Effect of Recycled Rubber-derived Carbon (CRR) on the Thermal Stability, Cure Behaviour, and Dynamic Mechanical Property of NR/SBR Compound

E C Danila¹, M Lanwang² and L L Diaz¹

¹ Department of Mining, Metallurgical and Materials Engineering, College of Engineering, University of the Philippines, 1101, Diliman, Quezon City, Philippines
² Materials Science and Engineering Program, College of Science, University of the Philippines, 1101, Diliman, Quezon City, Philippines
E-mail: edanila@up.edu.ph

Abstract. From an economic viewpoint, locally-sourced carbon from recycled rubber was identified to be a potential filler substitute to commercial carbon black in rubber tire. In this research, methodical measures were used to compare several properties of rubber compounds reinforced with carbon from recycled rubber (CRR) and commercial carbon black fillers to systematically qualify such substitution. Thermogravimetric analysis elucidated the overall thermal stability of the compounds, the degradation behaviour of their components and the purity of the fillers used. Differential Scanning Calorimetry and Rubber Process Analyzer test results revealed the difference in polymer network contribution and filler-filler interaction observed in the compounds, which collectively described the reinforcing effect of the fillers in the material. Conclusively, the difference in composition of fillers used resulted in the alteration of reinforcing effects in the rubber compounds.

1. Introduction
Rubber, as one of the most significant elastomeric composite material, exhibits remarkable viscoelastic properties that enable it to become an advantageous choice for various useful applications in the industry and everyday use. Such interesting properties arise from the integrated characteristics of its components which are the base elastomer, fillers, and additives [1], [2]. Of all its components, rubber fillers have been the focus of studies for decades. It has been proven that the physical, mechanical and thermal properties of the rubber compound can be enhanced by adding fillers [3], [4]. In the paper published by Fröhlich et. al., the primary filler factors affecting rubber reinforcement were thoroughly discussed using an elastic modulus curve. Such factors include the strain-dependent filler-filler interaction and the strain-independent polymer network contribution. The filler-filler interaction is highly dependent on the particle size, surface area, and amount of loading of the filler which, when treated as a whole, signifies the effective contact area between the filler and polymer matrix; while the polymer network contribution is highly related to the crosslink density of the matrix and the polymeric nature [5]. Since rubber has already been part of our daily lives, eco-friendly and sustainable materials for its production are also being widely studied. Aside from the traditional yet expensive filler, carbon black, many fillers from different sources are now being produced, studied, and reinforced with each other [3]. Now, as materials scientists and engineers, it is our roles to qualify and characterize these new fillers and to determine how they affect our rubber.
In the Philippines, the Rubber Project 3, a project under the umbrella of National Research and Development Program for Rubber Processing and Rubber Manufacturing, implemented through the University of the Philippines – Department of Mining, Metallurgical, and Materials Engineering (UP – DMMME), has identified several potential carbon black filler substitutes that can be sustainable and locally-sourced. One of the filler substitutes recognized was a pyrolytic carbon black derived from the pyrolysis of recycled rubber tires called Carbon from Recycled Rubber (CRR). CRR is a fine black powder with properties shown in table 1 [6].

| Properties                              | HAF            | CRR            |
|-----------------------------------------|----------------|----------------|
| Major Elemental Impurities              | S, K, Ca       | Zn, S, Ca      |
| Particle Size (80% passing)             | x>500 µm       | X<150 µm       |
| Surface Area, m²/g                      | 58.11          | 32.14          |
| Iodine Adsorption Number, g/kg          | 121.04         | 177.44         |
| pH                                      | 7.15           | 8.51           |

In this research, the effect of CRR as filler substitute to the in terms of thermal and viscoelastic properties of the synthesized compounded rubber material was evaluated. Specifically, the effect of filler substitution on thermal stability, polymer network contribution, and filler-filler interaction were determined.

2. Materials and methods

2.1. Sample preparation
Rubber compounds were blended using a Bharaj BMMM-6 twin roll mill in the Rubber Processing Laboratory of UP-DMMME. A specific tire wirebead formulation for compounding shown in table 2 dictated the amount of each reagent used. Compounded rubber were vulcanized using a thermal press in the Rhodoco Rubber Processing Services, Incorporated. Vulcanized products were properly stored prior to analyses.

| Compounding Ingredient | HAF-filled (phr) | CRR-filled (phr) |
|------------------------|------------------|------------------|
| Elastomer              | 100              | 100              |
| CRR                    | -                | 135              |
| HAF                    | 135              | -                |
| Additives              | 81.1             | 81.1             |

2.2. Thermogravimetric analysis
The thermogravimetric curves of rubber compounds were determined using ASTM D6370 - 99 [7] in a TA Instruments Q500 Thermogravimetric Analyzer in the Materials Characterization Laboratory of UP-DMMME. Curves were analyzed to identify the composition and degradation temperatures of the components in the compounds.
2.3. Differential scanning calorimetry
The heating profiles of unvulcanized rubber compounds were established following the procedure stated by ASTM D3418-12 [8] in a Q200 Differential Scanning Calorimeter in the D&L Industries to determine curing characteristics and polymer network contribution of both compounds.

2.4. Rubber process analysis
The elastic modulus curves of rubber compounds were established by employing ASTM 6601 [9] in a Rubber Process Analyzer in the Mechanical Testing Laboratory of UP-DMMME to investigate the filler-filler networking within the compounds.

3. Results and discussion

3.1. Compositional Analysis and Thermal Stability Measurements
Figure 1 shows the thermogravimetric (TG) curve, in green, and the derivative (DTG) curve in blue, of the HAF compound.

![TG and DTG plots showing the two-stage degradation and the three degradation events of the HAF compound.](image)

The TG curve showed the two-stage degradation of the HAF compound. The first shoulder signifies the degradation of elastomers while the second is that of carbon. From the DTG, 2 peaks were observed, a broad peak was seen around 350°C to 500°C and a sharp peak at 590.44°C. A curve fitting software was used to accurately identify the events that occurred in the broad region. Two identified peaks at 388.71°C and 442.83°C were elucidated to be the degradation temperature of natural rubber (NR) and styrene-butadiene rubber (SBR) [10], while the peak at 590.44°C confirmed the degradation of carbon [7]. Analyzing the TG, the composition of the compound was determined following the calculations stated from ASTM D6370 – 99. It was found out that the HAF compound contained 47.42% volatile organic compounds (VOC), 44.16% carbon, and 8.45% of remaining ash. For the CRR compound, analysis of its TG and DTG curve, shown in figure 2, gave rise to its composition and the degradation temperature of its components. Similarly, the TG and DTG curve also showed two-stage degradation, and three degradation events. From the curves, it was found out
that the compound contained 47.89% VOC, 37.51% carbon, and 14.54% of remaining ash and the degradation peaks of its components were at 385.15°C, 435.07°C, and 488.13°C.

Figure 2. TG and DTG plots showing the two-stage degradation and the three degradation events of the CRR compound.

Calculated compositions and degradation temperatures were compared and are presented in tables 3 and 4. Calculations showed that the HAF compound contained more carbon and less VOC and ash content as compared to the CRR compound. These differences can be attributed to the purity of the fillers used. CRR contains more impurities than HAF that might be remnants from its source material.

### Table 3. Compositional analysis showing substantial differences in the carbon and ash content of the two compounds.

| Component                  | HAF-filled (phr) | CRR-filled (phr) |
|----------------------------|------------------|------------------|
| Volatile Organic Compounds | 47.42            | 49.79            |
| Carbon Content, %           | 44.16            | 35.71            |
| Ash Content, %              | 8.425            | 14.54            |

Comparing, identified degradation peak values of CRR occurred in lower temperature in contrast to the peaks found in the HAF-filled compound. The most noticeable difference was the degradation temperature of carbon in CRR-filled compound at 488.13 °C, which is a 100°C earlier than its HAF-filled counterpart. This degradation temperature confirms that the carbon in CRR is a pyrolytic carbon black as expected based on the thermal history that its source has undergone [4].

### Table 4. Lowered degradation temperatures were observed for CRR-filled rubber compounds.

| Component | HAF-filled | CRR-filled |
|-----------|------------|------------|
Natural Rubber & 388.71 & 385.15  
Styrene-Butadiene Rubber & 442.83 & 435.07  
Carbon & 590.44 & 488.13  

### 3.2. Polymer network contribution

Figure 3 shows vulcanization peaks snipped from the DSC heating profile of the unvulcanized rubber compounds. It is observed that the vulcanization peak of the CRR-filled compound is less intense than that of the reference HAF-filled compound.

![Figure 3](image)

**Figure 3.** The extent of curing is reduced when CRR is used as filler as manifested by the decrease in peak height.

In Table 5, it is shown that the substitution of HAF with CRR lowers the curing temperature and the vulcanization peak values. The impurities found on the high ash content-CRR might have obstructed the cross-linking process which resulted in the inferior cure properties of CRR-filled rubber compounds.

|                         | HAF-filled | CRR-filled |
|-------------------------|------------|------------|
| Curing Temperature, (°C)| 201.50     | 198.88     |
| Peak Height             | 0.0773     | 0.0616     |
| Peak Area               | 3.2238     | 3.0035     |

This decrease in the heat of curing indicates fewer cross-links formed in the CRR-filled compound after vulcanization, which in turn, lowers the polymer network contribution.

### 3.3. Filler-filler interaction

The strain amplitude dependence of complex modulus of the rubber compounds is presented in Figure 4. Despite CRR having smaller particle size than HAF, lowered G' values throughout the strain sweep were still observed, deviating from the expected results. In theory, CRR having more effective contact area should have a higher reinforcing effect than HAF filler [5]. The researchers believe that
this deviation from theory is a consequence of the impurities in the CRR filler, in agreement to the results of our thermogravimetric and cure characteristic analysis. The substantial amount of non-reinforcing impurities present, i.e. the increased ash content, played a major role in lowering the filler-filler interaction in the compound. The reinforcing effect of carbon present in CRR is hindered by the non-reinforcing effect of impurities it contained.

![Figure 4. Lowered strain amplitude dependence of complex modulus was observed for the CRR-filled compound.](image)

4. Conclusions
Thermogravimetric analysis of rubber compounds revealed that the use of CRR instead of HAF as fillers lowers the overall thermal stability of a rubber material as the carbon component of the CRR-filled compound degrades at a much lower temperature than that of the HAF-filled compound. DSC and RPA tests expose the lowered reinforcing effect when CRR filler is used due to the decrease in polymer network contribution and filler-filler interaction. CRR-filled compound showing inferior observed properties as compared to the HAF-filled compound is a result of the substantial amount of non-reinforcing impurities present in the CRR filler as observed in the compositional analysis. Researchers recommend the employment of beneficiation techniques to CRR to further remove non-reinforcing impurities present.

5. References
[1] Wang J and Chen D 2013 J. Nanomater. 2013 496584
[2] Leblanc J L 2002 Prog. Polym. Sci. 27 627–687
[3] Polynuclear aromatic hydrocarbons, Part 2, Carbon blacks, mineral oils (lubricant base oils and derived products) and some nitroarenes 1984 IARC Monogr. Eval. Carcinog. Risk. Chem. Hum. 33 1–222
[4] Berki P, Göbl R and Karger-Kocsis J 2017 J. Polym. Test. 61 404-415
[5] Fröhlich J, Niedermeier W and Luginsland H 2005 Compos. Appl. Sci. Manuf. A 36(4) 449-460.
[6] Diaz L 2017 Enhancing and increasing local content in rubber for motorcycle tire application Quezon City, Department of Mining, Metallurgical and Materials Engineering, University of the Philippines
[7] ASTM Standard D6370 – 99 2003 Standard Test Method for Rubber – Compositional Analysis by Thermogravimetry (TGA) ASTM International, West Conshohocken, PA 19428-2959 United States
Acknowledgments
The authors would like to thank the Department of Mining, Metallurgical, and Materials Engineering for the use of their twin roll mill, thermogravimetric analyzer, and rubber process analyzer in the Materials R&D and Consulting Facility laboratories. The authors also thank the Engineering Research and Development for Technology of the Department of Science and Technology (DOST-ERDT) for the funding of this research.

[8] ASTM Standard D3418 2015 Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry ASTM International, West Conshohocken, PA 19428-2959 United States

[9] ASTM Standard 6601 2015 Standard Test Method for Rubber Properties—Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer ASTM International, West Conshohocken, PA 19428-2959 United States

[10] Varkey J, Augustine S and Thomas S 2010 Polym. Plast. Technol. Eng. 39(3) 415-435