

Surface treated natural rubber latex sludge as a potential filler for natural rubber compounds

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Abstract

Natural rubber (NR) latex sludge, a byproduct generated from centrifuged latex manufacturing industry, contains a large portion of inorganic materials and presently treated as a waste material. In this study, the sludge was converted to a powdery material through drying and grinding processes followed by a surface modification with a long chain fatty acid with a view improving its compatibility with rubber composites.

Composition and structure analysis of the latex sludge powder showed that it is mainly a crystalline material of phosphate mineral with approximately 8% of trapped rubber particles within the sludge material. Processed NR latex sludge powder was surface treated with a long chain fatty acid to offer organophilic character to the sludge. FTIR analysis confirmed that latex sludge was successfully modified with the long chain fatty acid.

A series of NR compounds were prepared with different loading levels of the surface treated sludge using a laboratory scale internal mixer to study the effect of the surface modified sludge on curing and mechanical properties in comparison to unmodified latex sludge filled NR compounds. Curing characteristics measured under low shear strain rate have shown that surface modification improves the processing safety without a significant impact on other curing characteristics.

Mechanical properties of surface treated sludge filled NR vulcanizates have shown an improvement in tensile properties, especially strength and elongation at break, in comparison to untreated counterparts. However, on the other hand, stiffness as measured with hardness was reduced at higher loadings of surface treated sludge filled NR vulcanizates. Both surface treatment and the increase of filler loading increased the compression strength and abrasion weight loss of the compounds.

Key words: fatty acids, mechanical properties, Natural rubber, NR latex sludge, surface treated

Introduction

Fillers are a group of materials frequently incorporated in to rubber composites as one of the major additives

among all the other rubber compounding ingredients such as activators, accelerators, vulcanizing agents, antioxidants, softeners, thickeners, *etc.*

to meet various product performance requirements (Okiemen *et al.*, 2003). It has been well established for decades that incorporation of filler has two main advantages; improvement of the reinforcement of the rubber composites and/or reduction of the cost of the final product (Hepburn & Blow, 1971). Incorporation of reinforcing filler into NR matrix improves physico-mechanical properties such as oil resistance, abrasion resistance and tensile strength of rubber vulcanizate by increasing the number of cross-links in rubber chains, which share load applied to the matrix. The reinforcement efficiency of the particulate filler depends on particle size, particle size distribution, particle shape, surface activity, and the interaction between the filler and the rubber matrix. (Ski, 1970; Parkinson, 1957; Hepburn, 1984). Non reinforcing fillers, known as diluents increase the bulk volume of the composite while reducing the cost of the materials.

A large number of studies on effective usage of various industrial and agricultural by-products such as wood flour, rice husk, palm kernel husks, fly ash as low cost filler materials, in rubber composites has been reported by many research groups (Okiemen & Imanah, 2003; Sae-Oui, P. *et al.*, 2002; Muniandy *et al.*, 2012; Pangamol *et al.*, 2018). These studies have revealed that the use of such materials in NR composites has multiple benefits such as low cost, certain property enhancements and in addition, the positive environmental impacts offered by restricting their disposal to the

environment. However, preparation of rubber composites filled with these types of fillers derived from industrial waste materials to yield useful technical properties, overcoming unnecessary agglomeration within the rubber matrix, is a challenging task.

Surface modifications of filler using various modifiers such as titanates, silanes, phosphates, fatty acids *etc.* have been widely reported as one of the main techniques to overcome the above challenge (NikNurAzzaNikAdik *et al.*, 2016). Stearic acid, a low molecular weight organic compound, has been used successfully to modify the surface of the different filler types like calcium carbonate and magnesium hydroxide. Coating with stearic acid on filler surface can improve the compatibility between rubber matrix and the coated filler, resulting in improved interfacial interaction and improved uniform dispersion within the rubber matrix due to the bi functional character (polar head and non-polar tail) of the stearic acid structure. Consequently, rubber composites with improved properties could be generated (Mihajlovic *et al.*, 2009).

Latex sludge containing magnesium ammonium phosphate which is a by-product generated in the magnesium removal process during centrifuged latex manufacturing process is one of the potential source for deriving a such low cost filler. Manufacture of 100 kg (dry rubber) of concentrated NR latex generates about 4-5kg of latex sludge. This is a considerable quantity when consider the total concentrated latex production of approximately 30,600 MT

(Rubber Development Department, 2016). In general practice, this sludge is disposed as a waste material, creating environmental issues such as emanating bad smell, contamination of water bodies and increasing the soil basicity. Even though agronomic benefits of the latex sludge have been investigated (Okiemen *et al.*, 2002), there is no reported literature available on its wide usage in the agriculture sector. This may be probably due to the presence of rubber particles trapped in the sludge which could decrease the rate of biological degradation. Effect of natural rubber processing sludge on the degradation of crude oil hydrocarbons in soil has also been investigated and found out that the extent of crude oil degradation was markedly increased by the sludge (Okiemen & Okiemen, 2002). A study on potential use of sludge ash as a filler in NR has revealed that there is a potential of using sludge ash as filler in the rubber industry (Intiya *et al.*, 2016). Use of untreated sludge as a semi reinforcing filler along with Carbon black for NR compounds has been reported by (Priyanka & Rathnayake, 2012). This study has revealed the use of sludge as a partial filler in carbon black filled rubber composites suitable for selected industrial applications.

Modification of sludge surface is a potential route to achieve the improved compatibility between latex sludge filler and the rubber matrix and subsequent enhance the dispersibility, widening its applications in the rubber industry.

Therefore, this study was carried out to investigate the effect of surface modification of latex sludge on the performance of NR compounds

filled/treated sludge. Sludge material was first characterized for its chemical composition and structure. Filler surface was treated with stearic acid and curing and mechanical performances of latex sludge filled NR compounds were investigated with a view to studying the effect of surface modification of latex sludge.

Materials and Methods

Materials

RSS No 1 grade of natural rubber obtained from Dartonfield Factory, Rubber Research Institute of Sri Lanka was used as the rubber material. NR latex sludge, a by-product of centrifuged latex manufacturing process, used in this study was obtained from Lalan Rubber (Pvt.) Ltd., Bulathsinghala, Sri Lanka. Other compounding ingredients used were of commercial grade chemicals supplied by local rubber chemical suppliers.

The latex sludge collected from Lalan Rubber (Pvt.) Ltd., was first sun dried for 4 days and further dried at 100°C in an oven for 24hrs and ground in to a powder. This powder was further dried at 120°C in an oven for 2hrs to assure a moisture free material.

Preparation of surface treated sludge

A volume of water (172ml) was heated to 75 ° C and stearic acid (20.3 g) was added in to the heated water. The mixture was further heated for another 15min. Ammonia solution (25 w/w %) was then added while stirring and the mixture was homogenized for 30min. Sludge suspension was prepared by mixing 640 g dried sludge powder into 3.2 L of

water. The temperature of the suspension was adjusted to 75 °C. Two mixtures were then mixed together and the mixture was stirred for one hour at 75 °C. Coated sludge was separated off and dried in an oven at 55° C for, 24hrs, and again ground to a fine powder.

Characterization of latex sludge

Chemical composition, especially metal iron concentration, of dried latex sludge powder was characterized with Atomic Absorption Spectrophotometer (AAS), model GBC Avanta 1, whilst phosphate content was determined using ASTM 4500-P (Vandomolybdophosphoric acid colorimetric method).

Structural analysis of sludge carried out using an X-ray diffractometer (Bruker D8 diffractometer and the analysis was performed at a wave length of 1.54Å of Cu K α radiations to determine the crystalline structure of the sludge, scanning over a two theta (2 θ) range from 1 to 60 degrees, at a rate of 0.01^o/seconds.

Rubber hydrocarbon content, acetone extract, and volatile material content were determined using ISO test methods, ISO 5945-19 2E, ISO 1404 and ISO 1976-E, respectively.

Fourier Transmission Infra-red Spectroscopy (FTIR) analysis was

carried out in order to find out the presence of stearic acid coating on the latex sludge using Nicolet 380 FTIR spectrometer. The analysis was done within the wavelength range of 400 to 4000 cm⁻¹.

The morphology of the sludge particles were studied with the HITACHI SU 6600 scanning electron microscope after the samples were sputter coated with a thin gold layer.

Compounding

Table 1 shows the formulation for each compound containing different loading levels of coated and uncoated sludge as filler.

For the compounding and mixing, a Brabender plasticorder (model: PL-2000) was used. Latex sludge filled NR composites were prepared by mixing them in the Brabender for 15 minutes at temperature of 60 °C and rotor speed of 60rpm. Various rubber additives were added to the masticated natural rubber prior to the addition of NR latex sludge and carbon black. Finally, accelerator and sulfur was added. Six natural rubber composites were produced incorporating different sludge loading levels from 0-100 phr at 20 phr intervals.

Table 1. Formulations of sludge filled NR composites

Ingredients	Amount (phr)	
	Uncoated Sludge filled Composites (USC)	Coated Sludge filled Composites (CSC)
Natural Rubber (RSS)	100	
Zinc oxide	5.0	
Stearic acid	2.0	
N-isopropyl n-phenyl,4-phenylendiamine	1.0	
Carbon black	30	
N-cyclohexyl-2-Benzothiazole sulphenamide (CBS)	1.2	
Tetramethyl thiuram monosulfide (TMTM)		
Sulfur	0.4	
Processing oil	2.0	
Sludge uncoated	5.0	
Sludge coated with stearic acid	Variable	(0-100) -
	-	Variable (0 -100)

Cure characteristics

Cure characteristics of the composites were determined using a moving die rheometer, model (MDR:Ekron EKT-2000s) according to ASTM 5289 at 130 °C. Cure characteristics of the latex sludge filled NR compounds were derived from the respective rheographs.

Mechanical properties

NR vulcanisates were prepared by compression molding of rubber compounds according to respective optimum cure times (t_{90}) using a Hot press (KAO-Tech compression Moulding Machine) at 130°C. Tensile properties and tear strengths of the rubber vulcanisates containing coated and uncoated sludge were analyzed using an Instron, model 3365 Universal

Tensometer following ASTM D 412-68 and ASTM 624-54 standards methods respectively. Five specimens were analyzed from each composite and the average results were recorded.

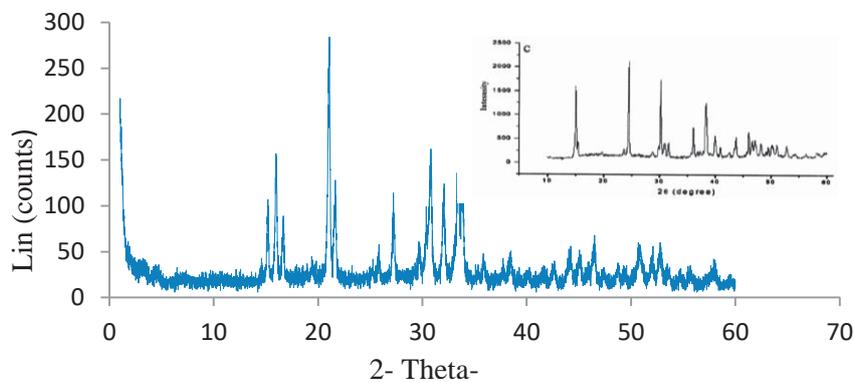
Results and Discussion

Composition and structure characterization

Composition of the latex sludge dried at 120°C is presented in Table 2. The results show that magnesium and phosphorus are the main inorganic constituents in the sludge. There is also a considerable amount of polyisoprene which indicates the natural rubber (measured as polyisoprene) trapped in the sludge material. Volatile matter percentage is about 5.54 (w/w) which consists of both ammonia and moisture of the sample.

Table 2. Chemical composition of NR latex sludge dried at 120°C

Constituent	(w/w %)
Oxygen (based on phosphate content)	36.0
Magnesium	27.73
Phosphorus	18.26
Poly isoprene content	8.31
Volatile matters	5.54
Ammonical Nitrogen content	0.16
Zinc	0.001
Other materials	add to 100

**Fig. 1.** The XRD spectrum of uncoated NR latex sludge

The diffraction peaks are appeared at 15^o, 45^o, 46^o, and 47^o in the -XRD spectrum of the sludge are analogous with the characteristic peaks for magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), a phosphate mineral known as struvite. Therefore, XRD analysis suggests that sludge is a phosphate rich mineral with a structure similar to struvite (Fig.1).

Morphological studies

Figure 2 (a) illustrates the SEM micrographs of the latex sludge. It could be seen that uncoated sludge particles exist as agglomerates with irregular sizes and shapes. SEM micrographs of the sludge observed at higher magnification

are shown in Figure 2 (b). It clearly shows platelet like laminated sheets structure of the sludge particles. Due to these laminated structure, sludge particles have a higher aspect ratio, which has a potential reinforcing effect in a polymeric composites matrix. When the micrographs of untreated and surface treated filler samples at same magnification (Figures 2(a) and 2 (c) are compared, agglomerates of relatively smaller sizes could be seen in surface treated sludge. It could be suggest that the surface coating has restricted the sludge particle agglomeration to a certain extent.

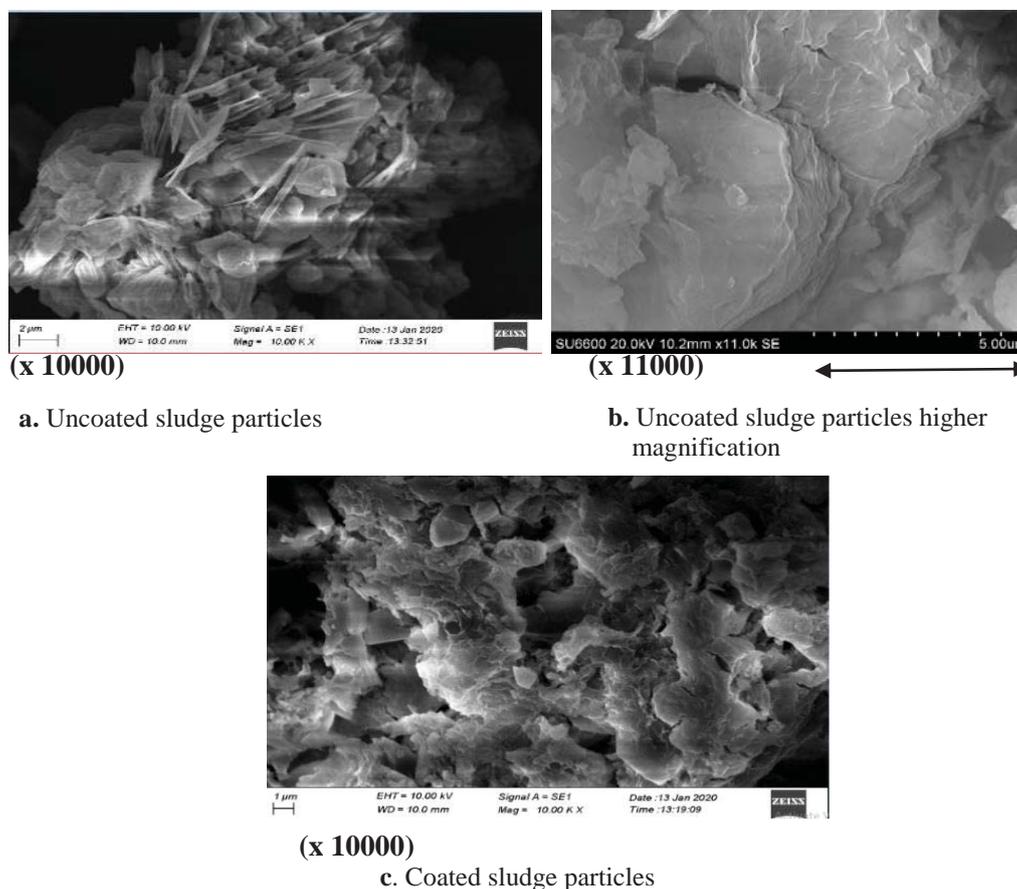


Fig. 2. Illustrates the SEM micrographs of the sludge

FTIR analysis

Figure 3 shows the infrared spectra of coated sludge and uncoated sludge samples. Peaks at 2326 cm^{-1} due to stretching vibration of NH_4 group, 1480 cm^{-1} due to bending and vibration of crystalline water, 1070 , 990 and 913 cm^{-1} peaks due to bending and vibration of PO_4^{3-} (Stefov *et al.*, 2005) they are common to both coated and uncoated spectrums and further confirmed the sludge as crystalline magnesium ammonium phosphate hexahydrate. IR band appear at 1241 cm^{-1} due to CO-O

stretching in esters and two additional peaks at 2854 cm^{-1} and 2919 cm^{-1} seen in the FTIR spectrum of coated sludge. These two additional peaks correspond to symmetric and asymmetric stretching and vibrations of aliphatic groups $-\text{CH}_2-$ groups. Presence of these peaks in the spectrum of stearic acid coated sludge suggests that, there is CO-O groups and C-H bonding typical to CH_2 groups of stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$). Therefore, it is evidenced that modification of the sludge surface with stearic acid is successful.

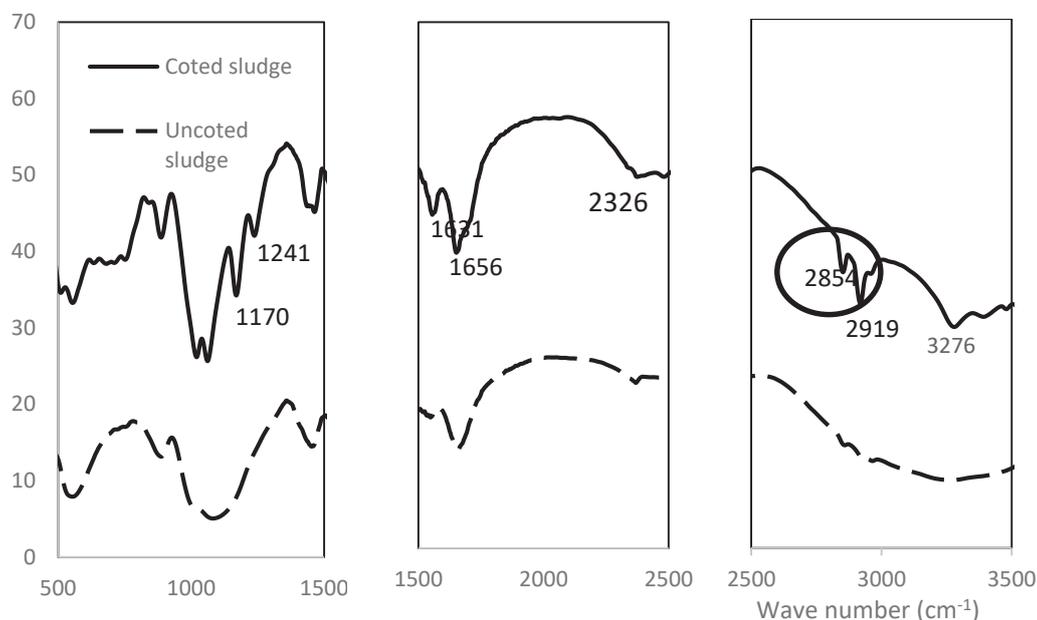


Fig. 3. FTIR of Stearic acid coated and uncoated sludge

Cure characteristic and processability of NR/sludge compounds

Figures 4 to 8 show the effect of stearic acid coated sludge and uncoated sludge on the curing characteristics of the rubber compounds.

Figure 4 shows that incorporation of sludge has initially resulted an increase in the scorch time in both uncoated and coated composites. Maximum increase was registered at 20phr sludge loading for both types of compounds. For unmodified filler incorporated composites, the scorch time gradually decreases after passing through the maximum values while treated composites remains its scorch time almost unchanged. Incorporation of filler may retard the formation of activator-accelerator pre-cursors due to the adsorption of them by the filler

agglomerates. The composition analysis of the sludge confirmed that it mainly consist of magnesium ammonium phosphate hexahydrate. Ammonium salt which could increase the basic nature of the rubber compounds and hence supports the curing reactions. Therefore, increase in ammonium salt content with increasing filler loading speeds up the formation of the activator-accelerator complexes loading at higher filler loading as the surface area of filler agglomerates dose not increase proportionally to its volume. Therefore, decrease in scorch time of un-coated sludge rich compounds could be elucidated. It has been reported in literature that addition of various types of fatty acids at high concentrations could retard the curing reactions due to the various complex reactions associated

with the soluble Zn ions formed in the compound (Coran, 1965, Poh & Tang 1995, Hanafi Ismail & Tajur Arus Ruhaizat,1997). In surface treated sludge, it has two major chemical substances namely Magnesium ammonium phosphates and stearic acid, both influence the curing reactions in two opposite directions. This may results in the almost unchanged higher scorch time of treated sludge incorporated compounds due to the compensation of opposite effects of each other. Therefore, it could be seen in Figure 4, that stearic acid coating has diminished the effect of filler loading on the scorch time of the treated sludge filled composites after a certain filler loading (20 phr).

In contrary to the effect on scorch time of the composites, there is a reduction in

T_{90} of the both types of filled compounds even at 20 phr sludge loading (Fig. 5). T_{90} of Uncoated Sludge Compounds (USC) exhibited a gradual reduction may be probably due to the presence of ammonium slats in the sludge. CSCs show an almost unaffected T_{90} values with sludge loading. The acceleration effect of ammonium salts and retardation effect of excessive fatty acid concentration in curing reactions of NR compounds incorporated with treated sludge explain this trend. Higher scorch time and lower T_{90} values of 20 phr sludge filled compounds than that of NR gum compounds suggests that adsorption of curing ingredients by filler particles has become significant only at the low loading levels.

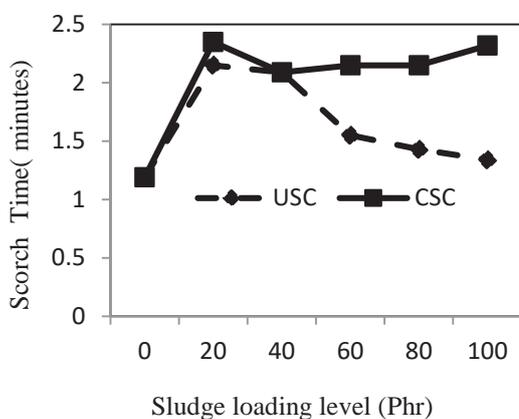


Fig. 4. Scorch time vs sludge loading

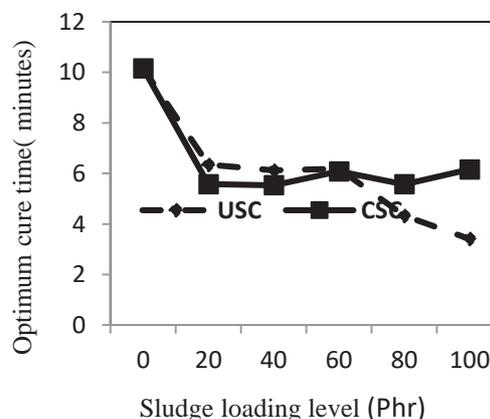


Fig. 5. Curve time vs sludge loading

As it could be seen in Figure 6, for uncoated sludge filled composites, cure rate index gradually increases with the sludge loading. In other words, a faster cure rate is obtained for the composites with increasing sludge loading. This may be due to the ammonia complexes formed between ammonia and compounding ingredients yielding new substances which accelerate the curing process. Coating of sludge may delay the curing reactions as it could be acted as a barrier in emitting moisture and ammonia which cause to increase the cure rate (Egwaikhide *et al.*, 2013) which is in par with the earlier observations made by other researchers (Poh & Tang 1995, Hanafi Ismail & TajurArus Ruhaizat 1997). From the results, it is evidenced that coating diminishes the effect of sludge loading on the cure rate of coated sludge filled NR compounds. Modification of sludge surface with stearic acid seems to allow incorporation of higher sludge loading without much adverse effect on the total cure time and processing safety. As expected, incorporation of sludge has increased the minimum torque which

indicates the processability of the rubber compound (Fig. 7). Higher the minimum torque, lower the material's processability. This is because of the restriction exerted by the filler particles against the mobility of rubber macromolecules. Maximum torque also increases for both types of composites, until it reached certain loading, beyond which maximum torque has again decreased with the sludge loading. When the composites are vulcanized, rubber molecules are cross linked and restrict their mobility in addition to the restriction applied by filler agglomerates. As the filler loading increases, larger agglomerates are formed in cross-linked rubber matrix and it may become unstable due to formation of larger agglomerates under experienced strain yielding lower torque values. It could be further seen in Figure 8 that the maximum torque of rubber compounds modified with stearic acid is lower than the corresponding uncoated sludge containing compounds. This may be due to the plasticizing effect of excess stearic acid in the modified sludge.

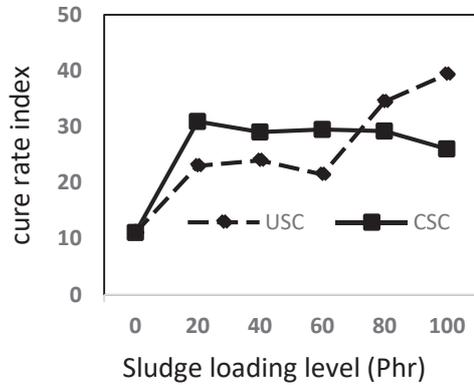


Fig. 6. Cure rate index vs sludge loading

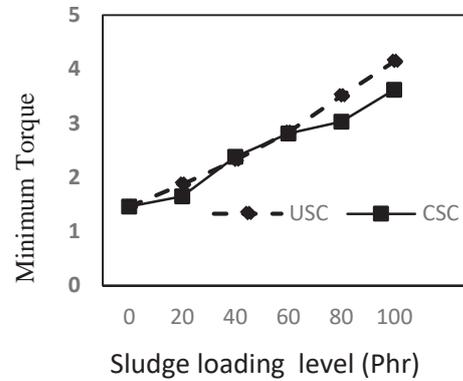


Fig. 7. Minimum torque vs sludge loading

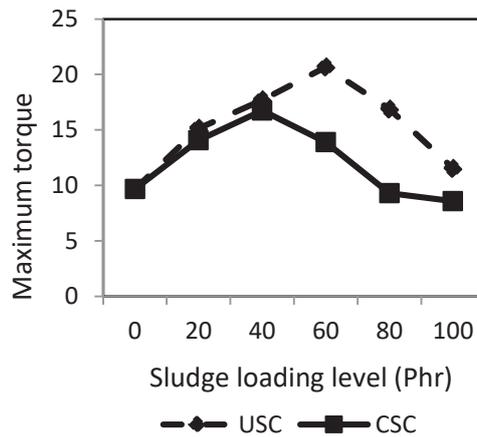


Fig. 8. Maximum torque vs. sludge loading

Mechanical properties

Figure 9 and 10 show the stress-strain responses of both unmodified (uncoated) and surface modified (stearic acid coated) latex sludge filled NR vulcanisates as a function of filler loading.

As expected, tensile strength (Fig. 9) of both uncoated and coated latex sludge filled vulcanisates was shown a reduction with the increase of sludge loading. In general, natural rubber gum

compounds have shown strain-induced crystallization and the material crystallizes under increasing stress (Ismail *et al.* 2010). However, incorporation of sludge (*i.e.* both modified and unmodified latex sludge) may disrupt the strain-induced crystallization process of NR. In addition, as the filler loading increases, there is a trend to form larger sludge agglomerates resulting in inhomogeneous distribution of sludge

agglomerates and poor interactions between sludge particles and rubber matrix and as a result of incompatibility of the filler and rubber. These agglomerates could serve as stress concentration points and flaws yielding poor tensile properties. Similar observations have been reported in literature for NR composites filled with other incompatible filler/natural rubber compounds (ShuhairiahDaud *et al.*, 2016). However, it could also be inferred from the results that surface modification with stearic acid has improved the filler dispersion within the rubber matrix and hinder the sludge agglomeration to a certain extent as evidenced by the higher tensile strength values of coated sludge filled NR vulcanisates in comparison to that of uncoated sludge filled NR vulcanisates (Fig. 9), especially, at lower

sludge loading up to 60 phr. Beyond 60 phr, coated and uncoated samples showed same values in tensile strength. This may be due to agglomeration of even coated latex sludge particulates at a higher loading.

According to Figure 10, % elongation at break is gradually decreased with increase of uncoated latex sludge in the compounds while gradual increasing tendency is observed for the surface coated sludge filled compounds. This may be due to the availability of excess unreacted stearic acids that acted as a plasticizer in the NR compounds. Due to the lubricating effect created by unreacted stearic acid, sludge particles could slide over one another during stretching the matrix which resulted in an extra extension.

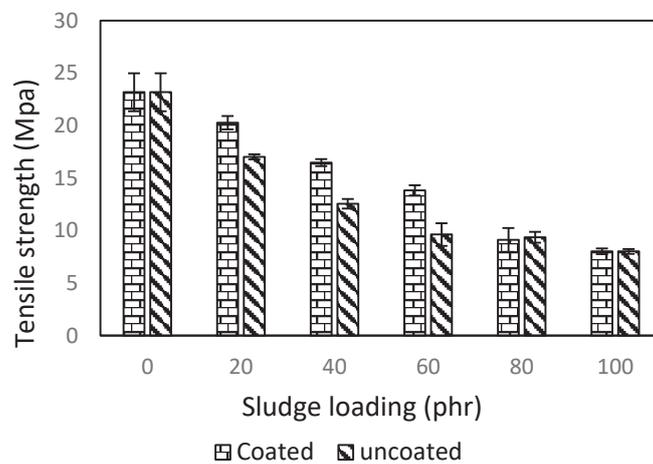


Fig. 9. Tensile strength of stearic acid coated and uncoated sludge containing vulcanizate

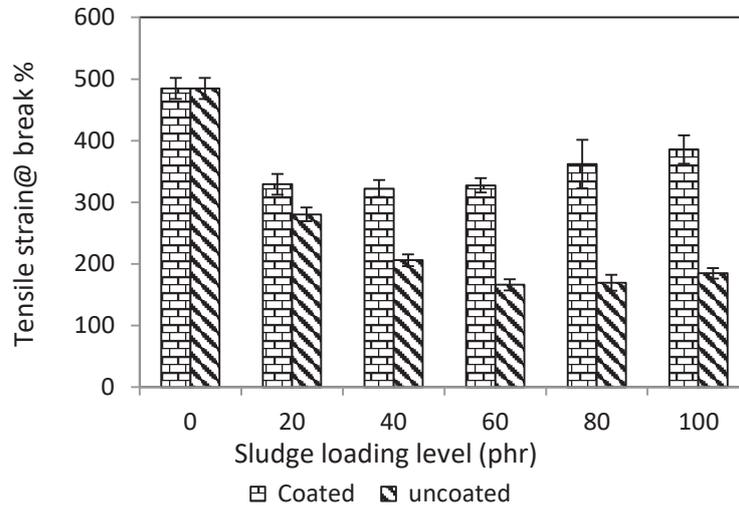


Fig. 10. The effect of filler loading on % elongation at break of stearic acid coated and uncoated sludge containing compound

Stress at 100% elongation related to degree of filler to rubber interaction and the dispersion of the filler in elastomer matrix. Table 3 shows the effect of filler loading on modulus at 100% elongation. Modulus of the filled compound increased with an increase of filler loading. When further increase of latex sludge loading, the rubber content decreases resulting in increase in the stiffness of the composites. As there is

no adequate rubber phase to wet the filler particles, the composite shows properties of a lightly bonded weak inorganic material yielding low modulus values at higher filler loading. The lower modulus values registered for coated composites may be again due to the presence of free stearic acids in the composites. They also follow the same variation of modulus with the loading as uncoated composites.

Table 3. The effect of filler loading on 100% modulus of stearic acid coated and uncoated sludge containing compound

Filler loading (sludge) (%)	Modulus @ 100% (Mpa)	
	Un-coated	Coated
0 (unfilled)	1.707	
20	4.003	3.418
40	4.924	3.886
60	5.399	3.34
80	5.109	2.314
100	4.036	1.736

Table 4. Mechanical properties of un-coated and coated sludge containing composites

Filler loading (sludge) (%)	Hardness (IRHD)		Resilience (%)		Compression Set (%)		Abrasion as volume loss (mm ³)	
	Un-coated	Coated	Un-coated	Coated	Un-coated	Coated	Un-coated	Coated
0(unfilled)	53.4		77.0		8.29		57.0	
20	64.1	60.5	71.5	72	10.93	8.57	77.85	197
40	67.75	66.6	70.5	70	11.26	11.17	216.6	234
60	72.58	63.9	69	62	13.96	11.56	258.8	300
80	70.35	56.8	63	51	13.4	27.8	275.2	367
100	65.39	55.1	54	49	26.6	32.5	313.4	360

Both vulcanisates, it has shown that hardness (IRHD) is increased at lower loading levels of latex sludge while it decreases gradually when the loading level is high. However, at any given sludge loading level, coated sludge filled vulcanisate shows a lower value than that of uncoated sludge filled vulcanisate. This is attributed to the fact that unreacted stearic acid present in the rubber matrix acts as a plasticizer, resulting in reduced hardness.

There is no considerable reduction of resilience up to 60 phr level indicating persistence of bouncing effect. It is evident from the results that there is no significant difference in compression set percentage in both coated and uncoated sludge incorporated compounds up to 60 phr level. Above 60 phr, there is a huge increment in percentage of compression set in both USC and CSC compounds. It could also be noted that at higher filler loading, percentage of compression has become higher in stearic acid coated sludge containing compounds when compared with uncoated sludge containing compounds.

In high filler loading levels such as 80 and 100 phr, agglomeration of filler is higher owing to poor filler dispersibility as well as the percentage of non vulcanisable materials in the composites. Consequently, lower cross linking density in the composites. It creates low strain recovery when the compression load relieved resulting in high percentage of compression set. Higher compression set is exhibited in stearic acid coated sludge containing higher filler loading due to presence of higher quantity of free fatty acids which increase lubricating effect. Fillers could slide over one another when compressed resulting low recovery on relieve due to stearic hindrance of stearic acid. (Nik Nur Azza NikAdik *et al.*, 2016). This may also lead to increase of percentages of compression set get higher at high loading levels.

Abrasion loss has significantly increased with incorporation of the sludge for both uncoated and coated composites. It has gradually increased with increasing sludge loading. Modified sludge containing compounds however, shows

relatively lower abrasion resistance over the uncoated counterpart. Lubricating effect of the stearic acid discussed earlier may be responsible for this observation too.

Conclusions

Studies on chemical composition and structural characterization revealed that processed latex sludge has a structure resembling the crystalline material known as struvite. In addition to magnesium salts and phosphates, it contains rubber and other inorganic materials trapped within the latex sludge. Inorganic latex sludge is successfully converted into organo-philic by surface modification with stearic acid treatment. Unmodified latex sludge accelerates the vulcanization reaction of NR compounds as shown by cure rate index data. However, surface modification of latex sludge with stearic acid neutralizes the curing acceleration created by latex sludge and consequently curing characteristics of NR compounds are not affected by surface modified latex sludge.

Surface modification of latex sludge with stearic acid improves the uniform dispersion of sludge within the rubber composite and, moreover, enhances the compatibility between the two components. As a result, failure strength characteristics under tensile deformation of coated sludge filled composites (CSC) is improved compared to that of uncoated sludge filled composites (USC). Although surface treatment of sludge has a significant impact to prevent latex sludge agglomeration and enhances in sludge dispersion within the NR

composite material, at higher loading levels of coated sludge, negatively affected on mechanical properties of composite due to higher amount of remaining free stearic acid in coating process. Therefore, this surface modified latex sludge material could be used in NR compounds as a semi reinforcing filler for different applications depending on the required vulcanizate properties.

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