International Journal of Advanced Research in Technology and Innovation
e-ISSN: 2682-8324 | Vol. 3, No. 1, 35-42, 2021
http://myjms.mohe.gov.my/index.php/ijarti

Preliminary Study of New Thermoplastic Elastomer (TPE) For Fused Deposition Modelling (FDM) 3D Printing

N.I. Nik Intan[1*], A. I. Dayang Habibah[1], S.S Salina[1], I. Suhawati[1], Y.W. Ngeow[1], K.C Yong[1]

[1] Engineering and Technology Division, Malaysian Rubber Board, Experimental Station, 47000 Sg. Buloh, Selangor, Malaysia

*Corresponding Author: nikintan@lgm.gov.my

Accepted: 15 February 2021 | Published: 1 March 2021

Abstract: *The present study describes the preliminary study of a new thermoplastic elastomer (TPE) Polylactic acid (PLA)-based filament with improved physical properties for Fused Deposition Modelling (FDM) 3D printing. The PLA was mixed with natural rubber (NR) and epoxidised natural rubber (ENR) at various blend ratios via melt blending. It was found that PLA blended with an 80/20 ratio of PLA/ENR offered balanced mechanical properties concerning tensile strength and elongation at break. Morphological studies revealed that ENR-25 droplets were distributed in the PLA matrix more uniformly than NR. Furthermore, the incorporation of NR and ENR-25 has significantly altered the PLA's blend thermal history, as confirmed by Differential Scanning Calorimetry and Thermogravimetric Analysis. The PLA/ENR-25 melt index was 14.12 g/min, three times higher than PLA/NR, demonstrating excellent rheological property essential in FDM 3D printing application.*

Keywords: Polylactic acid (PLA) blend, Thermoplastic elastomer (TPE), FDM 3D printing

1. Introduction

Nowadays, research on 3D-printing has an important role in promoting the development and progress of additive manufacturing (AM) technology. Hence, new scientific discovery, combined with material innovation, is highly demanding to infuse AM technology throughout all industries. Fused Deposition Modelling (FDM) printing is the most popular method since it has a low cost and less complexity. Generally, FDM uses thermoplastic polymers such as Polylactic acid (PLA), Polyethylene Terephthalate (PET) and Polyamide (PA) as printing materials. Thermoplastic elastomer (TPE) is another FDM 3D filament class that has received considerable attention recently. TPE consists of block copolymers or rubber mixtures with thermoplastics that provide high elasticity and improved toughness.

Polylactic acid (PLA) is a thermoplastic made from renewable resources such as corn starch, tapioca roots or sugar cane. PLA has become a common material within the 3D printing industry, particularly in medical applications due to its renewability and comparable properties to hydrocarbon-based polymers. Likewise, natural rubber (NR) is derived from the latex of rubber tree where it is one of the most important polymers in medical, tyre and engineering applications. PLA is a brittle thermoplastic with high strength and modulus (Rasal *et al.*, 2010). In contrast, the mechanical strength and modulus of NR are lower than that of PLA but exhibit excellent elasticity and ductility.

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

Because of their complementary properties, blending PLA with NR is worth trying to improve the properties of PLA, such as toughness and elongation at break without compromising biodegradability (Bijarimi *et al*, 2014). For example, Bitinis (2011) reported that 10wt% of NR is an optimum value for improving PLA's toughness. However, PLA and NR are thermodynamically incompatible due to their different solubility, PLA (10.1 cal/cm^3) (Abhishek, 2004) and NR (7.75 cal/cm^3) (Wohlfarth, 2010). Thus, to increase the compatibility between both materials, epoxidised natural rubber (ENR) was used as an alternative to NR. It is expected that ENR will have a compatibility with PLA since its polarity is closer to that of PLA. In this study, blends containing different ratio of NR and ENR with PLA were prepared via a melt blending approach. The effects of the different blends toward the mechanical properties and surface morphology were investigated. Crystallisation behaviour, thermal stability, melt flow index and printing ability of the PLA blends were additionally studied for selected blend ratios.

2. Experimental

Materials

An extrusion grade Polylactic acid (Ingeo™ 2003D, Natureworks, USA) was used in this study. It has a density of 1.24 g/cm^3 and melt flow index of 30 – 40 g/10 minutes, (190ºC/2.16 kg) and a melting temperature between 160 – 170°C. Natural rubber of the SMR L grade and Epoxidized Natural Rubber with 25% epoxy group (Ekoprena-25) with a Mooney viscosity of ML(1 + 4)100 °C =80 and 60 were used as the rubber matrix.

Sample preparation

The varied compositions of PLA, NR, and ENR-25 were as listed in Table 1. The PLA resin were dried in a vacuum oven at 70°C for minimum of 4 hours. All melt blends were prepared in a laboratory mixer (ThermoHaake. Polylab Mixer OS) at 180ºC with a capacity of 269 cm^3. The fill factor was held constant at 0.6 for all the variants experimented. Next, blending was carried out at 50 r.p.m. (rotor speed) for 5 minutes. The blend was then moulded at 180ºC under 45 MPa of pressure for 5 minutes using a hot press (Hexaplast) to produce a sheet measuring 100 mm in width × 125 mm in length and × 2 mm of thickness.

Table 1. Compositions of pure PLA, PLA/NR and PLA/ENR-25 blends

Materials	*weight (wt%)*						
	1	2	3	4	5	6	7
PLA	100	90	85	80	90	85	80
NR	0	10	15	20	0	0	0
ENR-25	0	0	0	0	10	15	20

Tensile properties

All compositions of blends were tested and compared for their tensile properties. Tensile tests were carried out according to BS ISO 37:2011 using an Instron 5564 universal testing machine with a 1 kN load cell and a crosshead speed of 50 mm/minute. At least five samples were tested for each blend, and the average 'stress' and 'strain' values were used to determine the stress at peak and elongation at break.

Optical Microscopy

The surface morphology of the samples were examined using an optical microscope (Olympus BX51M). A clean film sample was observed, and images captured at 20× magnification.

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

Differential Scanning Calorimetry (DSC)
The thermal behavior of selected PLA blends was analysed using Differential Scanning Calorimetry (DSC) Mettler STAR® SW 13.00 apparatus at a heating rate of 20°C minute^{-1} and nitrogenous (N_2) atmosphere. Analysis was performed at a temperature range of 100 to 200°C for a first heating scan with approximately 10 to 30 mg of sample sealed in 40 µL aluminum crucibles.

Thermogravimetric Analysis (TGA).
TGA was conducted using a Mettler STAR® SW 13.00 instrument. Specimens weighing 12 to15 mg were heated from an ambient temperature of 23°C to 400°C at a constant heating rate of 10°C per minute. TGA analyses were performed under a nitrogenous (N_2) atmosphere at a 60 ml/minute flow rate.

Melt Flow Index (MFI)
The melt flow rate (MFR) of the blended compounds was measured on a DYNISCO 4000 LMI indexer at 180°C and a load of 2.16 kg specified in the ASTM D1238–86 (Method AB) test method.

3D FDM Printing
A filament wire with 1.75 mm thickness was prepared using Xplore MC 15 Micro compounder. For the 3D-printing process, the PLA TPE was printed at 210°C, using a 3D GenceOne printer equipped with the 3DGence SLICER 4.0 software.

3. Results and Discussion

Tensile properties
Figure 1(a-b) presents the effects of blend ratio on tensile strength and elongation at break (EB) of PLA. As expected, the strength of PLA was suppressed by the presence of soft rubber phase. Compared with that of virgin PLA, the tensile strength of the PLA/NR blends were dramatically decreased by about 70 to 80%. However, in this case, the tensile strength of PLA/ENR-25 blends was less suffered than the PLA/NR blends, as shown in Figure 1a. The improvement in tensile strength indicated that ENR-25 provides better compatibility than NR in the PLA blends.

Interestingly, the EB of PLA was about 3.4%, and increased to 17.1% in the 80PLA/20NR blend, five times increment. Moreover, the use of ENR-25 from 10 to up to 20 wt% further increased the EB to seven times higher than that of PLA's. From this result, it is suggested that the 80/20 blend ratio offers optimum flexibility for both blends. The distribution of the rubber phase in the PLA matrix is responsible for the improvement in EB. This trend is well agreed with findings from a previous study. Wahit et al, (2015) reported that a similar blend ratio of 80PLA/20ENR exhibited balanced mechanical properties, including a flexural modulus of 2.8 GPa and an impact strength of 47 J/m. Therefore, the 80/20 blend ratio was selected for further characterisation and as a material of choice to make a thin filament for FDM 3D printing.

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

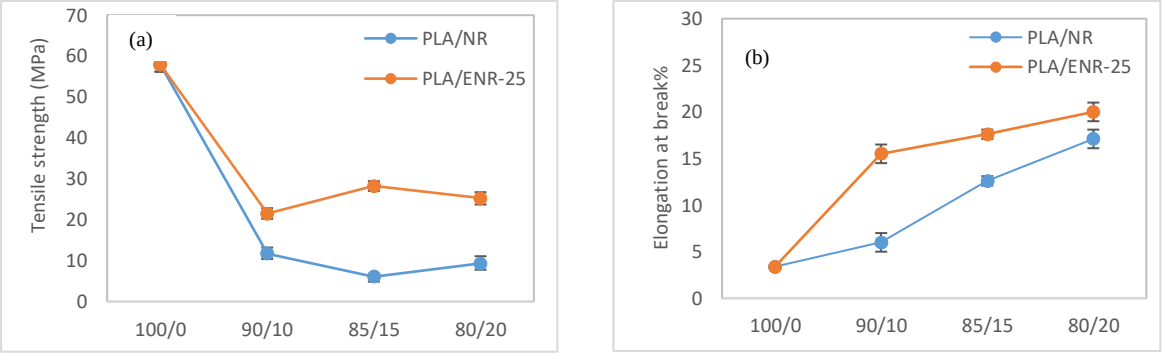

Figure 1: (a)Tensile strength and (b) Elongation at break (EB) of PLA/NR and PLA/ENR-25 blends versus blend ratio

Optical Microscopy

The morphology of PLA/NR and PLA/ENR-25 blends are shown in Figure 2(a-f). The bright and dark phases represent the PLA matrix and rubber particles, respectively. NR and ENR-25 were found dispersed in the PLA matrix as spherical particles, especially for samples with the rubber content of 10 and 15 phr (Fig 2a, b,d,e). Relatively, the ENR-25 droplets were smaller than NR. In the PLA/NR blend series (Fig. 2a-c), the increase in NR content led to larger rubber particles. The larger particles occurred due to poor interfacial adhesion between the PLA and NR phases, which consequently behaved as stress concentrator points that lower the mechanical properties (Nematollahi, 2018). The above reason could explain why the PLA/NR blends exhibited low tensile strength.

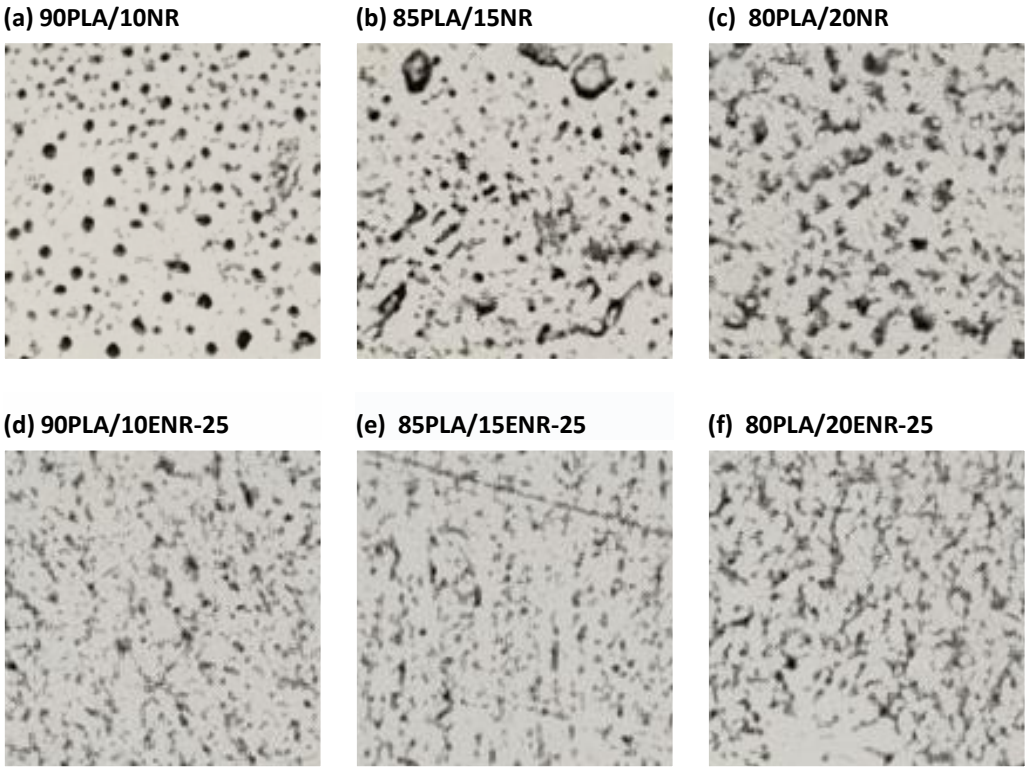

Figure 2: Optical micrographs (magnification 20x) of (a-c) PLA/NR and (d-f) PLA/ENR-25 at different blend ratios

Furthermore, co-continuous rubber phase was found for samples containing a high rubber content of 20 phr (Fig. 2c and 2f). However, the distribution of ENR-25 droplets (Fig. 2f) in the PLA matrix appeared more uniform than the NR (Fig. 2c). Also, the size and shape of the

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

ENR-25 particles were smaller than the NR particles. A similar observation was reported by Nematollahi, (2018) where the average rubber droplet size decreased due to the presence of ENR as compatibilizer. The study revealed that by increasing the ENR content (0-3 wt%), the adhesion of PLA and NR component in PLA/NR blends improved due to chemical interaction between the oxirane ring ENR and hydroxyl group in PLA.

Thermal Analysis

As shown in Figure 3 and Table 2, the neat PLA can be characterised with a T_g of 61.3°C, a cold crystallisation temperature (T_c) of around 123.3°C and a melting temperature (T_m) 145.2°C. The movement of T_g from their original values can be correlated to the compatibility of the polymer blend. Compared to the neat PLA, it was observed that PLA/NR and PLA/ENR-25 displayed two T_g indicating the PLA and rubber immiscibility. Nevertheless, with ENR-25 in the blend, the immiscibility level was relatively smaller, due to increased interactions between ENR-25 and PLA phases. As a result, T_g of the PLA shifted to ENR-25 (about -20.63 °C). This observation agrees with previous findings reported by Ishida *et al.* (2009).

It is clearly observed that the T_m of PLA/NR and PLA/ENR-25 blends was shifted to a lower temperature than the neat PLA. In this case, the decreased of T_m from the original value is more significant for PLA/NR blend than the PLA/ENR-25 blend. These phenomena can be attributed to the added NR, which acts as a crystallisation nucleation agent by providing nucleation spots during cold crystallisation (Jaqueline *et al.* 2016). It is possible that as a nucleating agent, rubber component induced heterogeneous mechanism resulted in faster crystallisation hence increase in crystallinity (Thongpin *et al.*, 2013).

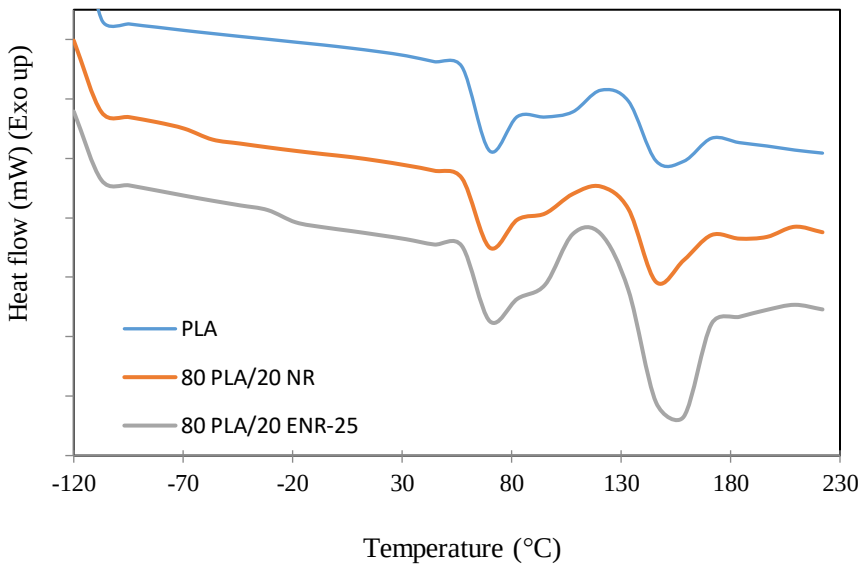

Figure 3: DSC curves (first heating scan) of PLA, PLA/NR and PLA/ENR-25 blends

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

Table 2: Thermal characteristics of PLA, PLA/NR and PLA/ENR-25 blends

Compositions	Tg of rubber (°C)	Tg of PLA (°C)	Tc (°C)	Tm (°C)	*Xc* (%)
100 PLA	-	62.18	123.3	145.2	10.11
80 PLA/20 NR	-66.17	61.31	116.7	140.5	16.26
80 PLA/20 ENR-25	-20.63	60.23	113.1	144.6	40.80

Figure 4 compares the TGA thermal degradation curves of PLA, PLA/NR and PLA/ENR-25 blends. Two steps degradation processes were observed for all the PLA blends where the first stage was at about 345 - 350°C, and the loss-weight was 48.20 - 43.22%, consistent with the decomposition of PLA. Whereas the second stage was about 375 - 380°C, corresponding to the degradation temperature of PLA blends. Table 3 summarises thermal degradation temperatures such as the onset of degradation temperature, temperatures degradation for 10% and 50% mass loss (T_{10} and T_{50}), and residue mass 400°C. The degradation temperatures showed that the PLA/ENR-25 blend's thermal stability was inferior to the PLA/NR blend. The above trend can be explained due to the epoxy group in the ENR-25. In this case, the oxirane structure in the PLA/ENR-25 blend has become more reactive at high temperatures. As a result, ENR-25 can act as an auto oxidant by initiating free radical reactions. Free radicals generated from the initiated reaction subsequently creates oxidation of the PLA in the blend hence reduced the thermal stability (Wahit, 2015).

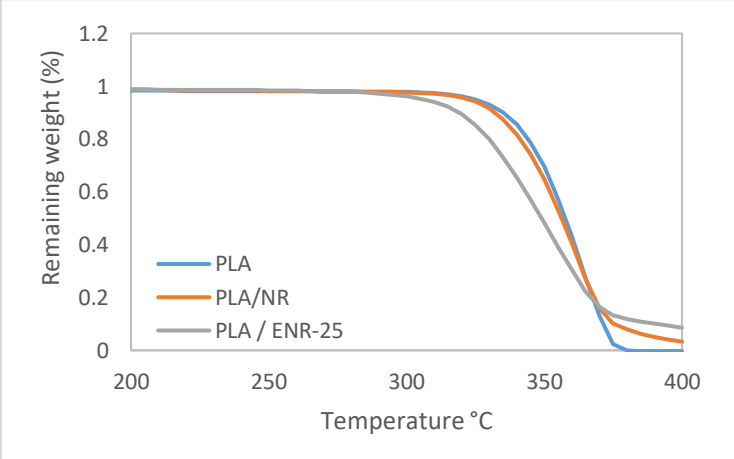

Figure 4: TGA curves of PLA, PLA/NR and PLA/ENR-25 blends

Table 3: Decomposition temperature of neat PLA, PLA/NR and PLA/ENR blends

Compositions	T_{onset} (°C)	T_{10} (°C)	T_{50} (°C)	Temp. peak of degradation (°C)	Final residue at 400°C (%)
PLA	325	335	355	364.97	1.0
80 PLA/20 NR	320	330	355	361.09	3.4
80 PLA/20 ENR-25	305	320	345	354.58	8.5

Melt Flow Index (MFI)

Melt Flow Index (MF1) is used to study melt viscosity under a constant load and low shear rates. The amount of mass or volume of a polymer that flows through a small die at a specified temperature and pressure are measured to obtain the MFI value. Figure 5 shows the MFI

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

comparison of PLA, 80PLA/20NR and 80PLA/20ENR-25 blends measured at 180°C and a 2.16 kg load pressure. MFI of pure PLA and 80PLA/20NR were almost equal. This result suggested that the addition of 20% NR to the PLA as a rubber modifier slightly altered the flow properties of PLA at a low shear rate. However, the MFI of 80PLA/20ENR-25 increased significantly to a value three times higher than that of the virgin PLA. The above results indicated that the use of 20% ENR-25 might offer improved flow properties to PLA.

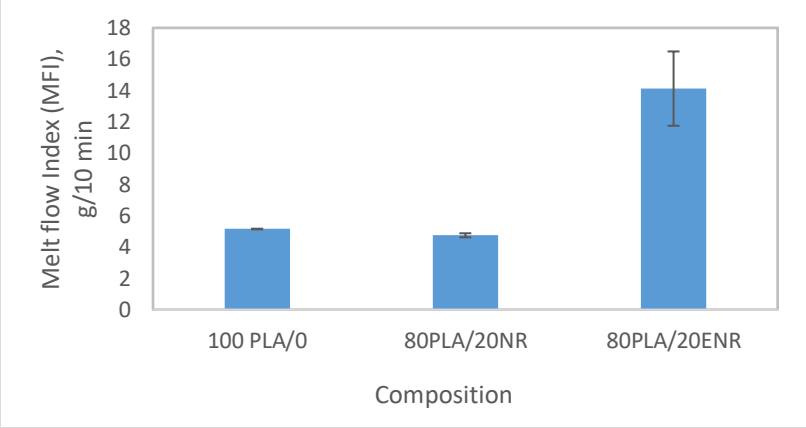

Figure 5: Melt flow index (MFI) of PLA, PLA/NR and PLA/ENR-25 blends

3D-Printing Study of the PLA blends

Figure 6(a-b) presents photographs of PLA blends fabricated as 1.75 mm filament and the printed digital model of 80PLA/20NR (left) and 80PLA/20ENR-25 (right). It was proven that both PLA blends could be printed smoothly under a controlled bed temperature. However, having a rubber modifier in the PLA blends might induce tackiness during the printing process, especially for the PLA blend that contained ENR-25. Hence, the bed temperature used for PLA/ENR-25 was reduced slightly to 55°C, from the initial 60°C, which is closer to the T_g of PLA in the 80PLA/20ENR-25 blend.

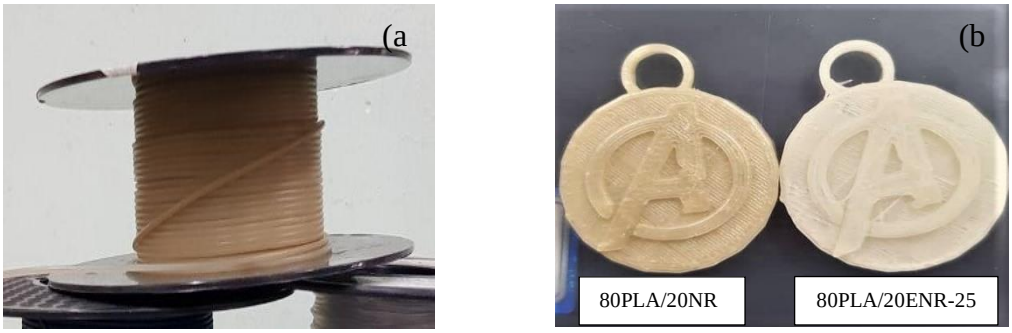

Figure 6(a-b): Photograph images of (a) PLA TPE filament prototype and (b) printed digital model of PLA/NR blend and PLA/ENR-25 blend

4. Conclusion

PLA TPE blends were prepared via melt blending. The elongation at break of 80PLA/20NR and 80 PLA/20 ENR-25 were five and seven times higher, respectively than that of neat PLA. Furthermore, the morphological analysis revealed that the ENR-25 particles were well dispersed in the PLA matrix compared to NR particles. It should be noted that the NR or ENR-25 particles act as plasticisers and thus enhance chain mobility resulting in a slight decrease in T_m and increase in the PLA's crystallinity, as confirmed through DSC analysis. Moreover, TGA

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved

curves revealed that an epoxy group in ENR-25 induced oxidative reactions at a high temperature, thus lowering thermal stability. Despite having better compatibility, the MFI value of PLA/ENR-25 was higher than 80PLA/20NR, which indicated improved flow properties and resulted in successful printing of the PLA blend filament. Thus, from the results obtained, it is suggested that the PLA/ENR-25 blend has great potential to produce filaments for 3D printing.

Acknowledgement
The Malaysian Rubber Board is acknowledged for the financial support of this project under the ISTC grant (S19ITE0708).

References

Rasal, R.M., Janorkar, A.V. & Hirt, D.E. (2010) Poly(lactic acid) Modifications. Progress Polymer Science, 35(3), 338−356

Bijarimi, M., Sahrim, A.& Rozaidi, R. (2014) Melt Blends of Poly(lactic acid)/Natural Rubber and Liquid Epoxidised Natural Rubber. Journal of Rubber Research, 17(2), 57-58

Bitinis, N., Verdejo, R., Cassagnau, P. and Lopez-Manchado, M.A. (2011) Structure and Properties of Polylactide/Natural Rubber Blends. Materials Chemistry and Physics, 129, 823-831.

Nematollahi, M., Jalali, A. and Modarress, H. (2018) High performance bio-based PLA/NR/ENR blend; Effect of ENR on microstructure, toughness, static and dynamic mechanical properties. Polymer International, 68 (3), 439-446

Abhishek, A., Amit D.S., Swagat S.R. & Ashok, K. (2004) Constrained nonlinear optimisation for solubility parameters of poly(lactic acid) and poly(glycolic acid)—validation and comparison. Polymer 45(25), 8603-8612

Wohlfarth, C. (2010). Solubility parameter of natural rubber: Datasheet from Landolt-Börnstein - Group VIII Advanced Materials and Technologies · Volume 6D2: "Polymer Solutions". In SpringerMaterials (pp 1467). Verlag Berlin Heidelberg

Wahit, M.U., Azman, H., Akos, N. I., Nurhayati, A. Z., & Kayathre, K. (2015) Mechanical, Thermal and Chemical Resistance of Epoxidized Natural Rubber Toughened Polylactic Acid Blends. Sains Malaysiana, 44(11), 1615–1623

Ishida, S., Nagasaki, R., Chino, K., Dong, T. & Inoue, Y. (2009) Toughening of poly(L-lactide) by melt blending with rubbers. Journal of Applied Polymer Science 113: 558-566.

Jaqueline G. L., Cosme, Vanessa M., Silva, Regina R. C., Nunes, Paulo H. S. & Picciani (2016) Development of Biobased Poly(Lactic Acid)/Epoxidized Natural Rubber Blends Processed by Electrospinning: Morphological, Structural and Thermal Properties. Materials Sciences and Applications, 7, 210-219

Thongpin, C., Klatsuwan, S., Borkchaiyapoom, P., & Thongkamwong, S. (2013) Crystallisation Behavior of PLA in PLA/NR Compared with Dynamic Vulcanized PLA/NR. Journal of Metals, Materials and Minerals, 23(1), 53-59

Copyright © 2021 ASIAN SCHOLARS NETWORK - All rights reserved