Microstructure-Properties of Dynamically Vulcanized Mengkuang Leaf Fibre/Ethylene Vinyl Acetate/Natural Rubber Thermoplastic Elastomer Composites

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Thermoplastic elastomer composites based on ethylene vinyl acetate (EVA), natural rubber (NR), and Mengkuang leaf fibre were prepared using the sulfur and peroxide vulcanization systems. Different curing systems and fibre loadings affecting the processing torque, tensile, thermal, and morphology of the composites were investigated. Addition of Mengkuang leaf fibre resulted in poor fibre dispersion and agglomeration in the matrix, which may have affected the efficiency of stress transfer and thus could explain a decline in tensile and thermal properties. Composites with dynamic vulcanization showed a rougher surface that might be due to the presence of crosslinking, which requires more force to fail. The increase in stabilization torque for the composites with dynamic vulcanization was observed due to the addition of curing agents, which implies some changes at the molecular level due to crosslinking. Tensile properties of Mengkuang leaf fibre filled EVA/NR composites indicated that the tensile strength, elongation at break, and Young's modulus of the peroxide cure system were higher than the sulfur cure system and unvulcanised composites. The sulphur cure system showed better resistance towards thermal degradation compared to the peroxide cure system. This was attributed to dicumyl peroxide (DCP), which degrades the polymer chain or the composites at high temperature.

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Keywords: Format; Mengkuang leaf fibre; Ethylene vinyl acetate; Natural rubber; Thermoplastic elastomer composites; Thermoplastic vulcanizates

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INTRODUCTION

The world's supply of natural resources is dwindling, while demand for sustainable and renewable raw materials is increasing. The incorporation of bioresources into today's materials, products, and processes of today can address environmental concerns while also reducing reliance on petroleum reserves. Bio-fibre reinforced polymer composites represent a potential and value-added source that could eventually replace petroleum-based composites in several applications. In fibre-reinforced polymer composites, the fibre serves as reinforcement by giving strength and stiffness to the structure while the polymer acts as a matrix to hold the fibre. Natural fibre have a number advantages over synthetic materials, including being less abrasive to the processing equipment, renewable, low density, and environmentally friendly (Pang *et al.* 2016; Surya *et al.* 2019). Among several existing natural fibres, Mengkuang leaf fibre has been selected as a reinforcement in the matrix. Mengkuang is a member of the Pandanaceous family, growing in mangrove swamps and jungles (Hashim *et al.* 2016). Mengkuang leaf fibre has been introduced into the composites as a filler to enhance their processability and mechanical properties, as well as to reduce material costs (Hashim *et al.* 2016; Abdullah and Aslan 2019). Sheltami *et al.* (2012) reported that Mengkuang leaf fibre consists of 37.3% cellulose, 34.4% hemicellulose, 15.7% pentosans, 24.0% lignin, and 2.5% extractives. After bleaching treatment, the contents of cellulose, hemicellulose, pentosans, and lignin after were 81.6%, 15.9%, 12.5%, and 0.8%, respectively. Research by Piah *et al.* (2016) using Fourier transform-infrared (FTIR) revealed that Mengkuang leaf fibre contained the same functional groups as found in natural fibres such as kenaf, jute, and flax, thus indicating its high potential as the reinforcement fibre in polymer composites.

Thermoplastic vulcanizates (TPVs) are a special type of thermoplastic elastomers (TPEs) prepared by dynamic vulcanization (DV), a dynamically cured reactive polymer blending technique. During blending, the elastic phase is dynamically crosslinked in the presence of a suitable curing agent to reduce the interfacial tension between two phases and also enhance the overall mechanical properties of TPV (Ning *et al.* 2018). Sulfur and peroxides are the most used curing agents in the fabrication of TPV. Through this process, the TPVs combine the good melt processability and recyclability of thermoplastics with the good elasticity and mechanical properties of the cross linked rubbers (Wu *et al.* 2016; Lopattananon *et al.* 2018). Therefore, TPVs have attracted considerable attention in recent years and have been widely used in industries such as automotive, building, and electronics. The earliest and most popular curing method for cross-linking of unsaturated rubbers is sulfur vulcanization. Different types of sulfidic cross-links, such as monososulfidic C-S-C, disulfidic $C-S_2-C$ and polysulfidic cross-links $C-S_x-C$, are formed between rubber chain segments during sulfur vulcanization (Kruželák *et al.* 2020). Peroxides, on the other hand can be used to vulcanize both unsaturated and saturated rubbers (Zhang *et al.* 2019). Crosslinking of elastomers with organic peroxides involves the action of free radicals. The process results in the formation of carbon-carbon bonds between macromolecular chains. Due to the strong thermal stability of C-C bonds, which is their main advantage, peroxide cured vulcanizates exhibit high-temperature ageing resistance and low compression set at elevated temperatures (Naebpetch *et al.* 2016).

TPV based on ethylene vinyl acetate (EVA) and natural rubber (NR) is a potential material since the NR phase provides excellent abrasion, tear, and fatigue resistance and the EVA phase guarantees good mechanical properties as well as excellent ozone and oxygen (Hashim *et al.* 2017). With the incorporation of Mengkuang leaf fibre, the distribution of the filler and degree of adhesion to the matrix are among the determining parameters that control the interfacial adhesion between the two phases and consequently the development of microstructure of TPVs. In recent years, several studies have been conducted in the field of multicomponent polymer systems on fibre addition, such as in TPVs systems. Goharpey *et al.* (2009) prepared polypropylene/ethylene propylene diene (PP/EPDM) TPVs reinforced by cellulose and found that incorporation of 5% and 10% of the fibres enhanced the properties of TPVs. This could be explained in terms of enhancement of three-dimensional networks formed between cured rubber particles through the interlinking between EPDM coated flexible fibres and PP chain segment. Meanwhile, Cao *et al.* (2020) correlated the microstructure and properties of polylactic acid/epoxidized natural rubber (PLA/ENR) TPVs reinforced with cellulose nanocrystal (CNC). They reported that CNC played a role in the reinforcement of the rubber phase and heterogeneous nucleating agents for the PLA phase, which enhanced the crosslinked rubber network and improved the crystallinity of the PLA phase, thus improving the tensile strength, Young's modulus, and dynamic storage modules of TPVs.

In this study, a series of EVA/NR/ Mengkuang leaf fibre TPVs that were cross-linked with peroxide or sulfur was prepared. The effect on different Mengkuang leaf fibre loadings and different curing systems on the mechanical and thermal properties of these TPVs properties was evaluated. In addition, the distribution of Mengkuang leaf fibre was followed by means of scanning electron microscopy (SEM) and processing torque curves.

EXPERIMENTAL

Materials

Ethylene vinyl acetate (EVA) in pellet form (commercial-grade H2020) was purchased from the Polyolefin Company, Singapore. The density of the EVA is 0.93 g/cm^3, with the melt flow index value of 1.5 g/10 min, and it contains 15% vinyl acetate. The natural rubber used was SMR L, obtained locally, and adhering to specification mandated by the Malaysian Rubber Board. Mengkuang leaves were obtained locally in Pulau Pinang, Malaysia. These leaves were dried under the sun for 4 to 5 days. Then, the leaves were ground into powder using a grinder, and sieved through a 250 µm pore size Endecotts sieve and kept in an oven overnight at 105 °C to remove moisture. Dicumyl peroxide (DCP), sulfur, stearic acid, tetramethylthiuram disulfide (TMTD), and dibenzothiazole disulfide were supplied by Bayer (M) Sdn Bhd, Malaysia.

Preparation of EVA/NR/ Mengkuang Leaf Fibre TPVs composites

The EVA/NR/ Mengkuang leaf fibre composites were prepared by melt mixing in a Haake Rheomix Polydrive R 600/610 at 120 °C with the rotor speed of 50 rpm over a constant mixing time of 10 min. The blend ratio of NR and EVA was fixed at 50:50 (Ismail *et al.* 2008; Hashim *et al.* 2016). The formulations of the composites are given in Tables 1 and 2. Mengkuang leaf fibre was varied from 0 phr (parts by weight per hundred parts of resin) to 40 phr. EVA was charged first to start the melt mixing. After 2 min, NR was added, followed by Mengkuang leaf fibre on the 4th min. Mixing was continued for another 6 min. For the peroxide cross-linking system, DCP curative was added at the 6th min, and mixing was continued. For the sulfur system, Mengkuang leaf fibre was added into the mixing chamber together with zinc oxide and stearic acid. Sulfur, dibenzothiazole disulfide, and TMTD were added after 6 min. Mixing was then continued until a constant torque was obtained. Mixing torque values were recorded during the mixing process in order to establish the potential chemical or physical response from the EVA, the NR, and the Mengkuang leaf fibre, based on the viscosity developed during the blending operation. The compounds were then compression-moulded using an electrically heated hydraulic press to obtain 1 mm composite sheets. Compression moulding was carried out at 120 °C involving 6 min of preheating followed by compressing for 4 min and subsequent cooling under pressure for 2 min. Dumbbell- shaped samples were then punched out using a Wallace die cutter from the 1-mm moulded composite sheets.

Table 1. The Formulation of EVA/NR/ Mengkuang Leaf Fibre Thermoplastic Elastomer Composites without Dynamic Vulcanization

Composition	Parts per hundred part of resin (phr)				
	1	2	3	4	5
NR	50	50	50	50	50
EVA	50	50	50	50	50
Mengkuang Leaf Fibre	0	10	20	30	40

Table 2. The Formulation of EVA/NR/ Mengkuang Leaf Fibre Thermoplastic Elastomer Composites with Dynamic Vulcanization

Composition	Parts per hundred part of resin (phr)									
	1	2	3	4	5	6	7	8	9	10
NR	50	50	50	50	50	50	50	50	50	50
EVA	50	50	50	50	50	50	50	50	50	50
Mengkuang Leaf Fibre	0	10	20	30	40	0	10	20	30	40
Sulfur	1.5	1.5	1.5	1.5	1.5	-	--	-	-	-
Zinc Oxide	1.0	1.0	1.0	1.0	1.0	-	--	-	-	-
TMTD	0.5	0.5	0.5	0.5	0.5	-	--	-	-	-
CBS	0.4	0.4	0.4	0.4	0.4	-	--	-	-	-
Stearic Acid	0.4	0.4	0.4	0.4	0.4	-	--	-	-	-
DCP	-	-	-	-	-	1.5	1.5	1.5	1.5	1.5

Tensile Properties

Tensile tests were carried out using an Instron 3366 universal testing machine (Instron Corporation, Norwood, MA, USA), according to ASTM D412 (2016), with a crosshead speed of 50 mm/min. Compression sheets obtained were cut into dumbbell shapes using a Wallace Die Cutter (H.W. Wallace & Co., Ltd., Surrey, UK). At least five specimens were tested for each formulation, and mean values and standard deviations for tensile strength, elongation at break, and modulus at 100% elongation (M100) are reported

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin-Elmer Spectrum One Series Instrument (Perkin Elmer System 2000; PerkinElmer Inc., Waltham, MA, USA). The samples were scanned 32 times over a 4000 to 400 cm^{-1} wavenumber range at a resolution of 4 cm^{-1}. The FTIR spectra were recorded in transmittance mode.

Morphological Study

The morphologies were studied using Field Emission Scanning Electron Microscope ((Zeiss Supra-35VP; Carl Zeiss AG, Oberkochen, Germany). Prior to SEM examination, the tensile fractured surface of each sample was mounted on aluminium stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging in order to obtain information on filler dispersion, filler-matrix interaction, and the mode of failure.

RESULTS AND DISCUSSION

Processing Torque

Figures 1 and 2 show the processing torque value for EVA/NR/Mengkuang leaf fibre composites that have been cross-linked using sulphur and peroxide system, respectively. From Figs. 1 and 2 it is clear that when EVA was introduced into the mixing chamber, the torque increased at first. For the unvulcanized blend, when the material reached the desired temperature and melted, the torque decreased until it reached an almost constant value at the end of the process, indicating a good level of mixing. However, after the curing agent was incorporated at 6 min, a significant increase in torque with mixing time was observed for the blends containing cross-linking agents, owing to the fact that the crosslinked matrix exerts increased resistance to the rotation of the rotor in the mixing chamber, which in turn results in increased torque value (Alias *et al.* 2020). The increase in torque is a direct function to the degree of curing that occurred, and the presence of a curing agent indicates that certain changes in the molecular level were caused by the curing agent (Ismail *et al.* 2014). When compared to EVA/NR blends cured with sulfur, the blends and composites prepared with DCP cross-linking agent possessed higher torque values. Such findings suggested that in the presence of peroxide, higher degree of crosslinking is achieved than in the presence of sulfur.

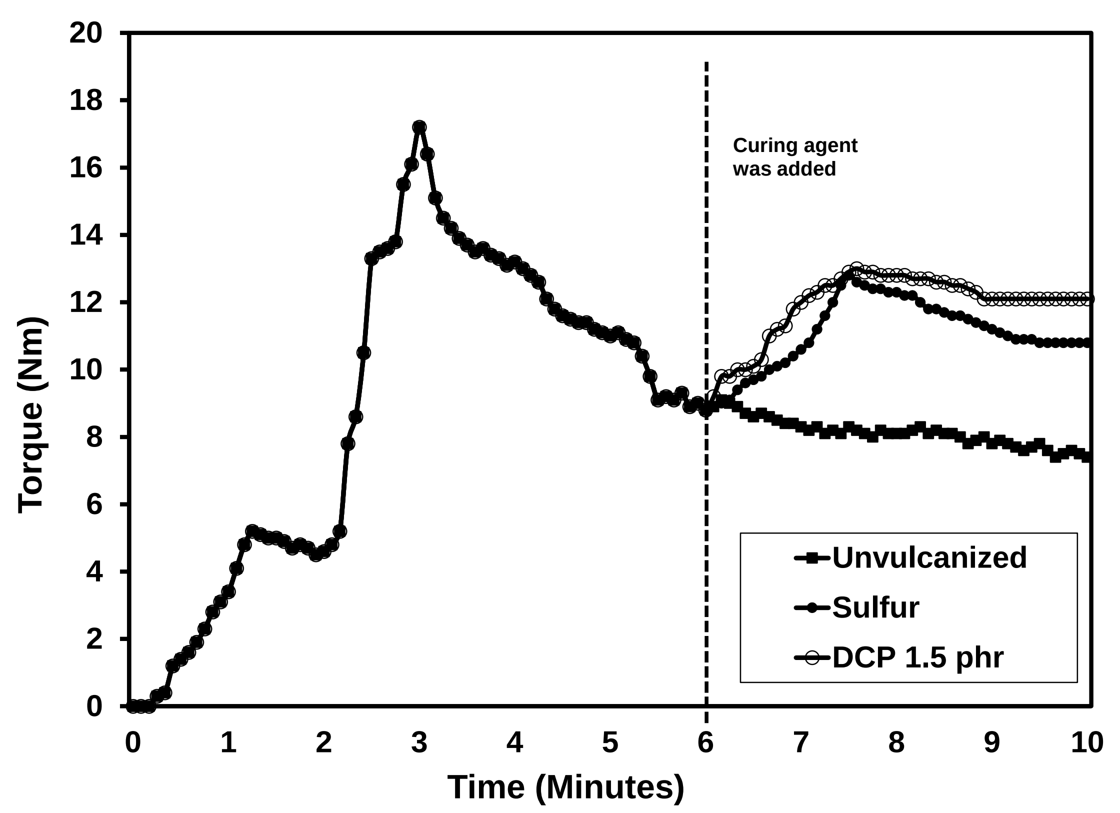

Fig. 1. Torque-time plot of unvulcanised and vulcanised EVA/NR blends of various vulcanisation system

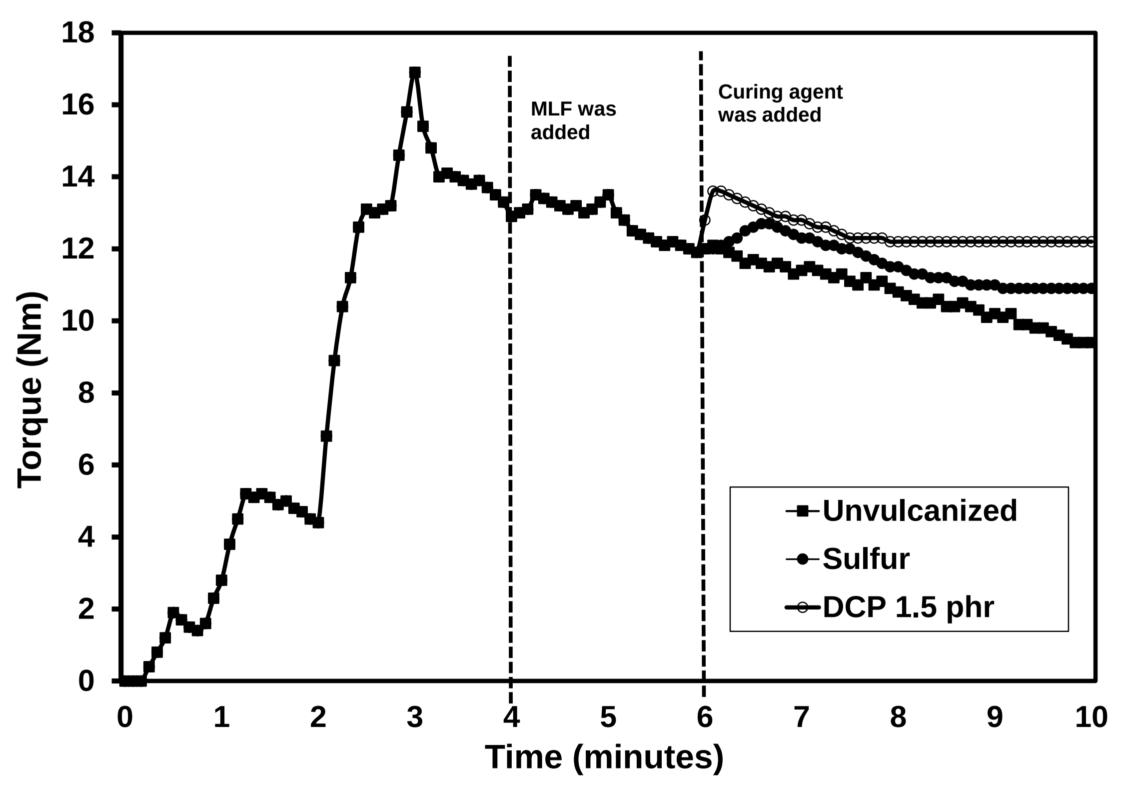

Fig. 2. Torque-time plot of unvulcanised and vulcanised EVA/NR/ Mengkuang leaf fibre composites of various vulcanisation system at 10 phr Mengkuang leaf fibre loading

The final torque values or stabilization torques of sulphur and peroxide crosslinked EVA/NR/ Mengkuang leaf fibre TPE composites, in comparison with the final torque values for unvulcanised TPE composites are presented in Fig. 3. The stabilization torque showed that the torque value increased with an increase in Mengkuang leaf fibre loadings. The increase in torque value can be attributed to the inclusion of Mengkuang leaf fibre, which is stiffer than the matrix and increases the viscosity of the composites. Dynamic vulcanization composites indicated higher stabilization torques than unvulcanised composites. The highest final torque values were obtained in DCP crosslinked TPEs. In sulfur vulcanizing system, only the elastomer phase will be crosslinked, and the viscosity of this phase will increase (Shi *et al.* 2019). The unvulcanised continuous thermoplastic phase will preserve the ease of processing of the thermoplastic elastomer. The same phenomenon occurs in EVA/NR/Mengkuang leaf fibre composites where only the dispersed NR phase was crosslinked, while the continuous EVA phase preserved the ease of processing. However, in DCP vulcanizing system, both the NR and EVA phases were crosslinked due to the ability of peroxide to crosslink both elastomers and thermoplastic phase (Shi *et al.* 2019). The proposed chemical interaction that occurred during the vulcanization process *via* DCP crosslinking can be referred to in Fig. 4. Consequently, the final torque values for the DCP curing system are higher than the sulphur system. The differences in stabilization torque are more pronounced with different vulcanization systems than with different amounts of Mengkuang leaf fibre, especially at high filler loading.

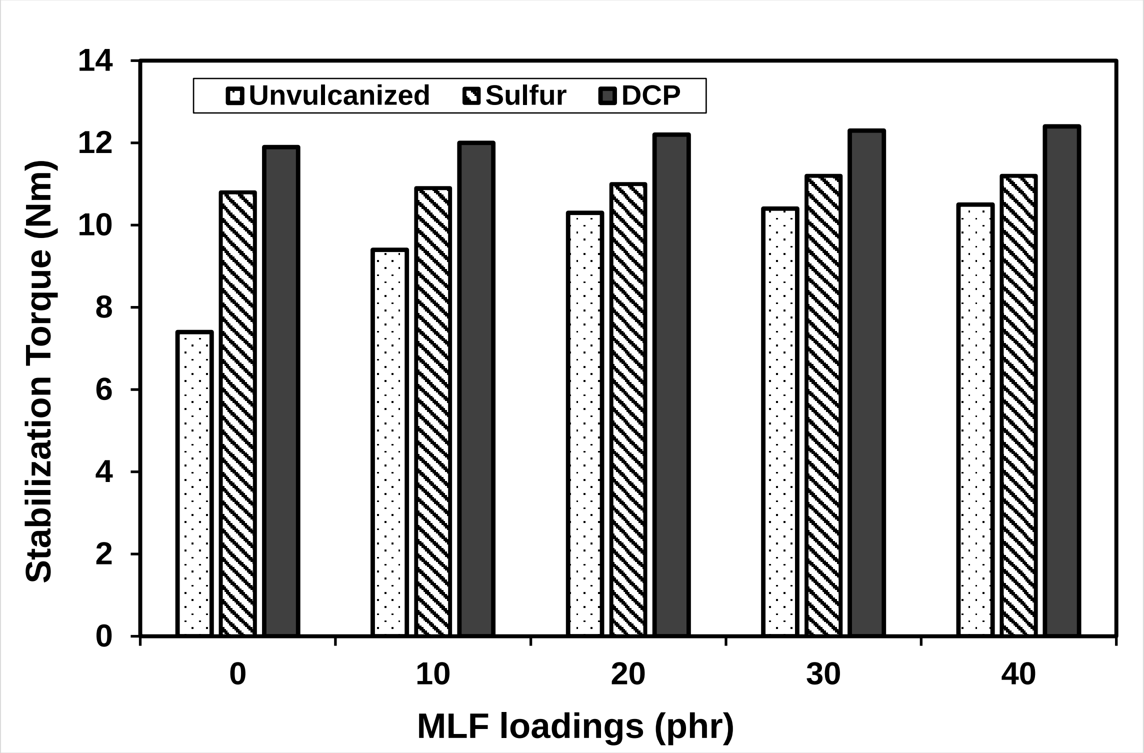

Fig. 3. Stabilisation torque of unvulcanised and vulcanised EVA/NR/ Mengkuang leaf fibre composite of different vulcanizing systems and Mengkuang leaf fibre loadings

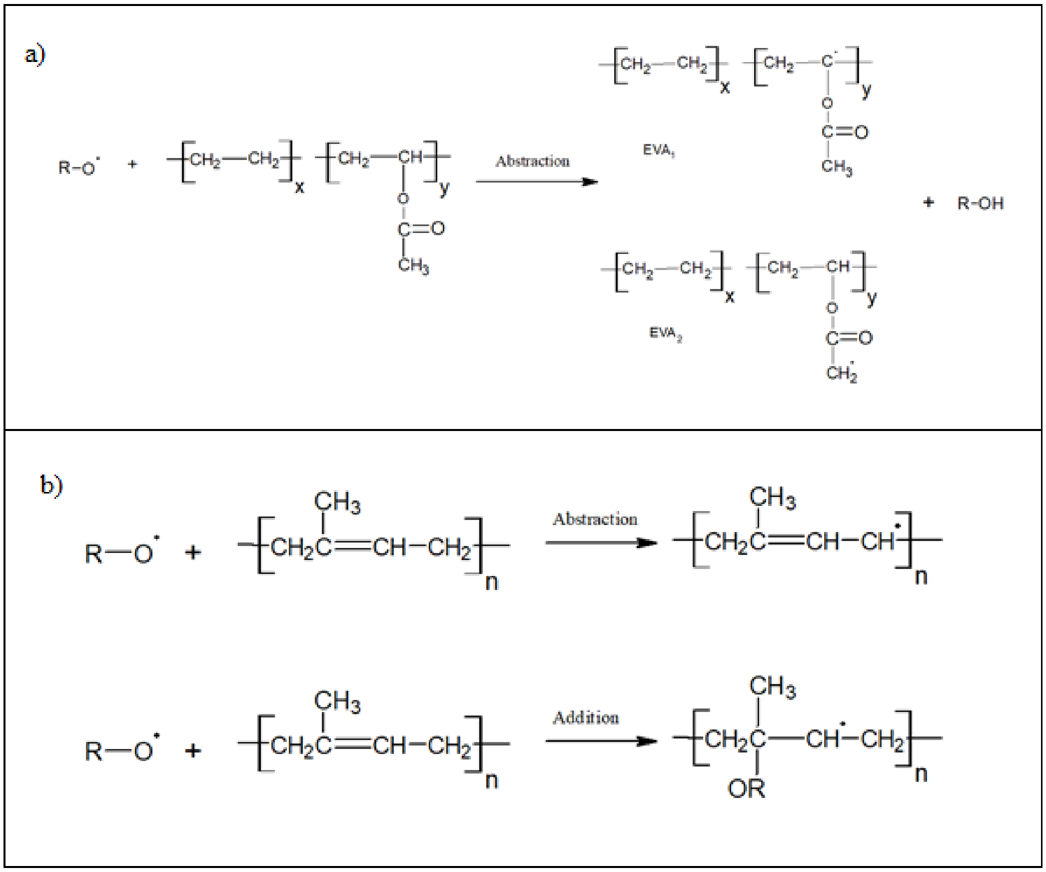

Fig. 4. Propagation reaction in the a) EVA phase and b) NR phase *via* DCP crosslinking

Fourier Transform Infrared (FTIR) Analysis

FTIR tests were carried out on unvulcanised EVA/NR blend and compared with their vulcanized counterparts (Fig. 5). The unvulcanised EVA/NR blend showed all the characteristics of pure EVA and pure NR. The characteristic peaks at 2922 and 2854 cm^{-1} in the spectra of EVA/NR blends were attributed to the asymmetric and symmetric vibrations, respectively, of aliphatic groups (-CH$_2$) of EVA. Strong peaks at 1740, 1242, and 1023 cm^{-1} correspond to the vibrations of vinyl acetate groups in EVA. Meanwhile, two distinguishing peaks were noticeable at 1452 cm^{-1} and 1372 cm^{-1}, indicating the CH stretching for the NR component in the blends. All of the observed peaks were in agreement with other works in the literature (Dikobe and Luyt 2009; Sefadi and Luyt 2012; Silviya *et al.* 2012). For vulcanized blends, two distinguished peaks at 2920 and 2853 cm^{-1} corresponded to the C-H asymmetry and symmetry stretching vibrations of CH$_2$ groups. This in agreement with those reported by Gunasekaran *et al.* (2007), and Kim *et al.* (2001) for the system of NR and poly(butylene terephthalate)and ethylene/vinyl acetate copolymer (PBT/EVA) blends, respectively. These peaks were found to be a strong intensity in vulcanized blends due to the presence of crosslinking.

Vulcanized blends with sulfur show the increasing the intensity of the peak at 1021 cm^{-1}, which was mainly attributed to the symmetry C-S-C group stretching vibrations in the C-S bonds. The peak shift could be attributed to the establishing of the crosslinking between the chains after the sulfur breaks the double bonds and forms sulfur atom bridge during vulcanization process (Gunasekaran *et al.* 2007). Meanwhile, for the DCP vulcanized blend, the presence peak at 964 cm^{-1} for EVA/NR (DCP) blend corresponds to the out-plane deformation (=C-H) due to the addition of radical on the double bond. This proves the propagation reaction mechanism by DCP in EVA/NR blend.

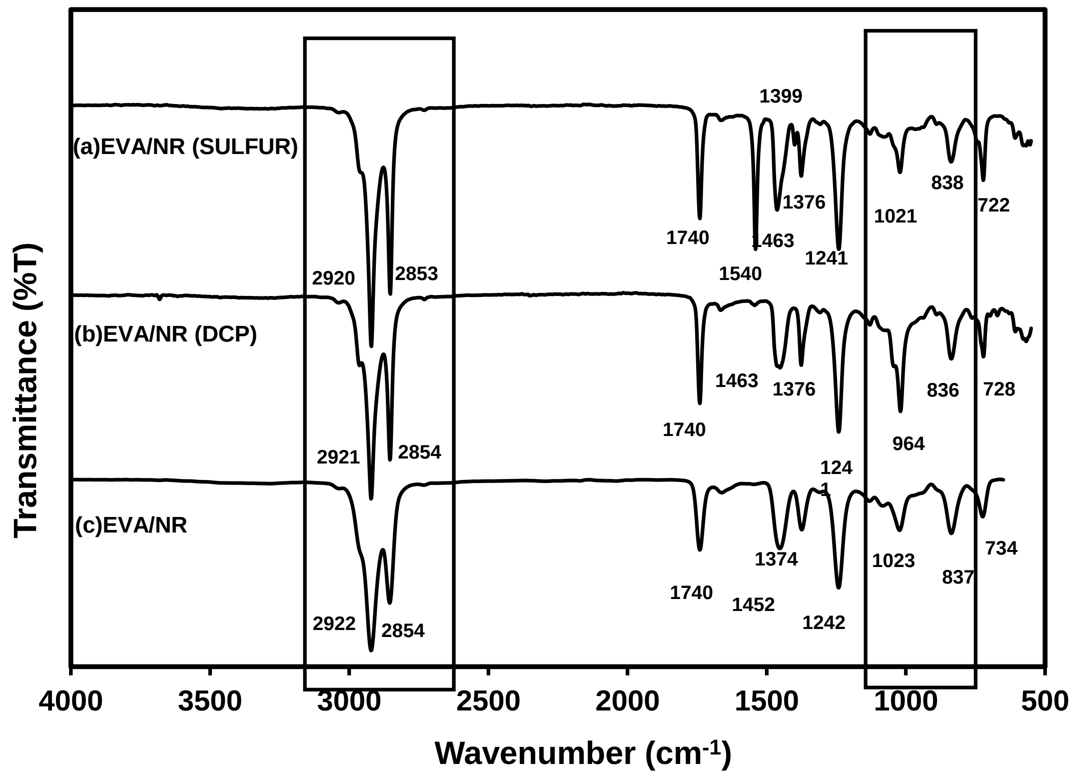

Fig. 5. FTIR spectra of EVA/NR blend at different vulcanisation system

Tensile Properties

The comparison of tensile strength, elongation at break and tensile modulus (M100) of various Mengkuang leaf fibre loadings in unvulcanised and vulcanized EVA/NR/ Mengkuang leaf fibre composite are shown in Figs. 6 to 8. As Mengkuang leaf fibre loadings increased, the tensile strength was found to decrease, as clearly shown in Fig. 6. This was due to the poor interfacial adhesion that lowers the ability of Mengkuang leaf fibre to support stress transfer from the EVA/NR matrix phase (Hashim *et al.* 2020). The effective stress transfer between the matrix and the fibre determines the tensile properties of the composites (Hayeemasae and Ismail 2021). The tensile strength of the vulcanised composites was improved after the addition of curative agents. When comparing DCP vulcanizates to sulphur vulcanizates, the increase was much more pronounced. This could be due to the higher crosslink density in DCP vulcanizates, as well as DCP's ability to induce cross-linking reactions in EVA. S-S and C-S linkages are formed in the sulphur curing system, whereas C-C linkages are formed in the DCP curing system (Nakason *et al.* 2006). Therefore, DCP influenced the crosslinking action both in NR and EVA phases while in the sulphur curing system, and the crosslinking reaction only occurred at the double bond in the NR phase only.

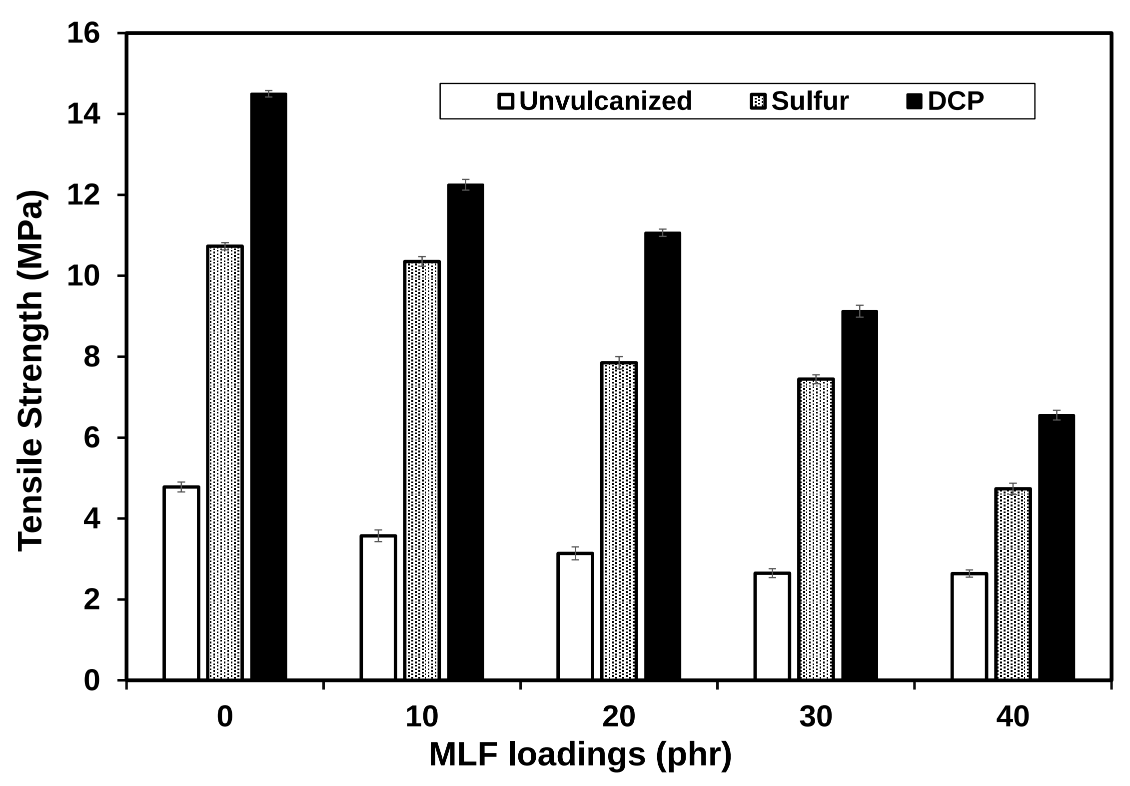

Fig. 6. Variation of tensile strength of unvulcanised and vulcanized EVA/NR/ Mengkuang Leaf Fibre thermoplastic elastomer composites with various Mengkuang Leaf Fibre loadings and different vulcanisation systems

Elongation at break of various Mengkuang leaf fibre loadings in unvulcanised and vulcanised EVA/NR/Mengkuang leaf fibre composite are shown in Fig. 7. The elongation of EVA/NR/ Mengkuang leaf fibre composites decreased with the increase in Mengkuang leaf fibre loadings. This phenomenon can be attributed to the agglomeration of Mengkuang leaf fibre as loading increased. For vulcanised composites, the result indicates that the sulfur curing system showed slightly higher elongation at break compared to the peroxide curing system. This was due to the vulcanizates with sulphur curing system that consist of more flexible C-S and S-S linkages, which provide higher extensibility compared to peroxide curing system (Nakason *et al.* 2011). Moreover, the cross-linked structure of the EVA gave more rigidity to the peroxide cured vulcanizates. Thus, DCP vulcanizates show lower flexibility as compared to sulphur vulcanizates.

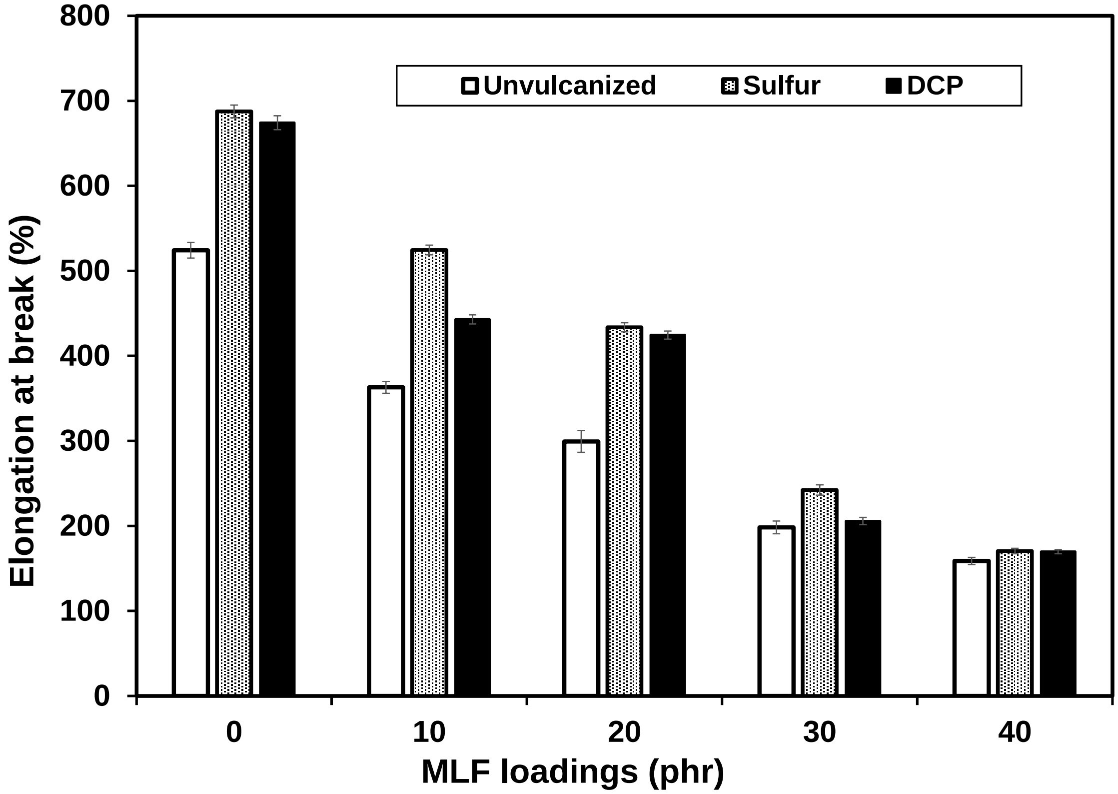

Fig. 7. Variation of elongation at break of unvulcanised and vulcanized EVA/NR/ Mengkuang leaf fibre thermoplastic elastomer composites with various Mengkuang leaf fibre loadings and different vulcanisation systems

Variation of the tensile modulus (M100) as a function of Mengkuang leaf fibre loadings and different crosslinking systems is shown in Fig. 8. The results indicated that M100 increased for all unvulcanised and vulcanized composites with increasing Mengkuang leaf fibre loading. This is due to the stiffening effect of the Mengkuang leaf fibre.

The presence of the rigid particles in the soft matrix gives the demobilizing effect on the matrix chain and thus improves the stiffness of the composites (Zaaba *et al.* 2016). M100 values are higher for composites vulcanized by the DCP compared to the sulphur system due to the presence of crosslinked in both phases in the former, which produce stiffer composites.

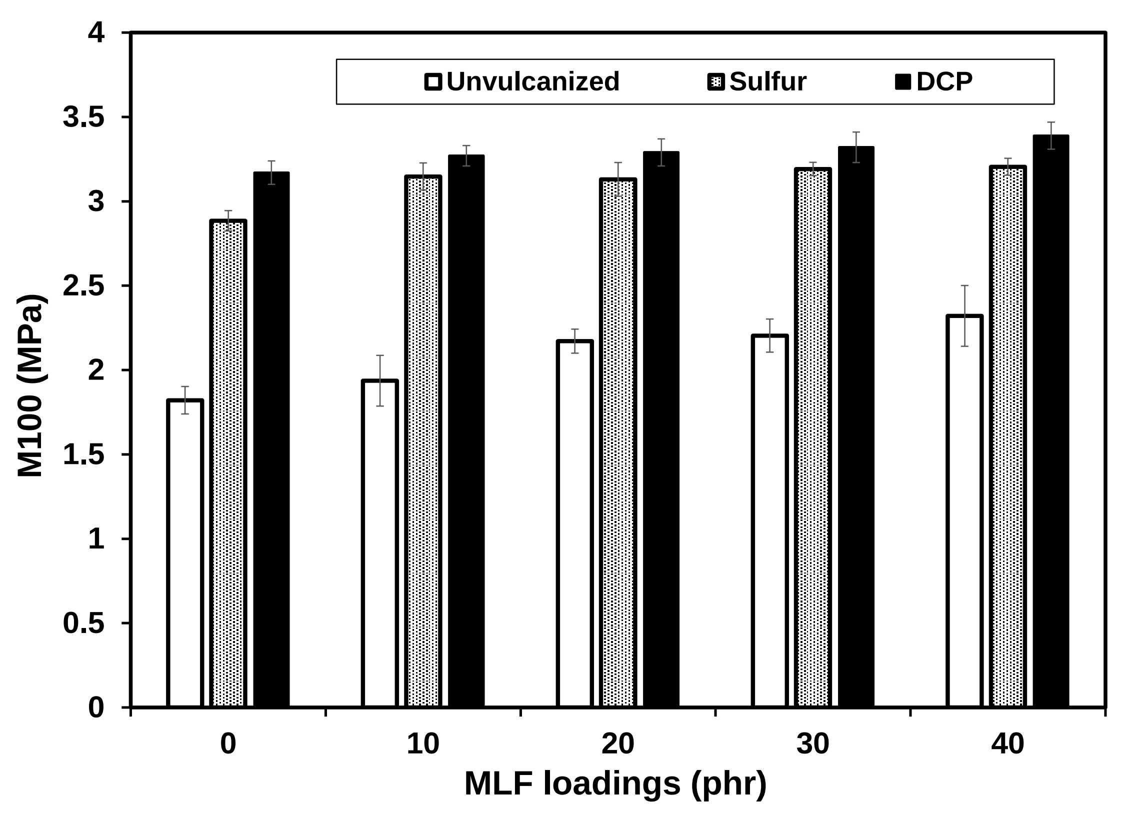

Fig. 8. Variation of tensile modulus of unvulcanised and vulcanized EVA/NR/ Mengkuang Leaf Fibre thermoplastic elastomer composites with various Mengkuang Leaf Fibre loadings and different vulcanisation systems

Thermogravimetric Analysis

Figures 9 and 10 show the thermograms (TGA) and differential thermogravimetry (DTG) of unvulcanised and vulcanised EVA/NR blends with different vulcanizing systems, respectively. The effect of incorporation of Mengkuang leaf fibre on the degradation of EVA/NR/Mengkuang leaf fibre composites with various vulcanizing systems are depicted in Figs. 11 and 12, respectively. The results show that a similar degradation pattern even with different vulcanization systems in EVA/NR blends and EVA/NR/Mengkuang leaf fibre composites, suggesting a similar degradation mechanism.

Table 3 summarizes the effect of Mengkuang leaf fibre loadings and various vulcanizing systems on the decomposition temperatures at various weight losses (10%, 30%, and 50% weight losses) for the EVA/NR blend and the EVA/NR/ Mengkuang leaf fibre composites. Increasing the Mengkuang leaf fibre loading generally decreased the thermal stability of the EVA/NR blend and the EVA/NR/Mengkuang leaf fibre composites for both unvulcanised and vulcanized system. This is simply due to the lower thermal stability of Mengkuang leaf fibre, as lignocellulose materials have lower thermal stability than thermoplastics. For vulcanised composites, it was found that at the early stages of decomposition (30 to 450 °C), peroxide vulcanizates showed a slightly higher decomposition temperature compared to sulfur vulcanising system and unvulcanised system, respectively.

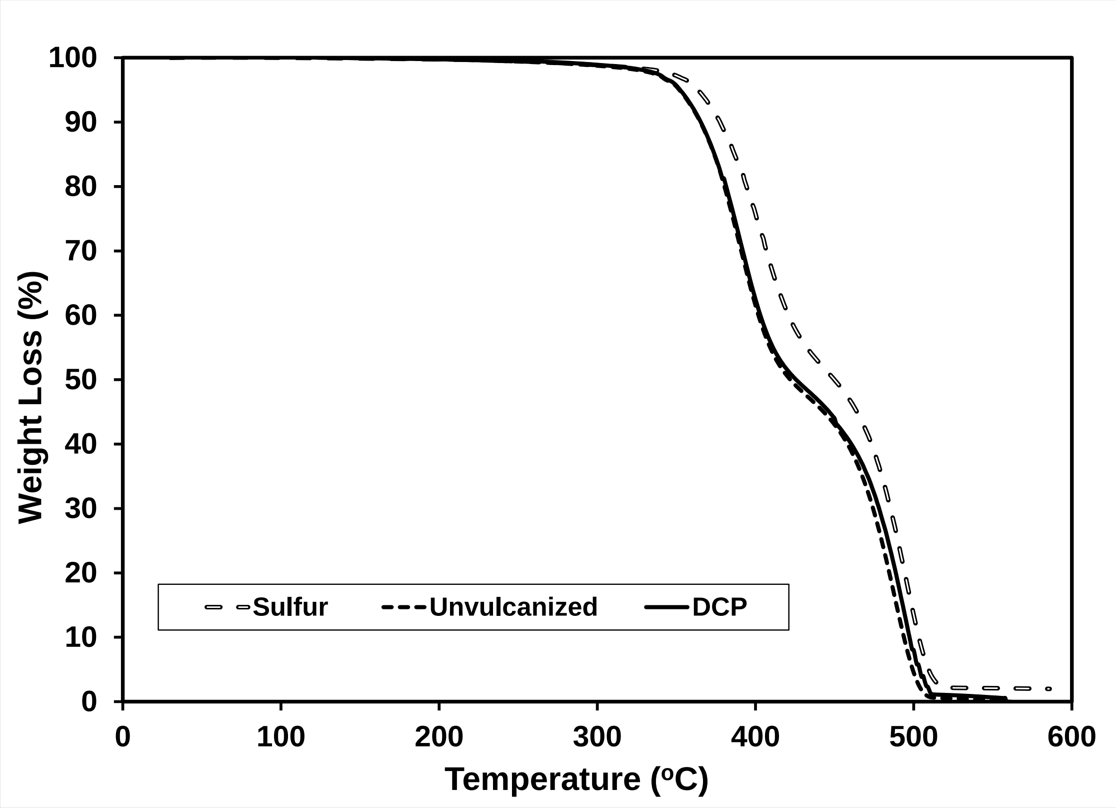

Fig. 9. Weight loss as a function of temperature (TGA curves) of unvulcanised and vulcanised EVA/NR blends of various vulcanization system

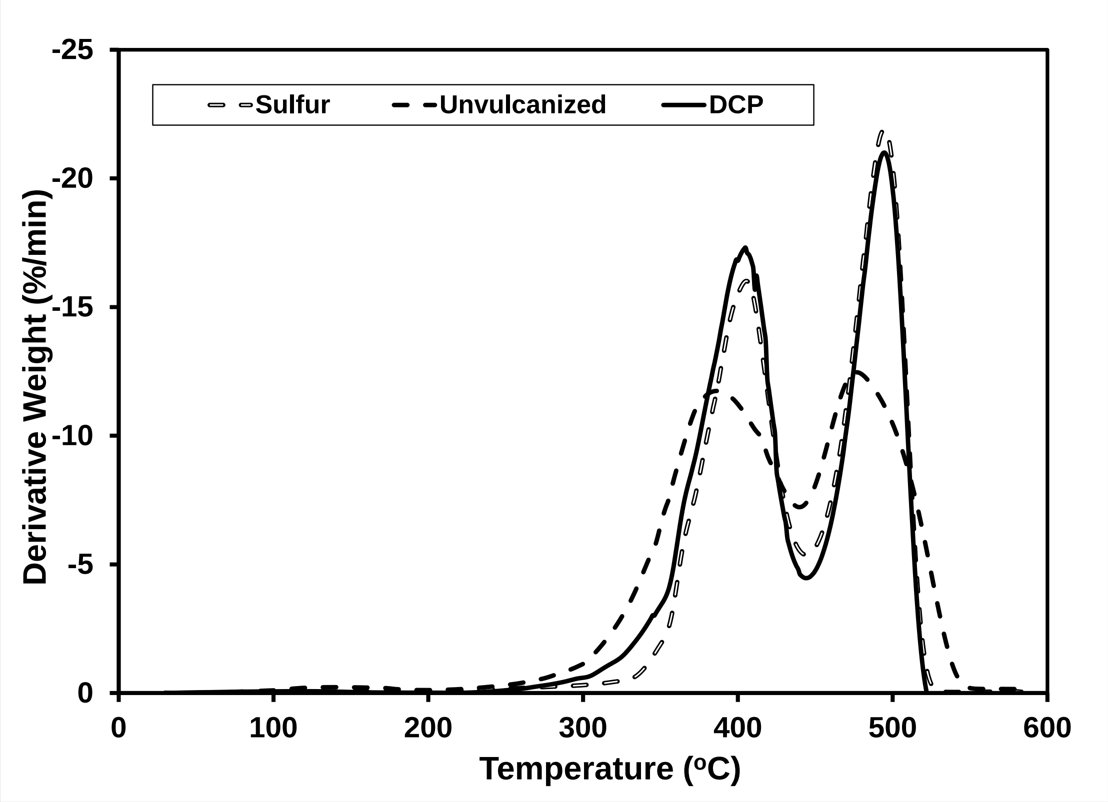

Fig. 10. Decomposition temperature at various weight losses of unvulcanised and vulcanised EVA/NR blends of various vulcanization system

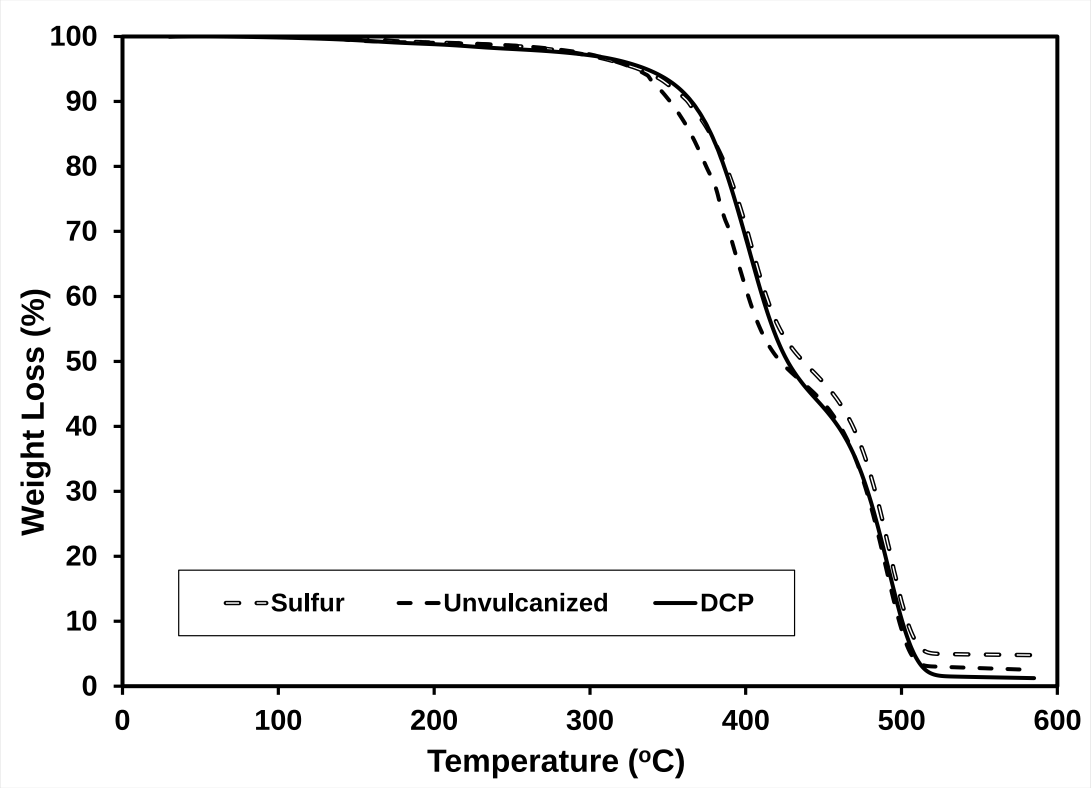

Fig. 11. Weight loss as a function of temperature (TGA curves) of unvulcanised and vulcanised EVA/NR/ Mengkuang leaf fibre composites at 10 phr loadings of various vulcanisation system

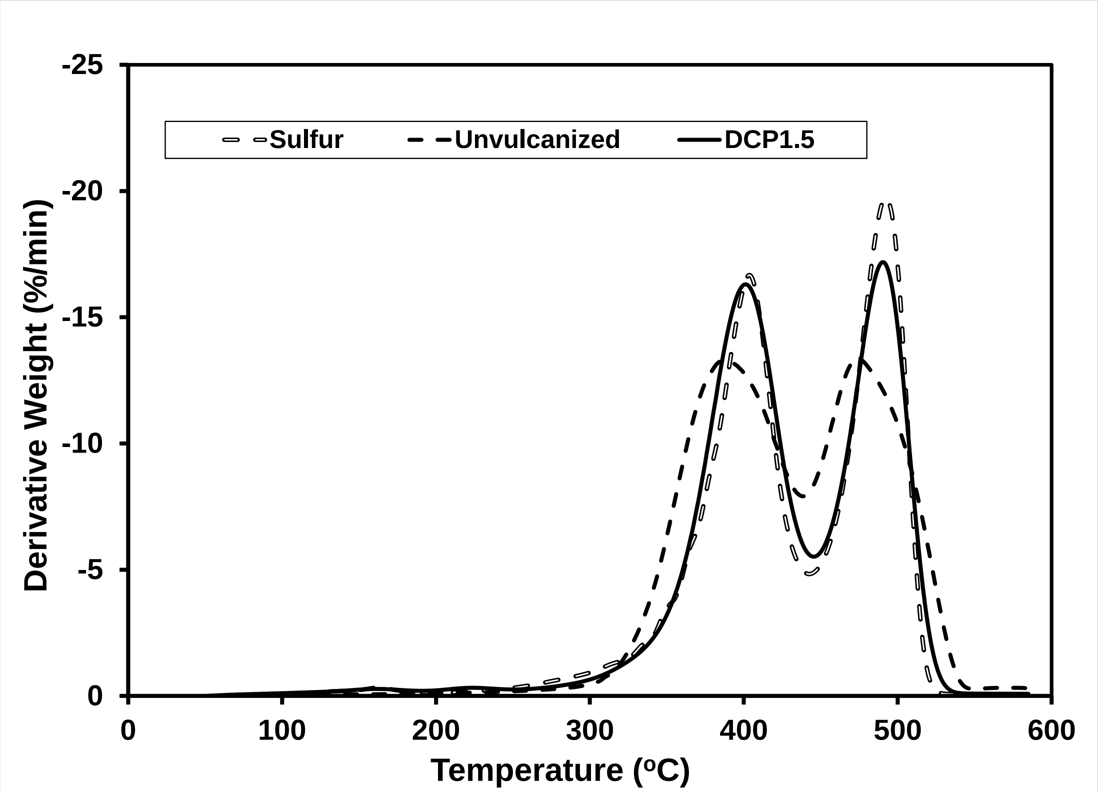

Fig. 12. Decomposition temperature at various weight losses of unvulcanised and vulcanised EVA/NR composites at 10 phr loadings of various vulcanisation system

Table 3. Decomposition Temperature at Various Weight Losses of Unvulcanised and Vulcanized EVA/NR/ Mengkuang Leaf Fibre Thermoplastic Elastomer Composites with Various Mengkuang Leaf Fibre Loadings and Different Vulcanisation Systems

Sample	**Degradation Temperature (ºC)**			**Char residue (%)**
	T_{10} (ºC)	**T_{30} (ºC)**	**T_{50} (ºC)**	
EVA/NR/MLF (0 phr)-Unvulcanized	**365**	**390**	**422**	**0.01**
EVA/NR/MLF (0 phr)-Sulfur	**376**	**406**	**449**	**2.01**
EVA/NR/MLF (0 phr)-DCP1.5	**378**	**407**	**450**	**0.06**
EVA/NR/MLF (10 phr)-Unvulcanized	**352**	**389**	**419**	**2.5**
EVA/NR/MLF (10 phr)-Sulfur	**359**	**401**	**436**	**4.78**
EVA/NR/MLF (10 phr)-DCP1.5	**355**	**392**	**429**	**0.02**
EVA/NR/MLF (30 phr)-Unvulcanized	**332**	**384**	**413**	**4.02**
EVA/NR/MLF (30 phr)-Sulfur	**331**	**392**	**429**	**8.81**
EVA/NR/MLF (30 phr)-DCP1.5	**348**	**390**	**426**	**4.02**

It is commonly known that high dissociation energy is required to cleave the C-C linkages obtained from peroxide vulcanizing system, thus providing the blends with higher thermal stability (Nabil *et al.* 2014). However, at high temperatures, sulphur vulcanizates exhibited better thermal stability compared to peroxide vulcanizates and unvulcanised compounds. In the sulphur cure system, crosslinks mainly consist of di- and polysulfidic crosslinkers that are less thermally stable but capable of changing to more thermally stable monosulfidic crosslinks. For the DCP vulcanization system, DCP caused degradation in vulcanizates due to the presence of the peroxide radicals, which can accelerate the degradation process at high temperatures. Other researchers in the study of polymer blend reported similar findings with DCP crosslink agents (Nakason *et al.* 2006; Liu *et al*. 2021).

Morphological Study

Figures 13a-c show the scanning electron micrograph of unvulcanised EVA/NR and vulcanized EVA/NR blends by peroxide and sulfur vulcanization systems, respectively. The tensile fractured of unvulcanized EVA/NR blend in Fig. 13(a) shows large size and non-uniform rubber particles dispersed in the EVA phase. Besides that, very little plastic deformation is observed. Meanwhile, the SEM micrograph for vulcanized EVA/NR blends (Fig. 13b-c) exhibited completely different characteristics. In contrast to the near brittle-type failure shown by unvulcanised blend, these fracture surfaces indicated rough surfaces with matrix tearing. The rough surface might be due to the resistance that occurred because of the crosslink chain that hinders the failure. In addition, the crosslink increased the stiffness of the blend, and thus required more force to fail.

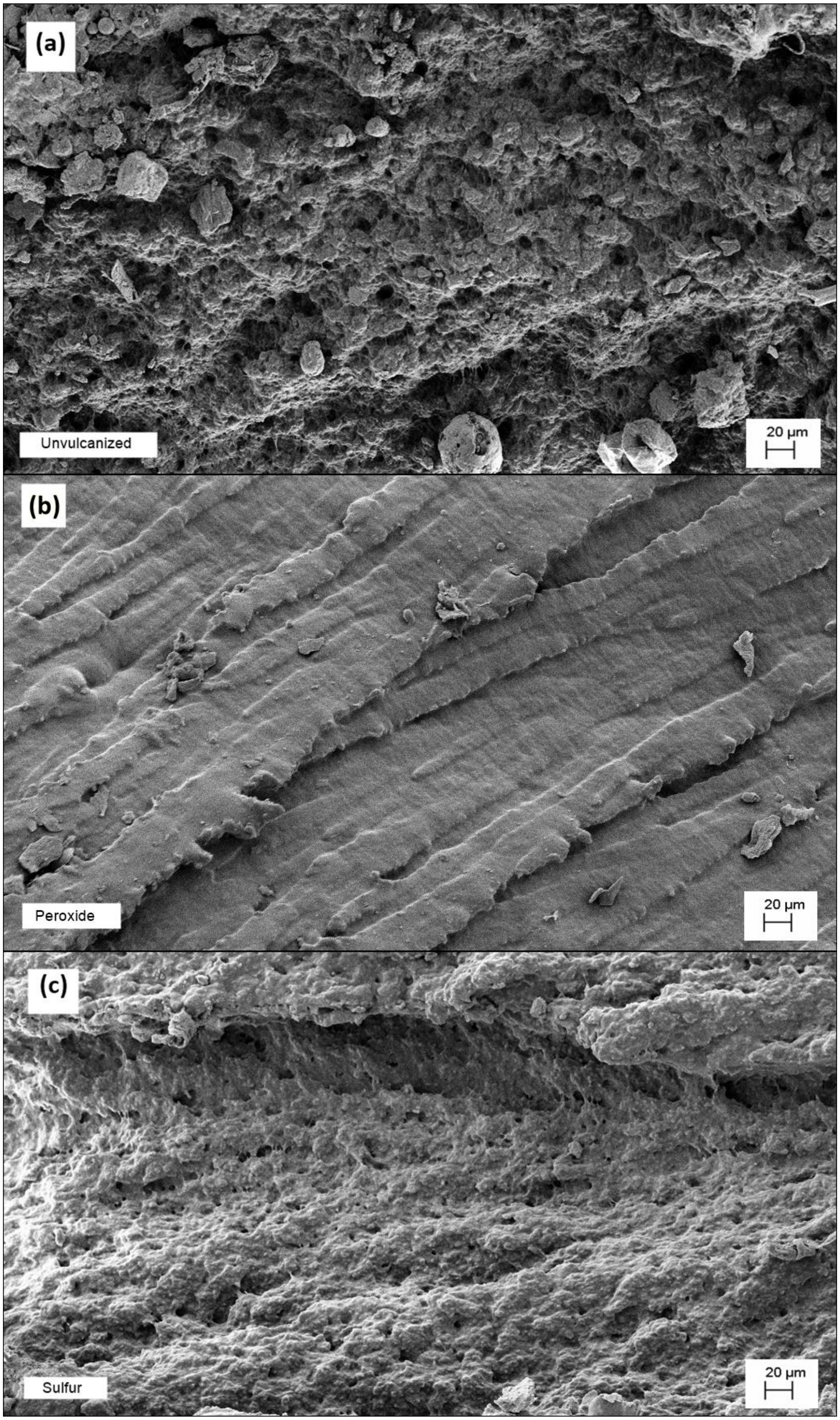

Fig. 13. SEM micrograph at the magnification of 200x a) unvulcanised EVA/NR blend and vulcanised EVA/NR blend: b) peroxide system c) sulfur system, respectively

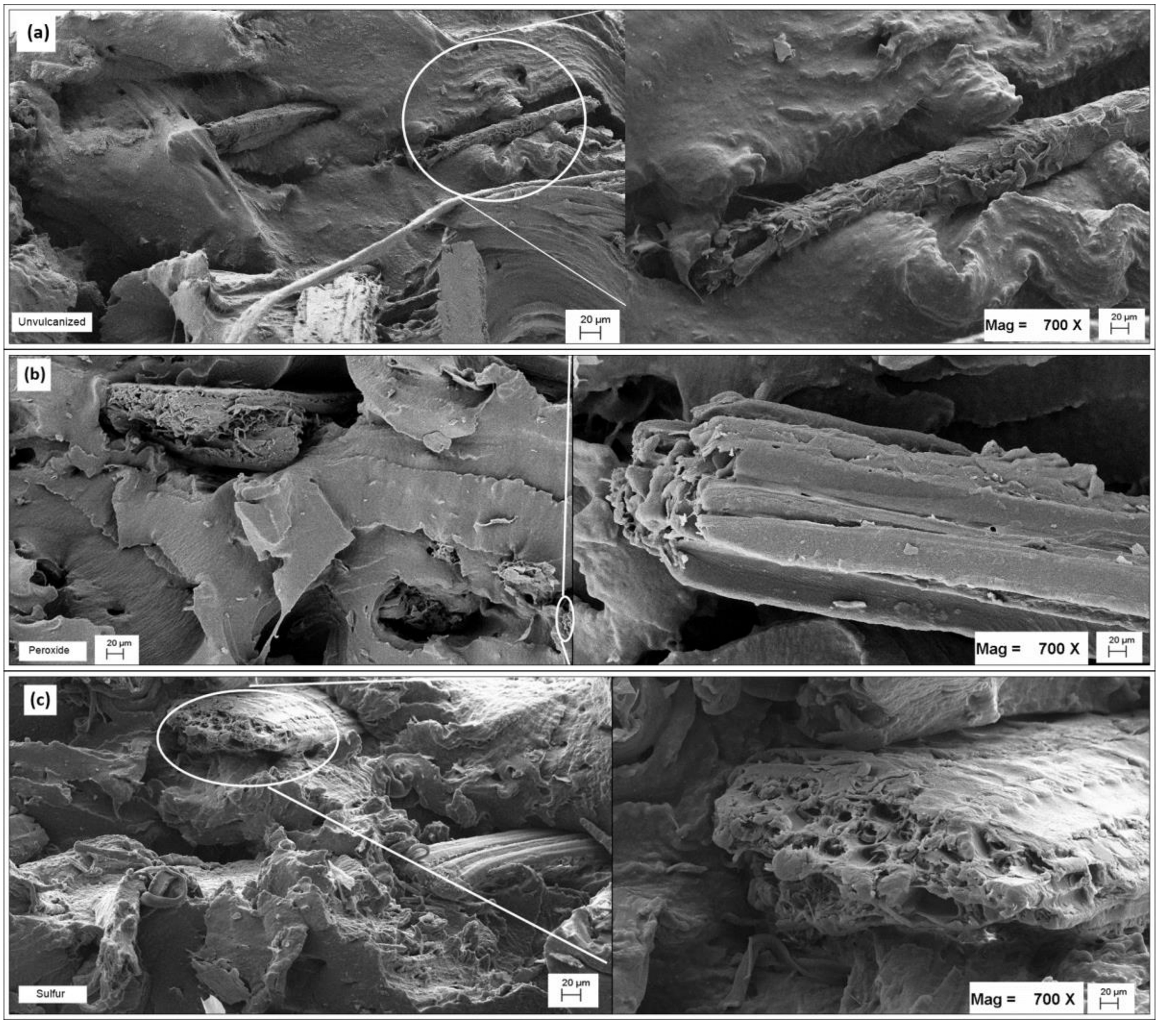

Fig. 14. SEM micrograph at the magnification of 200x a) unvulcanised EVA/NR/ Mengkuang leaf fibre composites and vulcanised EVA/NR/ Mengkuang leaf fibre composites at 10 phr loading: b) peroxide system c) sulfur system, respectively

Figures 14a-c show the scanning electron micrographs of unvulcanised EVA/NR and vulcanized EVA/NR composites by peroxide and sulfur systems with 10 phr fibre loading, respectively. Poor adhesion of the fibre and matrix is evident from the voids between the matrix and fibre particles. These voids act as stress concentration points and contribute to the decrement of mechanical properties (Sarifuddin *et al.* 2013). This is further evidence in supporting the trends in tensile properties as discussed earlier. However, vulcanized composites revealed that vulcanization greatly interrupted the fibre agglomeration and improved fibre dispersion. Simultaneously, the voids in the filled vulcanized systems were much less obvious. These factors contribute to the enhancement of the properties due to crosslinking formation.

CONCLUSIONS

1. The peroxide cure system exhibited higher improvement in tensile strength and modulus compared to the sulfur cure system and unvulcanised composites. The

crosslinking increased the stiffness of the blend, resulting in rough surface that required more force to fail.

2. The thermal stability of the vulcanized composites also improved by incorporating the curing agent with the sulfur cure system, showed better resistance towards thermal degradation compared to the peroxide system.
3. The processing torque of the composites increased with the increasing of Mengkuang leaf fibre loadings. The increase in stabilization torque for the composites with dynamic vulcanization is due to the addition of curing agents that implies some changes in the molecular level owing to the existence of crosslinking.
4. Scanning electron micrographs (SEM) showed poor interfacial adhesion between Mengkuang leaf fibre and EVA/NR matrix due to different polarities. However, less fibre pull out was observed during dynamic vulcanization owing to the existence of crosslinking.
5. Future studies are needed to assess the biodegradation study of the Mengkuang leaf fibre and the thermoplastic composites, since some of the raw materials are based on bioresources.

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