Nanotechnology & Applications

Effect of Chemically Modified Castor Seed (*Ricinus Communis*) Shell Powder on The Mechanical Properties of Natural Rubber Vulcanizate

Tenebe O.G^{1*}, Madufor I.C², Obidiegwu M.U² and Obasi H.C²

¹Department of Polymer Technology, Nigerian Institute of Leather & Science Technology, Zaria, Nigeria.

²Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, Nigeria.

*Correspondence:

Tenebe O.G, Department of Polymer Technology, Nigerian Institute of Leather & Science Technology, Zaria, Nigeria, Tel: +2348069332769.

Received: 29 June 2021; Accepted: 25 July 2021

Citation: Tenebe OG, Madufor IC, Obidiegwu MU, et al. Effect of Chemically Modified Castor Seed (*Ricinus Communis*) Shell Powder on The Mechanical Properties of Natural Rubber Vulcanizate. Nano Tech Appl. 2021; 4(1): 1-9.

ABSTRACT

Mechanical properties of natural rubber filled with modified castor seed shell powder for some engineering applications were studied. Castor seed shells were obtained and treated with 20% NaOH for 1h, washed and dried at 75oC and were pulverized and sieved to 75µm. Treated castor seed shell (TCSS) powder showed improved characteristics when compared to the untreated (UCSS) in terms of pH, bulk density, moisture content, lignin content, cellulose content, hemicelluloses content, thermal stability, SEM and FTIR spectra respectively. Natural rubber was compounded at varying filler loadings of 0, 10, 20, 30, 40 and 50phr on a two-roll mill. The cure characteristics of the compounded rubber were determined using a Mosanto Rheometer (model MDR 2000) and the result obtained were used for vulcanization in a hydraulic press. The cure characteristics, mechanical and morphological properties of the vulcanizates were analysed and compared with carbon black filled samples. The preliminary results showed that castor seed shell is hydrophilic which was chemically treated to decrease the hydrophilicity. The maximum and minimum torques increased with filler loadings. The result of the natural rubber filled vulcanizates showed improved mechanical properties such as; tensile strength, modulus, tear strength, hardness, abrasion resistance which increased with increased filler loadings while elongation at break, flex fatigue, compression set, impact strength and rebound resilience decreased with filler loadings. The TCSS filled vulcanizate showed superior abrasion resistance and compression set when compared with UCSS and CB filled. The sample morphology at 30phr revealed that TCSS was well dispersed due to strong interfacial adhesion between the filler and the matrices contributing to the improved mechanical properties investigated when compared to UCSS filled with poor interfacial interaction. The result reveal that TCSS is a reinforcing filler that can be used for the production of natural rubber-based products for some engineering applications.

Keywords

Castor, Fatigue, Filler, Loadings, Modulus, Resilience.

Introduction/Background of Study

Carbon black and other non-black filler such as calcium carbonate, kaolin clay, precipitated silica, barite, amorphous silica and diatomite is among the most commonly used traditional filler for the rubber and allied industries which are either to reduce cost or to modify end product properties [1]. Carbon black is the predominantly used filler, not only has the deficiencies of other traditional filler by being non-renewable, expensive, scarce, hazardous and non-degradable but also is limited to single colour application with low sustainability. It is obtained from petroleum which is a non-renewable material, thus making it very expensive and limited in supply on demand which is gradually becoming a threat to economic advancement and sustainability of the polymer based and allied industries [2]. These limitations and the concern for global environmental problems have made Scientists, Engineers, Technologists and Researchers to search for alternative green filler that are compatible with the environment in the development of bio-composites, which will give rise to products with lightweight, non-toxic, low-cost, biodegradable and easy to recycle [3]. The modification of natural fibres via chemical treatment approach offers reduction of moisture absorption, increase in the surface roughness, decreasing the hydroxyl groups [4]. The choice of castor seed shells as the reinforcement in natural rubber composites is because it is renewable, biodegradable, nontoxic, abundantly available in Nigeria which would add value to local content thereby promoting industrial growth and economic development and sustainability.

Objectives of Study

- · To obtain and chemically modified castor seed shells
- To pulverize and characterize chemically modified castor seed shells
- To study the effect of chemically modified castor seed shell powder on the mechanical properties of natural rubber vulcanizates

Materials and Method

Materials

The materials used in this research include Nigerian standard rubber of grade NSR-5 obtained from Rubber Research Institute, Iyanomo, Benin. Castor seed shell was obtained from Ososo, Edo State while sodium hydroxide, tetramethylthiuram disulphide, mercaptobenzothiazole sulphenamide, stearic acid, Sulphur, zinc oxide, carbon black, paraffin wax, trimethylquinoline, sulphonic acid, acetic acid, methanol and sodium thiosulphate, made by British Drug House were obtained from Rovet Chemicals, Benin City.

Method

Preparation and Chemical Modification of Castor Seed Shell

Castor shells were collected from Leventis Farms Ososo, Edo State. The shells were washed thoroughly using water and dried in open air for a period of 120 hours prior to pulverizing. The pulverized shells were further ball milled and soaked in 20% solution of sodium hydroxide solution for 1hour at room temperature. Then solution was decanted and the filler washed thoroughly to attain neutrality after which the powder was dried initially at room temperature and later oven dried at 75°C for 1hour [5]. The reaction equation is showed below. Carbon black were prepared and weighed in parts per hundred rubbers in accordance to weight percentage of fillers in rubber mix which vary from 10 – 50phr. The reaction involving chemical treatment of the fillers using sodium hydroxide is showed below;

Filler – OH + NaOH Filler – ONa + H₂O

Characterization of Castor Seed Shell Powder Filler

The chemically modified fillers were analysed in terms of particle size, iodine value, moisture content, bulk density, pH, thermal stability, lignin content, hemicelluloses content, ccellulose contents, FTIR and micro-structural analysis.

Characterization of Natural Rubber

The natural rubber was characterized in terms of dirt content, volatile matter, ash content and plasticity retention index.

Processing of Composites

Table 1: Formulation for Compounding Natural Rubber.

Ingredient	Parts per hundred rubbers (Phr)		
Natural Rubber	100		
Filler	Variable (10 - 50)		
Zinc Oxide	5.0		
Stearic acid	2.5		
Sulphur	1.5		
MBTS	1.5		
TMTD	3.5		
Paraffin Wax	5.0		

Compounding of Natural Rubber

The compounding of natural rubber was carried out in accordance to ASTM D4295-89 using the two-roll mill model ZL-3018, made in Taiwan maintained at 70oC to avoid crosslink during mixing. The process involves preheating the rolls of a two-roll machine prior to the introduction of crumb rubber between the moving roll which rotate counter wise for mastication to take place. After about 5min, the additives were added for effective compounding. Sulphur was added last because it introduces 3-dimensional network structure into the rubber compound.

Cure Characteristics of Compounded Rubber

The cure characteristic was determined using a Mosanto Rheometer model R-453-ST, made by Bagga Scientifc group, E-Polymers Company limited, Germany in accordance to ASTM D1415-88. The process involved cutting about 10g of the compounded unvulcanized rubber sample and placing it directly on the disc which operates electronically. The cut test piece was allowed to stay on the disc for about 30min. The cure time, cure temperature, scorch time, minimum and maximum modulus results of the sample were determined on the rheograph which was used to vulcanize the rubber samples using a hydraulic press.

Mechanical Properties of Vulcanizates Tensile Strength

The tensile test was conducted on using Instron universal tensometer, model SSTM-Smart-1-Series-20KN, made by Scientific Instrument Company limited, USA in accordance with ASTM D412. A dumbbell sample of known dimensions was loaded into tensile grips of the tensometer and clamped into the two jaws of the machine with each end of the jaws covering 30mm of the sample with the extensometer attached. The test begun by separating the tensile grips at a constant speed depended on sample dimensions. It ranges from 0.05 - 20 inch per minute and for 30 secs - 3 mins. Readings were obtained when the sample under tension were yielded.

Tear Strength

The tear strength, a measure of the resistance of a material to tear force was determined on the same universal testing machine in accordance with ASTM-D624. The tear strength was tested at angle 90°C and at crosshead speed of about 500mm per minute using 1kN load cell on each test sample.

Hardness

The hardness was carried out on a Durometer model JIS-K-6253, which consists of 12.7mm foot diameter, an operating stand with a mechanically controlled rate and 1kg mass centered on the axis of the indenter in accordance with ASTM D2240. The sample was placed horizontally with its major axis, the area in which the hardness was measured under the Durometer indenter by means of V-block. The hardness measurements were taken vertically while the presser foot was applied without shock until the full force was in contact with the wheel and the sample surface. Readings was taken at 5sec interval after the presser foot was in contact with the wheel surface. The method covered rubbers in the range of 30 - 85 according to international rubber hardness degrees (IRHD).

Compression Set

The procedure adopted for the measurement of compression set wers based on ASTM-D385 using Wallace Compression Set machine. The test samples were cut to standard dimensions and compressed between parallel steel plates under stress of about 2.8MPa. It was conditioned for a selected time of 24hours at 70°C after which the sample was removed and allowed to recover at room temperature for 30mins. It was calculated using equation below;

Compression Set =
$$\left(\frac{X-Z}{X}\right)x100$$

Where: X = initial thickness of sample, Z = Recovered thickness of sample.

Flex Fatigue

The measurement was carried out using flex tensometer, model SKZ137 in accordance to ASTM D430 which functioned by inducing surface cracking of the rubber vulcanizate samples. A specified mean load, which may be zero, and an alternating load were applied to the specimen, and the number of cycles required to produce failure (fatigue life) was recorded. The tests were repeated with identical samples at various fluctuating loads. The loads may be applied axially in torsion or in flexure depending on the amplitude of the mean and cyclic loading. Net stress in the sample may be in one direction through the loading cycles or may reverse direction.

Abrasion Resistance

The abrasion resistance of the compounded rubber was determined using Taber oscillating abrasion tester, model F735 in accordance with ASTM D5963-04. The original weight of test sample was initially measured and then placed on an abrasive surface or abrader. A load was placed on top of the abrader wheel and allowed to spin for a specified number of revolutions. Different abrading wheels were specified. A haze measurement as final weight was taken. The load and the wheel were adjusted for softer and harder materials. The abrasions were obtained using equation below;

Abrasion Resistance (%) = $\left(\frac{X}{Z}\right)x100$

Where: X = Weight Loss of Standard, Z = Weight Loss of Sample

It is the ratio of the energy released on deformation recovery to the energy that caused the deformation [6]. It was determined in accordance with ASTM D7121-05. A steel ball with a known diameter was released precisely via a magnet and allowed to fall from a specified height onto the sample specimen. The instrument electronics determine the rebound height of the ball by means of a triple light barrier, which is used to calculate the rebound resilience from it and the percentage rebound measured is inversely proportional to hysteretic loss.

Micro-Structural Analysis

The micro-structural analysis was carried out using Phenom Scanning Electron Microscope Model PoX in accordance to ASTM E2809-13. Specimen samples usually non-conductive were made conductive by coating with gold metal and into specified dimension of 5-nm thick by 2mm x 2mm square meter using a sputter cutting machine. The sample was placed on the column of the Scanning Electron Microscope (SEM) where the image was focused using navigation camera and was transferred to electron mode in accordance to the desired magnification, which reveals the cracks areas, pores, bundles and voids present in the sample. The specimen was scanned, namely, the unfilled NR which served as the control; UCSS; TCSS and CB at 30phr using a sieve size of 75µm respectively

Results and Discussion

The experimental results of mechanical properties are presented in Table 2 and Figures 1 - 10 while the results of the morphological properties are presented in Plate I – IV.

Discussion

Mechanical Properties of Vulcanizates

The mechanical properties of the natural rubber filled systems are showed in Table 2 and Figures 1 - 10. The tensile strength of various vulcanizates is presented in Figure 1, which was determined at the break point of the specimen. Figure 1 clearly showed the addition of these filler in their particular compounded system results in the improvement in the tensile properties. The tensile properties of unfilled NR and UCSS filled NR vulcanizates in Table 2 are compared with those of the compounds using TCSS and CB fillers. The tensile strength increased from 10phr to 50phr for UCSS, TCSS and CB loadings in the NR vulcanzates when compared to unfilled NR compound. However, the increased in the tensile strength values of NR/TCSS vulcanizates is higher than those of NR/UCSS and the results are closely related to NR/ CB filled systems, which may be caused by agglomeration of the filler particles, which increased at high filler loadings. The UCSS particles possibly interrupt matrix continuity, thereby decreasing the effective load-bearing cross-sectional area. Chemical treatment leads to fibre fibrillation which is breaking down of fibre bundles into smaller fibres by increasing the effective surface area available for contact with the matrices [7]. Chemically treated fibre reinforced polymer matrices often showed better tensile properties owing to the increased filler-matrix adhesion which has been explained

	Filler Loadings (phr)						
Property	Unfilled	10	20	30	40	50	
Tensile Strength (MPa)	16.85	(18.38) [24.01] {24.12}	(21.92) [24.05] {25.06}	(22.04) [29.78] {30.35}	(24.13) [31.11] {32.94}	(24.88) [34.69] {35.25}	
Modulus (MPa)	3.15	(5.09) [7.45] {7.59}	(6.93) [9.08] {9.61}	(7.19) [11.85] {12.05}	(9.01) [12.52] {12.93}	(9.18) [12.92] {13.47}	
Elongation at Break (%)	503.45	(450.03) [461.57] {466.89}	(430.26) [441.01] {442.36}	(401.02) [435.28] {444.08}	(382.08) [430.09] {436.15}	(355.46) [414.56] {419.38}	
Fear Strength (MPa)	10.67	(11.06) [13.04] {14.98}	(11.48) [14.12] {14.76}	(13.34) [15.33] {16.25}	(13.96) [16.85] {16.86}	(15.03) [18.60] {18.83}	
Hardness (IRHD)	35.18	(46.25) [51.06] {51.34}	(47.97) [53.25] {57.15}	(50.26) [59.92] {60.85}	(56.20) [68.29] {70.11}	(60.92) [72.55] {78.05}	
Compression Set (%)	28.05	(23.09) [19.48] {19.93}	(20.53) [17.09] {17.24}	(17.01) [14.01] {15.11}	(15.18) [12.08] {13.07}	(15.03) [9.11] {10.36}	
Abrasion Resistance (%)	27.62	(30.39) [38.25] {37.95}	(33.05) [44.05] {39.28}	(34.14) [46.08] {45.95}	(37.02) [52.09] {49.82}	(40.69) [60.05] {55.06}	
Flex fatigue (kc x 10 ³)	8.95	(4.91) [7.41] {7.72}	(3.18) [6.06] {6.35}	(3.04) [4.84] {4.93}	(2.76) [4.05] {4.46}	(2.09) [3.29] {3.95}	
mpact Strength (J/mm ²)	896.05	(655.08) [703.09] {706.48}	(628.81) [649.25] {695.08}	(603.01) [605.33] {642.93}	(568.32) [583.96] {614.05}	(505.65) [542.72] {606.07}	
Rebound Resilience (%)	38.25	(35.98) [32.35] {30.05}	(35.07) [30.14] {29.15}	(34.28) [30.01] {29.96}	(30.36) [29.64] {28.23}	(27.03) [23.05] {20.88}	

Table 2: Mechanical Properties of Vulcanizates.

Key: Untreated Filler (UCSS), Treated Filler [TCSS], Carbon Black {CB}.

on the basis of the changes in chemical interactions at the fillermatrix interface thereby improving the interfacial bonding by giving rise to additional sites of mechanical interlocking within the matrix so as to promote more polymer-filler interpenetration at the surface; hence the increase in the tensile strength observed [8]. However, for maximum reinforcement, the filler particles must be of the same size or smaller than the chain end-to-end distance. The degree of filler reinforcement increases with decrease in particle size or increase in the surface area [9]. In filled elastomers, the filler act as stress concentrators Smaller the particle size of filler, more efficient will be the stress transfer from the rubber matrix to the filler.



Figure 1: Tensile Strength of filled Vulcanizates.

Table 2 showed variation of modulus of the filler for both chemically treated and untreated. It is clear that the modulus of well bonded

vulcanizates as a result of treatment arises from the fact that the load transfers between the fibre and the matrix occur through the strong fibre matrix interface [10]. Hence, it is observed that the modulus of the chemically treated vulcanizates exhibit higher modulus values than the untreated samples which is compared to have proximate values with the carbon black filled systems. It also showed that it was due to the presence of a strong interface between the TCSS and matrix [11]. The effect of filler loadings in all cases of UCSS, TCSS and CB in NR vulcanizates on modulus is presented in Figure 2. It can be seen that the modulus increased with the increased in filler contents. Usually, the modulus is related to the stiffness of the rubber. The increased in TCSS and the CB mass ratios enhances the stiffness of the composites which may have led to the increased modulus of the concerned vulcanizates [12]. Most agro-filler exists as crystalline in nature with the irregular shape of particles while petroleumbased filler tends to amorphous with spherical shaped agglomerates. At similar loading of UCSS, TCSS and CB filler contents, it is clearly observed that the modulus of NR/TCSS vulcanizates is considerably higher than that of NR/UCSS and best compared with NR/CB samples. The effect of filler loading on modulus is due to the complexity of reactions taking place in curing rubber compound [13]. This modification results in polymer chain scission, which decline in molecular weight observed and molecules entangled with a high cross-link density.

The result of elongation at break is presented in Table 2 and Figure 3. It can be observed that percentage (%) elongation at break decreased with increasing loading of UCSS, TCSS and CB filler contents. Since TCSS has smaller particle size, which is closely

related to that of CB, it is expected that the interfacial adhesion between TCSS and NR matrix is better than UCSS. This might be as NR matrix allowed more rheological flow due to excellent filler rubber interaction. As the loading of UCSS, TCSS and CB increases the composites cannot resist crack propagation efficiently and as a result promulgate a calamitous crack which minimizes the elongation at break. The elongation at break for TCSS vulcanizates is lower than that of UCSS but can be compared to CB filled NR compounds.



Figure 2: Tensile Modulus of filled Vulcanizates.

The result of elongation at break is presented in Table 2 and Figure 3. It can be observed that percentage (%) elongation at break decreased with increasing loading of UCSS, TCSS and CB filler contents. Since TCSS has smaller particle size, which is closely related to that of CB, it is expected that the interfacial adhesion between TCSS and NR matrix is better than UCSS. This might be as NR matrix allowed more rheological flow due to excellent filler rubber interaction. As the loading of UCSS, TCSS and CB increases the composites cannot resist crack propagation efficiently and as a result promulgate a calamitous crack which minimizes the elongation at break. The elongation at break for TCSS vulcanizates is lower than that of UCSS but can be compared to CB filled NR compounds.



Figure 3: Elongation at Break of filled Vulcanizates.

The elongation at break of the compounds filled with chemically modified fibre was attributed to the changes in the chemical structure and bonding ability of the fibre [14]. The decrease in elongation was due to better strength and stiffness achieved from strong adhesion between TCSS and rubber matrix. However, higher extension is obtained from weak interfacial adhesion between fillers and polymer matrices [3].

Table 2 and Figure 4 compared the tear strength of raw rubber and natural rubber filled vulcanizates. The investigated result is evident that the tear strength of UCSS, TCSS and CB filled rubber is nearly 10times higher than that of raw rubber. However, TCSS filled vulcanizates showed higher and improved tear resistance ability when compared with UCSS and has closely related values when compared to CB filled samples. The results indicated that the inherent reinforcing potential of TCSS arises from the filler and filler rubber interactions. The tear strength also follows the same pattern as that of tensile strength. It is observed that as the content of both filler increases the tear strength also increases which owes to good filler rubber interaction [15]. This oblique that samples with the best cross-linked structures had the greatest tear resistance.



Figure 4: Tear Strength of filled Vulcanizates.

Hardness of a material is its resistance to localized deformation. It applies to deformation from indentation, scratching, cutting or bending [16]. In most polymers, the deformation considered is plastic deformation of the surface [17]. Hardness measurements are widely used for the quality control because they are quick and nondestructive tests when the marks or indentation produced by the test are in low stress areas. The shore is used to determine the indentation depth of materials. Characteristics of a material are considered prior to selecting the testing method employed during hardness test. These characteristics include; Sample size, Thickness, Scales etc. [18]. Average hardness of these vulcanizates with different loadings of UCSS, TCSS and CB in NR is presented in Table 2 and Figure 5.

Obviously for all vulcanizates, the hardness increased continuously

with increased filler loadings of UCSS, TCSS and CB contents. This is comprehensible as the TCSS filled systems becomes more rigid when compared to UCSS samples. Thus, increasing the mass ratio gave rise to the reduction of the deformable rubber portion in the compound which is widely known as the dilution effect [19]. This result is expected because the treatment increases the interaction between the rubber matrices and the filler hence; the increase in hardness. Thus, at higher concentrations, the fibers might be destroyed chemically leading to poor filler-matrix interaction. At higher interaction, the elasticity of the rubber chain decreases resulting in more rigid behaviors in vulcanizates [20]. Furthermore, the maximum hardness was found at 50phr for both filled NR compounds.



Figure 5: Hardness of filled Vulcanizates.

The results of compression set in Table 2 and Figure 6 showed that as UCSS, TCSS and CB filler loading increases, the compression of filled polymer matrices decreased for both filled vulcanizates. This observation is connected with the degree of filler dispersion and its particle size, which may have enhanced the resistance of TCSS-filled vulcanizates than UCSS samples. The result showed that TCSS filled vulcanizates had superior values when compared to UCSS and commercially grade N330 CB filled vulcanizates respectively. However, compression set is affected by the affinity of rubber matrices to interact with the filler surface energy, which may have enhanced the filler interaction [21].



Figure 6: Compression Set of filled Vulcanizates.

Abrasion resistance is the material's ability to with stand mechanical action such as rubbing, scraping or erosion. The result showed that TCSS filled vulcanizate had better resistance [22]. The variation of abrasion resistance with the filled systems is presented in Table 2 and Figure 7. The investigated result showed a progressive increase with increase in filler loadings. This observation may be as a result of improved affinity between the rubber and the filler contents. However, TCSS filled vulcanizates showed higher resistance when compared to UCSS and commercially grade N330 CB filled matrices, which may be due to higher filler interaction and compatibility as a result of filler treatment leading to proper filler matrix adhesion.

Fatigue is the weakening of a material caused by repeatedly applied loads. It is the progressive and localized structural damage that occurs when a material is subjected to cyclic deformation forces [23]. The nominal maximum stress values that cause such damages may be much less than the strength of the material typically quoted as ultimate tensile stress limits or the yield stress limit. It occurs when a material is subjected to repeat loading and unloading. If the loads are above a certain threshold, microscopic cracks are set up at the stress concentrators such as the surface, persistent slip bands and the grain interfaces [24]. Eventually a crack will propagate suddenly, and the structure will fracture and the shapes of such structures are affected by fatigue life. The stresses induced due to the flexural load are combination of compressive and tensile stresses which is often used to select material for parts that will support load without flexing and is used as an indication of a material's stiffness when flexed [25]. Since the physical properties of polymers can vary depending on ambient temperature. It is sometimes appropriate to tests materials at temperatures that simulate the intended end used environment. The effects of UCSS, TCSS and CB in NR on the flex fatigue are presented in Table 2 and Figure 8, which are found to be ultimately decreasing with filler loadings. The improvement in properties of TCSS filled vulcanizates when compared to UCSS filled systems is likely to be due to increased cellulose content, effective surface area, interfacial adhesion and physical and chemical changes induced by filler treatment [26]. The results also showed decrease with increased filler loading which is as a result of stiffening of the polymer chain due to the adherence of the filler to the polymer matrices.



Figure 7: Abrasion Resistance of filled Vulcanizates.



Figure 8: Flex Fatigue Resistance of Vulcanizates.

Table 2 and Figure 9 presented impact behaviour of UCSS, TCSS and CB in filled NR. The impact strength of vulcanizates is influenced by many factors which include toughness properties of the reinforcement, the nature of the interfacial region and frictional work involved in pulling out the filler from the matrix [27]. The nature of the interface region is of extreme importance in determining the toughness of the vulcanizates [2]. It was observed that the impact strength decreased gradually as filler contents increases for UCSS, TCSS and CB in filled NR matrices which are due to strong interface existing between the polymer matrices and the reinforcement thus, decreased in toughness of the vulcanizates. However, in all cases, the TCSS and CB filled had higher impact values when compared to UCSS filled matrices which had been explained in terms of good filler-matrix interactions.

The rebound resilience of the various vulcanizates is presented in Table 2 and Figure 10 respectively. Resilience of a rubber compound is a measure of how elastic it is when exposed to various stresses [25]. It's the ratio of the energy released on deformation recovery to the energy that caused the deformation [6]. It was observed that the rebound resilience decreased gradually as filler contents increases for UCSS, TCSS and CB filled matrices which have been explained based on strong interface existing between the polymer matrices and the reinforcement. However, in all cases, the TCSS and CB filled had higher, better and improved rebound resilience when compared to UCSS filled matrices.



Figure 9: Impact Resistance of filled Vulcanizates.



Figure 10: Rebound Resilience of filled Vulcanizates.

The micro-structural result obtained revealed results 1500* magnifications in each case. The plate showed similar pore areas but relatively lower than the filled matrices. For both vulcanizates there was irregular surface defects and cracks while the unfilled natural rubber matrix was quite plane. The observation may be due to complex filler interactions and compaction within the vulcanizate material [28]. The morphologies of the filled matrices at 30phr loadings were examined for treated (TCSS), and untreated castor seed shell (UCSS) as well as carbon black (CB) powder filled vulcanizates. Plate I showed micro-graph of unfilled natural rubber with clear surface which is expected due to the absence of reinforcement of fillers in the matrix. The results in Plate II showed morphology of UCSS filled vulcanizates revealing micro-cracks with pores formation, which may be caused by lack of proper adherence of the fillers in the polymer matrices [29]. The noticeable voids could be points of possible crack formation when stress development set into the matrices The results in Plate III and IV showed proper distribution of CB and TCSS within the filled matrices. The vulcanizates showed proper interlocking potentials between TCSS and the matrices which was predominantly observed due to chemical treatment which opened up the fibre surface structure for interaction and compaction which led to the improved mechanical properties investigated. The results demonstrated that the fracture surface of NR/UCSS was the roughest with deeper tearing lines and angular cracking. In addition, the interface between CB and TCSS in the natural rubber matrix clearly indicated adequate filler dispersion. However, the fracture surface of NR/TCSS vulcanizate was a few fibre bundles which indicated that the interfacial adhesion was very strong. Higher crack propagation energy was required to fracture this vulcanizate [30].



Plate I: Unfilled NR Vulcanizate



Plate II: 30phr of UCSS filled Vulcanizate



Plate III: 30phr of CB filled Vulcanizate



Plate IV: 30phr TCSS filled Vulcanizate.

Conclusion

A comparative study was performed on the UCSS, TCSS and commercial grade N330 CB to evaluate the mechanical properties and morphological properties of the filled vulcanzates. The tensile strength, tensile modulus, elongation at break, tear strength, hardness, flex fatigue, impact and rebound resilience of the vulcanizates were significantly improved by the addition of the filler. However, the chemically modified castor seed shell present superior compression set and abrasion resistance when compared to commercial grade N330 carbon black. The morphological properties investigated reveal proper filler dispersion in the TCSS vulcanizate than the UCSS filled which exhibits surface defeats and microcracks. The results revealed the potential application of TCSS for use in the manufacture of natural rubber-based articles such as shoe soles, foot-mats, oil seals, shock mounts, exhaust pipe suspenders for some engineering applications.

References

- 1. Kabir M M, Wang H, Lau K T, et al. Chemical Treatments on Plant Based Natural Fibre Reinforced Polymer Composites: An Overview, Composites Part B. Engineering, 2012; 43: 2883-2892.
- 2. Moridian M, Khorsandi L, Talebi A R. Morphometric and Stereological Assessment of the Effects of Zinc Oxide Nano-particles on the Mouse Testicular Tissue, Bratislavske Lekarske Listy, 2015; 116: 321-325.
- 3. Taylor Robert A, Otanicar Todd P, Herukerrupu Yasitha Bremond, et al. Feasibility of Nano-Fluid Based Optical Filters. Applied Optics, 2013; 52: 1413-1422.
- 4. Van de Weyenberg I, Ivens J, De Coster A, et al. Influence of Processing and Chemical Treatment of Flax Fibres on their Composites. Composites Science and Technology, 2003; 63: 1241-1246.
- Ekebafe L O, Ekebafe M O, Akpa F A O. Effect of Chemically Modified Powered Rubber Seed Shell as Filler on the Rheological, Tensile and Equilibrium Swelling Properties of Natural Rubber Compounds. Journal of Chemical Society of Nigeria, 2011; 36: 70-77.
- 6. Mathew L, Joseph K U, Joseph R. Influence of Chemical Treatment on the Mechanical Properties of Isora Fibre Reinforced Natural Rubber. Progress in Rubber, Plastics and Recycling Technology, 2004; 204: 337-349.
- Rezende C A, Bragança F C, Doi T R, et al. Natural Rubber-Clay Nano-Composites, Mechanical and Structural Properties, Polymer, 2010; 51: 3644-3652.
- Salvetat J P, Bhattacharyya S, Pipes R B. Progress on Mechanics of Carbon nano-tubes and Derived Materials, Journal of Nano-Science and Nano-Technology, 2006; 6: 1857-1882.
- Shaji P T, Saliney T, Marykutty C V, et al. Evaluation of Effects of Various Nano-fillers on Technological Properties of NBR/NR Blend Vulcanized Using BIAT-

CBS System, Journal of Polymers, 2013; 13: 1155-1165.

- Song S Y, Youn R J. Influence of Dispersion States of Carbon Nano-tubes on the Physical Properties of Epoxy Nano-Composites, Carbon, 2005; 43: 1378-1385.
- 11. Sui G, Zhong H W, Yang P X, et al. Curing Kinetics and Mechanical Behaviour of Natural Rubber Reinforced with Pretreated Carbon Nanotubes, Material Science and Engineering, 2008; 485: 524-531.
- Sung K M, Mosley D W, Peelle B R, et al. Synthesis of Monofunctionalized Gold Nano-particles by Fmoc Solid-Phase Reactions, Journal of the American Chemical Society, 2004; 126: 5064-5065.
- Ayo M D, Madufor I C, Ekebafe L O, et al. Effects of Carbonization Temperature on the Mechanical and Swollen Behaviour of Natural Rubber Filled Groundnut shell. Researcher, 2011; 3: 6.
- Akbari B, Tavandashti M P, Zandrahimi M. Particle Size Characterization of Nano-particles; A Practical Approach, Iran J. Mater Science, Eng. 2011; 8: 48-56.
- 15. Thomas C P, Jose T E, Thomas S P, et al. High Performance Nano-Composites Based on Acrylonitrile Butadiene Rubber with Fillers of Different Particle Size, Mechanical and Morphological Studies, Journal of Polymer Composites, 2010; 31: 1515-1524.
- Hanley C, Thurber A, Hanna C, et al. The Influences of Cell Type and ZnO Nano-particle Size on Immune Cell Cytotoxicity and Cytokine Induction, Nano-scale Res. Letters, 2009; 4: 1409-1420.
- 17. Wang B, Zhang Y, Mao Z, et al. Toxicity of ZnO Nanoparticles to Macrophages Due to Cell Uptake and Intracellular Release of Zinc Ions, Journal of Nano-science and Nanotechnology, 2014; 14: 5688-5696.
- Yan H, Tian G, Sun K, et al. Effects of Silane Coupling Agent on the Polymer-Filler Interaction and Mechanical Properties of Silica-filled Natural Rubber, Journal of Polymer Science, Part B, 2005; 43: 573-584.
- Yue D, Liu Y, Shen Z, et al. Study on the Preparation and Properties of Carbon Nano-Tubes/Rubber Composites. Journal of Material Science, 2006; 41: 2541-2544.

- Zhao H, Qi S, Zhou W, et al. Progress in Carbon Nano-tube/ Rubber Composites, Hecheng Xiangjiao Gongye, 2008; 31: 315-318.
- Zhu A, Shi Z, Cai A, et al. Synthesis of Core Shell PMMA-SiO₂ Nano-Particles with Suspension-Dispersion-Polymerization in an Aqueous System and its Effect on Mechanical Properties of PVC Composites. Polymer Testing, 2008; 27: 540-547.
- 22. Lu L, Zhai Y, Zhang Y, et al. Reinforcement of Hydrogenated Carbonxylated Nitrile Butadiene Rubber by Multiwalled Carbon Nano-tubes, Applied Surface Science, 2008; 255: 2162-2166.
- Kueseng P, Saeoui P, Rattanasom N. Mechanical and Electrical Properties of Natural Rubber and Nitrile Rubber Blends Filled with Multiwall Carbon Nano-tube, Polymer Testing, 2013; 32: 731-738.
- 24. Gosens I, Kermanizadeh A, Jacobsen N R, et al. Comparative Hazard Identification by a Single Dose Lung Exposure of Zinc Oxide and Silver Nano-materials in Mice, 2015; 10: e0126934.
- 25. Ismail H, Ramly F, Othman N. Multiwall Carbon Nano-Tube Filled Natural Rubber; Effects of Filler Loading and Mixing Methods, Polymer Journal, 2010; 49: 260-266.
- 26. Hanagata N, Morita H. Calcium Ions Rescue Human Lung Epithelial Cells from the Toxicity of Zinc Oxide Nanoparticles, Journal of Toxicological Sciences, 2015; 40: 625-35.
- Mostafa A, Abouel-Kasem A, Bayoumi R, et al. Effects of Carbon Black/Nano-Particulate Filler Loading on the Swelling and Compression Set Behaviour of SBR and NBR Rubber Compounds, Journal of Materials and Design, 2009; 30: 1561-1568.
- Balani K, Harimkar S P, Keshri A, et al. Multi-scale Wear of Plasma-Sprayed Carbon Nanotube Reinforced Aluminum Oxide Nano-Composite Coating: Acta Materialia, 2008; 56: 5984-5994.
- 29. Bokobza L, Chauvin P J. Reinforcement of Natural Rubber; Use of in-situ Generated Silicas and Nano-fibres of Sepiolite, Polymer Journal, 2005; 46: 4144-4151.
- Daeinabi K, Korayem M H. Indentation Analysis of Nanoparticles Using Nano-Contact Mechanics Models During Nano-manipulation Based on Atomic Force Microscopy, Journal of Nano-particles Res. 2011; 13: 1075-1091.

© 2021 Tenebe OG, et al. This article is distributed under the terms of the Creative Commons Attribution 4.0 International License