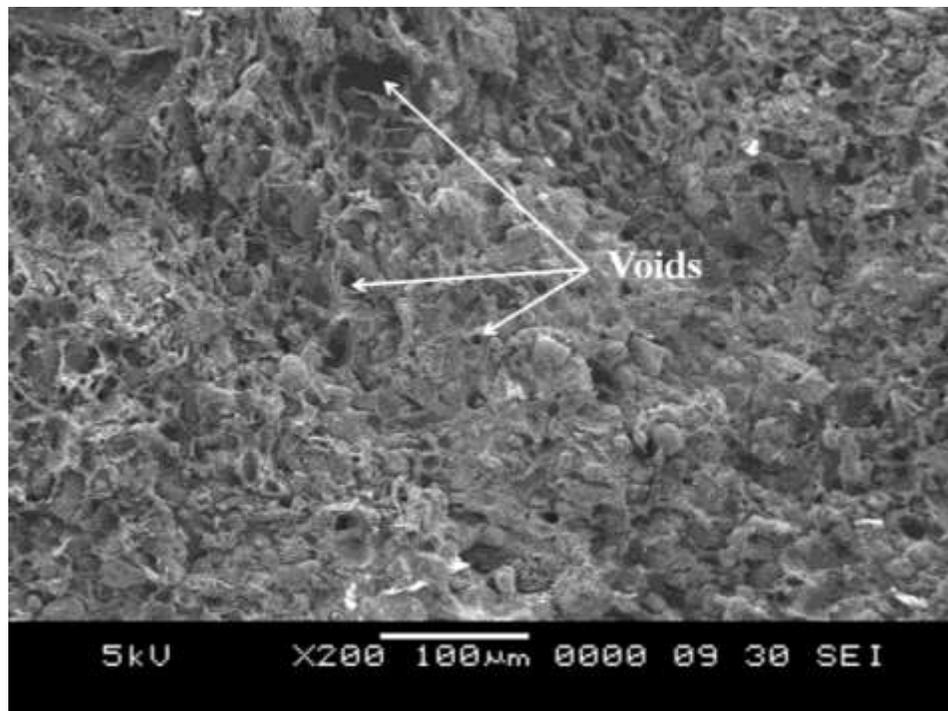


Fig. 7. SEM micrograph of untreated PLA/rLDPE/NF biocomposite (40 phr NF)

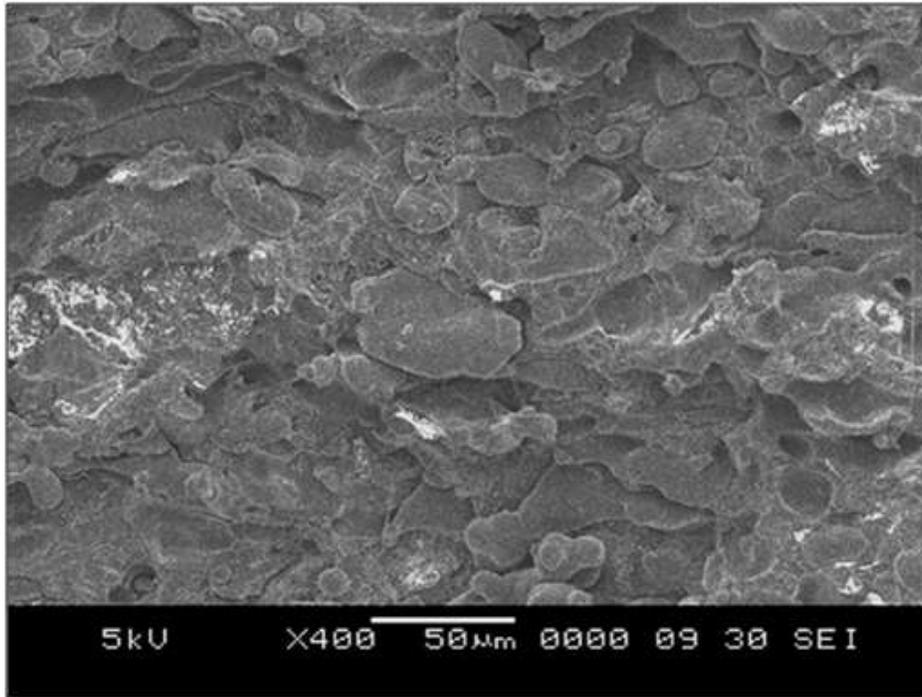


Fig. 8. SEM micrograph of tensile fracture surface of treated PLA/rLDPE/NF biocomposite with MMA (20 php NF)

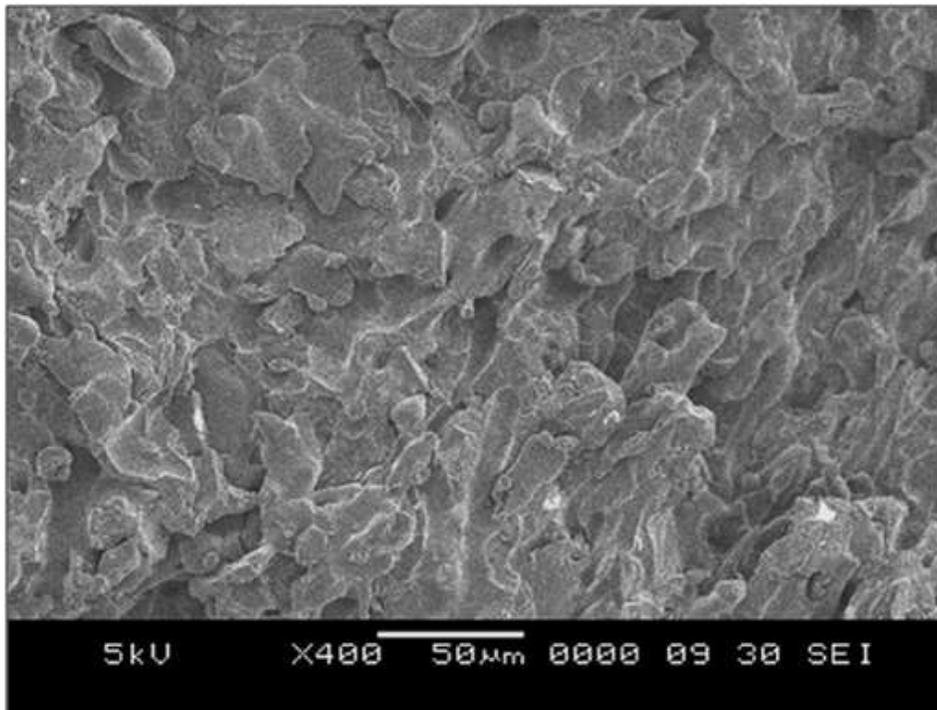


Fig. 9. SEM micrograph of tensile fracture surface of treated PLA/rLDPE/NF biocomposite with MMA (40 php NF)

Fourier Transform Infrared Spectroscopy Analysis

Figure 10 shows the FTIR spectra of untreated and treated NF. The main characteristic peaks of NF are summarized in Table 3.

Table 3. Functional Groups of *Nypa fruticans*

<i>Nypa fruticans</i>	
Wave number (cm ⁻¹)	Functional group
3339	Hydroxyl group (-OH) of NF and absorbed moisture
2919	C-H stretching vibration
1727	Carboxyl (C=O) from hemicellulose
1607	C=C stretching from hemicellulose
1515	C=C stretching of lignin
1440	CH ₂ group deformation from cellulose or C-H deformation of lignin
1368	C-H groups deformation in cellulose and hemicellulose
1315	C-H group vibration in cellulose
1243	C-O groups from acetyl group in lignin
1000 - 1150	C-O-C and C-O groups from main carbohydrates of cellulose and lignin
700 - 900	C-H vibration in lignin

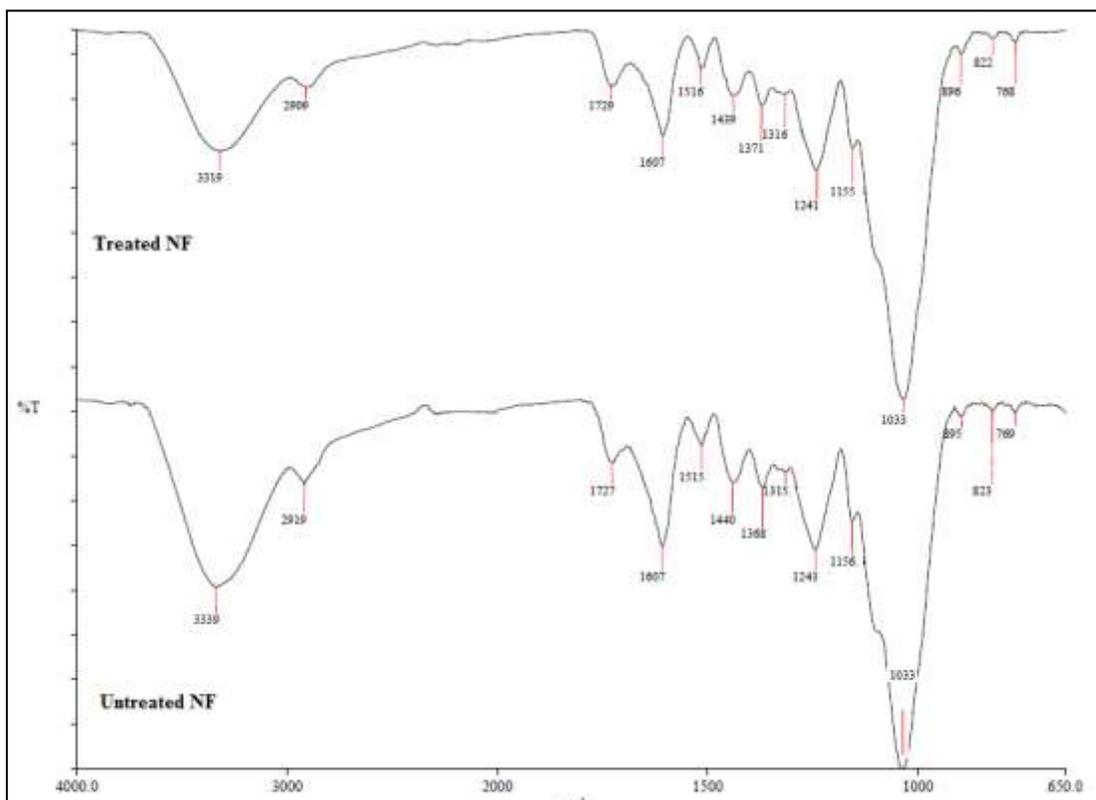


Fig. 10. FTIR spectra of untreated and treated NF with MMA

The IR spectrum of untreated NF at peak 3339 cm^{-1} corresponds to the -OH group. The IR spectrum of treated NF with MMA shows a decreased absorption band of the hydroxyl group from 3339 to 3319 cm^{-1} , due to the decreased hydrophilic character of treated NF. The decrease of NF hydrophilicity is attributed to the presence of esterification reaction between methyl methacrylate and hydroxyl group of NF, which can be identified by the absorption band at 1729 cm^{-1} . The schematic reaction of MMA and NF is illustrated in Fig. 11.

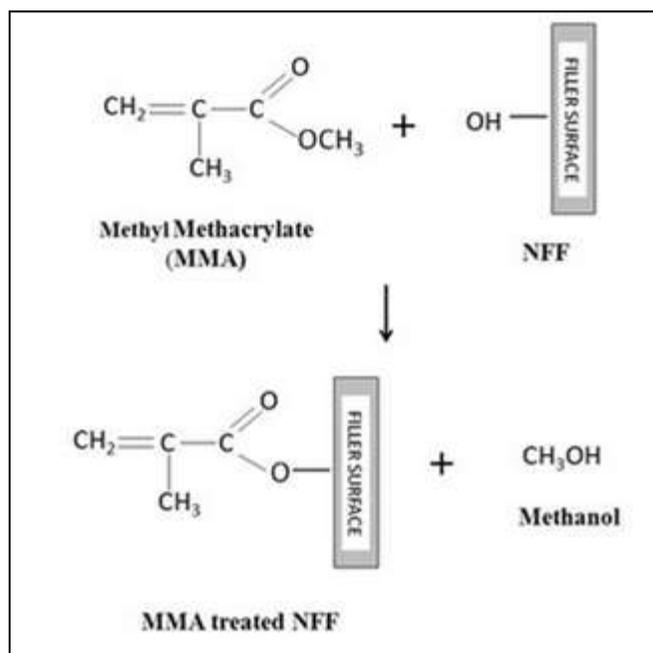


Fig. 11. Schematic reaction of NF with MMA and PLA/rLDPE

Thermogravimetric Analysis (TGA)

The TGA curve of untreated and treated PLA/rLDPE/NF biocomposites is shown in Fig. 12. The data obtained from the TGA curves are summarised in Table 4. The T_{dmax} is the temperature at which the maximum rate of weight loss of the biocomposites was observed. The table shows that the weight loss of untreated biocomposites at temperature $300\text{ }^{\circ}\text{C}$ increased with increasing NF content due to the early thermal decomposition of the hemicelluloses of NF from 250 to $300\text{ }^{\circ}\text{C}$. At the higher temperature of $600\text{ }^{\circ}\text{C}$, it is apparent that the weight loss of untreated biocomposites decreased with increasing NF content. The value of T_{dmax} was found to be increased with increasing NF content. The enhancement of thermal stability can be attributed to char formation during the pyrolysis of NF, as the char acts as a protective barrier that suppresses the thermal decomposition of the PLA/rLDPE matrix. However, at similar NF content, the treated biocomposites exhibited lower weight loss at temperature $300\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ compared to untreated biocomposites. The T_{dmax} values of the treated PLA/rLDPE/NF biocomposites were higher than those of the untreated biocomposites. This can be explained by the fact that MMA enhanced the filler–matrix interaction and caused better dispersion of NF particles in the PLA/rLDPE matrix, which ultimately resulted in the formation of a char layer, providing better thermal protection.

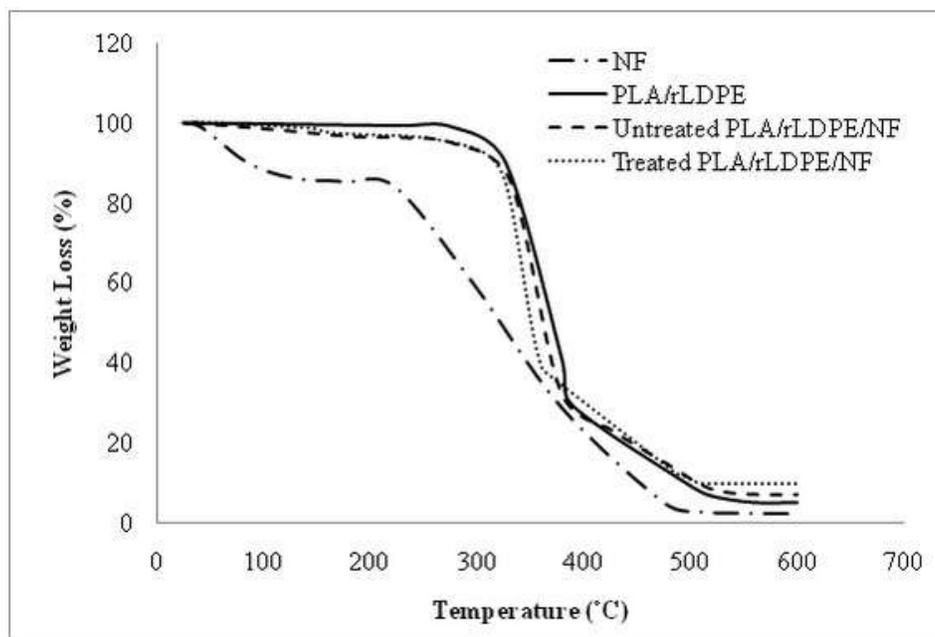


Fig. 12. TGA curve of untreated and treated PLA/rLDPE/NF biocomposites with MMA

Table 4. TGA Data of Untreated and Treated PLA/rLDPE/NF Biocomposites with MMA

Biocomposites	T_{dmax} (°C)	Weight Loss (%)	
	PLA	300 °C	600 °C
PLA/rLDPE: 70/30	481.99	1.25	100
PLA/rLDPE/NF: 70/30/20 (Untreated)	487.73	6.31	98.46
PLA/rLDPE/NF: 70/30/40 (Untreated)	488.78	9.68	94.90
PLA/rLDPE/NF: 70/30/20 (Treated)	493.96	5.32	96.16
PLA/rLDPE/NF: 70/30/40 (Treated)	505.97	7.84	92.28

The derivative thermogravimetric (DTG) curves corresponding to untreated and treated PLA/rLDPE/NF biocomposites are illustrated in Fig. 13. It can be seen that neat PLA/rLDPE biocomposites was decomposed in two stages, at temperature ranges between 300 and 380 °C and between 380 and 480 °C. This behavior is attributed to the two different degradation temperatures of PLA and rLDPE, respectively. The NF decomposed in a three stage process. The temperature from 30 to 110 °C contributed to initial weight loss due to the evaporation of water contained in the NF filler. At the second peak, NF filler begins to significantly lose weight in the range from 250 to 300 °C, which was attributed to the decomposition of hemicelluloses in NF, while the third peak at the temperature range of 350 to 440 °C was attributed to the decomposition of cellulose and lignin. For both, untreated and treated PLA/rLDPE/NF biocomposites exhibited three stages of degradation due to the combination degradation of NF and neat PLA/rLDPE. The degradation temperatures of PLA/rLDPE/NF biocomposites gradually decreased with increasing NF content. The figure shows that the introduction of MMA onto the surface of NF changed the thermal degradation of PLA/rLDPE/NF biocomposites. The temperature of degradation of the third peak degradation temperature stage was shifted to a higher temperature. This shows that treated PLA/rLDPE/NF

biocomposites with MMA had higher thermal stability compared to untreated PLA/rLDPE/NF biocomposites due to the improvement of inter-facial bonding and better dispersion between NF and PLA/rLDPE matrix. This was caused by the char layer, which protected the polymer from thermal degradation.

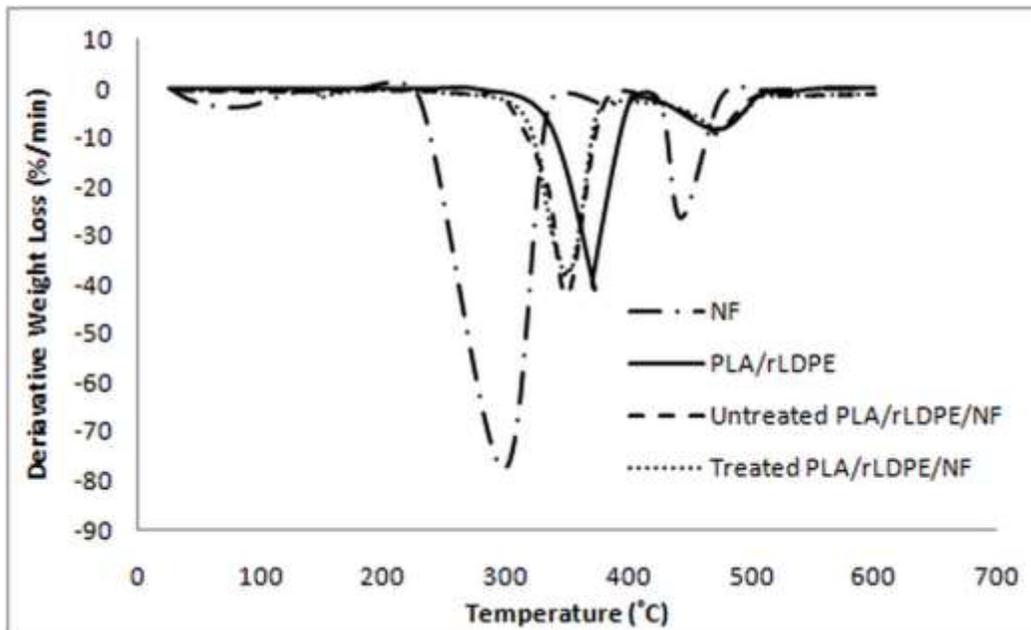


Fig. 13. DTG curve of untreated and treated PLA/rLDPE/NF biocomposites with MMA

Differential Scanning Calorimetry Analysis

Figure 14 shows the differential scanning calorimetry (DSC) curves of untreated and treated PLA/rLDPE/NF biocomposites.

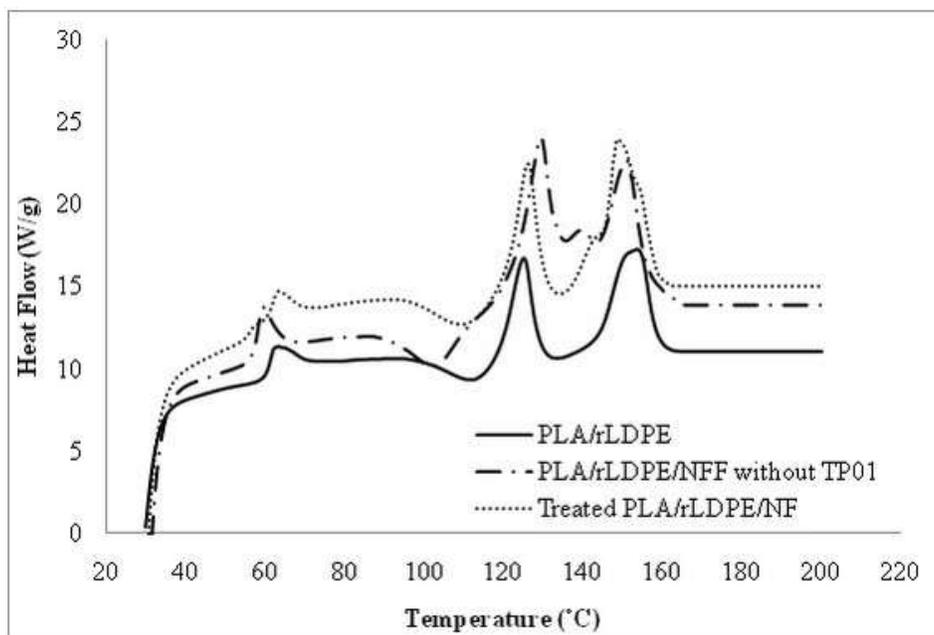


Fig. 14. DSC curves of untreated and treated PLA/rLDPE/NF biocomposites with MMA

The DSC data of untreated and treated PLA/rLDPE/NF biocomposites are summarised in Table 5. The figure indicates that the blend of PLA and rLDPE is an endothermic immiscible blend with the presence of two peaks. Table 4 indicates that the T_g , T_c , and X_c PLA values of untreated PLA/rLDPE/NF biocomposites decreased as NF content increased. In addition, the T_m of PLA and rLDPE was not significantly changed by the NF content. For untreated biocomposites, the X_c of rLDPE decreased in PLA blend. The decreasing of X_c of rLDPE was due to the smaller content of rLDPE in the PLA blend. The effect of NF content increased the crystallinity rLDPE of untreated biocomposites, but decreased the crystallinity of PLA. The presence of MMA increased the T_g and X_c of PLA and rLDPE of treated biocomposites. The MMA enhanced the nucleating effect of filler by promoting stronger filler-matrix interfacial adhesion and dispersion. Furthermore, T_c and T_m of treated PLA/rLDPE/NF biocomposites were not significantly changed with MMA treatment.

Table 5. DSC Data of Untreated and Treated PLA/rLDPE/NF Biocomposites with MMA

Biocomposites	T_g PLA (°C)	T_c PLA (°C)	T_m rLDPE (°C)	ΔH_f rLDPE (J/g)	X_c rLDPE (%)	T_m PLA (°C)	ΔH_f PLA (J/g)	X_c PLA (%)
PLA	58	-	-			151.8	28.3	30.2
rLDPE	-	-	126	101.1	34.5	-	-	-
PLA/rLDPE	61	111	125	5.8	2.0	153	19.5	20.9
Untreated PLA/rLDPE/NF: 70/30/20	60	110	126	13.5	4.6	150	15.4	16.4
Untreated PLA/rLDPE/NF: 70/30/40	59	105	126	22.2	7.6	151	11.2	12.0
Treated PLA/rLDPE/NF: 70/30/20	62	110	126	16.1	5.5	148	27.5	29.4
Treated PLA/rLDPE/NF: 70/30/40	63	110	126	24.2	8.3	152	17.1	18.3

CONCLUSIONS

1. The incorporation of NF in the PLA/rLDPE matrix reduced the tensile strength, elongation at break, and crystallinity of untreated PLA/rLDPE/NF biocomposites.
2. The Young's modulus and T_{dmax} of untreated biocomposites were increased with increasing NF content.
3. The chemical modification of NF with MMA in biocomposites led to positive results on the tensile and thermal properties.
4. The presence of MMA resulted in the treated biocomposites exhibiting higher tensile strength and Young's modulus compared to untreated biocomposites.
5. The treated biocomposites with MMA also had higher crystallinity and thermal stability.

6. The morphology study of treated biocomposites showed better interfacial interaction between NF and PLA/rLDPE matrix.

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