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A Comparative Study on the Thermal Behaviour of Natural Rubber Filled with Carbon Black and Plant Residues

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Authors' contributions

This work was carried out in collaboration among all authors. Authors NJN, EE and AE designed the study. Authors AA, SAI and NJN managed the laboratory analysis. All authors read and approved the final manuscript.

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ABSTRACT

Aims: A comparative study on the thermal behavior of natural rubber (NR) filled with different plant wastes and carbon black was carried out with the aim to evaluate green fillers that can replace carbon black filler in natural rubber vulcanisates for thermal applications.
Study Design: The plant wastes used for this study were carbonized and un carbonized cocoa pod husk, corncob and empty palm fruit bunch. Natural rubber vulcanisates filled with 10 phr carbon black (reference) and the various plant waste materials were prepared.
Methodology: The thermal behaviour of the vulcanisates and the fillers was studied by thermogravimetric analysis (TGA). The glass transition temperature (Tg) for the vulcanisates was determined by differential scanning calorimetry (DSC). The shape of the decomposition curve was obtained from the derivative of the TGA curve (DTGA). The amount of residue remaining at various

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temperatures for the different samples was calculated from the TGA curve. Activation energies of degradation were calculated using Horowitz–Metzger equation.
Results: The carbonised fillers and carbon black were more thermally stable than the un carbonised fillers and raw rubber. The decomposition behavior of vulcanisates followed a similar trend; with a single main decomposition peak at about 380°C. Samples with un carbonised fillers had higher residues than those filled with carbon black and carbonized plant wastes. From the activation energy values, it was found that vulcanisates, filled with carbonized corncob and carbonized cocoa pod husk were very close in thermal stability to those filled with carbon black and they were more stable than those filled with un carbonised plant wastes. DSC studies revealed that the fillers had non-significant effects on the Tg of the vulcanisates. This was evident from the very close nature of the Tg values for the different vulcanisates. Among the plant wastes studied, carbonised cocoa pod husk and corncob presented very close values of Ea and Tg to carbon black as fillers for raw natural rubber.
The vulcanisates with un carbonised fillers were less thermally stable than vulcanisates filled with carbonized fillers and carbon black.

Keywords: Degradation; glass transition; natural rubber; plant wastes.

1. INTRODUCTION

Natural rubber (NR) obtained from the latex of a tropical plant *Hevea brasiliensis* has found great value in many applications [1,2]. As a single material natural rubber may not be good enough for any useful application so there is the need for the addition of other materials (hard and soft) which help to enhance its properties [3,4]. These additives include fillers which make up the highest volume of additives [5]. Carbon black has been the major filler used in the rubber industry. The main disadvantage of using carbon black is that its cost is high and it is a petroleum product, a source which is non-renewable. Therefore, the need to source for alternative material from local sources which can replace carbon black with little or no modification. Several studies have been carried out to find alternatives (local sources) for carbon black. Notably among these studies are those on the use of agricultural by- products, such as rice husk, groundnut shell, rubber seed shell, cocoa pod husk, corncob, palm kernel fibre, jute fibre etc. [6,7] as fillers for NR. These filler materials are used in their raw form or they are modified before use. Organic materials as fillers have these advantages; completely renewable, environmental friendly, low cost, biocompatibility, and bio-degradability [8,9] Cocoa pod husk, corncob and empty palm fruit bunch are cheap, renewable and locally available agricultural waste products [10,11] which are still underutilized. For end use application of filled polymers, their properties need to be evaluated and one of these properties is thermal stability. The degradation and thermal stability analyses give valuable information about the performance of materials and the suitable conditions of usage and storage [12]. Thermal analysis is an important tool in polymer technology that is used to investigate the thermal stability of polymers and composites. Plant wastes may have lower thermal stability than other components in the polymer matrix which will affect the overall thermal behavior of the compound. Thus it is necessary to evaluate these effects when considering application at elevated temperatures. Several workers, [13,14,15] have reported on thermal properties of some elastomers filled with agricultural waste products.

Although much work has been reported on the use of different agricultural waste products as fillers for elastomers, [16,17,18] a gap still exist on the comparative studies on using different carbonised and un carbonised agricultural waste product as fillers for rubber with focus on their thermal properties. The aim of the present work is to evaluate the effect of some carbonised and un carbonised agricultural waste materials (cocoa pod husk, corncob and empty palm fruit bunch) in comparison with commercial grade carbon black N330 as filler on the thermal behaviour of natural rubber vulcanisates.

2. MATERIALS AND METHODS

2.1 Materials

Natural rubber used in this study conforming to the Cameroon Standard Rubber Grade L (CNR3L) was obtained from the Cameroon Development Cooperation (CDC) -Tiko. The vulcanizing ingredients such as stearic acid, zinc oxide, sulphur, tetramethylthiuram disulphide (TMTD), trimethyl quinine (TMQ), and carbon

black (N330) were of standard laboratory grades obtained from Sigma. Carbonised and un carbonised corncob (CC), carbonized and un carbonised cocoa pod husk (CPH) and carbonised and un carbonised empty palm fruit bunch (EPFB) powders were used as fillers in the preparation of natural rubber (NR) composites. The corncob, cocoa pod husk and empty palm fruit bunch were sourced locally around IRAD Ekona research farms and they are among the waste produced from the production of maize, cocoa bean and palm oil respectively. The CC, CPH and EPFB were individually washed to remove dirt particles, sun dried to maximum of 10% water content. The low moisture content, ensures a lesser degree of a defect arising from shrinkage during the curing process at elevated temperatures [19]. The dried samples were milled to fine powders of less the 0.35mm diameter (un carbonised fillers). Part of the dried CC, CPH and EPFB were carbonised to produce carbonized fillers. The carbonised materials were also milled into fine powder. These fillers as well as carbon black (N330) were filtered with a 0.35mm sieve. The sieved fine powders were then collected and used for composite preparation. Fig. 1 shows the different steps in the preparation of carbonised and un carbonised fillers.

2.2 Preparation of Natural Rubber Vulcanisates

Table 1 gives the ingredients used in compounding natural rubber. The ingredients are arranged in the order in which they were used during the compounding process. A two-roll mill was used in the compounding process with the temperature maintained at 70°C to avoid cross linking during mixing [17]. After compounding, samples were obtained, coded accordingly, and processed further by curing.

2.2.1 The curing process

Each rubber vulcanisate produced was placed in a rectangular shaped mould and introduced into a compression moulding machine for 5 min at 150°C, and pressure of 1800 psi to produce a rectangular sheet. After curing, samples were cut from the sheets and set for property testing.

2.3 Thermogravimetric Analysis (TGA)

The thermal stability of the produced materials was investigated by means of thermogravimetric analysis (TGA). The measurements were performed with a TA instrument Thermo Analyser Q500 in nitrogen atmosphere with a flow rate of 40 mL/min. It consisted in dynamic scans with 10 ±1 mg of the samples in platinum pans, heated from room temperature up to 750 °C at a rate of 10 K/min till 100 °C then at 20 K/min till 750 °C. The TG curves were analysed as percentage weight loss as a function of temperature and decomposition stages identified using the derivatives of the TG (DTG) curves.

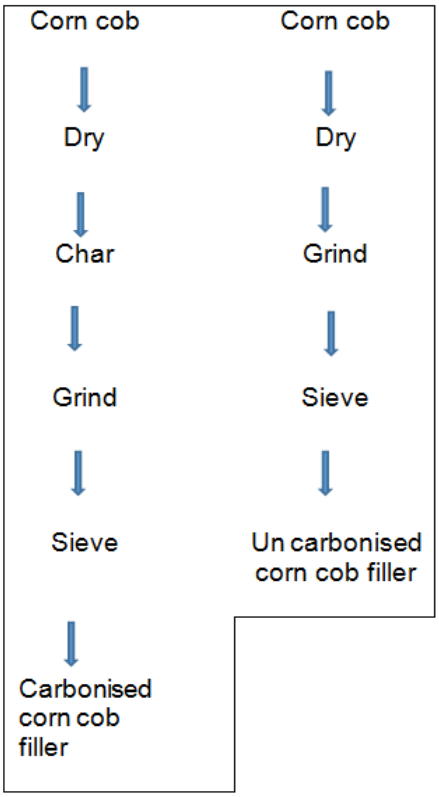

Fig. 1. Schematic procedure for the production of carbonised and un carbonised fillers with corncob as an example

Table 1. Compounding formulation used in the study

Ingredient	Amount (phr)
Natural Rubber	100
ZnO	5
Stearic acid	2.5
Tetramethylthiuram disulphide (TMTD)	1
Sulfur	2.5
Mecaptobenzothiazole (MBT)	1
Fillers	10

phr = parts per hundred rubber

2.3.1 Activation energy of degradation process

The activation energy for decomposition, Ea, can be calculated from the TGA curves by the integral method proposed by Horowitz and Metzger [20] using the following equation

$$\log\{-\log(1-\alpha)\} = (Ea\theta)/\{2.303RT^2_m\}$$

Where

α is the decomposed fraction, Ea is the activation energy of decomposition, T_m is the temperature at the maximum rate of weight loss, θ is the value of $T-T_m$ and R is the gas constant. From the plots of $\log\{-\log(1-\alpha)\}$ versus θ, the activation energy Ea for decomposition can be determined from the slope of the straight line of the plots.

2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed using the TA instrument, DSC Q2000 equipped with a liquid nitrogen cooling system, with the temperature range from -150 to 150 °C at a heating rate of 3 °C/min under 25 ml/min flow He atmosphere. The vulcanized natural rubber samples (~10 mg) were encapsulated in standard, aluminum pans then pretreated at 150 °C at a rate of 3 °C/min for 5 min at this temperature in order to remove the volatile impurities. The samples were then cooled down to -150 °C at a rate of 3K/min. A temperature modulation of 0.5 K amplitude and 60 second period was superimposed on the continuous heating and cooling runs. The glass transition temperature, Tg of each sample was taken as the midpoint of the transition in the reversible heat flow thermographs, which is not significantly affected by the baseline drifts.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis (TGA)

Curves for thermogravimetric analysis (TGA) for individual fillers and NR are presented in Fig. 1. The carbonised fillers were more thermally stable than the un carbonised fillers. The un carbonised cocoa pod husk (CPHuc) was the most thermally unstable filler. The lower thermal stability of natural fillers observed in this study is similar to the results of another study [21] that showed that EPFB had lower thermal stability than low density polyethylene and its incorporation reduced the thermal stability of its composites. The thermal degradation of EPFB fiber was due

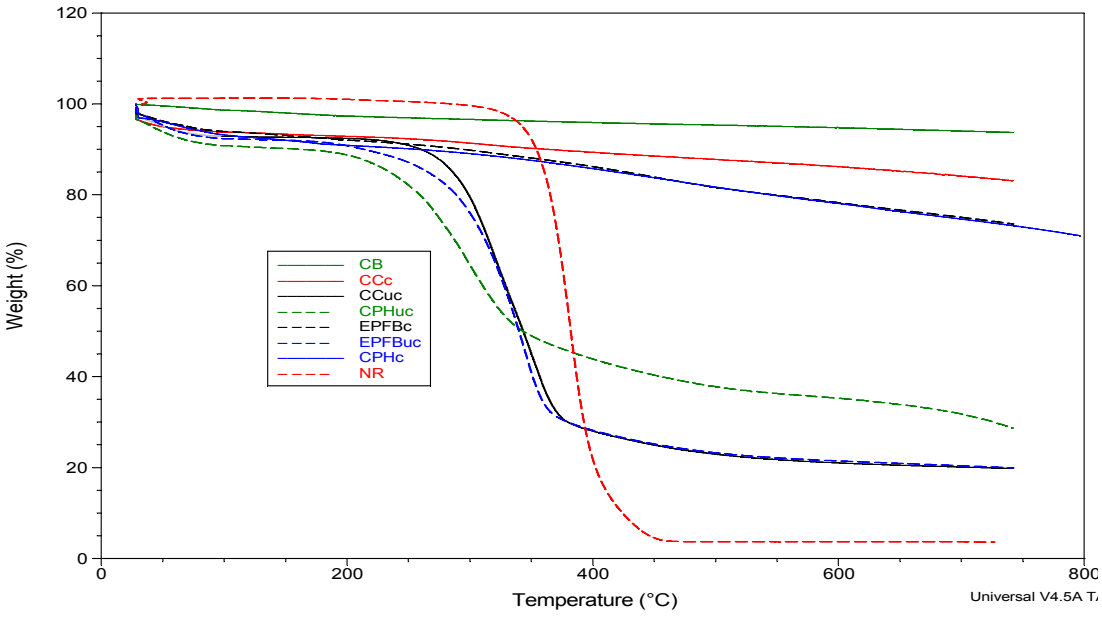

Fig. 2. TGA curves for NR (natural rubber) and fillers

CB = carbon black, CCc = carbonisedcorncob, CCuc = un carbonised corncob, CPHc = carbonized cocoapod husk, CPHuc

to the decomposition of cellulose, lignin and hemicellulose to give off volatiles [22]. Thermal decomposition began at 100°C for the un carbonised fillers while the raw NR was relatively very stable till 300°C where it degraded with the least amounts of residues at 450°C (Fig. 2) [1,23]. NR has been reported to undergo thermal degradation in the temperature range of 287–400°C to give 39% isoprene, 13.2% dipentene and small amounts of *p*-menthene [24]. The lower thermal stability of un cabonised fillers compared to carbon black and cabonised fillers is attributed to the presence of more volatile components in the un cabonised fillers which may reduce rubber-filler interaction [25]. Among the un carbonised fillers, the un carbonised cocoa pod husk (CPHuc) had the highest amount of residues at 500°C.

The thermal decomposition behavior and derivative weight thermograms of cabon black and plant waste filled natural rubber vulcanisates are shown in Figs. 3 and 4 respectively. The weight losses at various decomposition temperatures and char residues are also listed in Table 2.

TG and DTG curves of all vulcanisates evaluated have shown the same general shape, suggesting that the decomposition mechanisms are similar. All samples studied exhibited an initial small mass loss attributed to the elimination of volatile components such as water. Considering these curves, natural rubber vulcanisates were quite stable up to 200 ◦C for samples filled with un carbonised fillers and 300◦C for samples filled with carbon black and carbonized fillers.

It can be seen that the TG curves have only one large plateau and the DTG curves have one primary degradation peak, indicating that thermal degradation of the NR vulcanisates is mostly a one-stage process. The major stage in the degradation of the vulcanisates started at about 340°C and was completed at around 470°C. This is attributed to the degradation of NR segment. These results are similar to those obtained on thermal studies of natural rubber (NR) filled with titanium dioxide (TiO2) nanoparticles [26] and NR filled with strontium ferrite [27].

The primary particles of the filler form aggregate and agglomerate as a result of binding with physicochemical forces. The nature of the agglomerates depend on the nature of the filler and its activity [28]. From Table 2, it is observed that sample decomposition began at 100°C, and the rate was slow till 300 °C (maximum of 10%

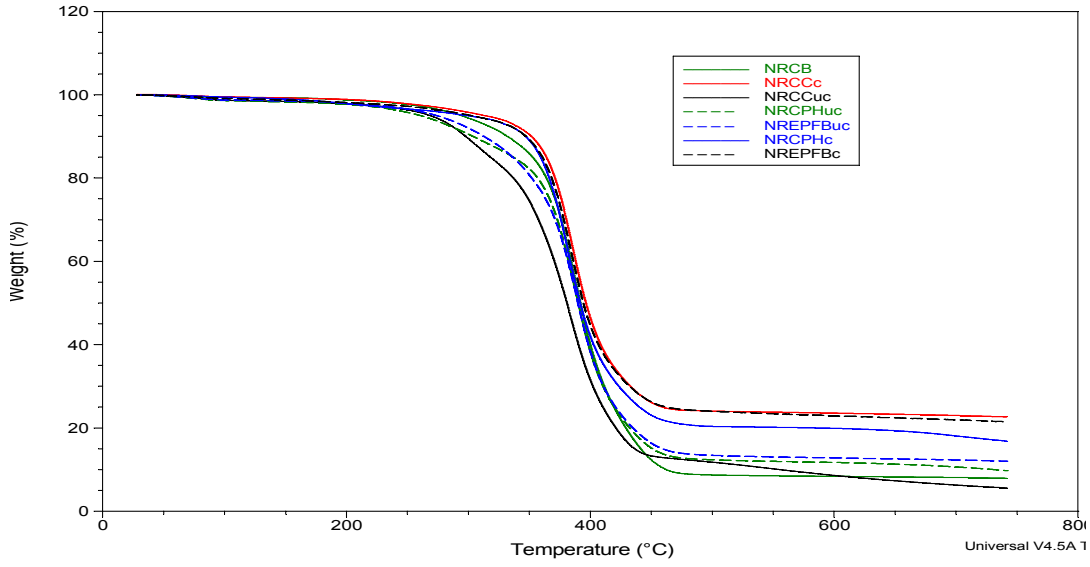

Fig. 3. TG curves for filled natural rubber (NR)

(NRCB = Natural rubber/carbon black, NRCCc = Natural rubber/carbonised corncob, NRCCuc = Natural rubber/un carbonised corncob, NRCPHc = Natural rubber/carbonised cocoa pod husk, NRCPHuc = Natural rubber /un carbonised cocoa pod husk, NREPFBc =Natural rubber/ carbonised empty palm fruit bunch, NREPFBuc = Natural rubber/un carbonised empty palm fruit bunch)

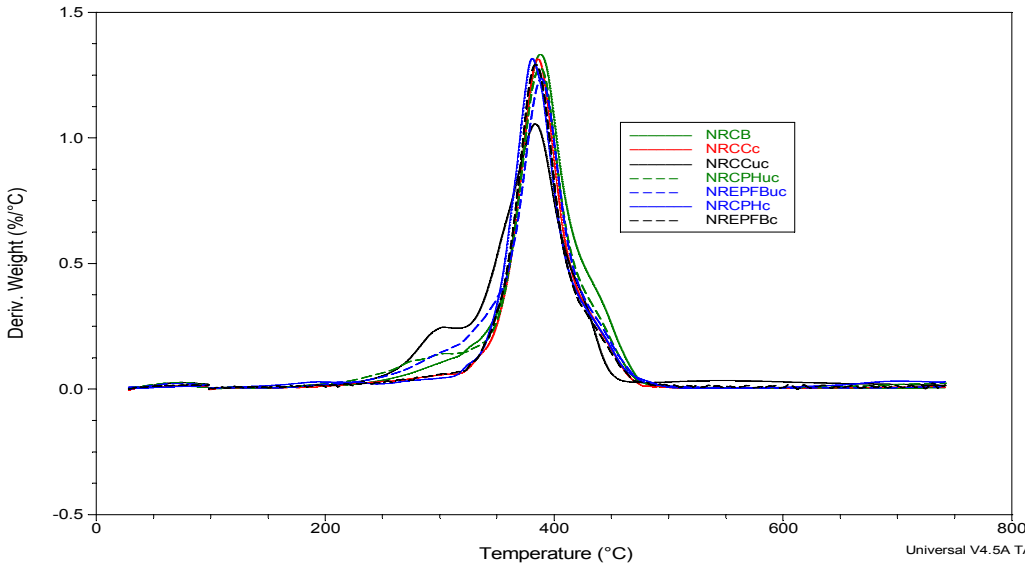

Fig. 4. Derivative of thermogravimetric (DTG) curves for filled natural rubber (NR)
(NRCB = Natural rubber/carbon black, NRCCc = Natural rubber/carbonised corncob, NRCCuc = Natural rubber/un carbonised corncob, NRCPHc = Natural rubber/carbonised cocoa pod husk, NRCPHuc = Natural rubber /un carbonised cocoa pod husk, NREPFBc =Natural rubber/ carbonised empty palm fruit bunch, NREPFBuc = Natural rubber/un carbonised empty palm fruit bunch)

mass loss). Similar results were obtained for rice husk filled natural rubber composites [29]. This region could be associated with the decomposition of hemicellulose in plant waste materials which are enriched with carbon sugars chain and branched structures, which are susceptible to decomposition at low temperature (200 - 260°C) [30]. The greatest mass loss (70%) was observed between 350°C and 450°C with decomposition for most samples ending at 500°C. The amount of sample loss at each temperature is higher for samples with un carbonised fillers than those with carbonised fillers and carbon black. This is attributed to higher volatile components in un carbonised plant wastes filled samples. The vulcanisates with carbonized fillers and carbon black are more thermally stable than vulcanisates with un carbonised fillers. This could be explained from the fact that the carbonised materials provided a shielding effect on the composites and delayed the thermal decomposition process [31,32,33]. Carbonised corncob, cocoa pod husk, empty palm fruit bunch though lower values are very close to carbon black in natural rubber compounding when thermal properties are considered. The vulcanisates with un carbonised fillers can be used with applications below 250°C. The char residues of vulcanisates were higher for samples filled with cabonised plant material then those filled with un carbonised plant material and carbon black (Table 2). The amount of char is very much dependent on the type of filler [34]. The difference in char amount mainly concerns the char formation process. The higher amount of char residues suggest a higher amount of inorganic matter in the samples [35]. The smallest amount of char residue was obtained for samples filled with carbon black and this is as expected because carbon black is mostly pure carbon.

The maximum decomposition temperatures of all the compounds were similar as they contain the same elastomer. The thermal degradation of the rubber results in the scission of crosslinking network and the chain cleavage, which in turn decreases the crosslink density and molecular weight of the vulcanisates.

3.2 Activation Energy of Degradation Process

Thermal stability of polymers can be evaluated in terms of activation energy of degradation from TGA curves [36]. The activation energy of degradation was calculated by using the Horowitz-Metzger equation. The activation energy of degradation is the energy required to decompose the substance. Higher values in the

Table 2. Mass loss and activation energy of NR vulcanisates

Sample	Mass loss /%						% residue left	Activation energy, *Ea*/kJ mol–1
	100°C	200°C	300°C	350°C	400°C	500°C	500°C	Ea
NRCB	0.61	1.24	5.61	14.27	60.29	91.3	8.7	58.56
NRCCc	0.52	1.11	4.22	9.62	53.81	76.03	23.97	55.71
NRCCuc	1.32	2.18	10.58	25.82	68.99	88.23	11.77	53.72
NRCPHc	0.59	2.14	5.06	11.01	58.16	79.63	20.37	55.25
NRCPHuc	1.41	2.33	9.54	17.93	62.04	87.66	12.34	49.21
NREPFBc	0.86	1.86	4.92	10.82	55.78	76.03	23.97	48.76
NREPFBuc	1.22	1.98	8.07	19.45	62.12	86.58	13.42	51.71

(NRCB = Natural rubber/carbon black, NRCCc = Natural rubber/carbonised corncob, NRCCuc = Natural rubber/un carbonised corncob, NRCPHc = Natural rubber/carbonised cocoa pod husk, NRCPHuc = Natural rubber /un carbonised cocoa pod husk, NREPFBc =Natural rubber/ carbonised empty palm fruit bunch, NREPFBuc = Natural rubber/un carbonised empty palm fruit bunch)

activation energy indicate that more energy is needed to decompose the material and hence the material is thermally more stable [37]. The activation energy of degradation was filler dependent and was generally lower for vulcansates filled with un carbonised fillers except for empty fruit bunch filler where the reverse was true. The higher value of Ea for vulcanisates with carbonised filler indicates that treatment of some plant wastes through carbonisation before compounding improves the thermal stability of the vulcanisates. Carbon black filled composites had the highest activation energy (58.56 kJ/mol) (Table 2). However, it is interesting to note that the Ea for vulcanisates filled with carbonized fillers (about 55.23 kJ/mol) were very comparable to the vulcanisate filled with carbon black and these values were within the range obtained for raw natural rubber under Nitrogen atmosphere in other studies [37].

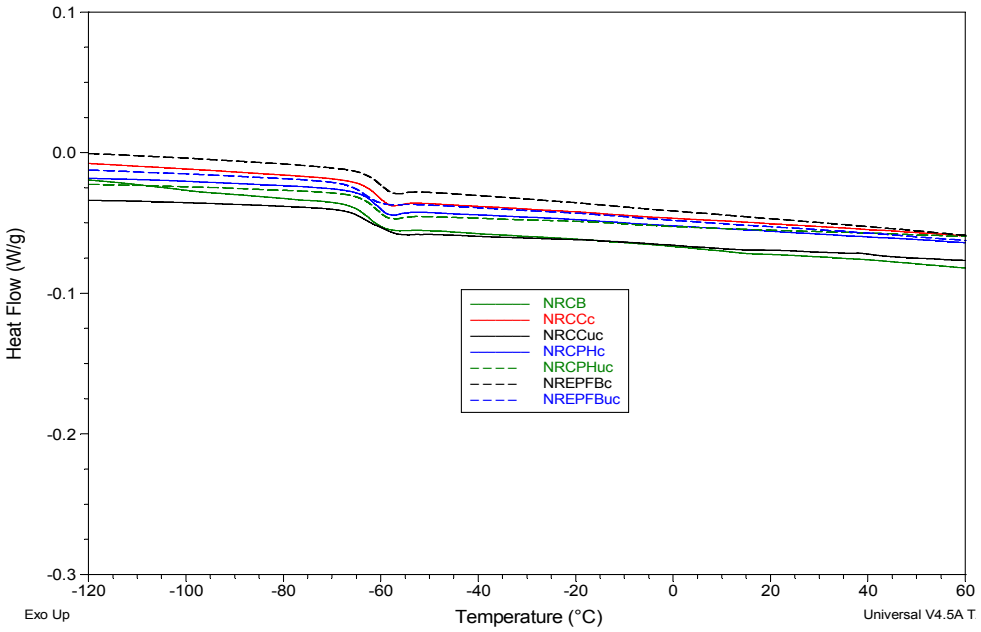

Fig. 5. DSC curves for vulcanised natural rubber (NR)

(NRCB = Natural rubber/carbon black, NRCCc = Natural rubber/carbonised corncob, NRCCuc = Natural rubber/un carbonised corncob, NRCPHc = Natural rubber/carbonised cocoa pod husk, NRCPHuc = Natural rubber /un carbonised cocoa pod husk, NREPFBc =Natural rubber/ carbonised empty palm fruit bunch, NREPFBuc = Natural rubber/un carbonised empty palm fruit bunch)

3.3 Differential Scanning Calorimetry (DSC)

Fig. 5 presents the DSC curves for the vulcanisates filled with carbon black and plant wastes.

4. CONCLUSION

Thermogravimetric analysis and differential scanning calorimetric analysis were carried out to study the thermal behavior of plant waste and carbon black filled natural rubber vulcanisates. The effect of filler treatment on the thermal behavior of vulcanisates was analyzed.

It was found that carbonizing the fillers improved the thermal stability of the fillers making them close to those of carbon black (N330). The mass loss for the vulcanisates was found to be lower for vulcanisates filled with un carbonised fillers than that of vulcanisates filled with carbonised fillers and carbon black. It is found that the vulcanisates filled with carbonized corncob and those filled with carbonized cocoa pod husk were very close to that filled with carbon black. All the vulcanisates studied presented a single degradation peaks from their DTG curves. DSC studies reveal similar glass transitions for the vulcanisates and hence plant waste filled NR are very close in Tg with carbon black filled NR vulcanisates.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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