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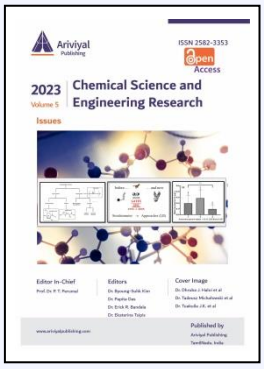

Comparative Study on Thermodynamic Properties of Clay and Carbon-Filled Natural Rubber Composites

Jacob Olalekan Arawande,*[a,b] Gabriel O. Orodepo[b] and Modupe Olatide[a]

[a]*Department of Science Laboratory Technology, University of Medical Sciences, P. M. B. 536, Ondo City, Ondo State, Nigeria.*
[b]*Department of Chemistry, University of Medical Sciences, P. M. B. 536, Ondo City, Ondo State, Nigeria.*

***Corresponding author E-mail address**: jarawande@unimed.edu.ng (Jacob Olalekan Arawande)

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Abstract: The mechanical properties (such as tensile strength and Young's modulus) of rubber composites were evaluated from the thermodynamic parameters (ΔG, ΔH, and ΔS) obtained for natural rubber composites filled with clay and carbon black at varying volume fractions of fillers (5%-25%). The tension developed in each rubber composite due to changes in temperature was used in determining thermodynamic parameters via the Arrhenius equation and plots. The result showed that between 8.50-23.50% volume fractions of filler, clay-filled rubber composites exhibited higher spontaneity of elasticity and higher tensile strength than the corresponding carbon black-filled composites. At lower filler concentration (5-7%), clay-filled composites exhibited higher modulus than carbon black-filled rubber composites and between 7.50% and 23.50% filler concentration, carbon black reinforced composites showed superior modulus values. An almost two-fold increase in modulus was observed for carbon black-filled composites when the filler concentration was increased from 15% to 20% and beyond 20% the modulus decreased drastically. For clay-filled rubber composites, the entropy change increased with increasing filler concentration up to 15% and decreased beyond 15%, while for carbon black reinforced composites, it decreased to a minimum as the filler loading increased from 5% to 10% and then increased gradually as filler concentration increased between 10-25% volume fractions. Low value of entropy change obtained at a 5% volume fraction of clay conferred excellent mechanical properties on the composite almost comparable with what was observed at a 10% volume fraction of carbon black.

Keywords: Carbon black; clay; natural rubber; filler; composites; Arrhenius equation; thermodynamic

1. Introduction

The recent advances in rubber technology have led to the development of rubber materials with improved properties such as high tensile strength, hardness and elongation at break.[1] Natural rubber in its raw form suffers from certain characteristics such as low modulus and strength,[2] in order to prepare rubber materials for several applications including military,[3] engineering and biomedical, natural rubber is usually compounded with different substances such as fillers.[4] These fillers have been found to improve the mechanical, electrical, thermal conductivity, and barrier properties of natural rubber.[1-5] Carbon black is the most commonly used filler in the rubber industry.[6] However, due to the high cost of this petroleum-based filler coupled with the problem of decolouration of materials after its use and the global demand for environmental sustainability, there has been a continuous search for renewable and low-cost fillers for use in the rubber processing industry. The research activities in the development of environmentally friendly fillers recently have been focused on the use of agricultural and industrial wastes such as oil palm ash,[7-10] cherry seed shell,[11] coconut fiber,[12-16] soy hull,[17-19] palm kernel husk,[20] eggshell powder,[21-26] snail shell powder,[27] cocoa pod husk,[28] Palmyra palm fibre,[29] and sawdust.[30] The effect of reinforcing natural rubber with carbon black and organoclay/clay on the mechanical properties of the resultant rubber composites has been well reported in the literature.[1,27,31-48] In order to obtain rubber composites with better mechanical properties required for engineering and specialized applications, a better rubber-filler interaction is essential. Thermodynamic study of rubber composites provides information on enthalpy, free energy, and entropy change of mixing,[49,50] which further supply important insight into the reinforcement mechanism of natural rubber with filler.[51] Various techniques such as synchrotron X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to obtain thermodynamic parameters for natural rubber-filler composites, however, these are highly sophisticated techniques that require high-level skills. The present study has employed a less sophisticated technique to investigate and compare the effects of clay and carbon black on the thermodynamic properties of resultant natural rubber composites.

Table 1. Compounding formulation for natural rubber composites

Ingredient	Part Per Hundred of Natural Rubber (phr)					Part Per Hundred of Natural Rubber (phr)				
Natural Rubber	100	100	100	100	100	100	100	100	100	100
Carbon filler	5	10	15	20	25	-	-	-	-	-
Clay filler	-	-	-	-	-	5	10	15	20	25
Zinc oxide	5	5	5	5	5	5	5	5	5	5
MBTS	1	1	1	1	1	1	1	1	1	1
Stearic acid	3	3	3	3	3	3	3	3	3	3
Sulphur	3	3	3	3	3	3	3	3	3	3
Volume fraction filler (phr)	5	10	15	20	25	5	10	15	20	25

Theoretical Background of studies

For elastic bodies such as natural rubber, the thermodynamic of stretching has been related to a rate process where the temperature dependence of tension or force is found to have the Arrhenius equation of the form

$$F = d\ exp^{(-\Delta E_a/RT)} \quad (1)$$

Where F is the force or tension acting on the material, d is the density of the material, T is the absolute temperature, E_a is the activation energy and R is the universal gas constant.
The change in activation energy, ΔE_a has been shown to be equal to the change in molar free energy of activation,[49] such that

$$F = d\ exp^{(-\Delta G_a/RT)} \quad (2)$$

$$\log F = \log d - \left(\frac{\Delta G_a}{2.303R}\right)\frac{1}{T} \quad (3)$$

The plot of log F against $\frac{1}{T}$ gives a slope whose value equals $\left(-\frac{\Delta G_a}{2.303R}\right)$ from which ΔG_a can be evaluated.
The enthalpy of stretching ΔH is an important thermodynamic parameter and has been deduced from the expression

$$\left[\frac{\delta \ln\left(\frac{F}{d}\right)}{\delta\left(\frac{1}{T}\right)}\right] P = -\Delta H/R \quad (4)$$

$$\log(F/d) = \left(\frac{-\Delta H}{2.303R}\right)\frac{1}{T} \quad (5)$$

The slope of the linear plot of log $\left(\frac{F}{d}\right)$ against $\frac{1}{T}$ gives$\left(\frac{-\Delta H}{2.303R}\right)$ from which ΔH can be calculated.
The entropy change ΔS is determined from the second law of thermodynamics as given in equation 6, and it is evaluated at 40°C (313 K).

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad (6)$$

2. Materials and Methods

2.1. Materials

The natural rubber latex (clone titrance TJI) employed for this study was obtained from the rubber plantation at the Federal College of Agriculture, Akure, Ondo State, Nigeria. It was freshly tapped using half coconut shells attached to the rubber tree via a short sharp stick. The latex was preserved with the ammonia solution (0.6% v/v) and further stabilized by sodium sulphite (2.5% v/v). The rubber compounding ingredients such as zinc oxide, stearic acid, sulphur, and mercapto benzothiazole sulphonamide (MBTS) were of commercial grade. Carbon black (N330) and clay which were used as fillers were sourced from Owo, Ondo state, Nigeria.

2.2. Carbon black and clay filler preparation

Carbon black was purchased from a commercial merchant and clay was obtained from Owo locality in Ondo State.

2.3. Sample Preparation

The method described by Adeosun et al., 2000[52] and Arawande et al., 2012[53] was adopted in preparing rubber composites. The composites were prepared according to the compounding formulation given in Table 1. The compounds were treated with 2% v/v acetic acid, pressed into a rectangular mat of dimension 35 by 18 cm. This was then sundried followed by oven drying to constant weight at 60°C for 24 hours. The dried master batches were masticated on water-cooled two roll mills followed by the blending with other ingredients. Each batch was mixed for 8 minutes then rapidly cooled and weighed. The composites were cured in rectangular heavy-duty steel moulds, which were pre-warmed before being filled with the compounds. The curing was done under the steam press (2000 psi) at 150°C for 35 minutes to produce vulcanized rectangular sheets of rubber composites of dimension (2.0 x 7.5 x 22.5) cm. The composites with varying concentrations of both fillers-carbon black (5-25%) and clay (5-25%) were prepared at the laboratory of Dunlop Nigeria PLC Lagos and stored in dark plastic bags at room temperature for twenty-four months.

3. Experimental Methods

The thermodynamic parameters have been obtained from the data generated by following the approach reported by Adeosun et al., 2000[52] with little modification. An Ohaus beam balance model dial-o-gram 310 g was employed for the experiment. The experimental set-up was as described in our earlier publication.[53] The dumbbell-shaped test pieces (in accordance with ASTM D-412) used for the study were cut from the vulcanized sheets. The balance was rested on a suitable level and a 1000 mL capacity beaker was placed on the left-hand side of the balance. The setup was arranged such that the whole dumbbell test pieces hung onto the hook of the balance were completely immersed inside the beaker. 300 g standard weight was hung on the lower part of the dumbbell test pieces by means of a small hook. This arrangement resulted in tension on the test piece

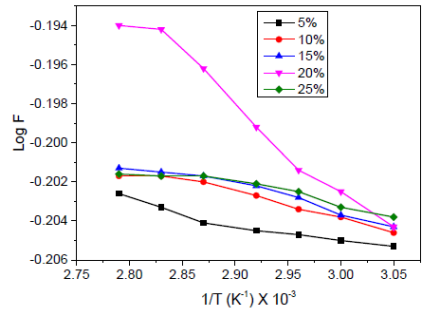

Fig. 1. Arrhenius plot of log F against 1/T for carbon-black filled natural rubber composites.

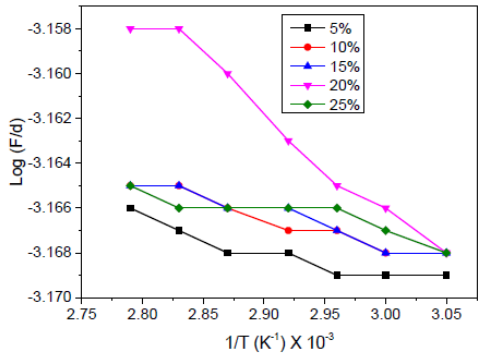

Fig. 2. Arrhenius plot of log F/d against 1/T for carbon-black filled natural rubber composites.

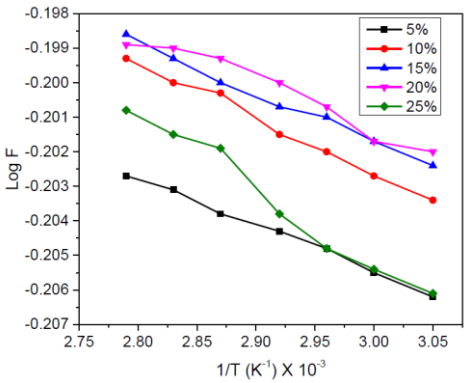

Fig. 3. Arrhenius plot of log F against 1/T for clay filled natural rubber composites.

and the pointer of the balance was adjusted to zero. Hot boiling water was poured into the beaker until the whole length of the test piece was completely immersed in the hot water. The fall in the temperature of the hot water is monitored by the thermometer and the corresponding weight required to restore the balance back to zero point was recorded and converted to tension F (in Newton) against temperature, ranging between 358 K and 328 K at an interval of 5 K.

4. Results and Discussion

The thermodynamic parameters reported in this study were determined as follows. The change in Gibbs free energy, ΔG was determined from the slope of Arrhenius plot of log F versus the reciprocal of absolute temperature (1/T) for each of the test piece of

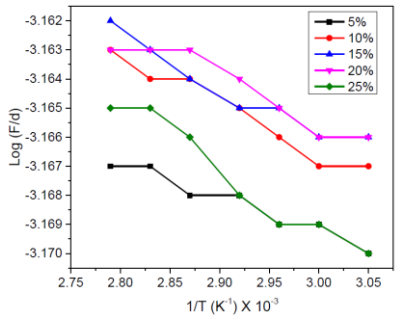

Fig. 4. Arrhenius plot of log F/d against 1/T for clay filled natural rubber composites.

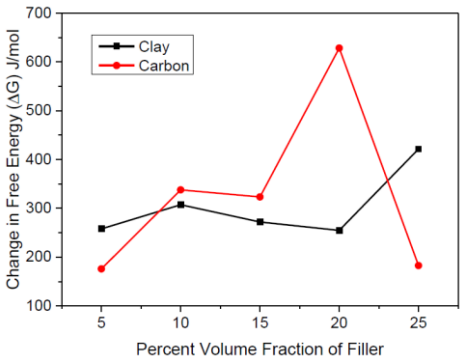

Fig. 5. Plot of change in Gibbs free energy (G) versus percent volume fraction of filler.

natural rubber composites containing varying volume fraction of fillers. Similarly, the change in enthalpy, ΔH was evaluated from the gradient of the plot of log (F/d) versus 1/T (where d is the density of natural rubber, 920 kg/m^3). The corresponding values of change in entropy, ΔS at 313 K were calculated from the values of ΔG and ΔH obtained.

Arrhenius plot of log F against 1/T for carbon-black filled natural rubber composite containing varying volume fraction of filler is shown in Fig. 1. The trend averagely reflected that the values of log F decreased as 1/T increased.

Arrhenius plot of log F/d versus 1/T for carbon-black filled natural rubber composite containing varying volume fraction of filler is presented in Fig. 2. The values of log F/d decreased as the values of 1/T increased.

Arrhenius plot of log F versus 1/T for clay filled natural rubber composite containing varying volume fraction of filler is depicted in Fig. 3. The trend of the plot showed that the values of log F decreased as the values of 1/T increased.

Arrhenius plot of log F/d versus 1/T for clay filled natural rubber composite containing varying volume fraction of filler is revealed in Fig. 4. The plot showed that the values of log F/d decreased as the values of 1/T increased.

It is important to measure thermodynamic parameters during chemical reactions especially natural rubber compounding as this affords useful insights such as heat evolved or absorbed, the degree of randomness and spontaneity of such reaction. The plots of thermodynamic parameters (ΔG, ΔH, and ΔS) versus percent volume fraction of filler are presented in Figs. 5, 6, and 7.

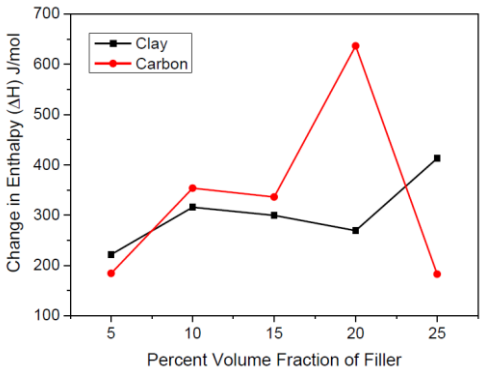

Fig. 6. Plot of change in enthalpy (H) versus percent volume fraction of filler.

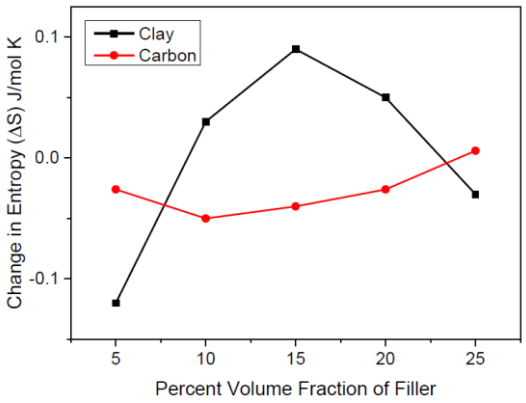

Fig. 7. Plot of change in entropy (S) against per cent volume fraction of filler.

Fig. 5 shows a plot of change in Gibbs free energy (G) versus percent volume fraction of filler. It was observed that the change in Gibbs free energy (G) attained optimal value at 20% filler volume fraction for carbon black filled composite, minimal values at 5% and 25% volume fraction of filler. For clay filled rubber composites, the Gibbs free energy had optimal values at 25% volume fraction of filler while the minimal values were at found at 5% and 20% volume fraction of filler. Above 10% filler volume fraction, there was a decrease in the Gibbs free energy (G) for both clay and carbon black filled rubber composites. Adeosun *et al.*[52] reported the relationship between the value of the free energy change (ΔG) and the spontaneity of rubber elasticity that the lower the value of ΔG the higher the spontaneity of elasticity. As depicted in Fig. 5, between 8.50-23.50% volume fractions of filler, clay filled rubber composites exhibited higher spontaneity of elasticity than the corresponding carbon black filled composites. It can be inferred from this result that between 8.50-23.50% volume fractions of filler, clay impacts higher tensile strength to natural rubber than carbon black filler. Similar observation was made by Todorova *et al.,*[54] Maiti *et al.,*[55] Alshangiti[45] and this was as a result of higher interfacial adhesion, better natural rubber-filler, and filler-filler interaction.

Plot of change in enthalpy (ΔH) against percent volume fraction of filler is presented in Fig. 6. As shown in Fig. 6, within 7.50% and 23.50% filler volume fractions, the enthalpy change for clay filled composites is lower than that of carbon black filled composites; this same trend was also observed for change in free energy. But outside 7.50% and 23.50% volume fraction of filler, the reverse trend was observed in the values of the enthalpy change of both composites.

The enthalpy change has been reported to be a measure of the modulus of the composites and it is also approximately proportional to the free energy change. At lower filler concentration (5-7.50%) and higher filler concentration (23.50%-25.00%), clay filled composites exhibited higher modulus than carbon black filled rubber composites but between 7.50% and 23.50% filler concentration, carbon black showed superior modulus values. An almost two-fold increase in modulus of carbon black filled composites was observed when the filler concentration was increased from 15% to 20%. Increasing the concentration of carbon black beyond 20% led to drastic reduction in the value of modulus of the rubber composites. This kind of effect of reduction in modulus of rubber composites at higher filler concentration has been attributed to possible agglomeration and poorer filler dispersion in the composite matrix.[56,57] Although, as revealed by the study, the mechanical properties of carbon black reinforced natural rubber composites are superior to that of clay filled composites within 7.50% to 23.50% filler concentration, the challenge was the higher loading of carbon black filler required to obtain the optimal mechanical properties has also been reported by Mohamed *et al.*[40]

The plot of change in entropy (ΔS) against per cent volume fraction of fillers (carbon black and clay) is shown in Fig. 7. Entropy change is a measure of the degree of randomness in a system. The entropy change increased with increasing filler concentration up to 15% for clay-filled rubber composites. However, at higher clay filler concentrations (beyond 15%), there was a reduction in the values of entropy change. For carbon black reinforced composites, the entropy change decreased to a minimum as the filler loading increased from 5% to 10% and then increased gradually as carbon filler concentration increased between 10-25% volume fractions. This is similar to the observation reported for corn cob reinforced natural rubber composites.[49] It is noteworthy that at lower (5-8%) and higher (beyond 23% volume fraction), carbon black reinforced composites were observed to have higher entropy change values than the clay-filled natural rubber composites. The study also revealed that between 8-23% volume fraction of filler, clay reinforced rubber composites exhibited more randomness than the carbon-filled composites. It has been shown by tubular model fitting that during rubber-filler interaction, the increase in chemical cross-linking points essentially reduces the movable radius of the molecular chain under dynamic loading. This restricts the easy movement of the molecular chain, suppresses the entropy change and consequently endows outstanding dynamic mechanical properties on the natural rubber composites.[3] The maximum entropy change for clay reinforced composite was obtained at 15% volume fraction of clay while it was found to be at 25% volume fraction for carbon black filled composite.

5. Conclusions

Within the filler volume fraction of 7.50-23.50% the enthalpy change for clay-filled composites is lower than that of carbon black-filled composites and similar trend was observed for change in free energy of the rubber composites. However, at low concentration 5.00%-

7.50% and higher concentration 23.50%-25.00% volume fraction of filler, the reverse trend was observed in the values of the enthalpy and Gibb's free energy changes of both composites.

At lower filler concentration (5.00-7.50%), clay-filled composites exhibited higher modulus than carbon black-filled rubber composites and beyond 7.50% filler concentration, carbon black showed superior modulus values. Thus, only 5% clay filler afforded a composite material with excellent mechanical properties while to obtain the same property with carbon black filler required up to 10% filler concentration. This study has established that the dynamic mechanical properties of rubber composites can be enhanced with low concentration of an alternative, less expensive and eco-friendly reinforcing agents such as clay. However, further research can be conducted in comparing other properties such as thermal conductivity of clay and carbon black filled rubber composites.

Conflicts of Interest

The authors declare no conflict of interest.

References

1 Bokobza L. Natural Rubber Nanocomposites: A Review. *Nanomaterials*, 2018, **9**, 12. [CrossRef]
2 Hakimi N.M.F.; Lee S.H.; Lum W.C.; Mohamad S.F.; Osman Al Edrus S.S.; Park B.D.; Azmi A. Surface Modified Nanocellulose and its Reinforcement in Natural Rubber Matrix Nanocomposites: A Review. *Polymers*, 2021, **13**, 3241. [CrossRef]
3 Chen G.; Wang B.; Lin H.; Peng W.; Zhang F.; Li G.; Ke D.; Liao J.; Liao L. Effect of Nonisoprene Degradation and Naturally Occurring Network during Maturation on the Properties of Natural Rubber. *Polymers*, 2022, **14**, 2180. [CrossRef]
4 Medupin R.O.; Abubakre O.K.; Abdulkareem A.S.; Muriana R.A.; Abdulrahman A.S. Carbon Nanotube Reinforced Natural Rubber Nanocomposite for Anthropomorphic Prosthetic Foot Purpose. *Sci. Rep.*, 2019, **9**, 1-11. [CrossRef]
5 Jacob A.; Kurian P.; Aprem A.S. Transport Properties of Natural Rubber Latex Layered Clay Nanocomposites. *J. Appl. Polym. Sci.*, 2008, **108**, 2623-2629. [CrossRef]
6 Fan Y.; Fowler G.D.; Zhao M. The Past, Present and Future of Carbon Black as a Rubber Reinforcing Filler–A Review. *J. Clean. Prod.*, 2020, **247**, 119115. [CrossRef]
7 Ismail H.; Haw F.S. Effects of Palm Ash Loading and Maleated Natural Rubber as a Coupling Agent on the Properties of Palm-Ash-Filled Natural Rubber Composites. *J. Appl. Polym. Sci.*, 2008, **110**, 2867-2876. [CrossRef]
8 Ooi Z.X.; Ismail H.; Bakar A.A. Synergistic Effect of Oil Palm Ash Filled Natural Rubber Compound at Low Filler Loading. *Polym. Test.*, 2013, **32**, 38-44. [CrossRef]
9 Bao C.A.; Kamaruddin S.; Yeow T.K.; Ing K.; Han B.T.J.; Ying C.S. The Effect of Oil Palm Fiber/Eggshell Powder Loading on the Mechanical Properties of Natural Rubber Composites. *ARPN J. Eng. Appl. Sci.*, 2016, **11**, 128-134. [Link]
10 Ming P.T.S.; Bao C.A.; Kamaruddin S. The Potential of Oil Palm Ash and Eggshell Powder as Hybrid Biofillers in Natural Rubber Biocomposites. In *IOP Conference Series: Materials Science and Engineering*, 2020, 859, 012013. IOP Publishing. [Link]
11 Osabohien E.; Egboh S.H.O. Cure Characteristics and Physico-Mechanical Properties of Natural Rubber Filled with the Seed Shells of Cherry (Chrysophyllum albidum). *J. Appl. Sci. Environ. Manag.*, 2007, **11**. [CrossRef]
12 Arumugam N.K.T.S.; Selvy K.T.; Rao K.V.; Rajalingam P. Coconut-Fiber-Reinforced Rubber Composites. *J. Appl. Polym. Sci.*, 1989, **37**, 2645-2659. [CrossRef]
13 Egwaikhide P.A.; Akporhonor E.E.; Okieimen F.E. Effect of Coconut Fibre Filler on the Cure Characteristics Physico-Mechanical and Swelling Properties of Natural Rubber Vulcanisates. *Int. J. Phys. Sci.*, 2007, **2**, 39-46. [Link]
14 Edirisinghe D.G.; Sampath W.D.M.; Wettasinghe P.C. Effect of Latex Coated Coconut Fibre on Cure Characteristics and Physico Mechanical Properties of Natural Rubber-Coir Composites. *J. Rubber Res. Inst. Sri Lanka*, 2015, **95**, 1-13. [CrossRef]
15 Patil Y.; Sharma S. Effect of Coir Fiber Reinforcement on Mechanical Properties of Vulcanized Natural Rubber Composites. *Sci. Eng. Compos. Mater.*, 2018, **25**, 517-528. [CrossRef]
16 Kongkaew T.; Kumneadklang S.; Panichpakdee J.; Larpkiattaworn S. Effects of Coconut Coir Powders on the Properties of Natural Rubber Composites. *Int. J. Sci. Innov. Technol.*, 2020, **3**, 53-60. [Link]
17 Alemdar A.; Sain M. Isolation and Characterization of Nanofibers from Agricultural Residues–Wheat Straw and Soy Hulls. *Bioresour. Technol.*, 2008, **99**, 1664-1671. [CrossRef]
18 Neto W.P.F.; Silvério H.A.; Dantas N.O.; Pasquini D. Extraction and Characterization of Cellulose Nanocrystals from Agro-Industrial Residue–Soy Hulls. *Ind. Crops Prod.*, 2013, **42**, 480-488. [CrossRef]
19 Neto W.P.F.; Mariano M.; da Silva I.S.V.; Silvério H.A.; Putaux J.L.; Otaguro H.; Pasquini D.; Dufresne A. Mechanical Properties of Natural Rubber Nanocomposites Reinforced with High Aspect Ratio Cellulose Nanocrystals Isolated from Soy Hulls. *Carbohydr. Polym.*, 2016, **153**, 143-152. [CrossRef]
20 Egwaikhide P.A.; Akporhonor E.E.; Okieimen F.E. An Investigation on the Potential of Palm Kernel Husk as Fillers in Rubber Reinforcement. *Middle-East J. Sci. Res.*, 2007, **2**, 28-32. [Link]
21 Mohammed M.R.; Hadi A.N. Effect of Egg Shells Powder on Some Mechanical and Physical Properties of Natural Rubber (NR). *Iraqi J. Mech. Mater. Eng.*, 2012, **12**, 446-458. [Link]
22 Intharapat P.; Kongnoo A.; Kateungngan K. The Potential of Chicken Eggshell Waste as a Bio-Filler Filled Epoxidized Natural Rubber (ENR) Composite and its Properties. *J. Polym. Environ.*, 2013, **21**, 245-258. [CrossRef]
23 Barrera C.S.; Cornish K. Novel Mineral and Organic Materials from Agro-Industrial Residues as Fillers for Natural Rubber. *J. Polym. Environ.*, 2015, **23**, 437-448. [CrossRef]
24 Sawere B.T.; Igbuku A.U. Evaluation of Some Mechanical Properties of Composites of Natural Rubber with Egg Shell and Rice Husk. *Int. Res. J. Adv. Eng. Sci.*, 2016, **1**, 71-75. [Link]
25 Akinlabi A.K.; Falope F.Y.; Oladipo G.; Ilesanmi N.Y.; Oni S.; Ugbaja R.N.; Mosaku A.M.; Diayi V.N. Properties of Vulcanizates Compounded from Modified Natural Rubber with Egg Shell. *J. Chem. Soc. Niger.*, 2018, **43**, 350-359. [Link]
26 Moonlek B.; Saenboonruang K. Mechanical and Electrical Properties of Radiation-Vulcanized Natural Rubber Latex with Waste Eggshell Powder as Bio-Fillers. *Radiat. Eff. Defects Solids*, 2019, **174**, 452-466. [CrossRef]
27 Igwe I.O.; Ejim A.A. Studies on Mechanical and End-Use Properties of Natural Rubber Filled with Snail Shell Powder. *Mater. Sci. Appl.*, 2011, **2**, 802-810. [Link]
28 Nkengafac N.J.; Alegria A.; Arrese-Igor S.; Edgengele A.; Eugene E. A Comparative Study on the Thermal Behaviour of Natural Rubber Filled with Carbon Black and Plant Residues. *J. Mater. Sci. Res. Rev.*, 2020, **6**, 21-30. [Link]
29 Nwabanne J.; Igbokwe P.; Ezeonyebuchi E.J.A. Effect of Palmyra Palm Fiber Filler on Properties of Natural Rubber Vulcanizate. *World J. Eng.*, 2014, **11**, 565-574. [CrossRef]
30 Oo H.N. Preparation and Characterization of Rubber Composites using Sawdust as Filler. *Int. J. Trend Sci. Res. Dev.*, 2019, **3**, 378-381 [Link]
31 El-Lawindy A.M.Y.; El-Guiziri S.B. Strain Energy Density of Carbon-black-loaded Rubber Vulcanizates. *J. Phys. Appl. Phys.*, 2000, **33**, 1894. [CrossRef]
32 Qing-xiu J.; You-ping W.; Ping X.; Xie Y.; Yi-qing W.; Li-qun Z. Combined Effect of Nano-clay and Nano-carbon Black on Properties of NR Nanocomposites. *Polym. Polym. Compos.*, 2005, **13**, 709-719. [CrossRef]
33 Ismail H.; Ramli R. Organoclay Filled Natural Rubber Nanocomposites: The Effects of Filler Loading and Mixing Method. *J. Reinf. Plast. Compos.*, 2008, **27**, 1909-1924. [CrossRef]
34 Bhattacharya M.; Bhowmick A.K. Synergy in Carbon Black-Filled Natural Rubber Nanocomposites. Part I: Mechanical, Dynamic

Mechanical Properties, and Morphology. *J. Mater. Sci.*, 2010, **45**, 6126-6138. [CrossRef]
35 Rezende C.A.; Bragança F.C.; Doi T.R.; Lee L.T.; Galembeck F.; Boué F. Natural Rubber-Clay Nanocomposites: Mechanical and Structural Properties. *Polymer*, 2010, **51**, 3644-3652. [CrossRef]
36 Bahl K.; Miyoshi T.; Jana S.C. Hybrid Fillers of Lignin and Carbon Black for Lowering of Viscoelastic Loss in Rubber Compounds. *Polymer*, 2014, **55**, 3825-3835. [CrossRef]
37 Ruamcharoen J.; Ratana T.; Ruamcharoen P. Bentonite as a Reinforcing and Compatibilizing Filler for Natural Rubber and Polystyrene Blends in Latex Stage. *Polym. Eng. Sci.*, 2014, **54**, 1436-1443. [CrossRef]
38 Vijay V.R.; Anitha A.M.; Menon A.R.R. Studies on Blends of Natural Rubber and Butadiene Rubber Containing Silica–Organomodified Kaolin Hybrid Filler Systems. *Polymer*, 2016, **89**, 135-142. [CrossRef]
39 Pajtášová M.; Micová Z.; Ondrušová D.; Pecušová B.; Feriancova A.; Raník L.; Domčeková S. Study of Properties of Fillers based on Natural Bentonite and their Effect on the Rubber Compounds. *Procedia Eng.*, 2017, **177**, 470-475. [CrossRef]
40 Mohamed R.; Nurazzi N.M.; Huzaifah M. Effect of Carbon Black Composition with Sludge Palm Oil on the Curing Characteristic and Mechanical Properties of Natural Rubber/Styrene Butadiene Rubber Compound. In *IOP. Ser.: Mater. Sci. Eng.,* 2017, **223**, 012008. IOP Publishing. [CrossRef]
41 Savetlana S.; Sukmana I.; Saputra F.A. The Effect of Carbon Black Loading and Structure on Tensile Property of Natural Rubber Composite. In *IOP Conf. Ser.: Mater. Sci. Eng.,* 2017, **223**, 012009. IOP Publishing. [CrossRef]
42 Wisojodharmo L.A.; Fidyaningsih R.; Fitriani D.A.; Arti D.K.; Indriasari, E.; Susanto H. The Influence of Natural Rubber–Butadiene Rubber and Carbon Black Type on the Mechanical Properties of Tread Compound. In *IOP Conf. Ser.: Mater. Sci. Eng.*, 2017, **223**, 012013. IOP Publishing. [CrossRef]
43 Jayaraj S.; Egodage S.M.; Walpalage S. Incorporation of Nanoclay into Field Latex to Develop Nanoclay Filled Dry Rubber Compounds. *J. Natl. Sci. Found. Sri Lanka*, 2017, **45**, 121-132. [CrossRef]
44 Burgaz E.; Gencoglu O.; Goksuzoglu M. Carbon Black Reinforced Natural Rubber/Butadiene Rubber and Natural Rubber/Butadiene Rubber/Styrene-Butadiene Rubber Composites: Part I: Rheological, Mechanical and Thermomechanical Properties. *Res. Eng. Struct. Mater.*, 2019, **5**, 233-247. [CrossRef]
45 Alshangiti D.M. Impact of a Nanomixture of Carbon Black and Clay on the Mechanical Properties of a Series of Irradiated Natural Rubber/Butyl Rubber Blend. *e-Polymers*, 2021, **21**, 662-670. [CrossRef]
46 Robertson C.G.; Hardman N.J. Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite. *Polymers*, 2021, **13**, 538. [CrossRef]
47 Paleri D.M.; Rodriguez-Uribe A.; Misra M.; Mohanty A.K. Preparation and Characterization of Eco-Friendly Hybrid Biocomposites from Natural Rubber, Biocarbon, and Carbon Black. *eXPRESS Polym. Lett.*, 2021, **15**, 236-249. [CrossRef]
48 Wirjosentono B.; Siregar A.H.; Nasution D.A. Mechanical, Thermal and Adhesion Characteristics of Natural Rubber/Epoxidised Natural Rubber (NR/ENR 25) Blends Containing Natural Microbentonite. In *IOP Conf. Ser.: Earth Environ. Sci.,* 2021, **912**, 012073. IOP Publishing. [CrossRef]
49 Arawande J.O.; Orodepo G.O.; Osungbemiro W.B. Studies on the Thermodynamic Properties of Natural Rubber Composites Filled With Clay and Corn Cob. *J. Chem. Soc. Niger.*, 2022, **47**, 350-362. [CrossRef]
50 Malomo D.; Adesigbin M.A.; Egharevba O.; Bello A.; Adewuyi S.O.; Idemudia L. Physico-Mechanical, Solubility and Thermodynamic Studies of Natural Rubber–Neoprene Blends. *J. Chem. Soc. Niger.*, 2019, **44**, 718-725. [Link]
51 Nie Y.; Huang G.; Qu L.; Wang X.; Weng G.; Wu J. New Insights Into Thermodynamic Description of Strain-Induced Crystallization of Peroxide Cross-Linked Natural Rubber Filled With Clay By Tube Model. *Polymer*, 2011, **52**, 3234-3242. [CrossRef]
52 Adeosun B. F.; Adu O. E.; Oyewusi P. A.; Ogunmade A. A. The Thermodynamics of Stretching of Filler Natural Rubber Vulcanizates. *J. Appl. Sci.,* 2000, **3**, 690-697.
53 Arawande J. O.; Adesina K. A.; Bello L. J. Comparative Studies On The Effects of Corn Cob and Carbon Filler Concentrations on Some Thermodynamic Parameters of Natural Rubber Composites *Int. J. Chem. Sci.,* 2012, **5**, 79–88.
54 Todorova Z.; Dishovsky N.; Dimitrov R.; El-Tantawy F.; Abdel Aal N.; Al-Hajry A.; Bououdina M. Natural Rubber Filled Sic and B4C Ceramic Composites as a New NTC Thermistors And Piezoresistive Sensor Materials. *Polym. Compos.*, 2008, **29**, 109-118. [Crossref]
55 Maiti M.; Sadhu S.; Bhowmick A.K. Effect of Carbon Black on Properties of Rubber Nanocomposites. *J. Appl. Polym. Sci.*, 2005, **96**, 443-451. [Crossref]
56 Yangthong H.; Pichaiyut S.; Jumrat S.; Wisunthorn S.; Nakason C. Novel Natural Rubber Composites With Geopolymer Filler. *Adv. Polym. Technol.*, 2018, **37**, 2651-2662. [Crossref]
57 Intapun J.; Rungruang T.; Suchat S.; Cherdchim B.; Hiziroglu S. The Characteristics of Natural Rubber Composites with Klason Lignin as a Green Reinforcing Filler: Thermal Stability, Mechanical and Dynamical Properties. *Polymers*, 2021, **13**, 1109. [CrossRef]

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