MECHANICAL PERFORMANCE ENHANCEMENT OF THERMOPLASTICS BY SURFACE-MODIFIED PYROLYTIC CARBON BLACK ADDITIVES FROM WASTE TIRES

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ABSTRACT

The objective of this work is to convert scrap tires into products with economic value within the framework of sustainable development. To this end, pyrolysis, a thermal degradation route, makes it possible to recover value-added products from used tires. The recovered carbon black (rCB) is in-situ functionalized during pyrolysis. This functionalization in the pyrolysis reactor depends on the nature of the reaction medium (air, vacuum, or nitrogen). The surface of the rCB was then modified by ethylene polymers on surface to make the solid compatible with the thermoplastic polymers.

Keywords: Vacuum pyrolysis — Recovered carbon black (rCB) — Functionalization — Catalytic grafting — composite materials – 3D printing – Thermoplastics.

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1. INTRODUCTION

Despite recycling efforts and government regulations on used tires, scrap tires represent a modern environmental and social risk and therefore a significant global challenge for their proper disposal. Worldwide, approximately 1.5 billion tons of tire waste are generated annually due to the rapid growth of the vehicle indutry[1-2]. Scrap tires, sometimes even dumped in an uncontrolled manner due to their lack of flexibility to be compacted, result in the rapid depletion of available sites for the storage of this waste. These sites can be at any time a source of major environmental problems1. Indeed, this waste can lead to negative effects such as fires, which lead to the release of toxic fumes with the presence of carbon monoxide (CO), nitric oxide (NO), sulfur dioxide (SO2), and styrene.

In the context of scrap tires, waste diversion means diverting tires from landfills. When a tire reaches the end of its useful life, the materials from which it is made from can be reused for other purposes to create eco-friendly products[3]. Certain techniques are used to process this waste and exploit it on a large scale (storage, disposal, recycling). However, these methods remain of limited effectiveness, as they eliminate waste, but remain unable to convert it into materials of economic value that support sustainable development.

Within the framework of the preservation of the environment, and to contribute to sustainable development, decisions have been made to impose the use of modern technologies which contribute to improving the treatment of this waste and to valorize it to obtain products with economic value. To deal with this reality, the most interesting alternative that meets ecological criteria is the pyrolysis process[4-5].It allows thermal decomposition of this waste in different environments, in the presence of a carrier gas (N2), under vacuum[6-8] (in the absence of oxygen), or in the presence of an inert carrier gas (N2) followed by air at the end of degradation at controlled temperatures in order to prevent the combustion of the decomposition reaction products.

The pyrolysis of used tires generates useful products, such as combustible gas, oil made up of combustible hydrocarbons, steel, and pyrolytic carbon black (rCB). The latter is used as a reinforcing filler in tires at a rate of 25-30% (weight)[9-11] and represents a valuable substance which the project focuses on.

Carbon black is an essential material in several industrial fields, particularly used in rubber factories as a reinforcement for increased stiffness and abrasion resistance thanks to its structural properties and chemical activity. The chemical composition of pyrolytic carbon black is altered due to various additives including residual rubbery carbonaceous deposits on its surface, which leads to a loss of chemical activity. Modifications have been considered to activate the surface of these particles, in particular the structural properties and the chemical composition of these fillers by functionalization techniques. The objective of this study is to develop a novel functionalization method to modify the surface of carbon black particles.

The Catalytic Grafting method[12-13] was evaluated, which would make it possible to graft functional groups while greatly reducing the costs associated with functionalization. It consists in growing oligomers of the target polymer of the composite on the filler surface to make the solid compatible with the polymer. The composite systems that are possible with these recycled fillers are numerous and varied, depending on the nature of the polymer and the production technology of the composite material. The fields of application are also very vast and expanding with, for example, the advent of 3D printing in which the thermoplastic yarns used are increasingly loaded with particles to improve the properties of the manufactured parts.

2. EXPERIMENTATION

2.1 Waste tire feedstock

The waste tire used as the feedstock in the pyrolysis process was provided by Pyrovac Inc.. This feedstock particle (ground rubber) with an average size of 1-3 mm has been obtained by shredding used tires.

2.2 Thermogravimetric analysis (TGA/DSC)

The Thermogravimetric analysis (TGA/DSC) was performed on the scrap tire to optimize the degradation conditions (temperature, heating rate and pyrolysis time) under nitrogen before using the pyrolysis reactor. The mass spectroscopy (MS) was used to identify the gaseous fraction during pyrolysis. Also, to characterize the rCB tires pyrolysis[14], the TGA/DTA was performed under N2 or air to analyze the carbon deposits on the rCB surface.

2.3 Thermal pyrolysis experiments

The thermal pyrolysis experiments were carried out in a small batch pyrolysis reactor (**Figure 1**) developed by Pyrovac Inc, with a 4-liter cylindrical sample holder. The rCB was recovered from vacuum (29 inHg), nitrogen (1.5 L/min), or air (1.5L/min) reaction at temperature of 450°C with a heating rate of 10°Cmin-1 and a total reaction time of 3h. The liquid fraction (pyrolytic oil) was collected in four consecutive traps, placed between the reactor and the vacuum pump, which were cooled to - 0°C (first trap) and -50°C for the last three traps.

Figure 1. Batch reactor pyrolysis used for pyrolysis process

2.4 Surface functionalization of commercial carbon black CB-N330

The controlled oxidation of CB-N330 was carried out in accordance with previous work published by the authors[15,16] to increase the concentration of surface functional groups with HNO_3 as a oxidant. The sample named after oxidation such as **CB_F-N330.**

2.5 Ziegler-Natta Polymerization of Ethylene on rCB_F and CB_F-N330

This technic was carried out in accordance with previous work published by the authors[12, 13]. During the first step, the metal catalyst was anchored at the surface of carbon black using the phenolic functional groups like an active site. The second step consisted in growing oligomers of the target polymer on the filler surface to make the solid compatible with the Thermoplastic polymers. The polymerization of ethylene on surface was conducted in a four-necked flask at 60°C under vacuum. After functionalization, the samples are named such as **rCB_{FP}** and **CB_{FP}-N330**.

2.6 Boehm titration

In the case of solid residue comes from pyrolysis rCB_F and oxidized commercial carbon blacks, the Boehm method was used to determine the nature and the concentration of different functional groups. By this method different basic solutions NaOH, Na_2CO_3, and $NaHCO_3$ are used to neutralized different acidic functional groups.

2.7 Scanning electron microscopy analysis (SEM)

To analyze the surface morphology of CB and rCB materials, the SEM analysis was used in this study. In the SEM analysis, a small quantity of dried samples was placed in the sample container of a JSM-840A (JEOL, US) scanning electron microscope equipped with an EDX spectrometer and sputtered with gold and palladium to acquire sufficient conductivity.

2.8 Preparation of HDPE/rCB$_{FP}$ or CB$_{FP}$

In this study, **Figure 2** illustrates the series of steps undertaken to prepare the HDPE/rCB composite materials.

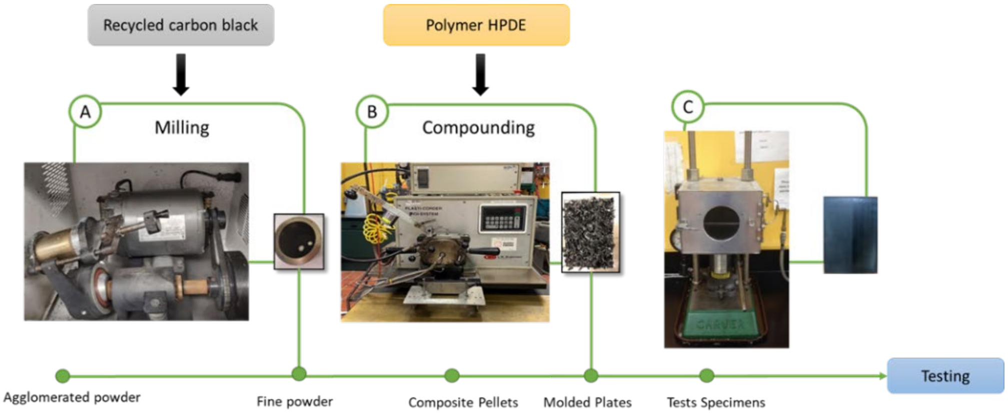

Figure 2. Processing steps for the preparation of composites test specimens

After milling powder, the composite material was prepared by mixing the melted polymer with carbon black particles **(3wt. %)** using a brabender (**Figure 2** Step B). The thermoplastic pellets and CB or rCB particles were compounded at a 175°C and a speed of 50 rpm for 10 min.

To create plates with a thickness of 2 mm, the polymer and composite pellets, produced by the brabender, underwent a compression molding process. This step (**Figure 2** Step C) involved utilizing a heated hydraulic press, as shown in Figure 3. Specifically, a Carver press with platen plates heated to a temperature of 170°C and a closing force of 2,500 kg was employed for the compression molding of rectangular flat plates.

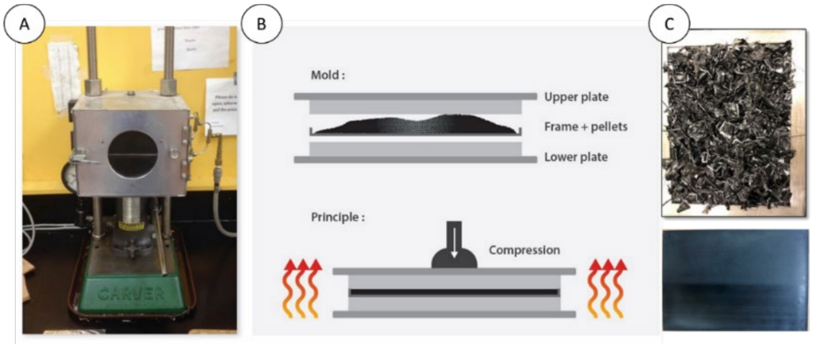

Figure 3. Plate molding: a) Carver hot press, b) mold and molding principle, c) frame containing composite pellets and molded plates.

3. RESULTS

3.1 The TG/DTA/DSC and DTA analysis of the waste tires

Figure 4A shows the TGA and DTA curves of waste tire powder under N_2 flow (50 $mLmin^{-1}$) at a heating rate of 10°Cmin-1 from 25 to 600°C. The DSC analysis curves obtained under the same conditions are given in Figure 4B).

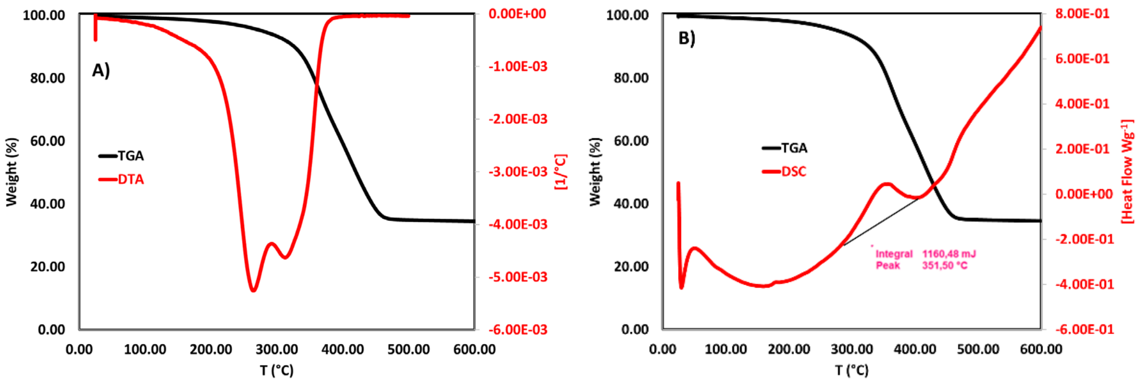

Figure 4. A) TGA and DTA **B)** TGA and DSC curves of the waste tire powder

The TGA curve shows a first stage between 25 and 320°C corresponding to the volatilization of additives such as plasticizers and extender oils[17]**.** Between 300°C and 450°C the mass loss corresponds to decomposition of rubber (naturel, styrene and -butadien)[17-19]. The remaining solid (35%) was attributed to filler material and rCB. The DSC analysis shows an exothermic event at 350°C due to vulcanization of rubber with an enthalpy of 1160 mJg^{-1}.

3.2 The influence of the pyrolysis medium on the yield and properties of rCB_F

During the thermal processing of tires waste, the reaction temperature near the raw material was monitored by a thermocouple placed inside the reactor (sample holder) to evaluate the temperature profile during degradation (Figure 5A). During the thermal conversion of waste tire with different reaction media (N_2, air and vacuum), the heating rate was less than 10°$Cmin^{-1}$ for the first 15 min due to heat transfer between the jacket and sample holder (reactor) whatever the reaction medium.

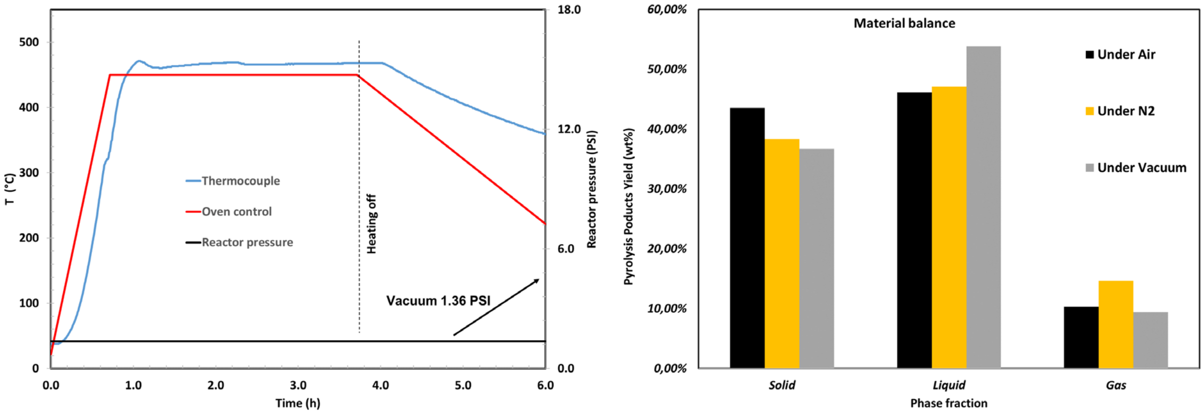

Figure 5. A) Pyrolysis temperature under vacuum and **B)** Material balance after pyrolysis process under Air/N_2/Vacuum during 3h

The influence of the reaction medium on the solid yield is shown in Figure 5B. It is noticeable that with changing the reaction medium, the solid yield reaches 37%, 38% and 43.5% under vacuum and N_2 and air respectively. The larger solid yield (by 5.5-6.5%) in presence of air was confirmed also by TGA analysis weight loss of rCB_F (Table 1), 4% weight loss of rCB_F from pyrolysis under N_2 and vacuum and 7% from pyrolysis under air. The difference can be attributed to the formation of residues / carbons [14, 16] in presence of air (thermal-oxidative).

Table 1. Physical proprieties and weight loss by TGA of rCB_F after pyrolysis process and commercial carbon black CB-N330

	Physical Properties^a			**TGA**^{b} **Analysis Weight loss (200°C-1000°C)**
Samples	S_{BET} (m^2g^{-1})	Pore size (nm)	Pore volume (cm^3g^{-1})	(%)
CB-N330	82	4.0	1.0	1
rCB_F-Air	66	3.0	0.3	7
rCB_F-N_2	44	3.0	0.4	4
rCB_F-Vacuum	46	4.0	0.5	4

[a] Calculated by BET method.
S_{BET}: Surface Area
[b]: TGA analysis under Nitrogen flow.

All rCB have smaller surface areas, pore size, and volume compared to commercial carbon black CB-N330 (Table 1), these differences reflect the presence of the residues / carbons on the rCB_F surface. The nature of these carbon deposits on the surface of all rCB will be discussed in the following paragraph concerning surface characterization. The morphology and the structure of rCB_F and CB-N330 were analyzed by scanning electron microscopy SEM (Figure 6) to provide answers on the presence of residues/carbons on the surface of rCB_F.

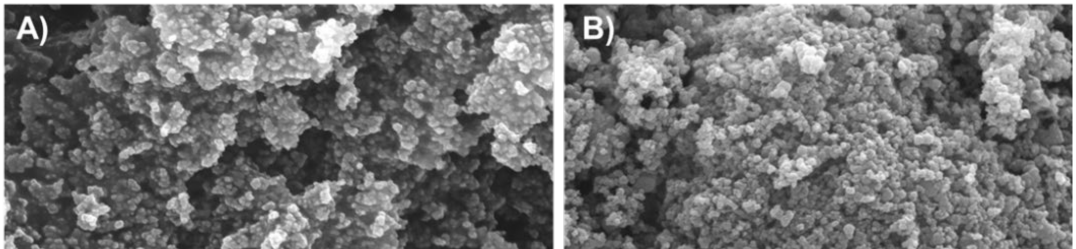

Figure 6. SEM images of **A)** CB-N330 and **B)** rCB_F-Air

It can be seen, that both CB-N330 and all rCB_F are spherical particles. However, in case of rCB_F the agglomerates are larger compared to smaller agglomerates with restricted space between them in case of CB-N330. The difference in agglomeration size between commercial and recovered carbon black is due to the presence of a layer oxygenated functional groups on rCB$_F$ during pyrolysis[14]. The nature of these deposits / carbons on the surface of all rCB will be discussed in the following paragraph concerning surface characterization by titration with basic solutions.

3.3 Surface characterization by Boehm titration of rCB$_F$ and CB$_F$-N330

To determine the nature and the concentration of different acidic functional groups of recovered samples by pyrolysis (rCB$_F$) and oxidized sample of commercial carbon black (CB-N330) the Boehm titration method was used. The concentration of different groups is listed in **Table 2**. The results show that the functionalization of the rCB surface during pyrolysis (in-situ in reactor) is greater than that of the CB-N330 particles oxidized by HNO$_3$.

Table 2. The concentration of the acidic surface functional groups analyzed by Boehm titration.

Samples	**Carboxylic groups* (mmolg^{-1})**	**Phenolic groups* (mmolg^{-1})**	**Lactonic groups* (mmolg^{-1})**	**Total acid groups (mmolg^{-1})**
CB-N330	0.06	0.04	0.05	0.10
CB$_F$-N330	0.40	0.20	0.10	0.70
rCB$_F$-Air	0.50	0.20	0.10	0.80
rCB$_F$-N$_2$	0.40	0.10	0.10	0.60
rCB$_F$-vacuum	0.30	0.10	0.20	0.60

3.4 Catalytic grafting to modify the surface's chemical nature of rCB$_F$ -Air and CB$_F$-N330

When reinforcing thermoplastics with fillers, the nature of the polymer/filler interface has a major influence on the mechanical behavior of the composite. To make the solid compatible with the polymer, the recovered carbon black functionalized in-situ during pyrolysis process under air (rCB$_F$) and oxidized commercial carbon black CB$_F$-N330 is used to graft Ziegler−Natta catalytic sites to grow polyethylene oligomers by the catalytic grafting technic[12-13]. The samples after catalytic grafting and polymerization of ethylene on particles surface are referred as **CB$_{FP}$-N330** and **rCB$_{FP}$-Air** (Table 3).

Table 3. Physical proprieties of rCB$_{FP}$ and commercial carbon black CB$_{FP}$-N330 after grafting

	Ethylene Polymerization		Physical Properties^a		
Samples	**T$_p$** (°C)	**t$_p$** (min)	S$_{BET}$ (m^{2}g^{-1})	Pore size (nm)	Pore volume (cm^{3}g^{-1})
CB$_F$-N330	-	-	55	3.5	0.9
CB$_{FP}$-N330	60	30	38	3.0	0.3
rCB$_F$-Air	-	-	66	3.0	0.3

rCB$_{FP10}$-Air	60	10	50	2.7	0.3
rCB$_{FP30}$-Air	60	30	29	2.7	0.2

Tp: temperature polymerization, **tp:** reaction time

It can be seen in **Table 3** that, the grafting polymerization led to a decrease in the BET specific surface area, total pore volume, and the pore diameter. In case of rCB$_F$-Air surface modification by ethylene, only the BET specific surface area is more influenced by the time of reaction. So, for both supports (CB$_F$ and rCB$_F$), the polyethylene can be incorporated on the external surface of the particles. The thermal stability of modified particles by polyethylene (rCB$_{FP}$-Air) or not modified (rCB$_F$-Air) was investigated by TGA pyrolysis process under N_2. The thermal weight loss curves are shown in **Figure 7**.

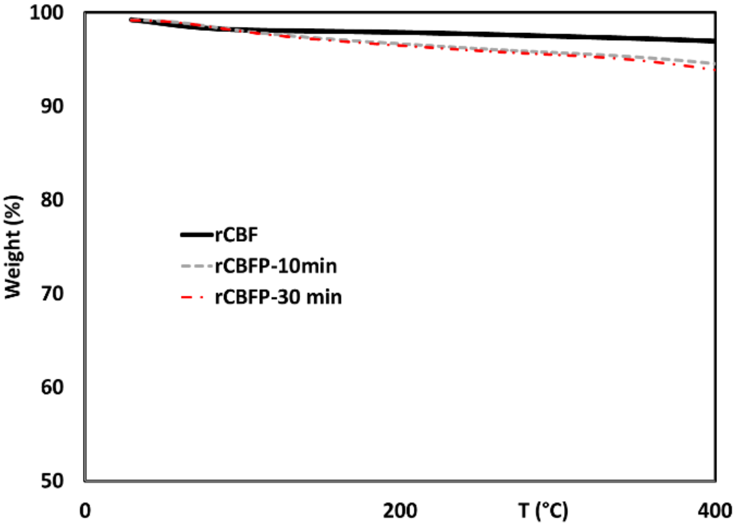

Figure 7**.** TGA analysis of non-functionalized rC$_{BF}$-Air and functionalized rCB$_{FP}$-Air after grafting and polymerization of ethylene during 10 and 30 min on the surface.

The relative weight losses in case of functionalized materials (during a reaction time of 10 and 30 mins) was relatively rapid after 150°C compared to pure rCB$_F$. This difference can be attributed to the pyrolysis of the organic polymers on the surface. The presence of polyethylene on the surface of carbon black particles after catalytic grafting was confirmed by SEM analysis of the morphology of these materials (**Figure 8**).

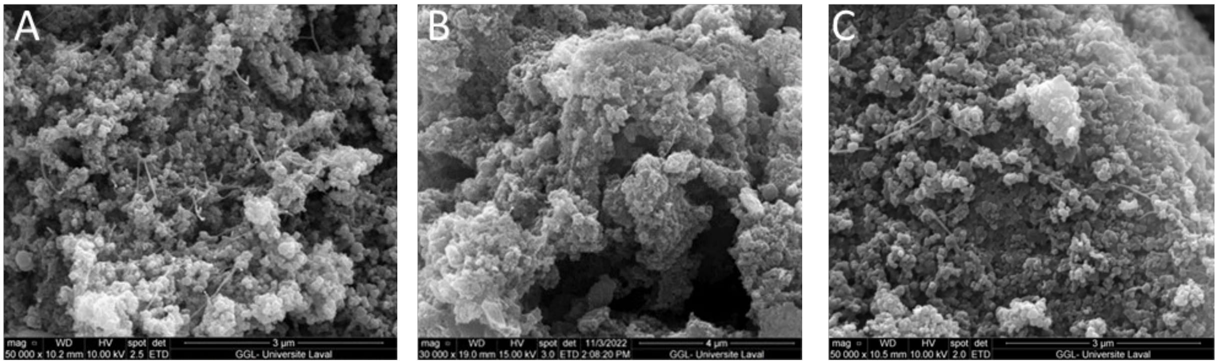

Figure 8. SEM images of **A)** CBFP-N330 and **B)** functionalized rCBFP-Air after 10 min and **C)** rCBFP-Air after 30min of reaction.

3.5 Tensile tests and impact of additional CBF-N330, rCBF-Air, and rCBFP-Air particles on HDPE

The tensile properties of neat HDPE and modified HDPE by CB particles were evaluated following test standard ASTM D638. It can be seen from **Figure** 9 that the addition of 3 %wt. CB particles is beneficial on the tensile modulus of neat HDPE, with increase of 9 to 12 % in rigidity. Impact on the tensile strength is less pronounced. Also, recycled carbon black shows better tensile modulus and tensile strength than its commercial counterpart.

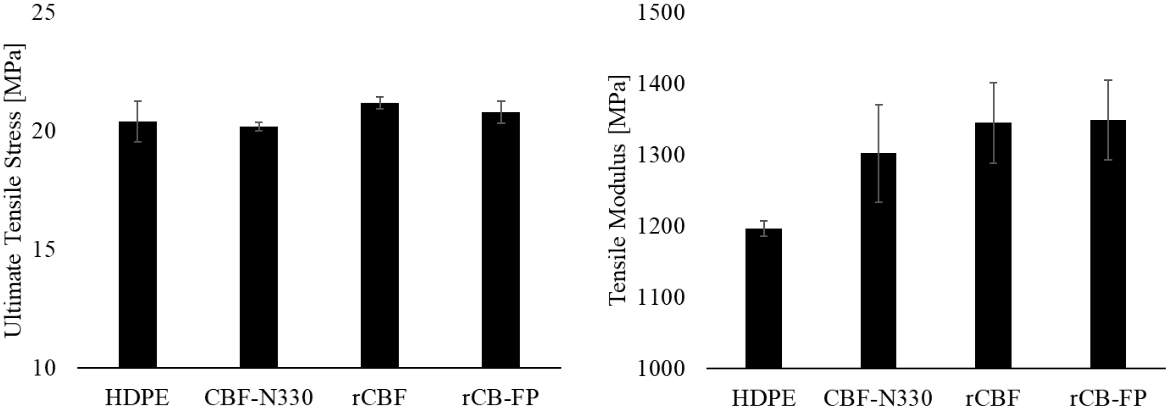

Figure 9. D638 tensile test results. Error-bars show ±1 standard deviation

4. CONCLUSIONS

The results of the preliminary work show that recycled carbon black with oxygenized functionalities at the exit of the reactor after the pyrolysis process can be obtained. Those materials were functionalized by a polymer (polyethylene) by grafting catalytical reaction and compared with commercial carbon black using the same reaction process. The two materials, after their incorporation into the HDPE, showed that the mechanical performance was increased. For future work, the optimization of the pyrolysis condition will be studied such as temperature and medium reaction during pyrolysis and the size particles of waste tire feedstock.

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