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Assessment of Physico-mechanical Properties of Natural Rubber and Modified Natural Rubber Vulcanizates with Watermelon Rind as Fillers

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ABSTRACT: Natural Rubber (NR) has a relatively low tensile modulus and strength, hence the need for reinforcing fillers to increase its tensile strength, hardness and abrasion resistance. In this study, NR was deproteinized, epoxidized and depolymerized. The functional groups of the NR and the modified NR were determined using Fourier Transform Infrared (FT-IR) spectroscopy. Watermelon Rind (WR) was used as fillers to replace Carbon Black (CB) in the compounding process. The shells were collected, dried, milled and sieved to 75 µm mesh size. Powdered WR was carbonized at 250^{o}C for 1.5 hrs to obtain Carbonized Watermelon Rind (CWR). The Uncarbonized Watermelon Rind (UWR) and CWR powder were characterized based on particle size, loss on ignition, volatile matter, moisture and ash content. The UWR and CWR were used to replace CB at 0, 50 and 100% for the NR and modified NR compounding. The physico-mechanical properties of the different vulcanizates were determined for the effect of modification on the NR. The FT-IR result of the NR samples showed the presence of O-H, C-H, C=C stretching with C=H wagging bands used as the fingerprint region of NR. The results of the physico-mechanical properties revealed that an increase in shell content in the NR decreased its tensile strength and elongation but improved the physico-mechanical properties of the modified NR. This study showed that watermelon rind can be a viable alternative source of carbon filler for improved physico-mechanical properties of modified natural rubber.

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The development in science required a variety of polymers with good properties and low cost. Therefore, there is a need to improve the properties of Natural Rubber (NR) through modifications in other to increase its applications. To achieve this, chemical and physical methods have been developed to carry out cross-links due to the presence of double bonds (C=C) NR chains (Phinyocheep, 2014). New polymeric materials with enhanced oil resistance or air permeability, improved aging resistance, improved adhesion to glass, metals, and fabrics, and altered abrasion and friction qualities have been produced by modifying NR chemically. Chemical modifications of NR, such as epoxidation, hydrogenation, halogenation, hydroboration, cyclization, and maleinization, provide a variety of options for improving NR characteristics (Okieimen *et al.*, 2003). NR is extensively used in many applications due to its high elasticity (reversible deformability). However, low tensile modulus and strength of neat NR are major concerns. For several applications, therefore, the addition of a reinforcing phase becomes necessary (Urushihara *et al.*, 2009). Rubber reinforcement requires increasing the rubber's tensile strength, tear resistance, abrasion resistance, and modulus which could be achieved by compounding with fillers (Kohjiya, 2000). Fillers increase efficiency by creating strong chemical bonds with rubber, a process known as filler-elastomer interactions. Carbon black (CB) obtained from petroleum products is the most common reinforcing filler and it is expensive Therefore, finding blends of polymers or additives that are cost-effective and environmentally friendly becomes essential (Akinlabi *et al.*, 2007). Using farm residue as an

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additive transforms unused, low-value materials into usable, great value materials. Agricultural residues are inexpensive and easily accessible resources in large quantities for use; considerably 300,000,000 tons are produced every year (Okieimen *et al*., 2003). Watermelon rind (WR) is the exocarp of the watermelon (*Citrullus lanatus*) fruit (Parmar and Kar, 2009). The edible rind is usually discarded or applied to feeds and fertilizers (Oko, 2012). Due to the high loss on ignition (70.5%) of the rind powder (Banerjee *et al*., 2012), it might be suitable as filler in rubber compounding. This research work is aimed at preparing a modified natural rubber vulcanized with watermelon rind as filters and compared with natural rubber by assessing their physico-mechanical properties.

MATERIALS AND METHODS

Materials: Natural Rubber Latex (NRL) was obtained from the Rubber Research Institute of Nigeria, Benin City, Nigeria. Watermelon was obtained from traders at the Eleweran market, Abeokuta, Ogun State, Nigeria. All the chemicals used were of the highest purity and obtained from suppliers in Nigeria.

Modification of Natural Rubber: Three different modifications were carried out separately on the NRL namely: Deproteinization (Kawahara *et al*., 2004), Depolymerization (Okieimen and Akinlabi, 2002) and Epoxidization (Perera and Brandbury, 1992). Functional groups present the NR and modified natural rubber samples were determined using FT-IR techniques (FTR, Bruker-Alpha, Platinum ATR)

Preparation and characterization of carbonized samples: WR was washed, dried and grounded to powder. The previously stated technique (Ishak and Baker, 1995) was used to carbonize a portion of the WR powder, with a minor modification. This was labeled Carbonized Watermelon Rind (CWR) while the uncarbonized portion was labeled Uncarbonized Watermelon Rind (UWR). Characterization in terms of moisture content, ash content, volatile matter, pH measurement and Loss on Ignition was carried out on the UWR and CWR following the methods described in the ASTM 1509.

Compounding of Different Vulcanizates: The compounding formulation for the NR and Modified NR samples with the filler is depicted in Table 1.

Physico-mechanical Analysis of Vulcanizates: The Tensile properties (Tensile Strength, Modulus and Elongation at Break) of the vulcanizates were determined using a Monsanto tensile tester model (I/M) at a crosshead speed of 500mm/min500mm/min using a dumbbell test specimen (Type II). Abrasion resistance of the test specimens was determined using the Wallace Croydon resiliometer 2A. The weight specimen was run for 500 revolutions of the abrasive wheel after which the specimen was reweighed and the volume loss was calculated from the density of the material. It was then calculated thus;

$$ARI\ (\%) = \frac{S}{T} \times 100$$

Where: ARI = abrasion Resistance Index; S = Volume loss per 500 revolutions of the abrasive wheel on the standard test piece T = Volume loss per 500 revolutions of the abrasive wheel on sample weight

Table 1: Composition for the compounding of vulcanizates

Compound component (phr)	Samples		
	Mix A	Mix B	Mix C
Natural rubber	100	100	100
CB	40	20	0
Filler	0	20	40
Zinc Oxide (ZnO)	4	4	4
Sulphur	2	2	2
Stearic acid	1.5	1.5	1.5
MBTS	1.5	1.5	1.5
Flectol H	2	2	2

*phr: Parts per hundred, MBTS: MercaptoBenzothiazoleSulphenamide. Flectol H: Polymerized 1,2-dihydro-2,2,4-trimethyl quinolone. *The same formulation was used for Deproteinized, Depolymerized and Epoxidized Natural Rubber with UWR and CWR respectively.*

The machine used for the compression test was the Wallace Compression Testing Machine, and the procedure involves placing the test sample on the compression parallel plate and conditioning the assembly for a selected time of 22 hours at 70^{o}C with a force of 72.5N. The compression set was calculated thus:

$$CS\ (\%) = \frac{T_f - T_i}{T_i} \times 100$$

Where: CS = compression set; T_i= Initial thickness, T_f = Final thickness

Hardness Test hardness of the test pieces were measured with the aid of the Deal Loaded Tester (Wallace) machine. The standard ASTM methods were used for these analyses.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FT-IR) Spectroscopy Result of Natural Rubber and Modified Natural Rubber: FT-IR spectroscopy was used to monitor the vibrational energy levels in the region of different molecules. FT-IR Spectroscopy confirms the

functional groups in the Natural Rubber (NR) and modified NR. The results show the presence of O-H stretching, C-H stretching, C=C stretching and C=H stretching summary of the wavenumbers given in Table 2. The peak at 840.11cm^{-1}, 840.04cm^{-1}, 835.48cm^{-1}and 835.75cm^{-1} correspond to C=H wagging bands (Silverstein *et al*., 2005) and is commonly used as the fingerprint region of NR. It is worth noting that the intensity and strength for the NR and DPNR seem close.

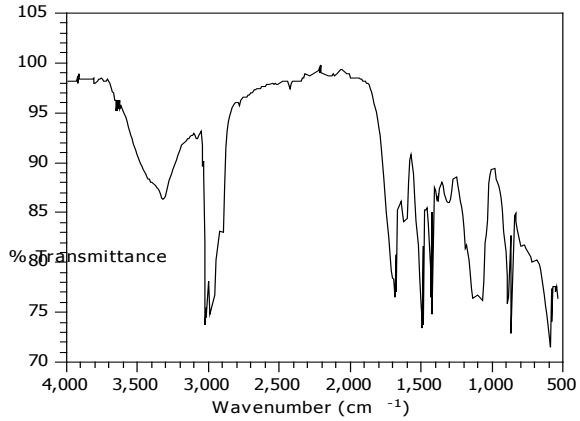

Fig 1: FT-IR spectrum of Natural Rubber (NR)

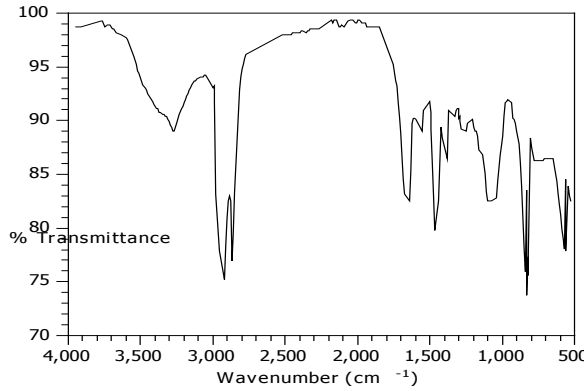

Fig 2: FT-IR spectrum of Deproteinized Natural Rubber (DPNR)

This is probably because the process of deproteinization is mainly to remove the nitrogen in the NR, so might likely not affect the various bonds. For the DNR, as expected, the C=C intensity reduced to medium when compare with the NR with strong intensity as shown in Figures 1 and 3, respectively. This is due to the breaking of some of the C=C bonds during the depolymerization process. This also made the C-H stretching for the DNR stronger when compared with that of the NR. The same trend as in that of DNR was noticed for the ENR (Figure 4). There is possibly a breakage of the C=C bonds for the reaction of the C-O-C bond. The intensity of the OH band reduced in the ENR, indicating that some of the OH have been epoxidized.

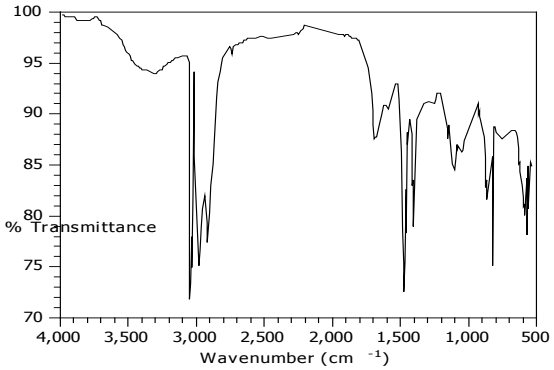

Fig 3: FT-IR spectrum of Depolymerized Natural Rubber (DNR)

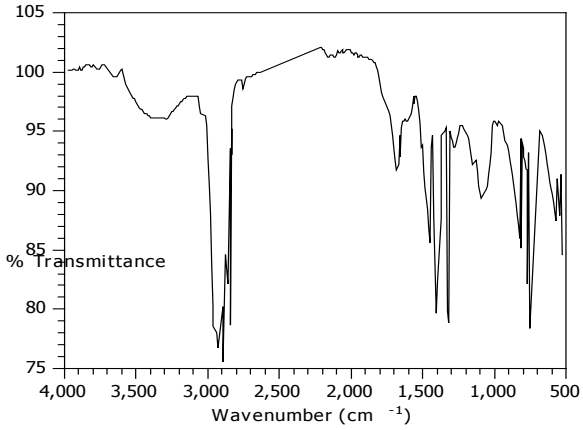

Fig 4: FT-IR spectrum of Epoxidized Natural Rubber (ENR)

Table 2: Summary of wavenumbers obtained from the FT-IR Spectra of NR, DPNR, DNR and ENR

Functional Group	NR	Wavenumber (cm^{-1}) DPNR	ENR	DNR
O-Hstr	3280.56	3278.04	3313.20	3306.10
C-Hstr	2960.23	2960.24	2960.04	2960.10
C=Cstr	1626.72	1626.97	1660.12	1660.09
C-Ostr	1232.20	1233.27	1241.57	1240.08
$C=H_{bend}$	840.11	840.04	835.48	835.75

Characterization of Watermelon rind Sample: The result for the characterization of the UWR and CWR is given in table 3 below. The particle size of both samples was reduced to 75µm to allow the samples to form a better cross-link with the rubber matrix. The pH result shows that both the UWR and CWR are alkali which makes it better for curing since acidity will not enhance the cure time and crosslink of the vulcanizates. The moisture content of the watermelon samples was reduced during carbonization as shown in the result. The loss of ignition is a method of determining the amount of carbon in a sample. The higher the filler's carbon concentration, the better the rubber is reinforced. The carbonized sample value was higher compared to the uncarbonized sample; this shows that carbonization increased the carbon content

and thus, result in better cross-linking and network formation. The result shows that watermelon rind has a high carbon percentage when compared to some biofillers that have been used (Pterocarpus santalinoides – 32.68 Akinlabi *et al*., 2011; eggshell – 47.8 Freire *et al*., 2006). This strongly suggests that the watermelon rind sample should have a good crosslink with the polymer matrix.

Table 3: Characterization of watermelon rind powder

Test	UWR	CWR
Ash %	12.92	14.1
Moisture content %	2.52	1.4
Loss on ignition %	72.51	88.4
pH	7.5	10.5
Particle size (µm)	75	75

Effect of modification 0f Physico-mechanical Properties of Vulcanizates: The results of the Tensile Strenght (TS) for the NR vulcanizates reduced as the percentage of the CWR increased in Mix B and Mix C. This result shows that the standard (carbon black) had the highest value of 24.5. There was a 53.9% reduction from Mix A to Mix B, while there was a 62.9% reduction for Mix C. The least standard permitted tensile strength for an NR mix is about 7.5MPa, according to technology, and considering the values for Mix B and Mix C, they have technologically good TS (Akinlabi *et al.*, 2020). The decreased tensile strength values reported in Mixes B and C when compared with the standard (CB), could be the weak intermolecular forces between the NR and the watermelon rind powder. For the modified NR (i.e. DNR, DPNR, ENR) the TS increased as the percentage of both the UWR and CWR increased respectively. The result shows clearly the TS of the modified NR vulcanizates was higher than that of NR in Mix B and C. This shows that the modified NR produced a stronger bond with the CWR than with carbon black unlike for NR where the strength reduced with an increased CWR.

This trend is the same for the modulus, the elongation at break, hardness and abrasion index i.e. the values decreased from Mix A to Mix C for the NR vulcanizates while it increased from Mix A to mix C for the modified NR. Compression refers to the elastomer's memory. It is the measurement of a rubber material's permanent deformation after being compressed for a while. Compression is a term that refers to a test that is performed under particular conditions and after a specific time, it calculates the permanent distortion as a percentage. The value of the compression decreased as more WR was added to the NR and modified NR. This shows that the vulcanizates with WR i.e. Mix B and C recover to their original thickness faster than the other vulcanizates. It can therefore be deduced from the physico-mechanical properties result that the WR samples are not as effective as CB for the NR vulcanizates. However, the WR samples reinforced all the modified NR than the CB, as there was a general increase in tensile strength, modulus, hardness and abrasion resistance with increasing filler loading. The increase in strength between the modified NR and the WR can be due to the chemical modification of the NR. Without the chemical modifications, the filler adheres to the polymer due to poor bonding., i.e., Vander Waals or induction interactions (Barone, 2005). Also, there could have been a better filler dispersion into the modified NR than the NR.

Effect of Carbonization on the Physico-mechanical Properties of Vulcanizates: Table 4 shows the various values for the physico-mechanical properties of NR, DNR, ENR and DPNR with CB, UWR and CWR respectively. The effect of carbonization was studied by comparing the values in Mix B (50% CB with 50% of WR) and Mix C (100% WR) where the carbonized and uncarbonized samples were used respectively. For the tensile strength, the values for the CWR were higher than that of the UWR for all the NR samples. This is an indication, that the CWR had a better network formation with the polymer chain since there were more bonds available for crosslinking. The increase in carbon content as indicated by loss on ignition (CWR 88.4% and UWR 72.51%) provided more bonds for crosslinking. Technologically, the higher the carbon content, the better the material in network formation which could lead to a high TS since there would be more bonds available for crosslinks (Akinlabi *et al.*, 2015). The hardness, abrasion and elongation at break values for the carbonized CWR were also higher than that of the UWR filled vulcanizate. This implies that the vulcanizates containing carbonized samples would be more resilient and as a result, the rubber articles made with the filler would have less heat build-up and hysteresis. Compression values for the CWR filled vulcanizates were found to be lower than that of the uncarbonized. The low values for the vulcanizates with carbonized samples indicate that it has a better ability to return to their original thickness than the ones with uncarbonized samples. A low compression set is required for molded rubber items such as seals and gaskets that must keep their dimensions to maintain an efficient seal. This shows that the vulcanizates with carbonized fillers would be better for molded rubber parts.

In general, the results show that both the uncarbonized and carbonized samples have a better reinforcing ability on the modified NR than the CB.

Table 4: Result of the physico-mechanical properties of the various vulcanizates

	CARBONIZED WATERMELON RIND											
	A				B				C			
	NR	DPNR	ENR	DNR	NR	DPNR	ENR	DNR	NR	DPNR	ENR	DNR
TS (Mpa)	24.5	7.2	10.8	10.8	11.3	10.9	12.1	11.7	9.1	20.4	19.5	21.8
E@break (%)	8357	7972	9026	10014	8122	10664	12259	10847	8001	12500	14812	13486
Modulus	1.9	1.4	1.5	1.5	1.2	2	2.1	2	1.3	2.8	2.5	2.4
Hardness (IRHD)	40	41	40	41	45	47	41	46	50	48	45	46
A.I.	77	63	29	23	77	65	38	29	33	75	42	38
Compression (%)	6.9	10.73	8.2	10.47	2.06	2.4	2.05	0.83	0.1	0.83	0.1	0.5
	UNCARBONIZED WATERMELON RIND											
	A				B				C			
	NR	DPNR	ENR	DNR	NR	DPNR	ENR	DNR	NR	DPNR	ENR	DNR
TS (Mpa)	24.5	7.2	10.8	10.8	8.5	9.8	11.1	11.2	7.2	15.5	13.4	18.7
E@break (%)	8357	7972	9026	10014	8025	9699	12156	10659	7956	11782	12785	13068
Modulus	1.9	1.4	1.5	1.5	1.3	1.2	2.1	1.7	1.2	2.5	2.5	2.1
Hardness (IRHD)	40	41	40	41	40	46	40	45	50	48	43	46
A.I.	77	63	29	23	42	63	33	25	29	65	38	30
Compression (%)	6.9	10.73	8.2	10.47	3.51	4.71	3.14	2.05	0.2	1.1	0.4	0.5

Conclusion: The physico-mechanical properties of the vulcanizates with watermelon rind investigated in this study showed comparable results with that of reinforcing standard carbon black. Vulcanizates with CWR samples have superior mechanical properties when compared to the UWR and these enhancements were attributed to the higher carbon content of the CWR. The study reports that the modification of NR followed by compounding with alternate fillers offers improved physico-mechanical properties of the vulcanizates when compared to unmodified NR with CB.

REFERENCES

Akinlabi, AK; Okieimen, FE; Okwu, UN; Oladoja, NA (2007). Thermal aging properties and molecular transport of solvents through vulcanizates prepared from thioglycolic acid modified epoxidized low molecular weight natural rubber blends filled with a mixture of carbon black and uncarbonized rubber seed shell. *Chem. Eng. Commun.* 194(1): 1-17

Akinlabi, AK; Olayinka, OM and Dare, EO (2011). The use of *Pterocarpus santalinoides* in rubber compounding. *SRE* 6 (1):229-234

Akinlabi, AK; Quadri, RK; Bankole, IAS; Koleoso, OK (2015). The use of coconut shell as an additive in natural rubber compounding. *JCSN 40(1):56-64*

Akinlabi, AK; Laleye, RN; Akinfenwa, SB; Mosaku, AM; Akinwunmi, F; Falomo AA; Oladipo, G; Oni, SO; Falope, FY; Ilesanmi, NY; Aborode, TO; Idowu TD (2020).The Use of Modified Sugarcane Bagasse in Natural Rubber Compounding. *JCSN 45 (6): 1092 – 1100*

Banerjee, K; Ramesh, ST; Gandhimathi, R; Nidheesh, PV; Bharathi, KS (2012). A novel agricultural water adsorbent, watermelon rind for the removal of copper from aqueous solutions. *IJEE* 3(2): 143-156

Barone, JR; Scmidth, WF (2005). Polyethylene reinforced with keratin fibres obtained from chicken feathers. *Compos. Sci. and Technol.* 65:173–181

Freire MN; Holanda JNF (2006). Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste. *Cerâmica* 52: 240-244

Ishak, Z; Baker, AA (1995). An investigation on the potential of rice husk ash as fillers for epoxidized natural rubber. *Eur. Polym. J.* 31(3):259-269

Kawahara, S; Klinklai, W; Kroda, H; Isono, Y (2004). Removal of proteins from natural rubber with urea. *Polym. Adv. Technol.* 15:181

Kohjiya, S (2000). Reinforcement of tyre rubber by silica generated in-situ. Tyretech Smithers Rapra Publishing. pp39-44

Okieimen, FE.; Akinlabi, AK (2002). Processing characteristics and physico-mechanical properties of natural rubber and liquid natural rubber blends. *J. Appl. Polym. Sci.* 85:1070

Okieimen, FE; Akinlabi, AK; Aigbodion, AI; Bakara, IO; Oladoja, NA (2003). Effect of epoxidized natural rubber. *NJPS T* 3 (1):233

Oko, O (2012). Evaluation of anti-nutrient contents of watermelon *Citrullus lanatus*. *Ann. Biol. Res.* 3 (11):5145-5150

Parmar, HS; Kar, A (2009). Protective role of Mangifera indica, Cucumis melo and Citrullus vulgaris peel extracts in chemically induced hypothyroidism. *Chem. Biol. Interact.* 177:254-258

Perera, MO; Bradbury, JH (1992). Epoxidized natural rubber. Australian National University, Chemistry Department, Canberra, A.C.T. 2600 Australia. pp1 - 12.

Phinyocheep, P (2014). Chemistry, Manufacture and Application of Natural Rubber: Chemical modification of natural rubber (NR) for improved performance. Woodhead Publishing Limited. pp 68-118

Silverstein, RM; Webster, FX; Kiemle, DJ (2005). Spectrometric Identification of Organic Compounds. 7th edition; John Wiley & Son: New York, NY, USA.

Urushihara, Y; Li, L; Matsui, J; Nishino, T (2009). In situ observation of filler displacement during tensile deformation of nano silica-filled natural rubber using field-emission scanning electron microscope, *Compos*. 40(2)232–234.