THE EFFECT OF COMPATIBILIZER ON THE TENSILE AND MORPHOLOGICAL PROPERTIES OF NYLON FIBRE REINFORCED THERMOPLASTIC NATURAL RUBBER COMPOSITES

Engku Zaharah Engku Zawawi[1*], Sahrim Ahmad[2], Rozaidi Rashid[2] and Noor Najmi Bonnia[1]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2]School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43650 Bangi, Selangor, Malaysia.

*engku946@uitm.edu.my

Abstract. In this study, the tensile properties such as tensile strength, modulus, and tensile strain of thermoplastic natural rubber (TPNR) composites reinforced with different volume fractions (vol%) of short nylon textile fibres (PA6) compositions were investigated. The TPNR was prepared from blending of high-density polyethylene (HDPE), natural rubber (NR), and liquid natural rubber (LNR) in the ratio of 50:40:10. The composites were prepared via the melt blending process with an internal mixer, and the compression moulding machine was used to mould the tensile test specimens. This study focuses on the effect of fibre loading with and without compatibilizer, maleic anhydride-grafted polyethylene (MAPE) on the tensile and morphological properties of the TPNR composites. Incorporation of fibre loading from 0 to 20 vol.% in TPNR resulted in increased tensile strength and tensile modulus to 16.11MPa and 287.67 MPa respectively, and the increments were 128.57% and 105.66 %, respectively. The addition of 4 wt.% MAPE in the composites of 20 vol% fibres increased the tensile modulus of the composites up to 26% compared to the composites without compatibilizer. The scanning electron micrograph of tensile fracture surfaced showed good adhesion between the fibres and polymer matrix with the presence of MAPE.

Keywords: thermoplastic natural rubber, compatibilizer, tensile strength, fracture surface, surface morphology

Article Info
Received 16th December 2021
Accepted 18th February 2022
Published 20th April 2022

ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Composites based on thermoplastic and elastomer blends (TPE) reinforced with particle filler or fibres have become increasingly popular, including thermoplastic natural rubber blends (TPNR). TPNR is classified as a thermoplastic elastomer and is prepared by melt blending natural rubber with polyolefins such as polypropylene (PP) and polyethylene (PE) [1-8]. Its properties combine the advantages properties of vulcanised elastomers and plastic. Therefore, TPNR can be processed by conventional thermoplastic processing machinery [4-5, 8]. However, blending the natural rubber or elastomer with polyolefin may reduce the strength and stiffness of polyolefin. Therefore, in order to obtain the unique mechanical properties of TPE, attempts have been made to enhance the strength by incorporating particulate fillers, natural or synthetic fibres such as glass-fibre into these blends [4-5, 9-12]. The reinforcement of short fibres in the TPE composites usually manifested as increased tensile strength and modulus, decreased elongation and swelling compared to the elastomer matrix [5, 11-12].

The short nylon fibres were chosen in this study to reinforce TPNR due to the advantages of short fibres, such as easy processability, anisotropy in technical properties, high stiffness, and short fibres can be incorporated directly into the polymer matrix during the moulding process. Thus, this TPNR-Nylon composites will have properties similar to other TPE composites. Therefore, becomes a very suitable material for various uses in the field of engineering, such as in the automotive industry, for making shock-absorbing seals and bumper stops that require the capability of withstanding weathering [13]. The mechanical properties of these composites are also highly dependent on the adhesion of the matrix and fibres interfaces.

Therefore, to achieve maximum reinforcement, attempts have been made to promote the interfacial adhesion of fibers to the matrix by using various compatibilizing agents [12, 14-16]. Studies by other researchers showed there were an improvement in tensile strength and modulus of thermoplastic elastomers composites with the addition of various compatibilizing agent. The use of a compatibilizer improve the compatibility and dispersion between the filler and the matrix by constructing a compatible hydrophobic coating of the polymer and the surface of filler. The effects of compatibilizing agent maleic anhydride-grafted polyethylene (MAPE) on the mechanical properties of recycled tire textile fibre (RTF) reinforced thermoplastic elastomer composites prepared from regenerated tire rubber (RR) and recycled high density polyethylene (rHDPE) blends have been studied by Ali and Denis [12]. Their results showed an improvement in tensile properties with the addition of MAPE compatibilizer. A morphological result showed the level of blend interaction surface of RR particles with MAPE highly enhanced the interfacial adhesion between the fillers and rHDPE resulting in improved homogeneity RR and RTF distribution.

The purpose of this article is to examine the effect of different loading of nylon short fibre with and without MAPE compatibilizer on the tensile properties and morphological aspect of TPNR-Nylon fibre composites. The fibre-matrix adhesion has been analysed by using scanning electron microscopy studies.

Materials and methods

Materials. The high-density polyethylene (HDPE) material used in this study with a density of 0.95 g/cm^3 manufactured by Polyethylene Malaysia Sdn. Bhd. Natural rubber, (SMR-L grade) was purchased from Guthrie (M) Bhd. The fibre used was short Nylon fibres

(PA6) with 6 mm long with the density of 1.14 g/cm^3 (product of Du Pont U.S.). Compatibilizer, maleic anhydride-grafted polyethylene (MAPE), was purchased from Aldrich Chemical Comp. Inc. Liquid natural rubber was prepared from SMR-L grade of natural rubber by photochemical oxidation [6-7].

Preparation of TPNR composites. All the samples used in this study were prepared by the melt blending method in an internal mixer (Haaker Rheomix, Model 600). The thermoplastic natural rubber (TPNR)-Nylon fibres composites were prepared by using 0, 5, 10, 15 and 20 vol.% fibres. The composition of the TPNR blend was fixed at 50 wt% HDPE, 40 wt% NR and 10% LNR (liquid natural rubber). The ~~N~~nylon fibre was dried at 80 ^{o}C for 6 hours before melt blending. The melt blending of TPNR was performed at the temperature of 160 ^{o}C with rotor speeds of 60 rpm for 13 minutes. For the preparation of composites, at the start of mixing, the NR, HDPE and LNR were added into the mixing chamber, followed by nylon fibres after 3 minutes later. Whenever compatibilizer was required, a 4 wt.% MAPE was added simultaneously with HDPE during the melt blending. Subsequently the composites compounds were compress moulding into standard dumbbell shape of tensile test specimens at the moulding temperature of 160 ^{o}C for 10 minutes and then cooled under pressure for 5 minutes.

Mechanical testing. Tensile test was performed according to ASTM D-638, at room temperature. The test was measured using a universal tensile tester at a 50 mm/min crosshead speed. The values of tensile modulus and tensile strength were determined. At least five specimens of each composition were used for the tensile test, and the average values reported.

Scanning electron microscope. The fracture surfaces of the gold-coated tensile test specimens were examined with a LEO 1450VP scanning electron microscope (SEM) at an acceleration voltage of 5 kV to evaluate the possible differences in fracture behaviour and analyse the dispersion of the fibres.

Results and Discussion

Tensile test. Tensile test was performed to determine the tensile modulus, strength and tensile strain at break of this discontinuous fibre reinforced composites system. Fig. 1 shows the effect of nylon fibres loading on the tensile strength of TPNR composites with and without MAPE compatibilizer. The results show tensile strength of TPNR blends without MAPE increased up to 128.57% with the incorporation of 20% fibres. It shows that nylon fibres effectively enhanced the strength of the TPNR blend. This is due to the capability of fibres to support stress transmitted from matrix. A similar study by Ghanbari et al. showed that incorporation of glass fibres had increased the tensile strength of neat matrix prepared from thermoplastic polyolefin elastomers up to 190% but accompanied by a 60% decrease in the strain at yield [11]. Meanwhile, Figure 1 also indicates that the tensile strength of the composites with 5 vol% nylon fibres had increased up to 10% with addition of MAPE compatibilizer, and then gradually increased to 25% as increasing the fibre content to 20 vol.%. These results indicate that MAPE successfully enhances adhesion between nylon fibres and the TPNR matrix.

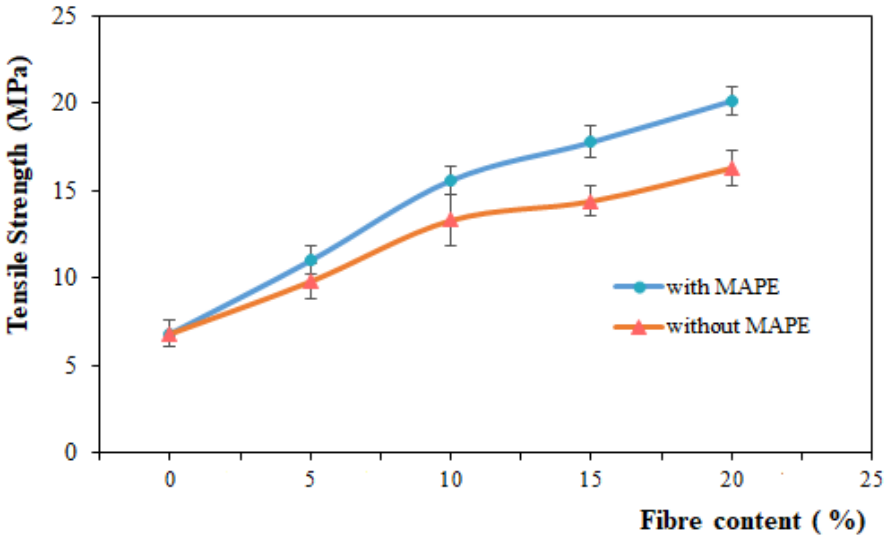

Figure 1. Tensile strength as a function of fibre volume fraction for TPNR-nylon fibre composites with and without MAPE.

Figure 2 shows the effect of nylon fibres on the tensile modulus of TPNR composites with and without MAPE. The addition of 20 vol% nylon fibres to TPNR without MAPE results in an increased in tensile modulus of the TPNR composites up to 105.66%. This indicates the ability of nylon fibres to impart greater stiffness to the TPNR blend. Other researchers also found that incorporating organic fibres gives rise to the more rigid material, showing a gradual increase of the modulus value as fibre content in the composite was increased [5].

It also can be observed in Figure 2 that addition of 4 wt.% MAPE into composites results in a substantial increase in stiffness at 5% fibre loading, while the rate of increase at higher fibres loading was more pronounced. The tensile modulus of TPNR composites with 20 vol% fibre increases to 26% with the addition of MAPE compatibilizer as compared without MAPE at the same fibre loading. The same trend was observed by Wang et al. [16] on the effects of compatibilizing agent (PP-g-MAH) on the mechanical properties of glass-fibre-reinforced polypropylene (PP) composites. They observed that the addition of a compatibilizing agent increased the tensile strength due to the physical compatibility between the compatibilizer and PP matrix. Other researchers studied MAPE compatibilizer's effect on the mechanical properties of fibres reinforced thermoplastic elastomer [12, 14-15]. Their results showed that MAPE had significantly enhanced the tensile strength and modulus of the composites.

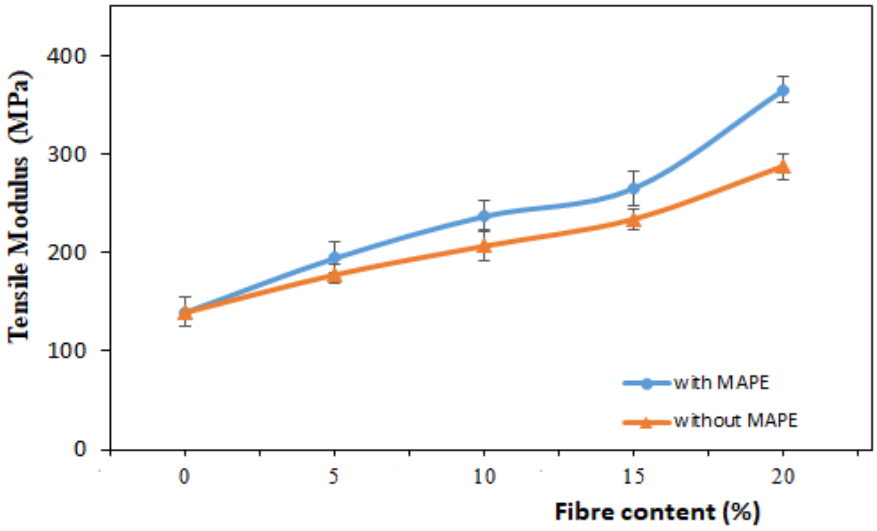

Figure 2. Tensile modulus as a function of fibre volume fraction for TPNR- nylon fibre composites with and without MAPE.

Although the tensile results show that the addition of nylon fibre had significantly improved the tensile strength and modulus of TPNR, the disadvantage was that the composites lost the extensibility property of the rubber matrix. Figure 3 indicates that the strain at break of TPNR decreases sharply with incorporation of nylon fibre at a very low fibres content (5%) and drops off more slowly at the higher fibre content. The reduction in the strain at break was contributed by embrittlement effect as the stiffness of the composites improved. Nevertheless, the results show that the addition of MAPE was slightly improved the tensile strain at break of the TPNR composites. Therefore, these results demonstrated that the mechanical properties are very much system dependent for a short fibre reinforced composite.

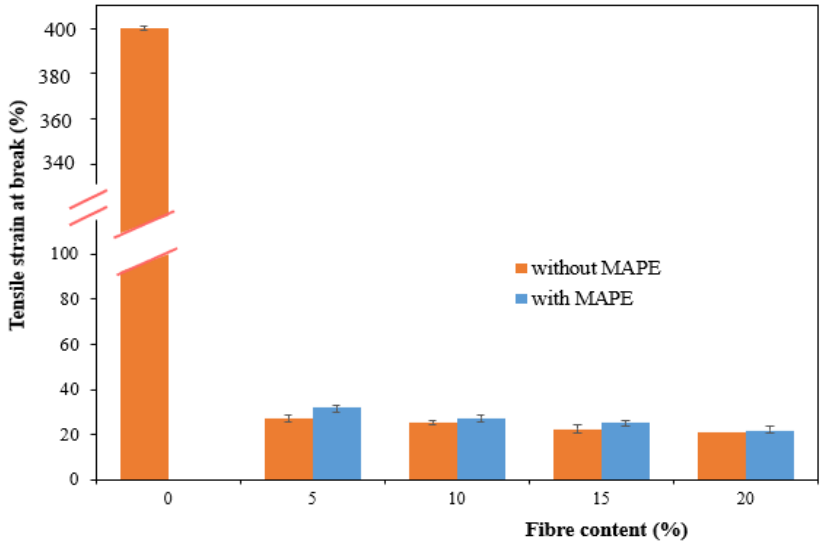

Figure 3. Tensile strain as a function of fibre volume fraction for TPNR-nylon fibre composites with and without MAPE.

Morphological examination. The microstructural characterization of TPNR-nylon fibres composites was examined using scanning electron microscopy (SEM). Observation via SEM is one of the ways to study the effect of MAPE compatibilizer on the interaction of fiber-matrix interface. The fibre–matrix interface properties are very important for the macroscopic mechanical properties of composite materials. Observations were made on the tensile fractured surfaces of the composite samples. Figure 4(a) shows the fracture of composites with 10 vol% fiber loading. The circle marking in Figure 4(a) indicates the debonding of the fibers due to poor adhesion of fibers to the matrix. Meanwhile, Figure 4(b) shows the micrograph of composites with the addition of MAPE at the magnification of 100X indicating that the nylon fibers (10 vol.%) are evenly distributed in the TPNR matrix.

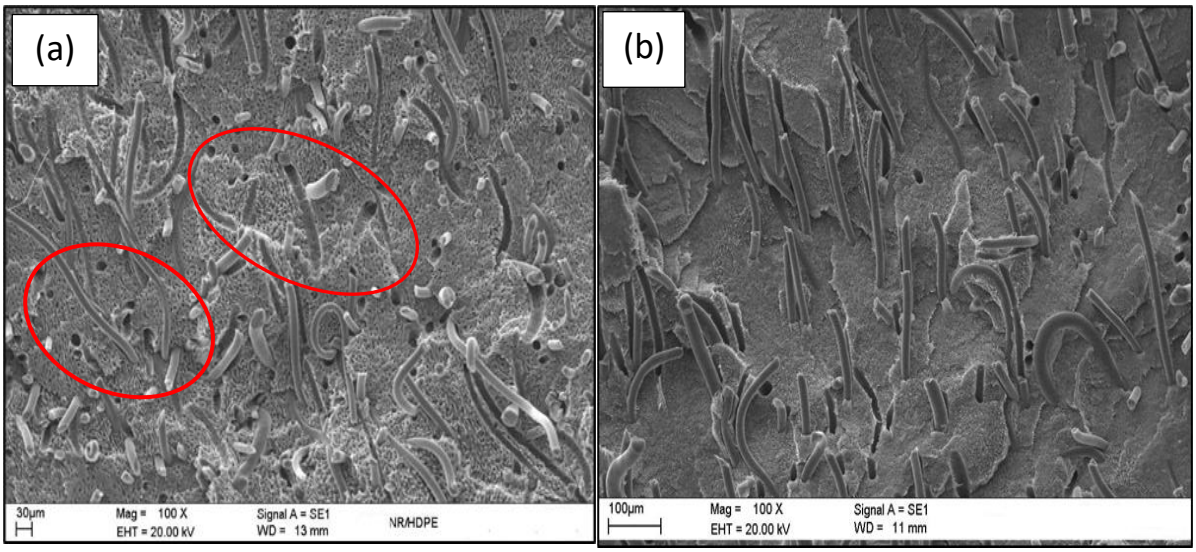

Figure 4. SEM micrographs of facture surface TPNR-nylon fibres composites: (a) without MAPE and (b) with MAPE at 100x magnification.

The fracture surface analysis of composites without MAPE compatibilizer at 500X magnification is shown in Figure 5(a). The results show the loose fibre ends sticking out of the surface of the TPNR matrix. The fibre surface is smooth and clean, and only a slight adhesion effect with the matrix. This indicates there was a lack of adhesion between the fibres and the matrix. Meanwhile, Figure 5(b) shows SEM micrographs of the fracture surface composite with the addition of MAPE. The micrograph shows the fibers being pulled-out from the matrix, where the surface of the fibres had been coated with a layer of the TPNR matrix. The fibres did not fracture but were pulled out of the matrix caused by matrix failure.

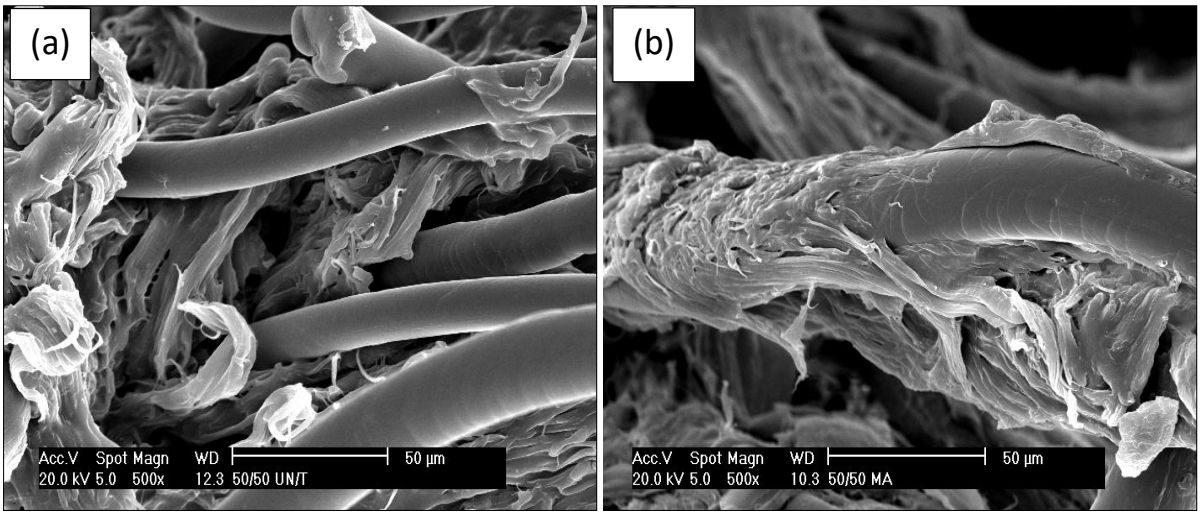

Figure 5. SEM micrographs TPNR-nylon fibres composites: (a) without MAPE and (b) with MAPE compatibilizer at 500x magnification

This showed that the micro-failure of the interface caused by the failure of the adhesion by the matrix was very close to the fiber and was not just debonding on the surface only. This result indicates that the interface adhesion was adequate, and it can be considered that the addition of MAPE was an effective way to promote better bonding between nylon fibers and the TPNR matrix. Therefore, increased the strength and stiffness of these composites. This may explain why the maximum stress of these composites was higher than that of composites without MAPE. It is already known that the mechanical properties are highly dependent on the composition of the composite as well as the interactions at the fiber and matrix interfaces.

Figure 6(a) and (b) shows the SEM micrograph of cross-section surface without and with the addition of MAPE after being immersed in the toluene for 24 hours. The samples were first cryofracture in liquid nitrogen prior to the immersion in the toluene. The dark voids in Figure 6(a) indicate traces of rubber droplets that have dissolved during the extraction process (shown with arrows). It can be seen that the thermoplastic forms a continuous phase and the rubber as a dispersed phase in this composites system. The voids around the fibers also indicate that the effect of the rubber was extracted out by toluene was poorly bonded to fibers.

Meanwhile, Figure 6(b) shows that the addition of MAPE caused the matrix to be even denser with small and homogenous distribution of rubber particles compared to Figure 6(a) and in turn helps better adhesion of matrix to the fibers. It can also be observed that the adhesions formed at the lower end of the fibers (after extraction with toluene) were well anchored to the TPNR matrix due to the presence of a compatibilizing agent. This observation was further confirmed by the increase in tensile strength and modulus of the composites, as discussed previously.

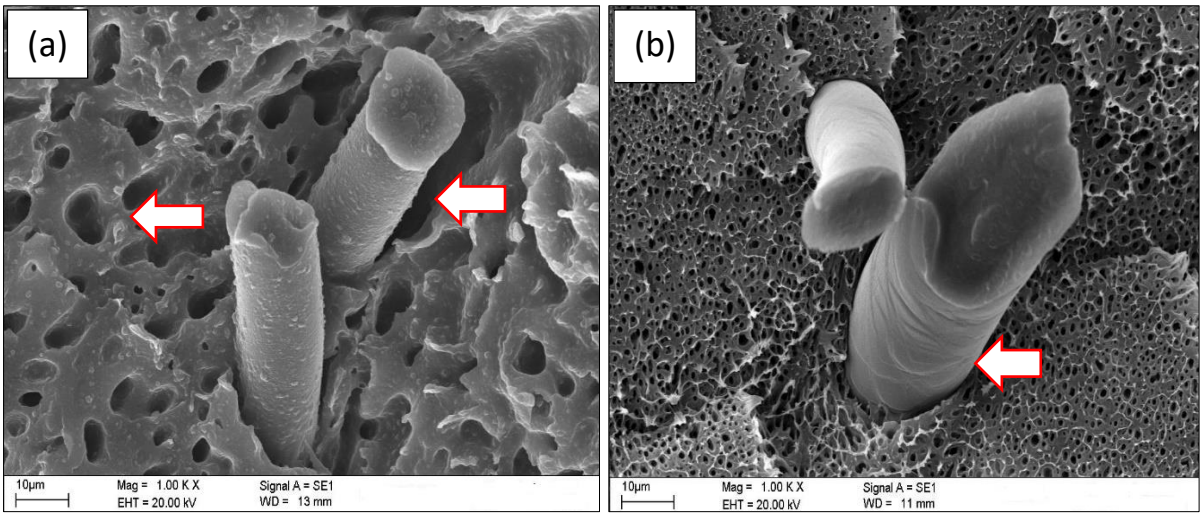

Figure 6. SEM micrographs of TPNR-nylon fibres composites after immersion in toluene (a) composite without the addition of MAPE and (b) with MAPE at 1000x magnification.

Conclusion

In conclusion, the polymer composites of TPNR reinforced with nylon (PA6) fibre was successfully prepared and investigated. It was found that the tensile strength and tensile modulus of the TPNR composites have increased with the increase of nylon fibre content from 5 to 20 vol.%. However, the tensile strain at break decreased with the incorporation of fibres. The result also shows that, the addition of compatibilizer (MAPE) increased the tensile modulus and tensile strength of the TPNR composites. Scanning electron micrograph results of the tensile fracture surfaces of TPNR composites indicated good adhesion between fibres and the matrix, thus contributing to increase in tensile strength of the composites.

Acknowledgments

The authors would like to thank Faculty of Applied Sciences, Universiti Teknologi MARA Malaysia, and Faculty of Science and Technology, Universiti Kebangsaan Malaysia for the research facilities and the assistance throughout this research.

Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

Not applicable

References

[1] Varaporn, T., Kesinee, K. & Pasaree, L. (2009). Polypropylene/natural rubber thermoplastic elastomer: Effect of phenolic resin as a vulcanizing agent on mechanical properties and morphology. *J. Appl. Polym. Sci*., 112 (6) 3177-3774.

[2] Safia, M., Farid, R. & Abdelmalek, D. (2012). The Physical Modification of a Natural Rubber-Polypropylene Thermoplastic Elastomer Blend by Azobisformamide Blowing Agent. ISRN Polym. Sci., 2012 1-6.

[3] Wickramaarachchi, W. V. W. H., Walpalage. S. & Egodage, S. M. (2019). Identification of the Best Blend Composition of Natural Rubber-High Density Polyethylene Blends for Roofing Applications. *Int. J. Chem. Eng*., 13 (4) 1-5.

[4] Zawawi, E. Z. E., Sahrim, A. & Rasid, R. (2012). Effect of Melt-Blending Conditions on the Properties of HDPE/NRBlends/Organoclay Nanocomposites. Adv Mat Res., l. 576 322-325.

[5] Sameni, J.K JK., Ahmad, S. H. & Zakaria, S. (2004). Effect of MAPE on the Mechanical Properties of Rubber Wood Fiber/Reinforced Thermoplastic Natural Rubber. *Adv. Polym. Technol*., 23 (1) 18-23

[6] Sahrim, A., Ibrahim, A., Che Som, S., Kohjiya, S. & Yoon, J.R. (1994). Natural rubber-HDPE blends with liquid natural rubber as a compatibilizer. I. Thermal and mechanical properties. *J. Appl. Polym. Sci*., 51 1357–1363.

[7] Ibrahim, A., Sahrim, H.A. & Che Som, S. (1995). Blending of natural rubber with linear low-density polyethylene. *J. Appl. Polym. Sci*., 58 1125–1133.

[8] Fabio, R., Passador, G. J. A. R. & Luiz, A. P. (2013). Thermoplastic Elastomers Based on Natural Rubber/Polypropylene Blends: Effect of Blend Ratios and Dynamic Vulcanization on Rheological, Thermal, Mechanical, and Morphological Properties, *Journal of Macromolecular Science, Part B*, 52(8) 1142-1157.

[9] Justyna, M., Marcin, M. & Krzysztof, S. (2019). Thermoplastic Elastomer Biocomposites Filled with Cereal Straw Fibers Obtained with Different Processing Methods-Preparation and Properties. *Polym*., 11 641, 1-15.

[10] Justyna, M., Marcin, M. & Krzysztof, S. (2020). Thermoplastic Elastomeric Composites Filled with Lignocellulose Bioadditives, Part 2: Flammability, Thermo-Oxidative Aging Resistance, Mechanical and Barrier Properties. *Mater.,* 13 1608, 1-15

[11] Ghanbari, A., Jalili, N. S., Haddadi, S. A., Arjmand, M. & Nofar, M. (2020). Mechanical Properties of Extruded Glass Fiber Reinforced Thermoplastic Polyolefin Composites. *Polym. Compos*., 41 (9) 3748–3757.

[12] Fazli, A. & Rodrigue, D. (2021). Phase Morphology, Mechanical, and Thermal Properties of Fiber-Reinforced Thermoplastic Elastomer: Effects of Blend Composition and Compatibilization. *J. Reinf. Plast. Compos*., 07316844211051749.

[13] Drobny, G. (2014). *Handbook of Thermoplastic Elastomers.* Second edition (Elsevier) pp. 301-337.

[14] Abderrahmane, B., Samia, B. & Farid, R. (2020). Compatibilization of Natural Rubber–Polypropylene Thermoplastic Elastomer Blend. *J. Elastomers Plast.*, 52(8) 728–746.

[15] Harekrishna, P., Paradesiparampil, R. Sreenath & Dinesh, K. K. (2020). Unique Compatibilized Thermoplastic Elastomer with High Strength and Remarkable Ductility: Effect of Multiple Point Interactions within a Rubber-Plastic Blend. *ACS Omega*, 5 (22) 12789-12808.

[16] Wang, Y, Cheng, L. Cui, X & Guo, W. (2019). Crystallization Behavior and Properties of Glass Fiber Reinforced Polypropylene Composites. *Polym.*, 11(1198) 1-17.