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DEVELOPMENT OF AN ENVIRONMENTALLY FRIENDLY THERMOPLASTIC COMPOSITE MATERIAL FROM BIO-SOURCED POLYMER AND RECYCLED WASTE TIRES

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ABSTRACT

The depletion of fossil fuels and environmental sustainability are critical concerns in contemporary society. Within this environmental context, the widespread landfilling of waste rubber tires has emerged as a global issue, significantly impacting the environment. Our research group addresses this challenge by creating a new eco-responsible composite material made by recovering waste tires solid particles to reinforce a bio-plastic as a mean to mitigate the environmental impact of mass produed plastics. Rubber tires, comprising 25-30% high-purity carbon black (CB) particles, can be thermally decomposed through vacuum pyrolysis for recycling the CB. CB is a high-value material commonly used to reinforce plastic composites, enhancing UV protection, electrical conductivity and abrasion resistance. Commercial CB used in reinforced plastics typically generates a carbon footprint of 1.08 kg CO2 per kg of CB. The Recycled CB (rCB) from waste tires vacuum pyrolysis reduces the carbon footprint to net zero emissions. However, rCB from waste tires is inherently heterogeneous due to variations in tire quality in the recycling process. Therefore, the key to obtaining a competitive recycled material lies in homogenizing particle size, removing impurities, and modifying surface functional groups. In this work, rCB was produced from waste tires through vacuum pyrolysis, and a methodology was developed to homogenize particles and modify surface functional groups, resulting in functionalized recycled carbon black (FrCB). High-density polyethylene (HDPE) was chosen as the thermoplastic resin due to its exceptional strength-to-density ratio, chemical resistance, and durability, making it ideal for various applications. A corn-based high-density polyurethane (bio-HDPE) was utilized in this study as a thermoplastic resin reinforced with rCB to produce a green composite achieving near carbon neutrality.

In this study, different percentages of commercial petroleum-based CB, ranging from 3% to 15%, were incorporated into bio-HDPE. Mechanical properties were studied and compared with new composite made of bio-HDPE/FrCB. This bio/recycled material is an alternative to commercially prevalent, petroleum-based reinforced plastics of mass consumption that are non-renewable and environmentally detrimental. The proposed material addresses pollution-related concerns, habitat alteration, and the disruption of natural processes essential for adapting to climate change.

INTRODUCTION

Polyethylene (PE) is mass procuded as one of the most utilized thermoplastics in the world. Its remarkable attributes include exceptional toughness, flexibility, chemical resistance, minimal permeability, and electrical conductivity. Moreover, its semi-crystalline nature and ease of processing make PE appealing for diverse products and usages. While PE is highly regarded for its utility in all market sectors, a considerable challenge resides in the long natural degradation period. Consequently, there is a need to develop innovative solutions to eco-friendly plastics and composites of mass production. The issue with PE usage frequently arises from its widespread application in single-use scenarios, leading to plastic waste and pollution. The environmental issues caused by plastic pollution become particularly concerning when individuals prioritize disposable materials over reusable options and environmentally sustainable alternatives [1]. As a result, there has been a considerable rise in plastic presence in the environment, characterized by a significant disparity between production and disposal rates. This has led to an accumulation dilemma primarily linked to the resistance of PE to degradation under ambient conditions [2, 3]. Bio-plastics can be a potential replacement due to the production from renouvable ressources, leading to a decrease in greenhouse gas (GHG) emissions by -2.6 kg CO2eq per kg compared to conventional fossil-based plastics [4]. With approximately 400 million metric tons of plastics manufactured annually, bioplastics could curtail GHG emissions by 73 million tons of CO2eq annually, presenting a notably positive impact on the ecosystem. This attribute position bio-based plastics as a viable alternative for reducing the carbon footprint in contrast to materials derived from fossil fuels [2]. Bio-HDPE exhibits mechanical and chemical properties similar to commercial-grade petroleum-based HDPE [5]. It demonstrates comparable performance with a density of 0.959 and a tensile strength at a yield of 30 MPa. However, despite these similarities, disparities in their sourcing, processing, presence of impurities, and environmental impact can lead to differences in mechanical, thermal, electrical, and frictional characteristics between bio-HDPE and fossil fuel-based HDPE. Hence, it is crucial to consider these factors when assessing the suitability of these materials for a wide range of applications [6]. Liu and Horrocks [7] examined the impact of reinforcing low-density polyethylene (LDPE) with CB on UV degradation resistance. Their research revealed that increasing the CB content from 1.5% to 3.5% improved UV stabilization in LDPE films with a thickness of 75 mm produced through extrusion. These films incorporated different types of CB with varying particle sizes. They were exposed to two accelerated artificial weathering devices: a xenon arc source and fluorescent tube sources, all while maintaining controlled temperature and humidity conditions. Billotte [8] studied the impact of reinforcing HDPE with recycled CB extreacted from waste tire. The results showed that have the rCB added to the polymer has not only an absorption protective action against UV radiation but probably play a significant role in oxygen diffusion through the sample.

Each year, the worldwide production of over 15 million metric tons of CB releases approximately 79 million metric tons of CO2 into the environment. Given their high cost and environmental impact, it is highly beneficial to find a recycling method to reuse CB particles. Therefore, an environmentally friendly and efficient tire decomposition process, which can repurpose waste tries as raw materials for new products, is essential for establishing a circular economy for waste tires [11-15]. Tire recovery has been traditionally divided into material and energy recovery, such as retreading, devulcanization, and pyrolysis. Among different approaches, pyrolysis of waste tires is considered the most practical technique for recycling and reducing waste tires. Pyrolysis refers to the thermal decomposition of organic materials in the absence of oxygen, typically induced by heat. The pyrolysis process is endothermic, meaning it absorbs heat and depends on the reactor's temperature to supply the necessary thermal energy for breaking down rubber molecules into oils and gases. This breakdown can occur under full vacuum, in the presence of inert gases, or even in rarefied air conditions [16, 17]. The quality and uniformity of pyrolytic rCB can fluctuate considerably. This is primarily due to the inclusion of various grades of CB used in tire manufacturing and the diverse range of tires processed during recycling (including those from cars, trucks, tractors, and bikes). The significant variability in tire types and particles poses challenges in optimizing pyrolysis processing conditions to target the recovery of a specific grade of CB particles for particular applications [18].Moreover, pyrolytic CB typically includes a portion of ash (12-17 wt.%) and carbonaceous deposits adhering to the surface of the particles. These deposits negatively impact the particles' surface area and bonding ability, diminishing their effectiveness in reinforcing plastics and elastomers [19, 20]. Consequently, improving the surface of rCB to be compatible with polymer is required. In this study, CB contained in waste tires (25-30%) is recovered by vacuum pyrolysis and is used as filler for a bio-polymer to provide an environmentally friendly material that can be produced in large scale. To do this, the rCB was subjected to functionalization treatments to improve adhesion to the polymer chains. Subsequently, FrCB was dispersed in a bio-HDPE matrix to prepare a composte sample. The mechanical and chemical properties of samples are studied to evaluate the performance of the proposed material for various applications.

Methodology

Material

The recycled carbon black (rCB) utilized is provided by Pyrovac Inc. and sourced through vacuum pyrolysis of waste tires in an industrial scale facility operating at a 540 kg/h capacity in Ville de Saguenay, Québec, Canada, and has undergone no subsequent treatment. Roy et al. [21] document the tire recycling process used in this work. The rCB employed in this study exhibits a surface area of 77.3 m2/g and a structure measuring 95.0 cm2/100 g [21]. The chosen comparative CB, CBc_EP100, is specifically designed for application in HDPE matrices for piping. Distinguished by a reduced moisture content compared to standard CBs, it showcases a narrow particle size distribution. Noteworthy characteristics include a specific surface area of 79 mg/g, a structure of 104 cm^3/g, and particle sizes smaller than 25 nm. Also, continexTM N330 by Continental Carbon was used to compare the microstructure of FrCB and commercial CB.
The polymer matrix of reference is HDPE SHC 7260, branded as "I'm Green" by Braskem. This matrix is formulated using ethanol derived from sugarcane, boasting an average molecular weight and a melt flow index (MFI) of 7.2 g/10 min, which has a low tendency to warp and high hardness and stiffness.

Surface functionalization

In the present study, catalytic grafting was employed to generate small polymer chains (oligomers) to enhance the compatibility of pyrolytic CBs with the polymer matrix. This technique was conducted following the methodology outlined in prior publications by the authors [22, 23]. In the first step, the metal catalyst was anchored to the CB surface utilizing phenolic functional groups as active sites. Subsequently, oligomers of the desired polymer were generated on the filler's surface to make the solid compatible with thermoplastic polymers. The ethylene polymerization on the surface was carried out in a four-necked flask at 60°C under vacuum conditions.

Sample Preparation

This work carried out two steps during the sample preparation of Bio-HDPE/FrCB composite materials. Firstly, different percentages of commercial carbon black, CBc_EP100, ranging from 3% to 15%, as well as 3% of FrCB were dispersed in bio-HDPE using a "HAAKE™ Rheomix Lab Mixer." Polymer pellets and CB particles are introduced through a hopper and mixed using two rotating screws. Temperature and mixing speed are controlled, and these parameters, in conjunction with the mixing duration, were adjusted for various dispersions containing different proportions of CB particles . The selected temperature for mixing was 175 °C, and the speed of the screws wass 70rpm. Subsequently, the test specimens were manufactured using a compression process in a hot/cold press. Three variables, time, pressure, and temperature, were optimized to improve the quality of samples. A Carver Press was used with platens heated to 170°C, and a closing force of 2,500 lb was applied for compression molding rectangular flat plates. Test specimens were cut from flat plates to meet the dimensions specified by the ASTM standards for mechanical testing.

Results and Discussion

Transmission Electron Microscopy Analysis

Electron Beam microscopy has been essential in tracking the changes in aggregation/compaction resulting from the treatment, providing valuable insights into the morphological and structural changes following the oxidation of pyrolytic carbon blacks. Moreover, it has been instrumental in detecting differences in the presence of inorganic compounds and residues/carbon deposits on the surface. Comparative analysis using TEM was performed to analyze structural alterations between commercial carbon blacks and pyrolytic carbon blacks after treatment application. The analysis was conducted for CBc_N330 and FrCB. Figure 1 shows no significant difference observed compared to the commercial carbon black. However, darker elongated structures are present. These structures are likely associated with the residual carbonaceous deposits from tire rubber.

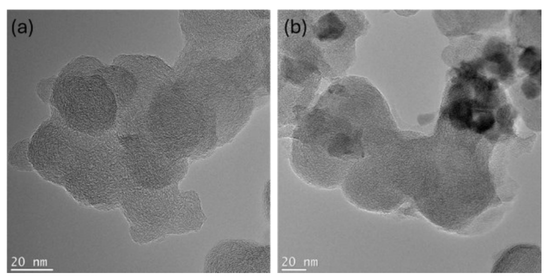

Figure 1. Transmission Electron Microscopy images of (a) commercial CB and (b) FrCB.

Mechanical properties

The tensile mechanical characteristics of various composite configurations were assessed using samples generated through the standard thermocompression procedure. Tensile mechanical testing utilized an MTS Insight 50 Electromechanical test Machine outfitted with a 50 kN load cell. A preload of 50 N was used, and all samples were tested at a uniform speed of 20 mm/min. The deformation of the samples was gauged using crosshead displacement. Each reported outcome is an average derived from three valid tests. Figure 2 shows the ultimate tensile stress and tensile modulus of bio-HDPE reinforced with different percentages of commercial CB and 3% of FrCB. By increasing the quantity of commercial CB to 15%, tensile modulus increases by 42% compared to sample prepared from pure Bio-HDPE. Also, it can be seen that the tensile modulus and ultimate tensile stress of Bio-HDPE reinforced by 3% FrCB increases by 18% and 5%, respectively.

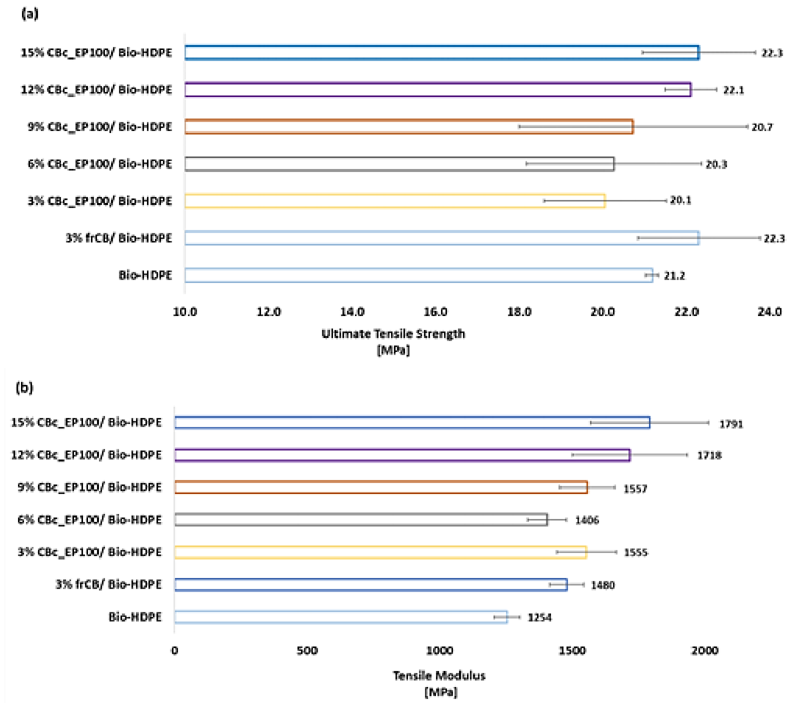

Figure 2. Mechanical test results from bio-HDPE reinforced with different percentage of commercial CB and 3% of FrCB.

Conclusion

The results of the primary work show a high potential to replace commercial HDPE with bio-HDPE at a fraction of much less carbon footprint. The mechanical performance of bio-HDPE can be improved by reinforcing polymer with rCB extracted from waste tires. In order to increase the tensile modulus of bio-HDPE significantly, we can increase the quantity of FrCB by 15%. In order to enhance the bonding between polymer and CB, functionalization of the CB surface can significantly impact mechanical properties. Current work focuses on replacing commercial HDPE with vegetable source polymer and reinforcing with FrCB to propose a multifunctional material. In the future, different characterization will be implemented on the proposed thermoplastic to extend its applications.

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