Evaluation of the cure characteristics and physico-mechanical properties of treated Oil Palm Fiber based Natural Rubber Composites

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Abstract

The global production of palm oil has grown with the emerging demand for vegetable oils in the past decades which produced 71 million tonnes of oil as at 2018 (Ritchie and Roser, 2021). This industry produces different types of waste materials such as empty fruit bunch, palm kernel shells, etc. during the process. This research was carried out to identify the application of the waste, mesocrap fiber part of the oil palm fruit (OPF) as a potential filler material in natural rubber composites by studying the cure characteristics and physico-mechanical properties. The fiber size of the OPF was reduced to micro size with a mechanical treatment followed by a chemical treatment and composites were prepared with different fiber sizes. The results revealed that the application of 2 phr loading of treated OPF enhances certain physico-mechanical properties and cure characteristics compared to a carbon black filled control compound.

Introduction

Natural fiber has attracted great interest in the rubber processing industry due to the growing concerns in developing green materials. Numerous types of natural fibers are being studied which are generated from animals, plants and other natural materials. The properties of the fibers again differ with the source of fiber generating area such as leaf, bast, seed, fruit, root etc. The chemical composition and structural variations within the fibers enable to generate different physico-mechanical properties in various applications. Plant fibers such as cotton, jute, hemp, coir has been widely used for different studies (Lila, *et al*., 2016) for full or partial replacement for hazardous filler materials such as Carbon black or Silica.

The adhesion of the interface between the rubber polymer and the fiber matrix acts as a crucial point when determining the physical properties (Zafeiropoulos, 2008). The common disadvantages existing in natural fiber materials are the heterogenic, hydrophilic nature and polarity. As a result, the incorporation of fiber to the rubber matrix requires a modification of the fiber or a modification in the rubber matrix to enhance the resultant properties.

The modification of the fiber material before incorporating to the rubber phase can be conducted by chemical treatment, physical treatment or both. Silylation, mercerization and other related modifications (Lila, *et al*., 2016) (Faruk *et al.*, 2012) can be considered for chemical modifications whereas the use of shearing based mechanical actions are widely used for particle size variation.

Several studies have been conducted by incorporating short fibers in rubber compounds*(Jacob et al.*, 2004). The main idea is to increase the interfacial adhesion by introducing a higher surface area with a low amount of

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loading. Additionally the ease of process, reduction of cost and at the same time improvement in the physical, chemical properties were expected with the substitution of natural fibers (Joseph *et al.,* 2006). In this study variation of fiber size was generated from the mesocrap part of the Oil Palm Fiber (OPF). The OPF used was generated as a waste material in the palm oil processing. When considering the palm oil process only 30% of the total weight of the plam oil tree's fresh fruit bunch is utilized for the oil production and the rest 70% is generated as a waste (Nugroho and Susanto, 2021)PKS (Palm Kernel Shell. Several studies have been carried out by incorporating empty fruit bunch fiber for plastic, PP, epoxy and polyester resin composites to investigate the reinforcement level, dynamic electrical properties and mechanical properties (Faruk *et al.*, 2012). OPF is a lignocellulosic fiber obtained from the oil palm tree (*Elaeis guineensis*) which is a hard, tough material which can be used with natural rubber as a potential reinforcing agent. Application of micro sized cellulose fibers can broaden its applications from next generation smart sensors, miniature computer components which requires high thermal stability, strechability to automotive components such as bumpers, which requires high level of shock absorbance (Kato *et al.*, 2015).

The main objective of this study is to compare and contrast the effect of OPF micro sized particles on cure characteristics and physico-mechanical properties at a low loading level.

Materials

Natural rubber (RSS 2) was supplied from the Dartonfield Estate, Agalawatta, Sri Lanka. Rubber compounding ingredients such as zinc oxide (ZnO), stearic acid, TMQ (2,2,4 trimethyl 1,2-dihydroquinoline), CBS (N-cyclohexyl-2-benzothiazole sulfenamide), sulphur were purchased from Glorchem Enterprise, Colombo, Sri Lanka. Chemicals for synthesizing micro size OPF namely sodium hydroxide, sodium chlorite and oxalic acid were purchased from Organic Trading (Pvt.) Ltd., Sri Lanka.

OPF waste of the oil palm fruit was sourced from Nakiyadeniya Oil Palm Mill.

Experimental Procedure

Synthesis of chemically treated micro sized OPF

The waste OPF was initially washed with clean water to remove the impurities and oven dried at 100°C for 48 hours. The samples were then cut into pieces and ground using a mechanical grinder.

Chemical treatment

Oil palm fibers were soaked in 2 % sodium hydroxide and placed for six hours at room temperature. Alkali treated fibers were then subjected to the steam explosion and a laboratory autoclave, which work with 0.1 MPa pressure was used for steam treatment. Steam explosion technique was applied on the alkali treated fiber for half an hour. Steam pre-treatment was performed by loading the lignocellulosic material directly into the steam gun and treating it with high pressure steam at a temperature of 120 °C.

The steam exploded fiber was then subjected to bleach. A sodium chlorite ($NaClO_2$) solution (pH 2.3) was used for this for 1 hour at 50 °C. This was performed to remove the remaining lignin.

The bleached sample was then subjected to mild acid treatment. 5 % oxalic acid was used for the acid hydrolysis followed by second step of steam explosion for half an hour. A pressure of 0.1 MPa was used and the fibres were then sonicated for half an hour to reduce the size further (Abraham *et al.,* 2013). The sonicated fiber sample was then centrifuged for half an hour in a centrifuge machine with a rotor speed of 9000 rpm. The fiber portion of the centrifuged sample was then separated and washed thoroughly using distilled water to remove the excess chemicals. Washed sample was then oven dried at 70 °C. The dried sample was sieved using meshes in the range of 25 µm to 350 µm.

Preparation of dry rubber composites

Six different types of dry rubber composites were prepared using the formulation described in Table 1. The sample with carbon black (2phr) was considered as the control sample C0 and the rest of the samples were classified as below according to the variation of fiber size.

C0 - Control sample with carbon black added as filler

C1 - (250 µm -350 µm) size fiber particles

C2 - (125 µm -175 µm) size fiber particles

C3 - (75 µm -125 µm) size fiber particles

C4 - (25 µm -75 µm) size fiber particles

C5 – (below 50 µm) size fiber particles

The compounds were then prepared using a two roll mill. The total mixing time was kept as a constant for 8 minutes as described in Table 2.

Table1: Formulation of NR/OPF fiber compounds

Ingredient	Phr (Parts per hundred parts of rubber)	
	C0 (Control)	C1-C5
RSS 2	100	100
ZnO	5	5
Stearic acid	2	2
TMQ	1	1
CBS	1	1
Sulphur	2	2
Carbon black	2	-
OPF	-	2

The mixing cycle used is stated in Table 2. Samples were then molded using a laboratory scale hydraulic hot press machine.

Table 2: Mixing cycle used in the preparation of NR/OPF compounds

Chemical added	Time (min)
NR	0
ZnO + Stearic acid + TMQ	2
Filler	3
CBS	5
Sulphur	6
Dump	8

Determination of the cure characteristics of the composites

Rheological properties of compounded samples were analyzed using D-RPA 3000 Dynamic Rubber Process Analyzer (MonTech) at the temperature of 150 °C.

Measurement of physico-mechanical properties of the composites

The tensile properties were measured using Instron tensile testing machine. The properties tensile strength of the vulcanisates were measured in accordance with ISO 37: 2017 at room temperature (27 ± 2°C) at a grip separation rate of 500 mm / min. Tear strength of the vulcanisates was measured using angle (Die B) test pieces with the aid of the same machine as per ISO 34-1:2010. The hardness (Shore-A) of the rubber compounds were determined according to the ASTM D2240 test method.

The water absorption percentage of the vulcanizates was measured by immersing vulcanized pieces of the composites for three days and calculating the results according to the following formula.

$$\text{Water absorption}\,(\%) = \frac{(m_2 - m_1)}{m_1} \times 100$$

Where,

m_1= Initial mass of the test piece (g)

m_2= Final mass of the test piece (g)

Morphology

Surface morphology of the treated fibers on the size range of less than 50 µm was examined by Scanning Electron microscopy (SEM) using a ZEISS EVO LS 15 Microscope (Figure 1). The specimen was sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

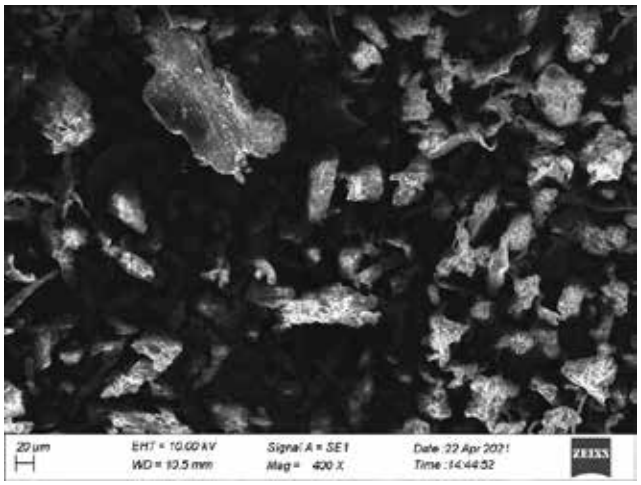

Figure 1. Morphology of treated OPF in the size range of less than 50µm

Results and Discussion

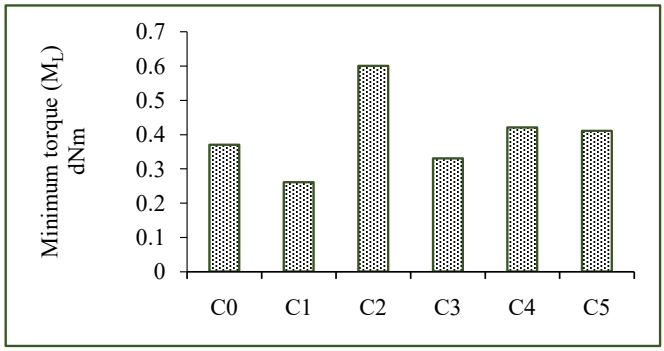

Figure 2. Minimum torque of NR/OPF composites

The minimum torque (M_L) of a compound relates to processability and stock viscosity of unvulcanized rubber (Edirisinghe *et al.*, 2015). According to the results obtained (Figure 2), it was perceived that the composite C2 (with 125 µm -175 µm size OPF) indicated a comparatively high value compared to the control composite and other composites. This indicates a poor dispersion of the OPF within the matrix with the size range of 125 µm -175 µm, which can lead to reduce processability. Additionally, the rest of the composites have indicated almost similar values to that of the control composite with satisfactory level of processability.

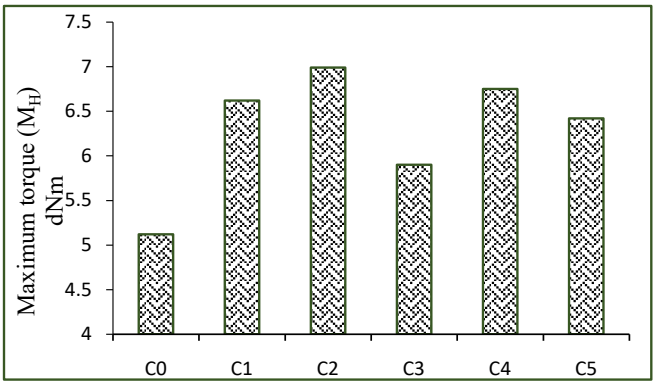

Figure 3. Maximum torque of NR/OPF composites

The stiffness of the fully vulcanized compound is represented by the maximum torque (M_H) value. With the initiation of the curing process the torque value tends to increase with the generation of crosslinks. According to the Figure 3, all the samples have torque values greater than the control composite. However, a systematic trend of the M_H values cannot be observed in the samples C1-C5. The reason for this can be the different levels of fiber entanglements occurring within the matrix. The highest stiffness can be expected with the composite C2, which has the highest torque value. This result is further evident from the hardness values obtained in Figure 10.

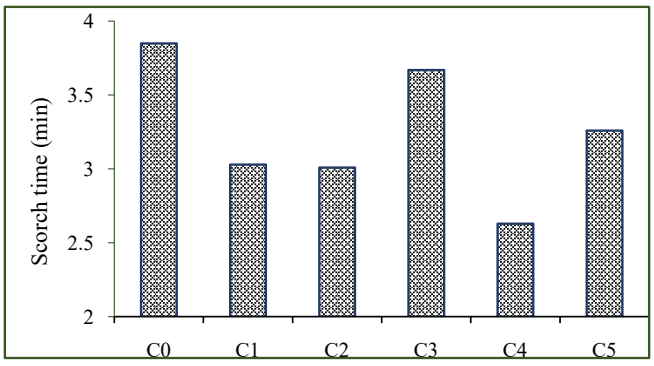

Figure 4. Scorch time of NR/OPF composites

The scorch time represents the processing safety feature of the sample (Formela *et al.*, 2015)static mechanical properties (tensile strength, elongation-at-break, hardness and resilience and according to the results (Figure 4) an increased processing safety can be seen with the C3 composite which has a close value to the C0 composite.

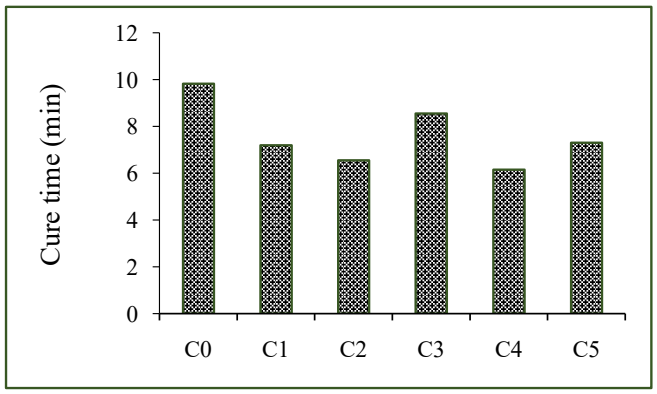

Figure 5. Cure time of NR/OPF composites

The variation of 90% cure time of the composites is represented in Figure 5 and according to the results the highest cure time has been obtained by the control composite. The values vary in the range of 6-10 minutes and the results reveal that the OPF fiber size range has no effect on the cure time since a significant trend is not available even though lower time has been consumed to cure the rubber article compared to the composite C0.

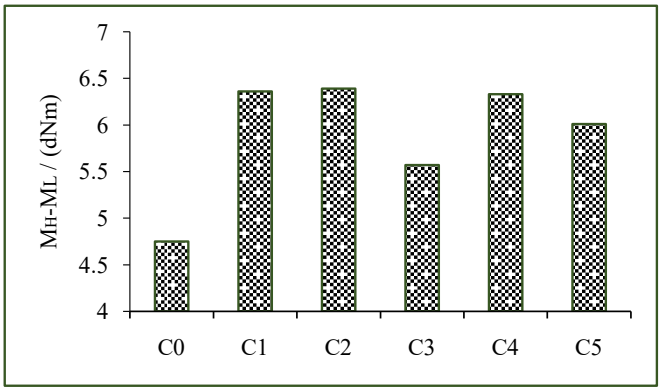

Figure 6. Delta cure of NR/OPF composites

The difference between maximum torque and minimum torque indicates the level of crosslink density of a composite. The variation of delta cure values of the composites is illustrated in Figure 6. The delta cure results of composites C1-C5 have generated high values compared to that of the control composite, which indicates greater rubber-filler interaction than filler-filler interaction existing in the OPF filled composites. This indicates that the addition of OPF to the matrix has uplifted the crosslink generation process.

Physico-mechanical properties

The variation of tensile strength of NR/OPF based composites is illustrated in Figure 7. The results indicate favorable values when compared to the control composite prepared with the filler carbon black. The

composites C1-C5 have generated 17-33% increment in tensile strength compared to the control composite with a tensile strength of 16.2MPa. This indicates that incorporation of treated OPF has generated better NR-filler adhesion than the carbon black filled composite. The highest value of 24.4MPa has been generated by the composite C2. However, the reduction in fiber size has not presented a significant property enhancement for the same level of fiber loading. A study carried out by Joseph *et al*. (2006) revealed that the physical properties of a composite can vary not only with the aspect ratio of the fibers, but also with different other factors such as fiber orientation, fiber dispersion and fiber-matrix adhesion. These can be possible reasons for the fluctuated values of tensile strength of the composites C1-C5.

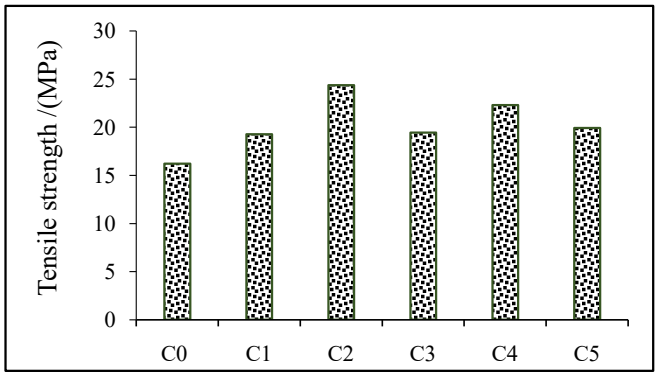

Figure 7. Tensile strength of NR/OPF composites

The elongation at break values has not shown a significant variation within the composites C1-C5 (Figure 8). However, when compared to the C0 composite, elongation at break values are lower. These values can be related to the trend in hardness observed in Figure 10, where the control composite has generated the lowest hardness of 28 Shore A and the NR/OPF composites have generated higher hardness values.

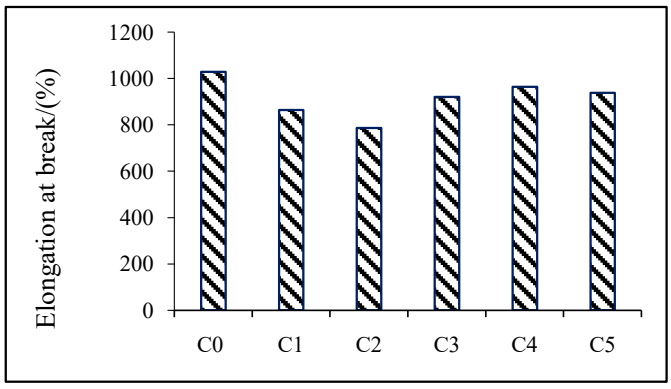

Figure 8. Elongation at break of NR/OPF composites

The tear strength of the composites C1-C5 has varied in the range of 27.44 N/mm to 175.1N/mm (Figure 9). A significant increase in tear strength in the latter composites can be observed with the decrease in fiber size. The control composite has generated a value of 131.9N/mm. This represents the variation of the dispersion of the larger fiber sizes compared to the smaller fiber sizes. The crack propagation has been a stress-free task for the composites C1, C2. One possible reason is the poor dispersion of the filler material in the NR matrix. This can be due to the reduced effective surface area of the larger size fibers and possible agglomerations. However with the higher effective surface area of the filler with lower fiber size, rubber-filler interactions have been improved, resulting in increased tear strength for the C3-C5 composites, which is greater than that of the control composite.

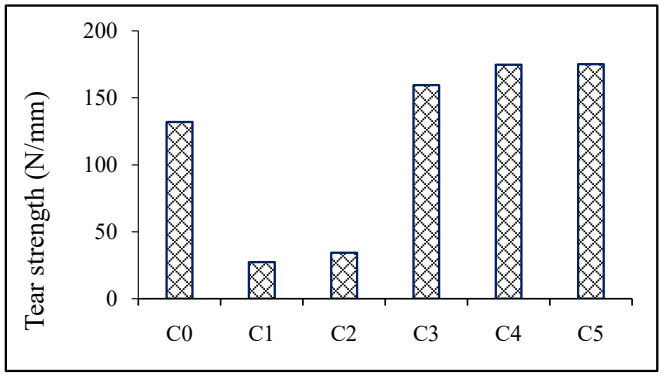

Figure 9. Tear strength of NR/OPF composites

The hardness values (Figure 10) are in agreement with the MH trend of cure characteristics (Figure 3) and the elongation at break results (Figure 8). All the composites with OPF has generated high hardness values when compared to the control composite (28 Shore A), which indicates enhanced compound stiffness generated by treated OPF. This can be attributed to increased compatibility between the treated OPF fiber and NR compared to that of carbon black filler. As the size of the OPF decreases, hardness has represented decreased values from C3-C5. This indicates that the larger fiber size has enhanced the hardness property than the smaller fiber sizes.

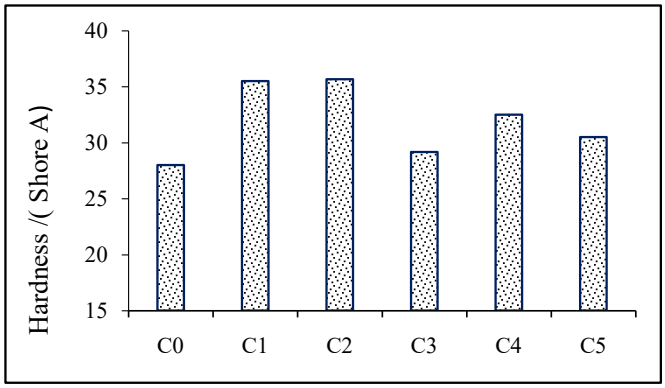

Figure 10 Variation of Hardness

The water absorption level of the fiber composites has generated higher values compared to that of the control composite (Figure 11). The main reason can be the affinity of cellulose rich natural fibers towards the water

molecules and the porosity existing with the OPF, which then results in providing a cooling effect to the matrix. A study carried out by Bopada *et al.* (2021) revealed that the mesocrap part of the OPF has increased the level of water absorption regardless of the duration of immersion in water of OPF based fiber cement mortar composite. The uptake of the water molecules has increased with the decreasing fiber size and a sudden drop can be seen in the final composite C5. This may be due to possible agglomerates generated within the composite leading to lower the effective surface area.

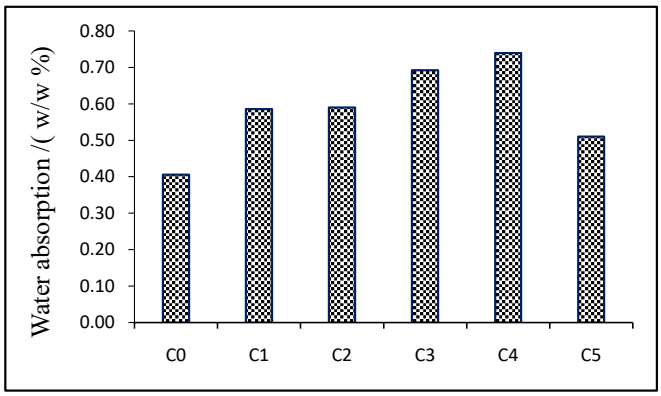

Figure 11. Water absorption of NR/OPF composites

Conclusions

The incorporation of chemically treated OPF into NR compounds has generated enhanced tensile strength and hardness for the composites compared to the control composite filled with carbon black. The analysis of cure characteristics indicated enhanced crosslink density and favorable cure time for the NR composites prepared with treated OPF, whereas the scorch time was reduced for the same. However, the reduction in particle size did not demonstrate a significant trend in regard to the cure characteristics. One possible reason is the amount of OPF loading (2phr) used to evaluate the effect of compatibility of micro size OPF with NR. Nevertheless, even with such a low loading level the enhancement of the mechanical properties provides an idea about the novel economical and eco-friendly approach to use treated OPF as a substitute to synthetic filler materials for highly flexible, low hardness property related applications.

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