International Research Journal of Advanced Engineering and Science
ISSN: 2455-9024

Evaluation of Some Mechanical Properties of Composites of Natural Rubber with Egg Shell and Rice Husk

B. T. Sawere[1], A. U. Igbuku[2]
[1, 2]Department of Science Laboratory, Delta State Polytechnic, Ozoro
Email address: [1]saweretesi@yahoo.com

Abstract— *Egg shell and rice husk were incorporated into natural rubber using a laboratory size two roll mixing mill. A conventional vulcanization was used for curing. The tensile strength, abrasion resistance, hardness as well as the equilibrium swelling characteristics of the vulcanizate in toluene were measured as function of filer loading. The composites were varied from 0pph to 70pph. The tensile strength of the egg and rice husk filled vulcanizates exhibited retardation with increase in filler contents. The egg shell retarded from 12.5Mpa to 6.6Mpa and the rice husk from 10.4Mpa to 4.7Mpa. The hybrid was erratic, decreased from 92Mpa to 84Mpa and thereafter increased to 14.4Mpa. The abrasion resistance showed an irregular pattern of initial decreased from 92Mpa to 84Mpa and thereafter increased to 92Mpa and finally decreased to 89Mpa with increase in filler loading for egg shell, with a maximum wear ratio of 10.8 x 10-2g/rub. The rice husk increased from 85Mpa to 80Mpa, decreased to 79Mpa, with a maximum wearratioof1.27x 10-2g/rub. The hybrid decreased from 88Mpa to 83Mpa, with a maximum wear ratio of 1.4 x 10-2g/rub as the filler load increased. Hardness of vulcanizate increased with increase in filler contents from Opph to 70pph*.

Keywords— *Natural rubber, composite, eggshell, rice husk, fillers, vulcanizate.*

I. INTRODUCTION

Natural rubber (NR) is one of the main elastomers and widely used to prepare many rubber compounding products (Khali et al., 2014). The wide commercial acceptance of rubber (NR) has been attributed to some of its outstanding properties' over some known elastomers. Natural rubber is a renewable agricultural resource that does not naturally possess the necessary hardness and modulus required for its commercial acceptability (Akinlabi et al., 2005). Natural fillers is frequently reinforced by assimilation of fillers to improve its mechanical properties like: tensile strength, modules, tear strength elongation at break, hardness, compression set, rebound resilience and abrasion resistance (Frohlich et al., 2005). For this, carbon black and silica are commonly used (Salaech, et al., 2012). The incorporation of various materials (additives as compounding ingredients) increases these aid characteristics to the level desired for NRs demands (Okiemen et al., 2002). The additives which are added to enhance the processibility and properties of rubber vulcanizates are usually sourced from combinations of any of the followings: accelerators, activators, fillers, antioxidants, vulcanizing agents, softeners, plasticizers etc. Filler is one of the major additives used in natural rubber compound and has marked effect and influence on rubber materials. Filler play a dominant role in modifying the physical properties of base polymer. (Teena et al., 2013). Particulate fillers are added to rubber either to extend or cheapen the rubber compound, or to add desirable qualities to the final compound and enhance the products service qualities. (Dannelly 1999). In rubber industry, fillers that are commonly in use are carbon black, China clay and calcium carbonate. Nowadays, there has been a growing interest in the use of individual an d Agricultural waste such as product like rice husk (Attharangsan et al., 2012) as fillers for rubber and their blend Rice husk is a major by-product obtained from the production of rice. The main constituents of rice husk are cellulose, lignin and sugar. In addition to organic compounds rice husk is also composed of approximately 20 wt% of amorphous silica by weight of burned pelt (Tzong-Horngs et al., 2004). It is the most important agricultural dregs and well recognized that the rice husk is a significant source of silica (Khali et al, 2014). Chemical analysis of rice husks revealed the following typical composition (referred to as substance free from loss on ignition); 9% water, 3.5% protein, 0.5 fats, 30-42% cellulose, 14-18% pentosan and 14-30% One of the not important phenomena in material science is the reinforcement of rubber by rigid entities, such as Rice husks, carbon black, clays silicates and calcium carbonate. Thus, these fillers or reinforcement aids are added to rubber formulations to optimize properties that meet a given service application or set of performance parameters (Walff, 1996). Although the original purpose is to lower the cost of the molding compounds, prime importance is now attached to the selective active filler fillers and its quantity that produce specific improvements in rubber physical properties. Natural rubber is usually considered to have good processing properties. Altogether it is tough and "nervy" at temperatures well below 100Oc, it breaks down easily to a useable plasticity. Generally it can adapted to any fabrication technique at the rubber factory. The viscosity of stabilize grades of natural rubber do not generally requires pre mastication before the incorporated of fiber and other compounding ingredients. For a non-stabilize grade, a short mastication time before compounding is common practice .The efficiency of mastication is lowest at around 100^oC.mastication is best carried out below 80^OC (well-cooled open mill) or above 120^0C intermixture. Chemical peptizers allow mastication to be carried out at lower temperature and are thus useful for increasing mastication throughout. The viscosity of the masticated rubber is strongly dependant on that of the bale rubber used. Rubbers with high initial viscosities tend to break down faster. Many attempts on research work have been carried out with different fillers in order to improve the mechanical properties of rubber and rubber composites. Egwaikhide et al. (2007) worked on an investigation on the potential of Palm Kernel Husk as filler in Rubber Reinforcement. The preliminary results show that palm Kernel Husk is potential reinforcing filler for natural rubber compounds. Helson et al. (2007) in analysis of variance of effect of rice husk ash and commercial fillers in NR compounds. The analysis reveals that BRHA shows little variation in the mechanical properties of NR compounds; in other words, it is non-reforcing filler and their use must be restricted to 20pht, approximately. For WRHA, NR compositions containing 10 and phr of filler shows a real increment in the tensile strength and the variation of this filler (0 up to 50phr) causes maximum variation upon tensile strength, according to FO value. Okiemen et al. (2007), worked on effect of coconut fibre filler on the cure of characteristics and physic –mechanical and swelling properties of natural rubber vulcanisates. The result shows that coconut fibre is a potential reinforcing filler for natural rubber compounds. It was found that vulcanizates with 60ph showed maximum tensile properties. Hardness of filled vulcanizate with coconut fibre increased in filler loading. Abrasion resistance decreased marginally with increasing filler loading. The resistance to swelling of natural rubber compound is dependent on the amount of filler loading; the higher of filler content the lower the equilibrium sorption values obtained. Manroshan et al., (2005) reported their work on effect of Nanozied Calcium carbonate on the mechanical properties of latex films. The result shows that the curing time decreased with filler loading because of the increased in interaction between the filler and the rubber matrix, as reflected by the apparent swelling index. Tensile strength and EL increased up to 10phr of filler and then decreased again. Rakdee et al. (2001) worked on use of Rice Husk Ash as filler in Natural Rubber vulcanizate: in comparison with other commercial filler. It was found that both grades of rice husk ash provide inferior mechanical properties (tensile strength ,modulus, hardness, abrasion resistance and tear strength) in comparison with reinforcing fillers such as silica and carbon black. Sobyhy et al. (2003) studied the cure characteristics and physioco-mechanical properties of calcium carbonate reinforced rubber composites. The results showed that the cure characteristic and the physic mechanical properties of $CaCO_3$ reinforced NR or NBR compound depend mainly on both the filler concentration and the type of the rubber used. The uses of $CaCO_3$ as reinforced filler improve the physicomechanical properties at the aging resistance to Y-irradiation. Da Costa et al. (2002) worked on Mechanical and Dynamic Mechanical properties of Rice Husk Ash Filled Natural Rubber compounds (WRHA). The vulcanizate with 20phr of this filler gave the best results, and showed physical properties not much inferior to commercial carbon black or silica filled vulcanizates. The mechanical properties of Natural rubber with flyash were investigated and compared with those filled with calcium carbonate (Hundiwale et al, 2002). From the result it was observed that the flash filled composites were better in mechanical properties compared to those filled with calcium carbonate .it was further observed that addition of filler increased the tensile strength and module so that to reach maximum and he property decreased with increased the volume fraction of the filler. This research work deals with effect of rice husk and egg shell on the mechanical properties of natural rubber vulcanizates. The objective is to enhance mechanical properties of natural rubber with eggshell and rice husk.

II. Material and Method

Materials

Natural rubber crumbs (Grade NR -10) were obtained from the Rubber Research Institute of Nigeria (RRIN), Iyanomo – Benin. The rubber compounding chemicals such as Zinc oxide, steric acid, Sulphur and CBS were of commercial grade.

Egg shell and rice husks were obtained from Kano metropoly and Danbatta LGA of Kano.

Filler preparation

Large quantity of both eggshell and rice husk were obtained, cleaned, dried and ground into fine powder; sieved with a mesh of the sizes 120um, respectively.

Dry ashing

1.0g of each samples of egg shell and rice husk were ashes in a furnace, at 450oc for about 8 hours.

Digestion

Eggshell was digested with 4 mol of HNO_3 and made up with deionized water to 100cm 3 flasks, filtered into a Labeled sample bottle.

Analysis of digested samples

The samples were analyzed for the element potassium (k), calcium (Ca), sodium (Na), copper (Cu), Zinc (Zn) Mangane (Mn), Magnsium (Mg), lead (pb) and Iron (Fe) with A.A.S.

Compounding

The recipient used in compounding of the natural rubber compound is given in table I.

TABLE I. Recipient for compounding the NR mixture.

Ingredient	Grade	Part per hundred (pph)	Part per batch (g)
Natural rubber	NR-10	100	400
Steric acid	Gen. Purpose	1.5	6
Zinc Oxide	Industrial	5.0	20
C.B.S	Industrial	0.6	24
Sulphur	Industrial	2.5	10

C.B.S. = Cyclohexyl Benthlexyl Sulpheamide

Curing

The gum stock of mixture from each formulation was pressed into sheet at the pressure 165kg / cm^3 and cured at 155^0c.

Determination of Vulcanizate Properties

Wear and abrasion resistance

A, Williance abrasion test was used in accordance with the British standard method for determination of Abrasion resistance, part A9, 1998 (903).

B. T. Sawere and A. U. Igbuku, "Evaluation of some mechanical properties of composites of natural rubber with egg shell and rice husk," *International Research Journal of Advanced Engineering and Science*, Volume 1, Issue 3, pp. 71-75, 2016.

International Research Journal of Advanced Engineering and Science
ISSN: 2455-9024

Tensile properties

The tensile strength of vulcanizate was measured using Z wick 1425 tensile machine - ASTM D419 98a at a cross sectional speed of 500mm/min on a dumbbell test specimen as contained in ASTM D412-87.

Density

The relative density of vulcanizate composites were determined using specific gravity balance (SG).

The density of rice husk filler was determined by achimedis principles while that of eggshell filler with gravitmetric method, using density bottle.

$$Rs = \frac{W_1 - W_0}{(W_4 - w_0) - (w_2 - w_1)}$$

Where W_1-W_0 = Weight of the filler

$(W_4 - w_0)$- $(w_2 - w_1)$ = weigh of Volume of water

Ph Measurement

This was determined using digital computer pH meter (Luttron 210).

III. Results and Discussion

Particle Size

The particles size of 120um of filler of egg shell and rice husk was used, respectively. Fine particles actually affect their greater interaction between the rubber matrix and the filler and hence provide a higher degree of reinforcement than the coarse ones.

Elementary analysis

It was observed from the result obtained in table II, that the egg shell has a higher concentration of the elements than that or rice higher, except for Ca, Mn, and Fe. Therefore, the higher density observed in egg shell us most likely due to the elements that make it up and the degree to which the egg shell particles are bound together in aggregate or agglomerization due to Vander Walls forces.

TABLE II. The concentration (mg/L) of elements of egg shell and rice husk.

Sample	Element								
	K	Ca	Ng	Cu	An	Mn	Mg	pb	Fe
Egg shell	23.12	32	4.250	0.050	11.23	0.016	92.13	0.243	0.041
Rice Husk	31.12	0.5	2. 023	0.024	10.62	0.055	91.23	0187	0.803

pH of filler.

The pH results obtained were 8.14 (basic) for egg shell and 5.50 (acidic) for rice husk. Alkaline substance (eggshell) increase the cure rate i.e the chemical cross linking of individual polymers.

Filler density

The densities for egg shell and rice husk were 2.313g/cm^3 and 0.833g/cm^3 respectively. This implies that for a given part per hundred (pph) of filler in the matrix, rice husk particles numerical strength will almost be thrice that of egg shell by magnitude present in the ratio 1:3 in density.

Wear and abrasion resistance (rub/g)

The resistance of a rubber compound to wearing away by contact

With a moving abrasion surface -weight.

Wear rate = wt lost/No of rubs (g/rob) – i

Wear resistance = 1/wear rate (rub/g) _ ii

Wear rate (g/rub)

The wear rate as shown in table III for egg shell was between E_{10} and E_{60}. The rice husk decreased with increase in filler loading in accordance with Harry and John (1997), that addition of any particles filler can reduce some of the physical parameters of a polymer more or less in proportion to the volume present. There was a noticeable wear rate effect on hybrid composite. The shell has more impact on wear properties than that of the rice husk.

Table III. Wear rate of egg shell, rice husk and hybrid composite.

Egg Shell		Rice Husk		Hybrid	
Formulation	Mean wear rate 10^{-2} (g/rub)	formulation	Mean wear rate10^{-2} (g/rub)	Formulation	Mean wear rate 10^{-2} (g/rub)
E_{10}	1.09	R_{10}	1.18	$E_{10}R_{50}$	1.14
E_{20}	1.11	R_{20}	1.18	$E_{20}R_{40}$	1.15
E_{30}	1.19	R_{30}	1.25	$E_{30}R_{30}$	1.14
E_{40}	1.09	R_{40}	1.27	$E_{40}R_{20}$	1.14
E_{50}	1.08	R_{50}	1.14	$E_{50}R_{10}$	1.20
E_{60}	1.09	R_{60}	1.19	R_0	0.31
E_{70}	1.13	R_0	0.71		

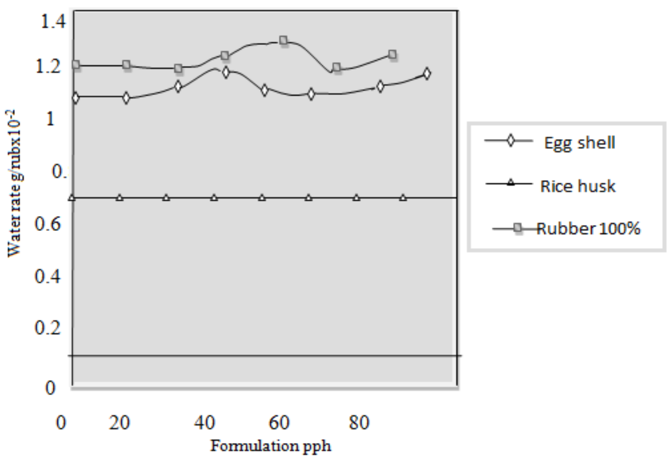

Fig. 1a. Effect of formulation on wear rate of egg shell and rice husk composites.

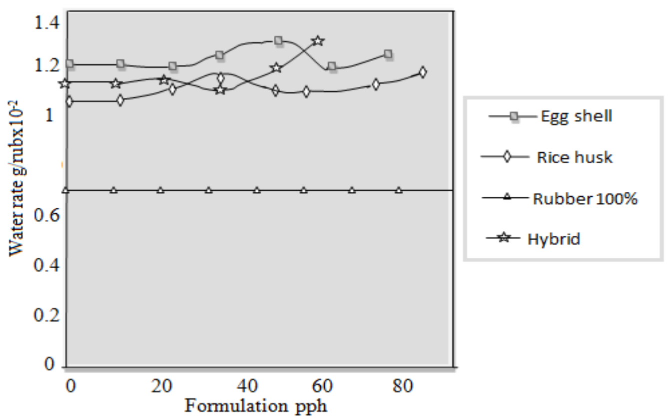

Fig. 1b. Effect of formulation on wear rate of egg shell and rice husk composites.

Abrasion resistance (rub/g)

The abrasion resistance from the result obtained in table 3.2 was better with the egg shell as filler than that of rice husk,

B. T. Sawere and A. U. Igbuku, "Evaluation of some mechanical properties of composites of natural rubber with egg shell and rice husk," *International Research Journal of Advanced Engineering and Science*, Volume 1, Issue 3, pp. 71-75, 2016.

with a maximum of 93 grub/g at 50pph when compared to that of rice husk at 88grub/g at 50pph, in accordance to Akinlabi et al. (2005), who has previously shown the successful usage and influence of filler (clay, silica, CB, and cocoa pod husk) on the physical properties of vulcanizates. The initial and final decrease of abrasion resistance with egg shell loading gives a similar effect on other inert fillers and is due to low surface activity of the filled vulcanizates in accordance with Rakdee et al. (2001). The increase in abrasion resistance between 30pph and 50pph is an indication that filler loading is not a function of the measure parameter but attributed to the degree of dispensation of filler, as reported by Okieimen et al. (2001). The hybrid fluctuated between 88 and 87 grub/g and finally decreased with no influence to filler loading.

TABLE IV. Abrasion resistance of egg shell, rice husk and hybrid.

Egg Shell		**Rice Husk**		**Hybrid**	
Formulation	Mean Abr. Resistance (rub/g)	Formulation	Mean Abr. Resistance (rub/g)	Formulation	Mean Abr. Resistance (rub/g)
E_{10}	92	R_{10}	85	$E_{10}R_{50}$	88
E_{20}	90	R_{20}	85	$E_{20}R_{40}$	87
E_{30}	84	R_{30}	80	$E_{30}R_{30}$	88
E_{40}	92	R_{40}	79	$E_{40}R_{20}$	88
E_{50}	93	R_{50}	88	$E_{50}R_{10}$	83
E_{60}	92	R_{60}	84	R_0	226
E_{70}	89	R_0	154		

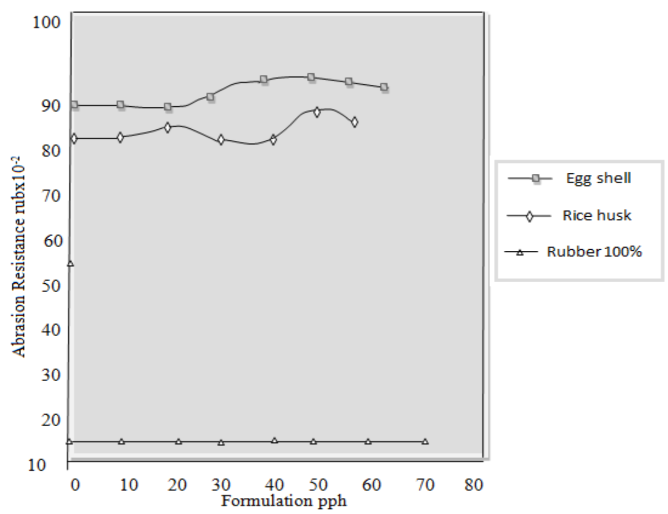

Fig. 2a. Effect of formulation on abrasion resistance of egg shell and rice husk composites.

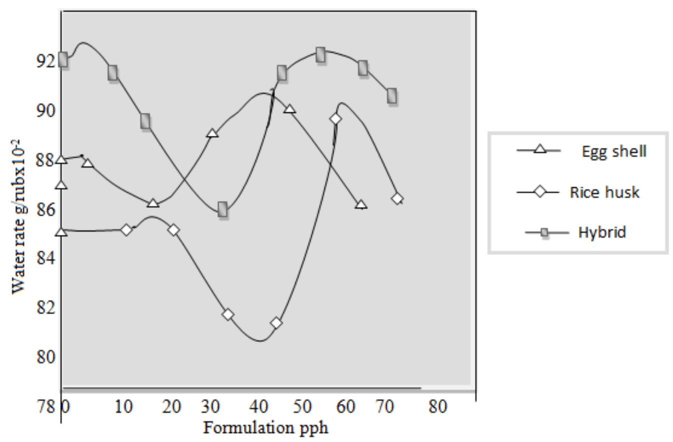

Fig. 2b. Effect of formulation on abrasion hybrid composites.

Tensile Strength

The tensile strength, from the result obtained as shown in table V decreases with increase in filler loading. This suggested that there was a negative interaction between the dispersion of filler particles with the rubber matrix, in accordance to Blackley (1999). The maximum tensile strength occurred at the same volume of filler in both cases but the value for the egg shell composite Was 12.5Mpa while that for rice husk at 10.4Mpa due to the spherical shape of the egg-shell Particles which provided substantial wetting whereas rice husk particles being random in shape, showed low strength. The hybrid composite increased to a maximum value of 16.2Mpa, at 50pph. This improvement suggested that there was positive interaction between egg shell and rice husk particles with the rubber matrix, thus giving extra reinforcement to the samples, while egg shell is being embedded in the matrix. Tensile strength for the gum vulcanizate was 20.8Mpa in accordance with Akinlabi (2007).

TABLE V. Ultimate tensile strength of egg shell, rice husk and hybrid.

Egg shell		**Rice-Husk**		**Hybrid**	
Formulation	Mean Ten. Stress (Mpa)	Formulation	Mean Ten. Stress(Mpa)	Formulation	Mean Ten. Stress (Mpa)
E_{10}	12.5	R_{10}	10.4	$E_{10}R_{50}$	14.7
E_{20}	11.8	R_{20}	9.0	$E_{20}R_{40}$	13.6
E_{30}	9.9	R_{30}	8.2	$E_{30}R_{30}$	12.8
E_{40}	9.3	R_{40}	8.0	$E_{40}R_{20}$	16.2
E_{50}	8.8	R_{50}	5.8	$E_{50}R_{10}$	14.4
E_{60}	8.2	R_{60}	4.7		
E_{70}	6.6	R_0	20.8		

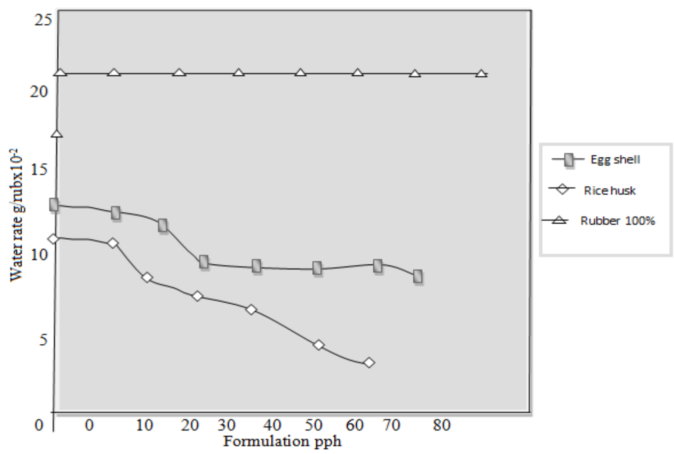

Fig. 3a. Effect of formulation on tensile strength of egg shall and rice husk composite

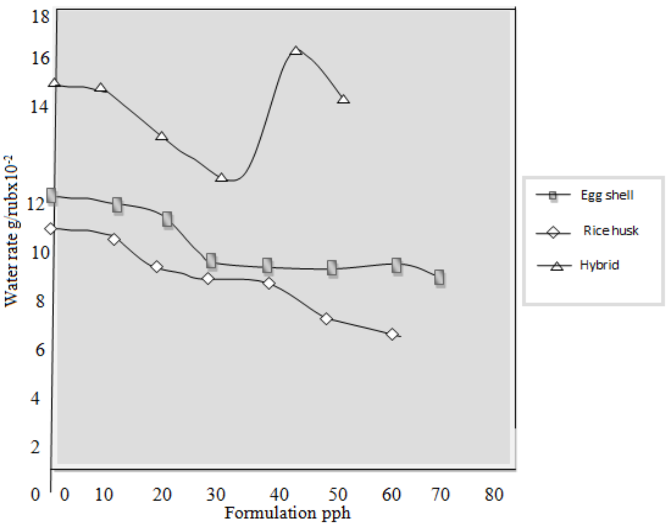

Fig. 3b. Effect of formulation on tensile strength of hybrid composite.

IV. Conclusion and Recommendation

The effect of NR and filler – filler interaction on rubber reinforcement was investigated by the use of egg shell and rice husk and the hybrid composites as filler, respectively. The result shows that both fillers were of low reinforcing filler for Natural rubber compounds. However, the eggshell composites exhibited relatively better reinforcing properties that the rice husk composites. It was observed that the tensile strength decreased as the filler content increased resulting to a poor dispersion of the filler on rubber matrix. This is an indication that a dilution effect occurs with disperse agglomerates preponderance. As for the egg shell and rice husk, the Vulcanizate at 10pph of filler gave the best result of tensile strength. The rice husk and hybrid had not much appreciable impact or improvement on the mechanical properties of NR. The analysis revealed that the eggshell showed a little variation better than that of rice husk in mechanical properties. The usage must be restricted to 10PPh and 20PPh appropriately, which shows an appreciable increase especially in tensile strength, for the variation of the egg shell and rice husk filler can be exploited further by controlling the parties size and distribution, in order to improve the filler dispersion and also its surface functionality.

Reference

[1] A. K. Akinlabi, U. N. Okwu, F. E. Okieimen, and N. A. Oladoja, “Properties of vulcanizates from blends of natural rubber and thioglycolic acid modified, epoxidized, low-molecular-weight natural rubber filled with carbonized rubber seed shell,” *Journal of Applied polymer Science*, vol. 104, pp. 2830–2838, 2007.

[2] A. K. Akinlabi, F. E. Okiemen, and A. I. Aigbedion, “Thermal aging properties and chemical resistance of blends of natural rubber and epoxidized low molecular weight natural rubber,” *Journal of Applied Polymer Science*, vol. 98, issue 4, pp. 1733-1739, 2005.

[3] D. C. Blackley, *Polymer Lacttices, Science and Technology*, 2nd Edition, Klwer Academic, Dordrecht, the Netherlands, 1997.

[4] C. R. G, *Journal of Applied Polymer Science*, vol. 55, pp. 995-1001, 2002.

[5] P. A. Egwakhide, E. E. Akporhonor, and F. E. Okieimen, “An investication on the potential of palm karnel husk as fillers in rubber reinforcement,” *Middle-East Journal of Scientific Research*, vol. 2, issue 1, pp. 28–32, 2007.

[6] D. C. Hundiwale, U. R. Kapadi, M. C. Desai, and S. H. Bidkor, “Mechanical properties of natural rubber filled with flyash,” *Journal of Applied Polymer Science*, vol. 85, issue 5, pp. 995–1001, 2002.

[7] H. M. Da Costa, V. D. Ramos, L. Y. Viscant, and C. R.G. Furtado, Design and analysis of single-factor experiments: Analysis of variance of the effect of rice husk ash and commercial fillers in NR compounds,” *Polymer Bulletin*, vol. 58, issue 3, pp. 597-610, 2007.

[8] S. K. Harry and M. V. John, *Handbook of filter for plastics van No strand Company London*, 1997.

[9] S. Manroshan and A Baharin, “Effect of nanosized calcium carbonate on the mechanical properties of latex films,” *Journal of Applied Polymer Science*, vol. 96, issue 5, pp. 1550 -1556, 2005.

[10] F. E. Okieimen, P. A Egwakhide, and E. E. Akporhonor, “Effect of coconut fibre filler on the cure characteristics physico–mechanical and swelling properties of natural rubber vulcanisates,” *International Journal of Physical Sciences*, vol. 2, issue 2, pp. 039-046, 2007.

[11] C. Rakdee, P. sae-Oui, and P. Thanmathorn, Use of rice husk ash as filler in natural rubber vulcanizates: In comparison with other commercial fillers,” *Journal of Applied Polymer Science*, vol. 83, issue 11, pp. 2485-2493, 2002.

[12] M. S. Sobhy, D. E. El-Nashar, and Nabila A. Maziad, “Cure characteristics and physicomechanical properties of calcium carbonate reinforcement rubber composites,” *Egyptian Journal of Solids*, vol. 26, no. 2, pp.241-257, 2003.

[13] S. Salaeh and C. Nakason, “Influence of modified natural rubber and structure of carbon black on properties of natural rubber compounds,” *Polymer Composites*, vol. 33, issue 4, pp. 489-500, 2012.

[14] P. J. Danhelly, “Medium Thermal black for cost reduction and property enhancement,” *Rubber Technology International*, vol. 99, pp. 52-56, 1999.

[15] K. Ahmed, S. S. Nizami, and N. Z. Riza, “Reinforcement of Natural rubber hybrid composites based on marble sludge/Silica and Marble Sludge/rice husk derived silica,” *Journal of Advanced Research*, vol. 5, issue 2, pp. 165-173, 2014.

[16] S. Attharangsan, H. Ismail, M. Abu Bakar, and J. Ismail, “Carbon black (CB)/ rice husk powder (RHP) hybrid filler- filled natural rubber composites effect of CB/RHP ratio on property of the composites,” *Polymer-Plastics Technology and Engineering*, vol. 51, issue 7, pp. 655-662, 2012.

[17] T.-H. Liou, “Preparation and characterization of nano-structured silica from rice husk,” *Materials Science and Engineering: A*, vol. 364, issue 1-2, pp. 313-323, 2004.

[18] J. Frohlich, W. Niedermeir, and H. D. Luginsland, “The effect of filler-filler and filler elastomer interaction on rubber reinforcement,” *Composites Part A: Applied Science and Manufacturing*, vol. 36, issue 4, pp. 449-460, 2005.

[19] T. Thomas, E. P. Ayswarya, and T. T. Eby, “Nano alumina as reinforcement in natural rubber composites,” *International Journal of Innovative Research in Sciences, Engineering and Technology*, vol. 21, issue 6, pp. 2319-2370, 2013.

[20] S. Wolff, Chemical aspects of rubber reinforcement by fillers,” *Rubber Chemistry and Technology*, vol. 69, issue 3, pp. 325-346, 1996.