

REINFORCEMENT OF THERMOPLASTICS NATURAL RUBBER COMPOSITE WITH LIQUID EPOXIDIZED NATURAL RUBBER TREATED TORCH GINGER FIBER

NUR KAHIRUL NABILA KAMARUDDIN, IBRAHIM ABDULLAH, ISHAK AHMAD*

*School of Chemical Sciences and Food Technology, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.*

**Corresponding author: gading@ukm.edu.my*

ABSTRACT

Effects of coating torch ginger fiber (TGF) with liquid epoxidized natural rubber (LENR) as a compatibilizer for TGF and natural rubber, and linear low polyethylene (NR/LLDPE) composite were investigated. LENR coated TGF reinforced NR/LLDPE composites were prepared by incorporation of 10% loading of TGF with the variation of LENR coating. Pre-treatment of TGF using 4% NaOH was done to expose more hydroxyl groups on TGF surface before coating with LENR to improve the adhesion between LENR and TGF. The scanning electron microscope (SEM) micrograph of TGF surface showed the LENR coated on the pre-treated TGF surface was homogeneous. The mechanical properties of TGF reinforced thermoplastic natural rubber were found to increase when TGF was treated with 4% NaOH followed by 5% LENR coating. Effects of TGF treatment on the rheological behavior of composites showed an increase in the adhesion of LENR treated TGF. SEM micrograph of the tensile fractured surface showed good interfacial interaction between NR/LLDPE matrix and 5% LENR coated TGF compared to untreated and NaOH treated TGF.

Keywords: Natural rubber, liquid epoxidized natural rubber, linear low density polyethylene, torch ginger fiber, thermoplastic composite.

INTRODUCTION

Reinforcement of polymer composites with natural fiber has been one of the main industrial and scientific research interests since few decades ago. The interest in natural fiber composites arises from its ability to be recycled and processable from renewable resources [1]. Natural fiber has the potential to replace conventional fibers in polymeric matrix such as glass, carbon and aramid because of the specific properties of natural fiber such as biodegradability, environmental acceptability, light weight and high specific mechanical properties [2]. The chemical composition of natural fiber is generally made up of cellulose, hemicellulose, and lignin [3-5]. This composition is dependent on the plant type that will have an impact on processing and properties of the composites. The high cellulose content will result in composites having high susceptibility to moisture absorption and a high silica content, and therefore will incur a higher cost in processing [5,6]. However, the major limitation of using natural fiber as reinforcement in thermoplastic matrix is the incompatibility between hydrophilic fiber with hydrophobic matrix that causes poor interfacial adhesion and hence inhomogeneous dispersal of filler particles in the matrix. Another serious drawback is the low thermal stability of lignocellulosic fibers above 200°C, which limits the choice of manufacturing techniques and type of matrix to be used for composite fabrication.

Chemical modification of natural fiber involves reaction of an active group of a simple chemical molecule with the lignocellulose fiber to form covalent bonds. The most abundant site for reaction on the cell wall is the hydroxyl group that has to be exposed prior to any reaction. Normally the fiber is treated with an alkali or acid solution to create active spots. Acetic anhydride is the most common reagent used to react with cell wall polymer hydroxyl to produce acetylated fiber. Mwaikambo and Ansell had reported the modification of surface structure of hemp, sisal, jute and kapok fibers on subjecting it to alkalization in sodium hydroxide solution [7]. Chemical modifications of pineapple leaf fiber were reported by Ray *et al.* via alkali treatment, diazo-coupling with aniline and cross-linking with formaldehyde [8]. The reaction of silane coupling agents with lignocellulose fibers was reported to occur only with pre-hydrolyzed silane [9]. Abdelmouleh *et al.* had reported the effects of three types of silane agents on the treatment of de-lignified cellulose fibers to improve interaction in low density polyethylene and nitrile rubber matrix [10].

A recent study to improve natural rubber-high density polyethylene (NR-HDPE) adhesion with liquid natural rubber (LNR) coated rice husk (RH) has been reported [11]. Surface modification with LNR under various conditions of ultrasonic agitation was studied. The process of coating on the RH particles and chemical bonding the rubber to the cellulose surface occurred on exposure to e-beam radiation [11]. Liquid epoxidized natural rubber (LENR) was also found to improve the tensile properties of RH filled polymeric composites by acting as a compatibilizer between the filler particles and rubber-thermoplastic phases [12]. The active groups such as –OH, exposed after alkali treatment reacted with the epoxy group on LENR chain to form bonds, physical and chemical, between the rubber film and RH surface. However, the interaction was not as strong as the radiation induced bonding. More active sites were probably formed on exposure of rubber to e-beam irradiation that promoted more interaction between the phases. Without radiation, LNR had insignificant effects on the compatibility of RH in the NR/PE matrix.

Various types of natural fibers are derived from plants. Their properties as well as applications may vary depending on the part origin of plants. Accordingly, the four principle categories are seed fibers, bast fibers, leaf fibers and grass fibers [13,14]. In this study, *Etilingera elatior. sp.*, commonly known as torch ginger plants, belonging to Zingiberaceae family fibers was used. Normally, only flower part in Torch Ginger Plant is used and the stem is just the by-product while it has a high potential as reinforcing filler in composite. In addition to that the whole stem is fibrous which gives vast amount of fiber sources. Torch Ginger fiber (TGF) is categorized under bast fibers that usually have high tensile strength as compared to other plant fibers. It is hydrophilic in nature as a large amount of hydroxyl group is present in a single fiber [15]. The potential of TGF as a reinforcing agent in thermoplastic composites is high provided that the fiber can be made to undergo physical and/or chemical surface modification to reduce the hydrophilic nature of fiber and subsequently induce interaction with the matrix.

The purpose of the study was to explore the effect of incorporation of TGF into NR/LLDPE matrix. Surface tension developed between the filler and matrix would be minimized by chemical modification of TGF with liquid epoxidized natural rubber. Pre-treatment of fiber with alkali would be required to create active sites prior to reaction with LENR. The rubber coated TGF, at different degree of coating, was then used as reinforcing agent in NR / LLDPE composites.

EXPERIMENTAL

Materials

Natural rubber (NR), SMR-L grade, was supplied by the Malaysia Rubber Board (MRB) and low linear density polyethylene (LLDPE) with a density of 0.93 g/cm³ by System Chemicals Co., Spain. Torch ginger plant was obtained locally from Mersing, Johor, Malaysia. Liquid Epoxidized Natural Rubber (LENR) was synthesized in our laboratory by photochemical degradation of ENR-50. Sodium Hydroxide (NaOH) was purchased from System Chemicals Co., Spain.

Methods

Fiber Preparation

Torch ginger stem was cut into small pieces, soaked in water for 24 hour, dried under sunlight, ground to powder and graded using a sieve (Retsch Test Sieve, model ZM200) to obtain 110µm-125µm in size. Alkali treatment of powdered fiber was done by stirring it in a 4 wt% solution of NaOH for 1 hour at room temperature. Torch ginger fiber (TGF) was then filtered and washed several times using distilled water until traces of sodium hydroxide was eliminated and dried it in an oven at 70°C for 24 hour. LENR surface modification of TGF was done by soaking treated TGF in LENR solution (5% and 10% polymer solution) for 30 min at room temperature. The mixture was mechanically stirred and finally subjected to sonication for 5 min. The TGF was then filtered out and dried in a vacuum oven at 70 °C for 24 hour.

Composite Preparation

Natural Rubber / Low Linear Density Polyethylene (NR/LLDPE) with 60/40 ratio were melt-blended in an internal mixer, Brabender PL2000, with a capacity 60 cm³. Blending was carried out at 135°C at 50rpm for 5 min. The composites were prepared using 10wt% of different TGF treatments (untreated TGF, NaOH treated TGF, and NaOH followed by 5% and 10% LENR treated TGF). The composites obtained were hot pressed into sheet of 1mm and 3mm thickness.

Characterization

Infrared Absorption

Fourier-Transform Infrared Spectroscopy (FTIR) was used to characterize the surface structure of the TGF particles. The sample was prepared in potassium bromide (KBr) pellet and scanned through 400-4000 cm⁻¹ (Perkin-Elmer, GX model).

Mechanical Testing

Tensile test was carried out using a Universal Testing Machine (Instron 5566) according to ASTM D412 98a standard with a load cell 10KN at a rate 50 mm/min. The samples were cut using Hollow Die Punch (ASTM D41268) into dumbbell shape of 1 mm thickness. The impact strength was measured by using Universal Fractoscope pendulum impact tester (CEAST 6545) based on ASTM D256.

Rheological Study

Dynamic frequency sweep and steady shear flow modes were used in the measurement using a rheometer (Physica MCR 301) with parallel plate geometry (25 mm diameter and 0.051 mm gap). A high frequency range from 0.05 to 500 rad/s with 5% strain amplitude was utilized in the dynamic frequency sweep. Steady shear flow was measured at low shear rate range from 0.001 to 10 (s^{-1}) at a similar temperature of 110⁰C.

Morphology

Scanning electron microscope (VPSEM LEO 1450 model) was used to examine the morphology of fiber and composite. The sample was spur-coated with a thin layer of gold prior to scanning. The effectiveness of surface treatment was analyzed from the surface morphology of TGF before and after modification. The morphology of fractured surface of composite sample used in tensile test was examined to study the TGF-matrix adhesion and distribution of TGF particles in the composite.

RESULTS AND DISCUSSION

Infrared Analysis

The chemical and physical interactions between TGF and LENR were analyzed from the infrared absorption. The FTIR spectra of untreated, alkali treated and LENR coated TGF are shown in Fig. 1. The band at 1735 cm^{-1} appears for the untreated TGF. This peak may be attributed to C=O groups from hemicelluloses [16]. After treatment with alkali, the band disappeared which could be due to the removal of C=O associated species or reaction of the C=O group with active species generated during alkalization [11]. The absorption band at 1722 cm^{-1} appears after treatment of TGF with LENR. This peak may be attributed to C=O stretching from hydrogen bonded to carbonyl groups.

A broad band appearing at about 3478 cm^{-1} in the spectrum of untreated TGF can be assigned to hydrogen bonding O-H stretching vibration. The peak is more defined in the spectra of NaOH treated and LENR treated TGF with absorption peaks at 3495 cm^{-1} and 3487 cm^{-1} respectively. Most probably more -OH groups is present resulting from treatment with NaOH. The surface of fiber was partially degraded exposing more OH groups. For LENR treated TGF, the peak is more defined by the LENR modification. Hydrogen bonding between -OH groups on TGF surface with epoxy from LENR will be formed [12].

The absorption peak at 2931 cm^{-1} , 2904 cm^{-1} and 2928 cm^{-1} are assigned to -C-H vibration peaks [18]. Peak observed at 1480 cm^{-1} in the spectrum of TGF treated with LENR is assigned to the ester groups which are often superimposed by the -CH₃ bending. In the spectrum of TGF treated with LENR, a band obtained at 875 cm^{-1} and 1251 cm^{-1} are assigned to epoxy groups [19]. These observations strongly indicate the presence of interaction, chemical or physical, between LENR coating and TGF fiber.

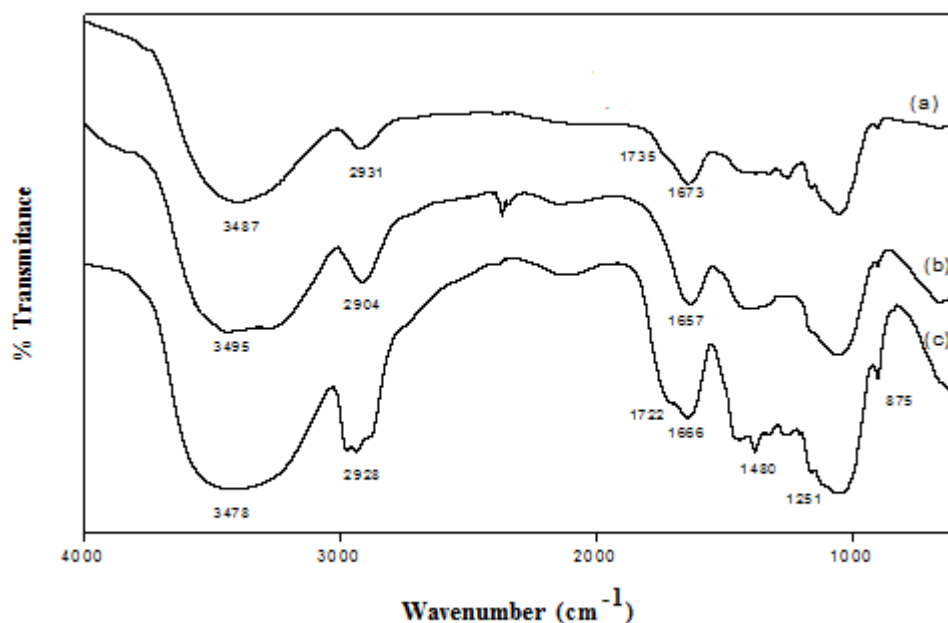


Fig. 1 FTIR spectra of (a) untreated TGF, (b) TGF treated with NaOH and (c) TGF treated with NaOH and LENR

Morphology

The surface morphology of TGF fiber was examined by scanning electron microscope as shown in Fig. 2. Coating of LENR on TGF fiber surface would enhance interfacial adhesion in polymeric composite but the coating thickness has to be optimized. It is anticipated that the fiber particles with thicker coating tend to agglomerate and disrupt proper dispersion of particles in the matrix due to the particles becoming sticky [8-10]. A rough surface of the fiber can be observed on the untreated TGF (Fig. 2(a)). After alkali treatment, the fiber surface looks more grooves and even as can be observed in Fig. 2(b). Alkali treatment is commonly used to remove impurities, wax and oil on the surface of natural fiber. Fig. 2(c) shows the micrograph of TGF after treatment with 5% LENR solution. LENR is seen to be homogeneously coated on the particle surface. In contrast, a thicker coating layer of LENR can be observed in Fig. 2(d) when treated using higher concentration of LENR.

Treatment with 5% LENR solution had caused the formation of a fine coating on the surface that can lead to good dispersion of fiber particles in the matrix during composite mixing. Pre-treatment with 1% NaOH is prerequisite to the formation of a fine LENR layer on TGF surface. NaOH solution reacts with the surface lignin to expose a number of hydroxyl groups which promote physical and chemical interaction with LENR. The probability of epoxy group on LENR surface to interact with TGF increased when the number of exposed hydroxyl groups on TGF is increased.

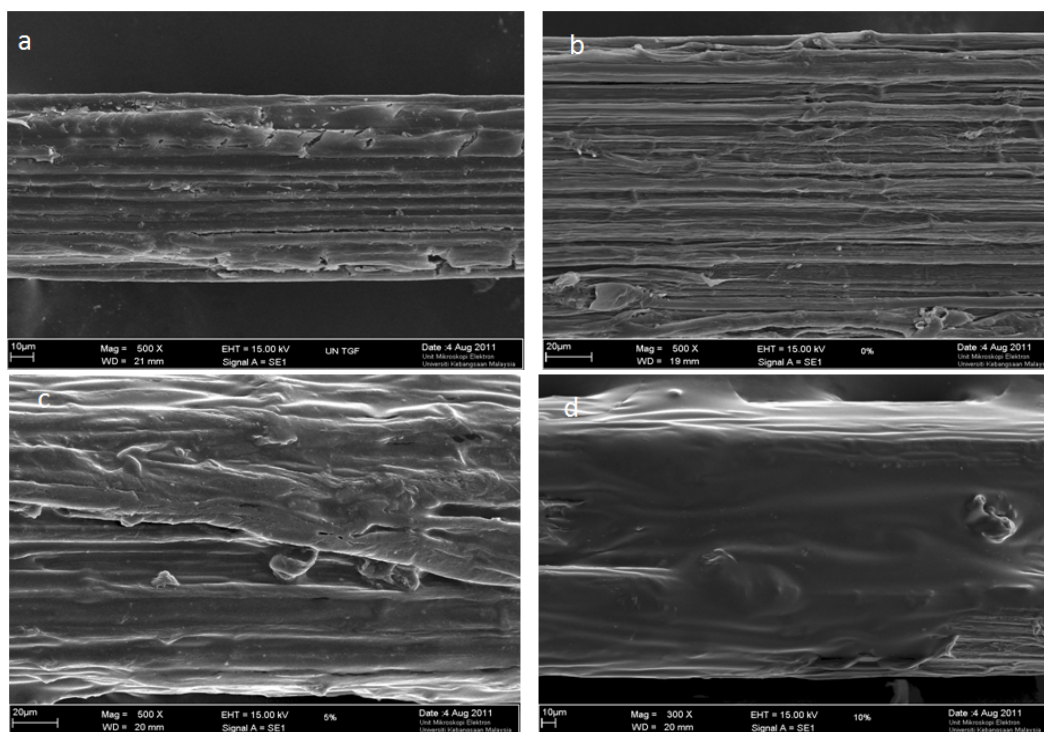


Fig. 2 SEM micrographs of TGF surface: (a) untreated TGF, (b) TGF treated with NaOH, (c) TGF treated with LENR (5%), (d) TGF treated with LENR (10%).

Analysis on the surface morphology of composites has been frequently used to study fracture mechanisms and fiber-matrix adhesion or distribution of filler particles. SEM micrographs of the fractured surface of composites filled with different types of treated TGF are shown in Fig. 3 at 500x magnification. Composite with untreated TGF shows very limited strands of polymer attached to the fiber indicating of poor interfacial interaction between the fiber and the matrix (Fig. 3(a)). A significant amount of micro-voids can be observed to form at the interface. Fig. 3(b) shows a slight increase in polymer matrix-fiber interaction but the fiber particles are larger. Thus treating the TGF with NaOH does not only help to improve the fiber-matrix interaction but also the fiber-fiber interaction leading to agglomeration. Fewer micro-voids are observed and the dispersion of TGF particles is more homogeneous. Chong *et al.* reported that interfacial interaction between rice husk and TPNR matrix can be improved with the modification using liquid natural rubber (LNR) [11].

Fig. 3(c) shows the micrograph of fractured surface of composite with LENR treated TGF. Significant surface adhesion is observed between the TGF particles and matrix suggesting an improved interfacial interaction. However a much better improvement in surface interaction can be seen in Fig. 3(d) where the fibers of TGF are completely obscured by the matrix. However, the fiber particles seem to be bigger in size due to agglomeration. Coating of LENR on TGF surface promotes good interfacial interaction not only between the fiber and polymer matrix but also between the fiber particles. However in thicker coated LENR, the increased compatibilization has led to the agglomeration of fiber particles causing formation of bigger filler particles.

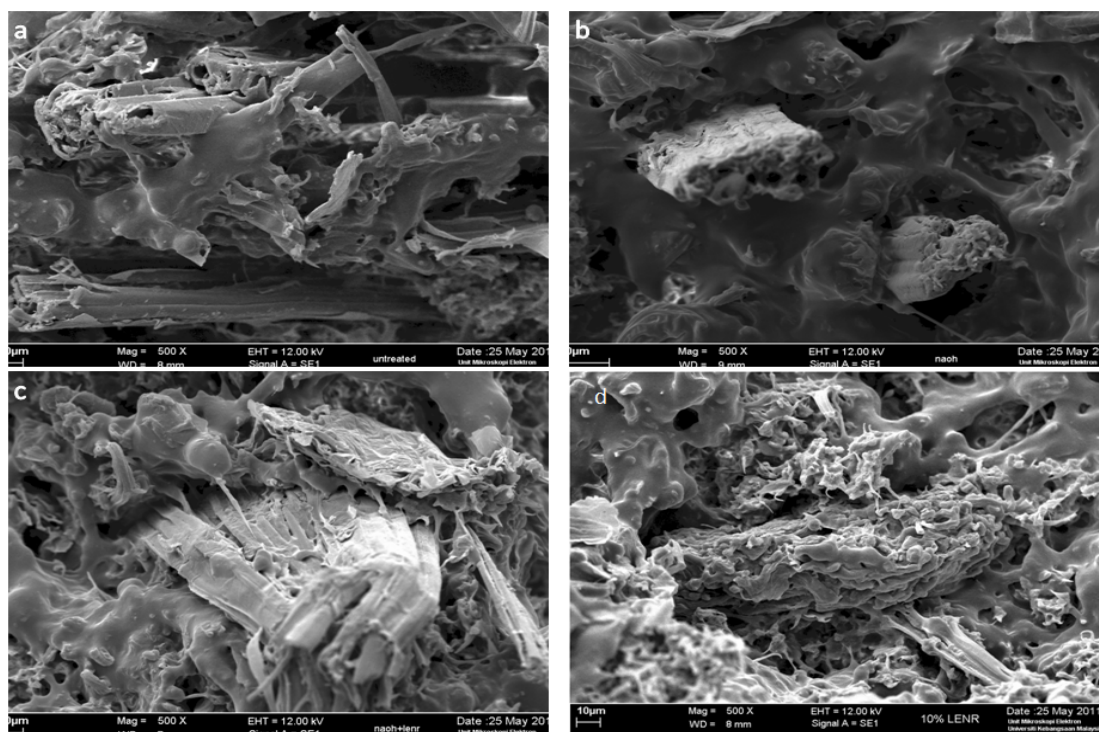


Fig. 3 SEM micrographs (500x) of fractured surface of composites NR/LLDPE/ TGF: (a) untreated TGF, (b) TGF treated with NaOH, (c) TGF treated with 5% LENR, (d) TGF treated with 10% LENR.

Mechanical properties

It can be seen in Fig. 4 that the highest tensile strength is shown by composites filled with NaOH and 5% LENR solution treated TGF whilst the lowest by NaOH treated TGF. Treatment of TGF with NaOH caused the fiber to lose parts of the surface wall giving rise to fragile fiber and hydrophilic surface due to exposure of hydroxyl groups. The fiber has poor interaction with the hydrophobic polymer matrix and the enforcement, if any, will be weak. The agglomeration of filler particles is also predominant and led to reduced tensile strength. Formation of LENR coating on the surface of fiber helped to create a compatibilizing layer at the NR/LLDPE matrix–TGF fiber interphase and hence the interaction between the phases would be enhanced. The epoxy groups of LENR are hydrophilic while the isoprenic component is hydrophobic. Interactions between epoxy groups on LENR with cellulose of TGF and isoprenic component with hydrophobic matrix are feasible.

The 10% LENR solution coating TGF produced lower tensile strength composites than the 5% LENR solution coating as shown in Fig. 4. The difference between the two TGF fillers was only the thickness of LENR coating which could affect the interaction between filler particles. Such a decrease of tensile strength can be rationalized to the homogeneity of the filler particles distribution in the matrix. Thicker coating filler particles would tend to agglomerate into bigger particles than thinner coating particles. It would be more difficult to disperse the thicker coating fillers in polymeric composites.

Fig. 5 shows the variation of tensile modulus of NR/LLDPE composites filled with various treated TGF fillers. Increased stiffness can be due to stiffer filler and reinforcing effect of the filler particles that depends on filler-matrix interaction and homogeneity of filler particles in

the matrix. TGF treated with NaOH followed by 5% LENR solution shows the highest tensile modulus. The enhancement in the stiffness of these composites is attributed to the improved interfacial interaction between filler and matrix, and homogeneity of particles distribution. Poor interaction in untreated fiber would be the cause for low modulus. The composite with alkali treated fiber has lower modulus compared to alkali treated followed by 10% LENR treated filled composites because more hydroxyl groups exposed after alkali treatment that make fiber incompatible with matrix. The adhesion to the matrix, which is low, is not expected to be a major factor in influencing the properties.

Fig. 6 shows the effect of TGF treatment on the impact strength of 10wt% filled NR/LLDPE composites. The highest impact strength shown by NaOH followed by 5% LENR treated TGF filled composite is due to better fiber-matrix adhesion and homogeneous distribution of the fiber in matrix. The value for the untreated fiber is also significant due to low fiber-matrix interaction and surface tension. The surface of untreated fiber particles contained substantial amount of lignin which is hydrophobic in nature and thus less repulsive to the polymer matrix phase. Alkali treated and alkali treated followed by 10% LENR TGF filled composites exhibit very low impact strength. These composites were filled with bigger agglomerated filler particles and poor interaction with the matrix. The impact stress is not able to be homogeneously dispersed in the matrix due to poor stress transfer across the filler-matrix interphase. The impact force is quite efficiently transmitted in the alkali followed by 5% LENR treated TGF filled composites where filler interaction is better. Interaction between fiber and matrix is considered to be the main factor determining the impact strength of composites.

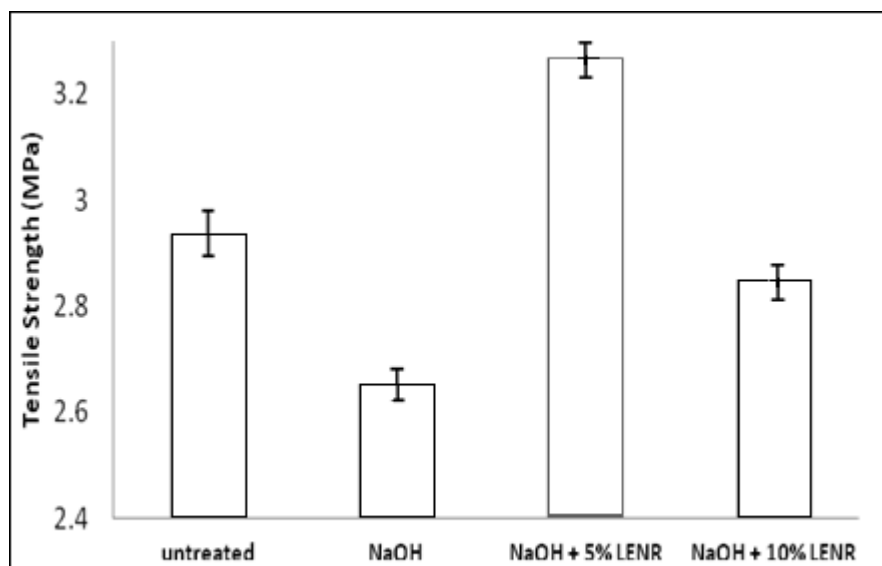


Fig. 4 Tensile strength of NR/LLDPE composite filled with Untreated TGF, TGF treated with NaOH, and TGF treated with NaOH followed by 5% and 10% LENR coating.

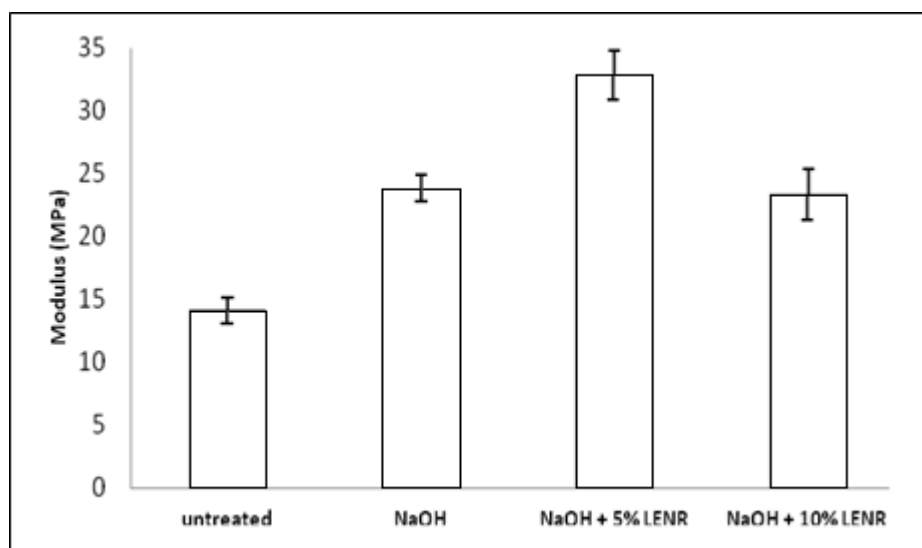


Fig. 5 Tensile modulus of NR/LLDPE composite filled with untreated TGF, NaOH treated TGF, and 5% and 10% LENR treated TGF.

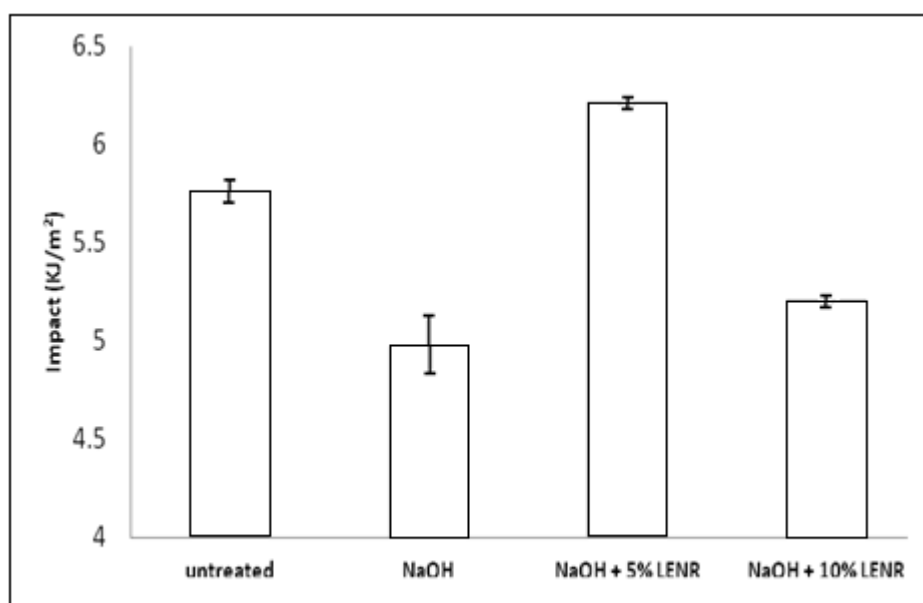


Fig. 6 Impact strength of NR/LLDPE composite filled with untreated TGF, NaOH treated TGF, and 5% and 10% LENR treated TGF.

Rheological Properties

The complex viscosity behavior of NR/LLDPE composites, with and without TGF fillers subjected to different treatments at 110°C is shown in Fig. 7. The NR/LLDPE blend shows a uniform decrease of the viscosity throughout the frequency swept indicating the shear thinning behavior or pseudo-plastic behavior of the polymer matrix. The complex viscosity of

NR/LLDPE/TGF composites, however, shows a slight deviation from the regular pattern depending on each treatment.

The pseudo-plastic behavior of fiber-reinforced polymer composites may come from the impact of high frequency that will try to weaken the interfacial bonding existing between fiber and matrix. When matrix and filler is strongly bonded or interacted, high frequency is needed to weaken the bond. In the filled polymer system the presence of fiber affects the normal flow of polymer and hinders the mobility of chain segments in the flow. The viscosity of the polymer will thus increase. The NaOH treated TGF composite exhibits a higher viscosity than the NR/LLDPE blend from high to low frequencies that can be rationalized as a result of poor filler-matrix interaction. The untreated TGF composite, however, shows similar interaction at low frequencies but decreases to lower than the blend on increasing the frequency. The viscosity starts to decrease above 0.5s^{-1} , when the filler agglomerate starts to degrade. Dislocation of the fiber and variation of agglomerated size in the process caused phase separation of filler from matrix, resulting in lower viscosity [16].

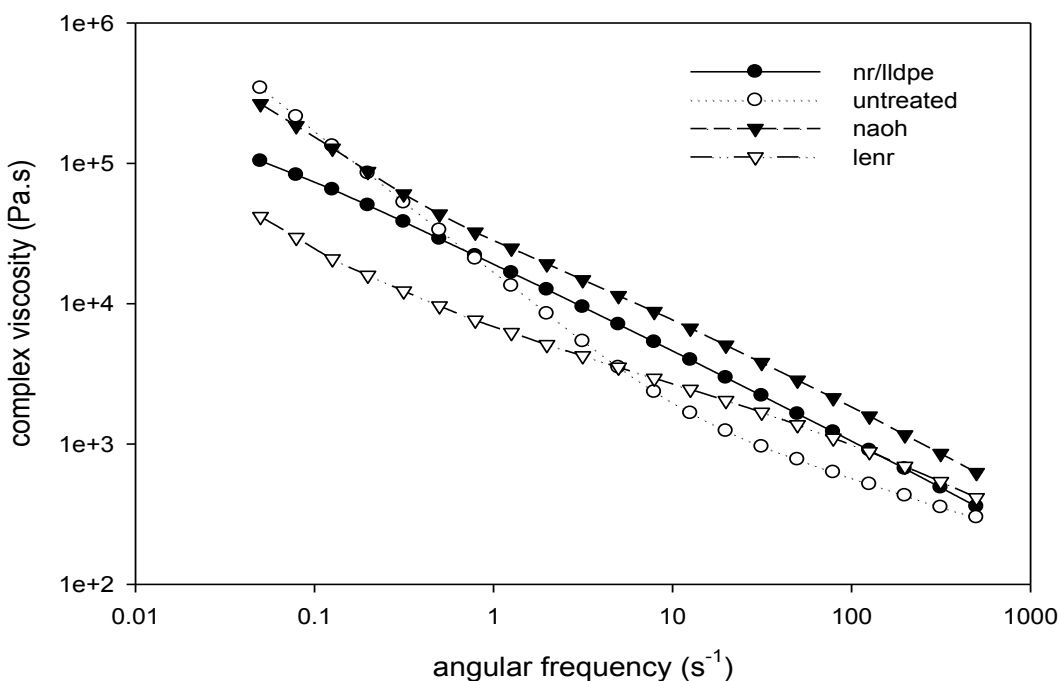


Fig. 7 Complex viscosity curve of NR/LLDPE composite filled with untreated TGF, NaOH treated TGF, and 5% and 10% LENR treated TGF.

CONCLUSION

TGF can be used as reinforcing filler for NR/LLDPE matrix. Untreated TGF has low mechanical properties due to poor interfacial interaction and particles agglomeration in the composite. NaOH treatment does improve slightly the fiber adhesion to the matrix but fiber-fiber interaction becomes more significant. Coating with a thin layer of LENR through treatment with NaOH solution followed by 5% LENR solution, has produced the most effective reinforcing filler particles. The composite exhibits the highest mechanical properties. The LENR coat on the fiber

surface has enhanced the interfacial interaction or compatibilisation between TGF and polymer matrix. A thicker LENR coating leads to fibers becoming sticky and will adhere together causing agglomeration. LENR has the potential to be a compatibiliser due to its co-polymeric in nature with regular epoxy groups at the interval in the polyisoprenal chain.

ACKNOWLEDGMENTS

The authors would like to acknowledge to Ministry of Higher Education, Malaysia for funding the project under the FRGS grant (FRGS/2/2013/SG06/UKM/02/2) and Polymer Research Centre (PORCE) of Universiti Kebangsaan Malaysia for their support in providing the infrastructure for the project.

REFERENCES

1. Igor, M. D. R., Carlo, S. & Fabrizio, S. Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated Phormium tenax leaf fibers. *Material and Design*, (2010) 31: 2397-2405.
2. Wong, S., Shanks, R. & Hodzic, A. Interfacial improvements in poly(3 hydroxy-butyrate)-flax fibre composites with hydrogen bonding additives. *Composites Science and Technology* (2004). 64: 1321-1330.
3. Bledzki, A. K., & Gassan, J. Composites reinforced with cellulose based fibre. *Progress in Polymer Science*, (1999) 24:221-274.
4. Juan I. M., Vera A. A. & Viviana P. C. Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, (2008) 15:149-159.
5. Mwaikambo, L.Y., Martuscelli, E. & Avella, M. Kapok/cotton fabric-polypropylene composites. *Polymer Testing*, (2000) 19: 905-918.
6. Rajeev, K. Mohan, K. And Ramani, N. Biofiber-reinforced polypropylene composite. *Polymer Engineering and Science*, (1997) 37: 516-523.
7. Mwaikambo, L. Y. & Ansell. M. P, Chemical Modification of Hemp, Sisal, Jute, and Kapok Fibers by Alkalization. *Journal of Applied Polymer Science*, (2002) 84: 2222-2234.
8. Ray, S., Bhowmick, A. K., Sarma, K.S S., Majali, A. B. & Tikku, V. K. Characterization of electron-beam-modified surface coated clay fillers and their influence on physical properties of rubbers. *Radiation Physics and Chemistry*, (2002) 65: 627-640.
9. Herrera-Franco, P.J. & Valadez-Gonza'lez, A. A study of the mechanical properties of short natural-fiber reinforced composite. *Composites Part B: Engineering*, (2005) 36:597-608.
10. Abdelmouleh, M., Boufi, S., Belgacem, M. N. & Dufresne. A. Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibre loading. *Composites Science and Technology*, (2007) 67:1627-1639
11. Chong, E.L., Ahmad, I., Dahlan, H.M & Abdullah I. Reinforcement of natural rubber/high density polyethylene blends with electron beam irradiated liquid natural rubber-coated rice husk. *Radiation Physics and Chemistry*, (2010) 79:906-911.
12. Rahmadini, S., Ahmad, I. Ibrahim, A. Effect of rice husk surface modification by lenr the on mechanical properties of NR/HDPE reinforced rice husk composite. *Sains Malaysiana*, (2011) 40(7): 749-756.

13. Bachtiar, D., Sapuan, S.M. & Hamdam, M.M. The effect of alkaline treatment on tensile properties of sugar palm fiber reinforced epoxy composites. *Material and Design*, (2008) 29: 1285-1290.
14. Li, X., Tabil, L.G., & Panighiri, S. Chemical treatments of natural fibre for use in natural fibre reinforced composite: A review. *Journal of Polymers and the Environment*, (2007) 15: 25-33.
15. Awang, M., Salit, M.S & Wirawan, R. A Review of Natural Fibre reinforced Polymer Composite. *Universiti Putra Malaysia Press*. (2009).
16. Mohanty, S. & Nayak, S. K. Dynamic and steady state viscoelastic behavior and morphology of MAPP treated PP/sisal composites. *Material Science and engineering A*, (2007) 443: 202-208.
17. Thomas, G M. *The rheology handbook: for users of rotational and oscillatory rheometers, 2nd Edition*, Hannover: Vincent network (2006) Coatings compendia, ISBN 3-87870-174-8.
18. Tharwat, F. Tadros, *Rheology of Dispersions, Principles and Applications, 1st Edition*, WILEY-VCH Verlag GmbH & Co. KGaA, (2010). ISBN 978-3-527-32003-5.
19. Chang, D. H. *Rheology in Polymer Processing. 1st Edition*, Academic press Inc. (1976). ISBN 0-12-322450.