

Thermal Properties of Nypa Fruticans Fiber Filled Polylactic Acid/Recycled Low Density Polyethylene Biocomposites : Effect Compatibilization with Ultra-Plast TP01

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ABSTRACT

Nypa fruticans (NF) is one type of lignocellulosic material that is abundance and from renewable resources. In this study to investigate the effect of NF content and compatibilizer on thermal properties of Polylactic acid (PLA)/recycled low density polyethylene (rLDPE) biocomposites. The thermal degradation and crystallisation behaviour of PLA/rLDPE/NF biocomposites was studied by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). ULTRA-PLAST TP01 (TP01) was used as compatibilizer in order to improve the interfacial adhesion between the NF and PLA/rLDPE matrix. The effect of NF content has decreased the crystallinity of biocomposites but increased the thermal stability. However, T_g decreased with increased NF content. The presence of TP01 have increased the thermal stability and crystallinity of biocomposites. The total weight loss of biocomposites with TP01 was lower compared to biocomposites without TP01.

Keywords: Nypa Fruticans, Polylactic acid, Recycled low density polyethylene, Biocomposites, Compatibilizer

1. INTRODUCTION

In the last decades, the development of biocomposites from biodegradable polymers and natural fillers has attracted a great interest in the industrial and academic research, because of the complete biodegradation in composting process without emission of any toxic substance (As'habi, et al., 2013; Bajpai, Singh, & Madaan, 2012; Balakrishnan, Hassan, & Wahit, 2010; Chun & Salmah, 2013). Among the biodegradable polymers, poly(lactic acid) (PLA) has recently gained an increasing commercial and industrial interest because of its relatively cheap cost. Poly(lactic acid) is a transparent and semi-crystalline polymer with a melting temperature of approximately 160°C, high strength and low elongation at break (Garlotta, 2001). To overcome some problems such as stiffness, brittleness and low thermo-mechanical properties that limit the use of PLA, filler, compatibilizer and other polymeric material can be added during its processing. Hamad and Deri reported that the blending of PLA

at 30% with LDPE show considerably higher elongation at break than pure PLA with an acceptable loss of strength (Hamad, Kaseem, & Deri, 2012). Despite from reducing the waste of LDPE, it also improve the properties of PLA by a cost-effective method.

Natural filler such as cellulose based fibers have been widely recognized as strong natural reinforcements for soft recyclable polymers to form relatively high strength biodegradable composites. Since these filler are fully extracted from the nature, they have significant advantages in biodegradability and reproductivity. Many studies have been carried out on the suitability of natural filler such as coconut shell powder, palm kernel shell, corn cob, hemp, ramie, and sisal as filler in biocomposites (Salmah, Koay, & Hakimah, 2012; Salmah, Lim, & Teh, 2012; Sawpan, Pickering, & Fernyhough, 2011; Wu, 2012; Yeng, Husseinsyah, & Ting, 2013; Zhou, Yu, Sun, Yao, & Qiu, 2012). *Nypa fruticans* belongs to the family *Palmae* or *Arecaceae*. *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. In our previous study has been reported that the utilization of *Nypa fruticans* had effected the mechanical and thermal properties of the biocomposites (Mohamad Syahmie, Salmah, & Pei Leng, 2014).

Besides their advantages, there are some drawbacks of using natural fibers, like poor thermal stability, mainly in processing conditions, high flammability and hydrophilicity. Due to their low thermal stability, natural fibers are generally processed with plastics where high temperatures are not required (less than about 200 °C). Above these temperatures, many of the polymeric constituents in natural fibers begin to decompose. For natural fibres, flammability is in part due to differences in chemical composition. Higher cellulose content results in higher flammability while higher lignin content results in greater char formation with lower degradation temperature. To overcome this drawback, some strategies to promote larger polymer fiber contact can be applied, like fiber surface treatment, polymer modification or introduction of compatibilizer (Faisal, Salmah, & Kamarudin, 2013; Ismail, Salmah, & Abu Bakar, 2005; Salmah, Faisal, & Kamarudin, 2011; Salmah & Ismail, 2008). Compatibilizers have been used to improve dispersion, adhesion and compatibility for systems containing a hydrophilic filler and hydrophobic polymer (Salmah, et al., 2011). The mechanical and physical properties of natural fiber-reinforced plastic composites strongly influenced by the interaction on interface between filler and matrix.

The aim of this research to study the effect of the NF content and compatibilizer on the thermal properties of PLA/rLDPE/NF biocomposites. The ULTRA-PLAST TP01 was used as compatibilizer to improve the properties of PLA/rLDPE/NF biocomposites.

2. EXPERIMENTAL

2.1 Material

The Polylactic Acid (PLA) was supplied by TT Biotechnologies Sdn. Bhd., Penang and recycled Low Density Polyethylene (rLDPE) with MFI value 0.6 g/10min at 230 °C was obtained from STL Plastic Sdn. Bhd., Penang. ULTRA-PLAST TP01 obtained from Performance Additives Sdn. Bhd. The *Nypa fruticans* (NF) that used as

filler was obtained at a plantation at Simpang Empat, Perlis. *Nypa fruticans* was cleaned and grinded. The NF was dried at 80 °C for 24 hours. The average particle size of NF was 31µm determined by using Malvern Particle Size Analyzer. The chemical composition of NF is presented in Table 1.

Table 1: Chemical composition of *Nypa fruticans* (Tamunaidu & 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

2.2 Preparation of Biocomposites

The biocomposites were prepared using Brabender EC Plus at temperature of 180°C and rotor speed 50 rpm. First, PLA and rLDPE charges to mixing chamber for 2 minutes until completed melt. After 2 minutes of mixing, NF was added and mixing continues for another 6 minutes. The total mixing was 8 minutes. Then the biocomposites were compress using compression moulding machine model GT 7014A. The specimen of dumbell followed ASTM 638 bar type IV was used. The compression of biocomposites was done at temperature of 180°C with 1 minute preheat, 4 minutes compress and subsequently cooling for 4 minutes. The similar procedure was done for biocomposites with TP01 where TP01 was added together with PLA and rLDPE. The formulation of PLA/rLDPE/NF biocomposites with and without TP01 is shown in Table 2.

Table 2: Formulation of PLA/rLDPE/NF biocomposites with and without TP01.

Material	Biocomposites	
	Without TP01	With TP01
PLA (php)	70	70
rLDPE (php)	30	30
NFF (php)	0, 10, 20, 30, 40	10, 20, 30, 40
TP01 (php)	-	3*

php = part per hundred of polymer

* 3% from weight rLDPE

2.3 Differential Scanning Calorimetry (DSC) Analysis

DSC analysis with a Q10 DSC (TA Instrument) was used to determine the glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and the crystallinity (X_c) of each biocomposite. The specimens were heated from 30 to 200°C at 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.

2.4 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.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis (TGA)

Figure 1 show the TGA curve of NF, neat PLA/rLDPE and PLA/rLDPE/NF biocomposites with and without TP01. The data obtained from the TGA curves is summarized in Table 3. The early thermal decomposition of biocomposites occurred at temperature range from 100 to 300°C due to the incorporation of NF. Moreover, at higher degradation temperature, the addition of NF provided better thermal resistant, which the total weight loss biocomposites was lower than neat PLA/rLDPE. The better thermal stability of biocomposites without TP01 due to the higher content of extractives and ash as shown in Table 1. This indicates that incorporating NF in the PLA/rLDPE matrix enhanced the thermal stability of the biocomposites due to char formation from pyrolysis of NF. Where, NF act as protective barrier which preventing the PLA/rLDPE matrix from thermal decomposition. For PLA/rLDPE/NF biocomposites with TP01 showed the total weight loss of the biocomposites was lower than biocomposites without TP01. This indicates that PLA/rLDPE/NF with TP01 have higher resistivity to thermal degradation. The presence of TP01 had a considerable effect on the thermal degradation behavior of biocomposites and promoting an increased in the temperature degradation.

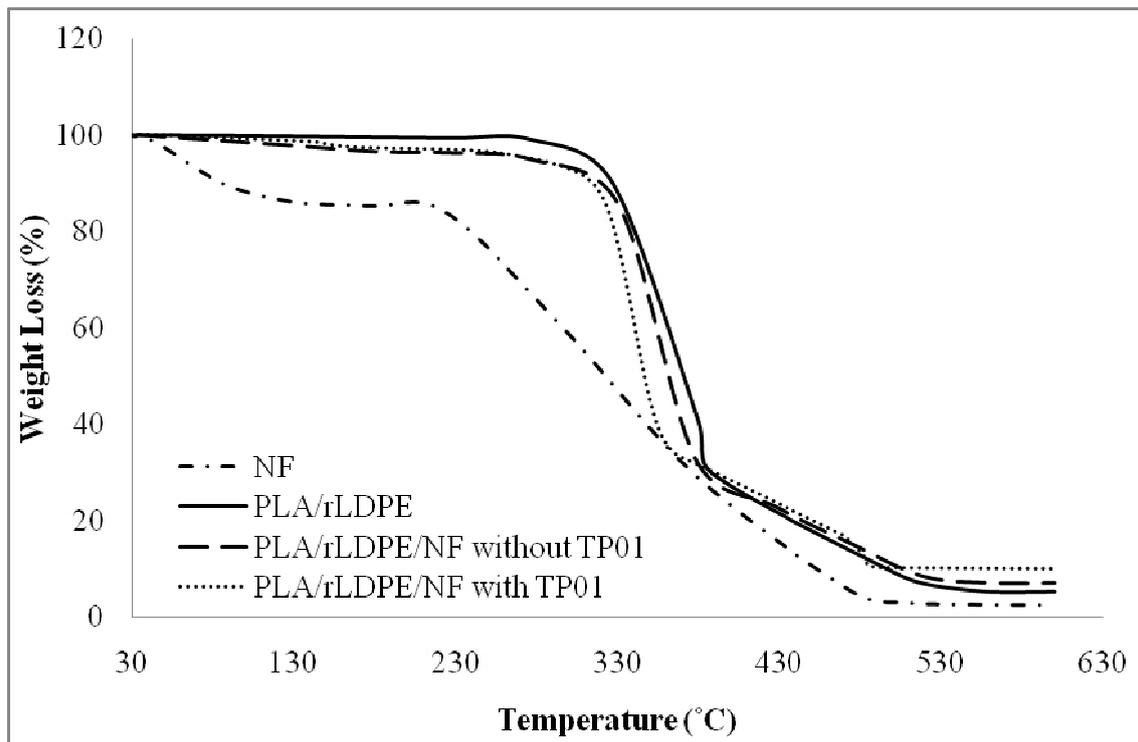


Figure 1: TGA curve of PLA/rLDPE/NF biocomposites with and without TP01

Table 3: Percentage of weight loss of PLA/rLDPE/NF with and without TP01 at different temperature

Temperature (°C)	Weight loss of PLA/rLDPE/NF				
	PLA/rLDPE	Without TP01		With TP01	
	70/30	70/30/20	70/30/40	70/30/20	70/30/40
0 - 100	0.169	1.574	2.135	1.210	1.916
100 - 200	0.363	2.042	3.180	2.054	2.881
200 - 300	0.713	2.697	4.363	4.134	4.298
300 - 400	72.533	62.988	53.429	61.748	52.269
400 - 500	21.844	21.190	20.670	20.028	19.783
500 - 600	4.378	8.351	11.124	8.769	10.898
Total	100	98.842	94.901	97.943	92.045

Figure 2 illustrate the DTG curve of PLA/rLDPE/NF biocomposites with and without TP01. The overall DTG curve show a three steps decomposition of biocomposites exhibited from the combination of neat PLA/rLDPE and NF decomposition behaviour . The first stage of weight loss was assigned to the evaporation of water from the sample . The second peak, NF fiber begins to significantly loss the weight in range 250 – 300°C was attributed by the decomposed of hemicelluloses in NF, while the third peak at temperature range of 350 – 440°C was due to the decomposition of cellulose and lignin. The addition of NF in PLA/rLDPE matrix has significantly affected the thermal degradation temperature. At lower

temperature in the range of 300 – 400°C, the biocomposites incorporated with NF were observed to be shifted to a lower temperature compared to neat PLA/rLDPE. However at higher temperature in the range of 400 – 500°C, the PLA/rLDPE/NF biocomposites with TP01 were found to shift at higher temperature than PLA/rLDPE/NF biocomposites without TP01. The improvement degradation temperature of compatibilized biocomposites was due to the better interaction between PLA/rLDPE and NF with presence of TP01.

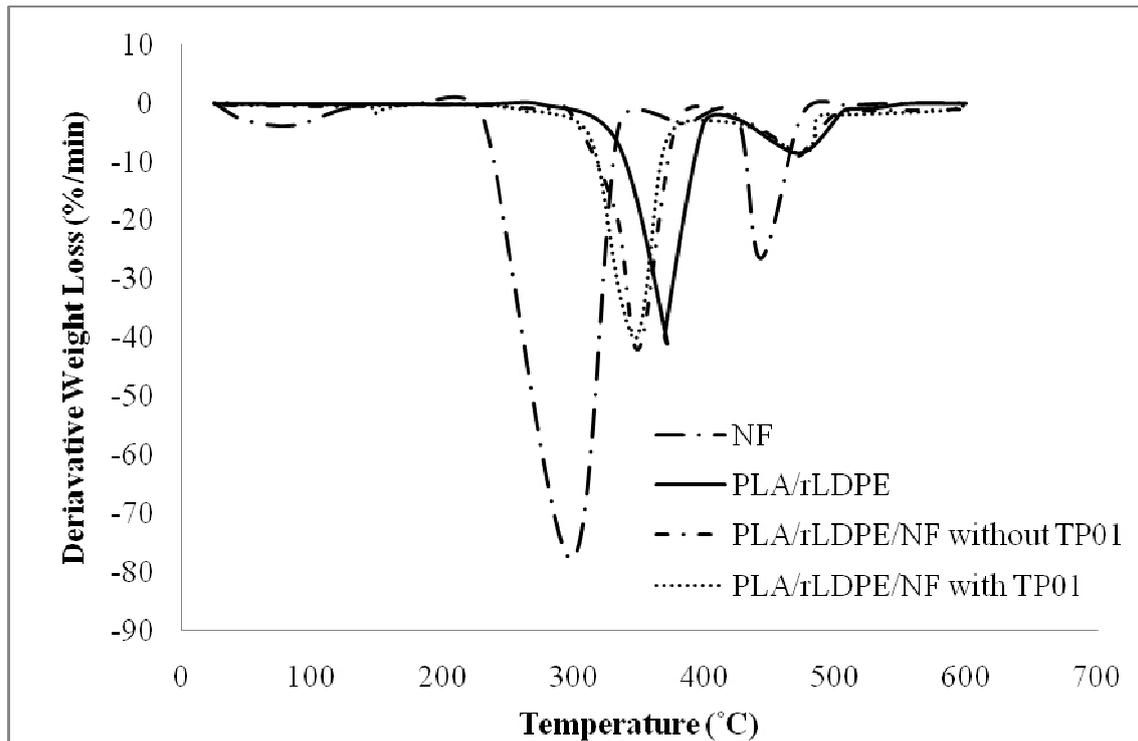


Figure 2: DTG curve of PLA/rLDPE/NF biocomposites with and without TP01

3.2 Differential Scanning Calorimetry Analysis (DSC)

Figure 3 shows the different scanning calorimetry (DSC) curve of PLA/rLDPE/NF biocomposites with and without TP01. The DSC data of PLA/rLDPE/NF biocomposites with and without TP01 is summarized in Table 4. The DSC scan of PLA/rLDPE matrix shows two melting peak, this due to the melting temperature of PLA and rLDPE. The presence of two peak indicated the immiscible blend of PLA and rLDPE. From Table 4 shows that T_g , T_c and X_c of PLA/rLDPE/NF biocomposites without TP01 decreased as the NF content increases. In addition, the T_m of PLA and rLDPE was not significantly affected by the NF content. At similar NF content, PLA/rLDPE/NF biocomposites with TP01 exhibit higher T_g , T_c , T_m and X_c compared to PLA/rLDPE/NF biocomposites without TP01. The increased of crystallization of biocomposites with TP01 was due to the increase of compatibility between the filler and matrix that improved the nucleation activity of NF.

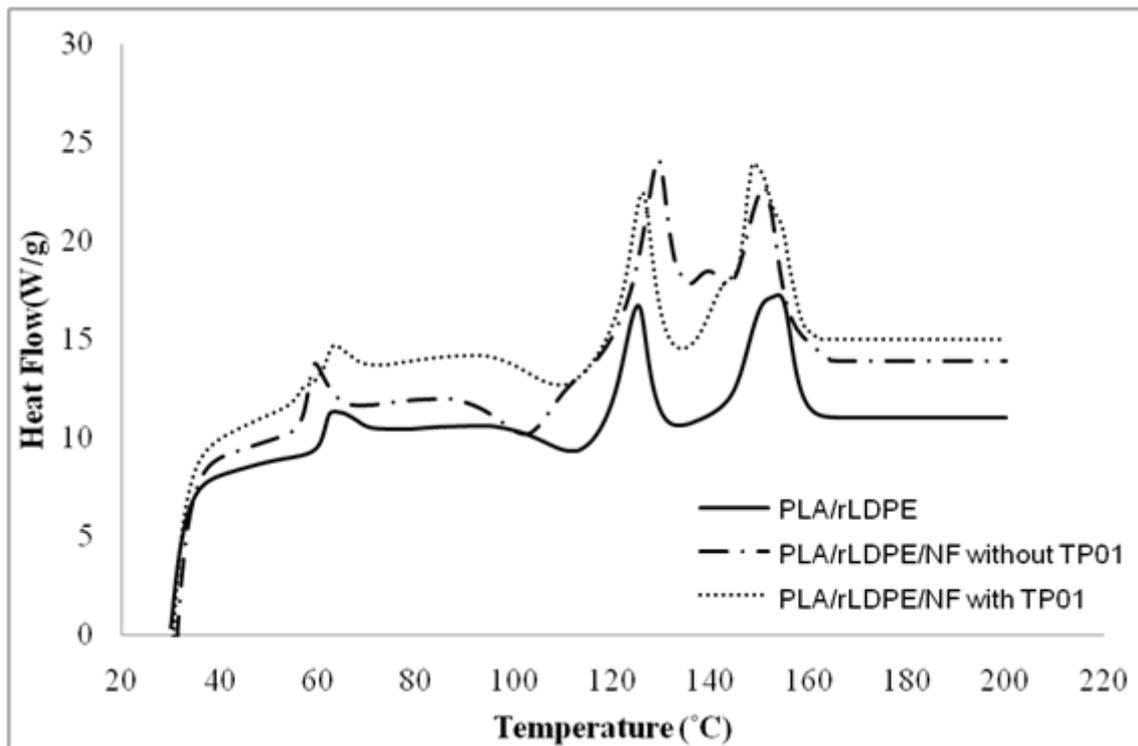


Figure 3: DSC curves of PLA/rLDPE/ biocomposites with and without TP01

Table 4 : DSC data of PLA/rLDPE/NF biocomposites with and without TP01

Materials	T_g	T_c	T_m	T_m	ΔH_f	X_c
	(°C)	(°C)	rLDPE (°C)	PLA (°C)	PLA	PLA (%)
PLA/rLDPE	61	111	125	153	19.6	20.90
PLA/rLDPE/NF without TP01: 70/30/20	60	110	126	150	15.4	16.40
PLA/rLDPE/NFF without TP01: 70/30/40	59	105	126	151	11.2	12.00
PLA/rLDPE/NFF with TP01: 70/30/20	60	104	126	153	22.0	23.5
PLA/rLDPE/NFF with TP01: 70/30/40	60	104	126	153	17.4	18.6

4. CONCLUSION

The incorporation of NF resulted in an early thermal decomposition of the PLA/rLDPE/NF biocomposites. However, at higher temperature degradation showed that NF provided better thermal stability of the biocomposites. At higher NF content, the thermal stability of the biocomposites were increased. The increased of NF content also effected the decreasing of glass transition temperature (T_g), crystallization temperature (T_c) and crystallinity (X_c) of the biocompoites. The addition of TP01 which acted as

compatibilizer improved the thermal stability of the biocomposites. Meanwhile, the T_g and X_c were found to be increased. However the T_c of the biocomposites decreased with the presence of TP01.

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