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RESEARCH ARTICLE

EFFECT OF HYDROTHERMAL CARBONS CONTENT ON WEAR PROPERTIES OF POLYETHYLENE MATRIX COMPOSITES

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ABSTRACT

Compared to commonly used carbonaceous materials such as carbon nanotubes or graphene nanoplatelets, hydrothermal carbons (HTCs) are obtained with environmentally friendly approaches at a lower cost. Although HTCs have a wide application area such as batteries, magnetic materials, supercapacitors, adsorbent materials, etc., there are few studies on the usage of HTC as reinforcement material for composites. In this study, polyethylene matrix composites containing different amounts (0.5 wt.%, 1 wt.%, 2 wt.%) of HTCs were fabricated via the injection molding process. The effect of HTCs content on the wear properties of polyethylene matrix composites was investigated. Reciprocating wear tests were performed by applying different loads at dry sliding conditions. To correlate with wear results, the mechanical properties of samples were determined by tensile and impact tests. Also, FTIR and DTA analyzes were conducted to understand the effect of HTCs on the structural and thermal properties of composites. Results show that the addition of HTCs led to the enhancement of mechanical and tribological properties of polyethylene at lower amount reinforcement ratios. Thus, it can be said that HTCs could be an alternative carbonaceous reinforcement material for polymer matrix composites.

Keywords: Hydrothermal carbons, Polyethylene, Wear properties, Composite materials, Mechanical properties

1. INTRODUCTION

Polyethylene (PE) is one of the most used polymers for tribological applications such as biomedical and military because of its high wear resistance [1]. However, the tribological properties of PE don't completely satisfy the requirements in these fields [2]. Therefore, the wear properties of PE need to be improved. For this purpose, many studies have been conducted to enhance wear resistance of PE with the addition of different types of reinforcements [3].

In recent years, carbonaceous reinforcements such as graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) have become popular for polymer matrix composites due to their superior mechanical properties. GNPs have a high elastic modulus (~1 TPa) while CNTs have nearly 0.27 TPa to 1.47 TPa of elastic modulus [4]. In addition to mechanical properties, these fillers act as a solid lubricant which causes a lower coefficient of friction compared to ceramic and metal fillers [5].

Johnson et al. [6] reported tribological properties of CNTs /PE composites. It was shown that the wear rates of the composites decreased with increasing CNTs content (1%, 3%, and 5%). Composites containing 5% wt. CNT presented a 50% better wear resistance compared to pure PE. In another study, Fouad and Elleithy [7] produced PE matrix composites containing GNPs at different weight ratios (2%, 4%, and 8%). It was observed that the hardness and wear resistance of pure HDPE were enhanced with the addition of GNPs up to 4 wt.%. However, when the GNP ratio increased to 8%, although the hardness value increased, the wear resistance decreased due to poor matrix-reinforcement bonding. McNally et al. [8] melt blended PE with 0.1, 0.5, 1, 3, 5, 7, 8.5 and 10 wt.% MWCNTs. It was reported that the yield strength of composites was improved up to 7 wt.% CNTs addition. In another similar study, Bourque et al. [9] reinforced PE with GNPs (0.1 wt.% to 15 wt.%) via twin-

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screw extrusion. Results show that the yield strength of samples enhanced with the increase in the GNPs ratio.

As mentioned above, GNPs and CNTs had a positive effect on the mechanical and wear properties of polyethylene matrix composites. However, they have been produced with high production costs [10]. Also, in their production, environmentally harmful chemicals are used [11]. Hydrothermal carbons (HTCs) can overcome the disadvantages of these carbonaceous reinforcements. HTCs are produced from eco-friendly biomass such as pure carbohydrates, lignocellulose, simple sugars sea plant derivate, food wastes, etc. without using harmful chemicals at low operating temperatures [12]–[14]. HTCs have a wide application area such as batteries [15], magnetic materials [16], supercapacitors [17], adsorbent materials [18], etc.

Previous studies show that using HTCs as a reinforcement material led to the enhancement of tribological and mechanical properties of metal matrix composites [10], [11]. However, to the best of my knowledge, there is no study on the effect of HTCs on the wear properties of polymer matrix composites. In this study, the effect of HTCs content on the wear properties of polyethylene matrix composites was investigated. Also, structural, thermal, and mechanical properties of PE/HTCs composites were studied.

2. EXPERIMENTAL METHODS

2.1. Materials

PE powders with trade code LUMICENE® M3427 were supplied from Total Polymers (Belgium). The melting point of PE powders is 123 ℃ and their melt flow index is 3.1. To synthesize HTCs, 1 gr of glucose (Merck) was dissolved in 15 ml distilled water. Then, obtained suspension was poured into stainless steel autoclave. The autoclave was put into a furnace at 210 ℃ for 24 hours of residence time. After the cooling, solid carbon products were separated by filter paper and dried in a furnace at 105 ℃ for 1 hour. SEM images of the produced HTCs was shown in Figure 1.

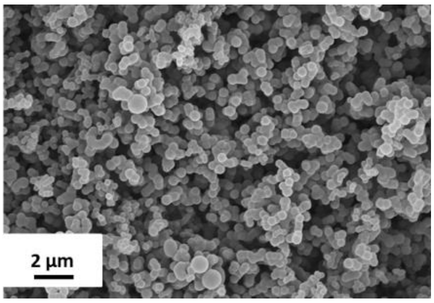

Figure 1. SEM images of produced HTCs.

2.2. Production of Samples

The production diagram of PE-HTCs composites was presented in Figure 2. The produced HTCs and PE powders were mixed in the 3D mixer (Turbula®) for 2 hours. Then, mixed powders were fed to an injection molding device. The temperature profile of the injection molding device was set at 235℃, 245℃, 265℃ from hopper to die. Dog-bone shaped samples were produced.

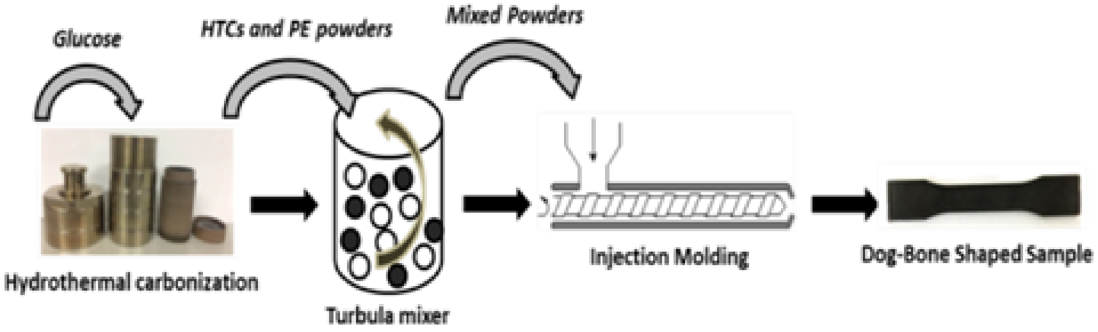

Figure 2. Production diagram of PE-HTCs composites

2.3. Characterization

Fourier Transform Infrared Spectroscopy (FTIR) spectrums of samples were obtained using the Bruker Alpha FTIR device. The resolution was set to 24 cm^{-1} and twenty-four scans were recorded for each sample in the range of 600–4000 cm−1. The thermal properties of the samples were investigated via Hitachi STA 7300 Differential Thermal Analysis (DTA) device. The samples were heated up to up to 200 °C with a heating rate of 10 °C/min. The analysis was conducted under nitrogen gas and the gas flow rate was 2 ml/min. The % crystallinity (Xc) of samples was calculated according to the following equation (1):

$$X_c = (\Delta H_m)/\Delta H^{\circ}_m) \text{ x } 100\% \qquad (1)$$

where ΔH_m is the melting enthalpy after thermal history, ΔH°_m is the enthalpy of 100% crystallization of HDPE [19]. The tensile test was performed with a Shimadzu tensile testing machine at room temperature at 5 mm/min test speed. For the impact test, the samples were cut in a dimension of 70 × 12.7 × 3.2 mm, and the test was applied to unfnotched samples using a Zwick/Roell RKP 450 device. The wear test was applied by using the UTS Tribometer device for samples under three different loads (20, 30, and 40 N), for 100 m sliding distance, using AISI 52100 steel ball, at 10 mm stroke distance. A schematic drawing of the wear test device was presented in Figure 3.

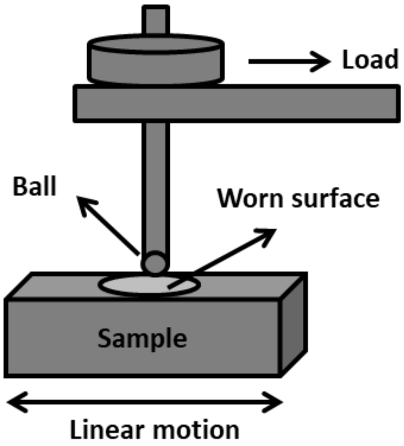

Figure 3. Schematic representation of the wear test device.

Wear rates of samples were determined using the volume loss method and calculated using equation (2).

$$\text{Wear rate } (W_r) = W_v/l \tag{2}$$

Where W_v is worn volume and l is the sliding distance. The worn surface area was measured with the Mitutoyo SJ-410 instrument. W_v was calculated by multiplying worn surface and stroke distance [20]. Zeiss Ultra Plus Scanning Electron Microscope was used for examination of the HTCs and worn surfaces of samples after gold coating.

3. RESULTS AND DISCUSSION

3.1. Structural and Thermal Properties

Figure 4 illustrates the FTIR spectra of samples. Samples have two peaks at nearly 2920 and 2852 cm^{-1}. These peaks can be attributed to C–H asymmetric and C–H symmetric stretching vibrations in -CH_2-, respectively. Also, there are smaller peaks at nearly 1466 cm^{-1} and 723 cm^{-1} due to C–H deformation vibrations in –(CH_2)n– and C–C rocking vibrations in –(CH_2)n–, respectively [21]. There is no new peak formation with the addition of HTCs to the PE matrix. Therefore, it can be said that there is no chemical interaction and HTCs were mechanically attached to the PE matrix.

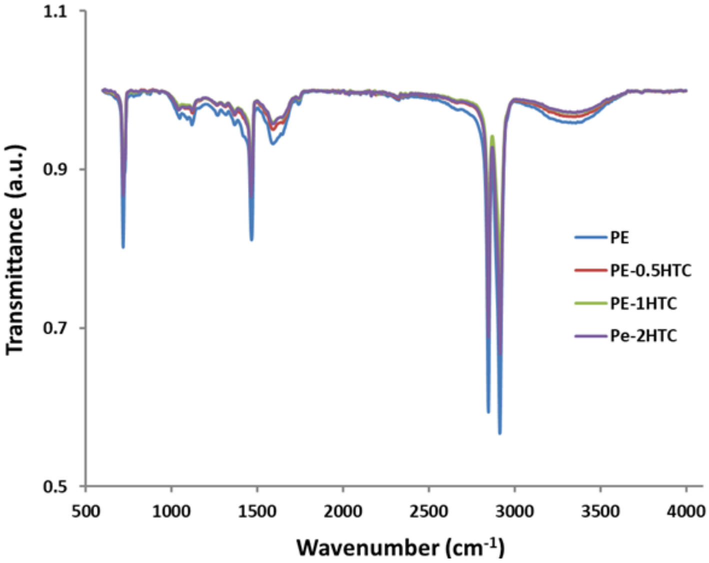

Figure 4. FTIR spectra of samples.

The melting temperatures and crystallinity of all samples were seen in Table 1. It can be said that melting points of composites were not changed with increasing HTCs content, significantly. The melting points of composites range from 119.2 °C to 119.5 °C, while pure polyethylene is 118.2 °C. This result was in good agreement with the findings of Thongruang et al [22].

On the other hand, HTCs reinforced composites have lower crystallinity than pure polyethylene. This can be attributed to the friction between HTCs and polymer chains may hinder the mobility of the macromolecular chain because hindering the mobility of the chains can obstruct formation of highly ordered alignment of the crystal lattice [23]. Also, it is worth the note that the crystallinity of composites was decreased with increasing HTCs content. PE-2HTC showed the lowest crystallinity and its crystallinity was %8 lower compared to PE.

Table 1. Melting temperature and crystallinity of samples

Sample	Melting Temperature (℃)	Crystallinity (%)
PE	118.2	75
PE-0.5 HTC	119.2	72
PE-1 HTC	119.3	70
PE-2 HTC	119.5	69

3.2. Mechanical Properties

Absorbed energies during the impact test and tensile strength of samples were shown in Figure 5. Addition of HTCs up to 1 wt.% reinforcement ratio improved the mechanical properties of pure PE. The tensile strength and absorbed energy amounts of PE increased from 12.4 MPa to 14.6 MPa and from 6.5 J to 8.5 J with the addition of 1 wt.% HTCs, respectively. As mentioned above, HTCs were only mechanically attached to the PE matrix. When force is applied during the tensile test, the polymer chains start to move, it can be estimated that HTC provides an increase in tensile strength by mechanically preventing polymer chain movement [5]. Also, it may be noted that HTCs can block crack propagation during the applied impact load.

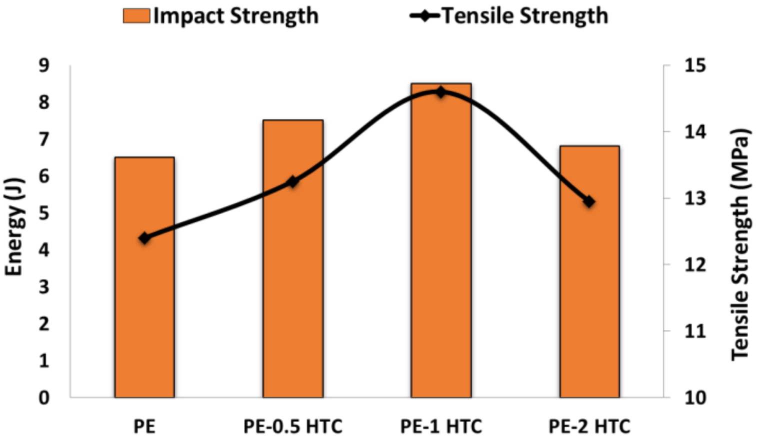

Figure 5. Absorbed energies and tensile strength of samples.

However, when the HTC ratio increased from 1 wt.% to 2 wt.%, there was a decrease in both tensile strength and impact strength. It is well known that solid micro-nano-particle reinforcements tend to agglomerate in polymer matrix. Therefore, it was thought that HTCs agglomerated in the matrix for PE-2HTC sample which have more HTC content compared to the others and this agglomeration caused a weaker matrix-reinforcement interface. Poor matrix-reinforcement interface can cause a decrease in mechanical properties.

3.3. Wear Properties

The wear properties of composites play an important role in the application of these materials in engineering applications [24]. The wear rates of produced samples under three applied loads (20, 30, and 40 N) were presented in Figure 6. It was observed that the wear rates of samples were increased with the increment of the applied load. This may be explained with that repeated higher loads on the surfaces of samples cause higher friction force [25].

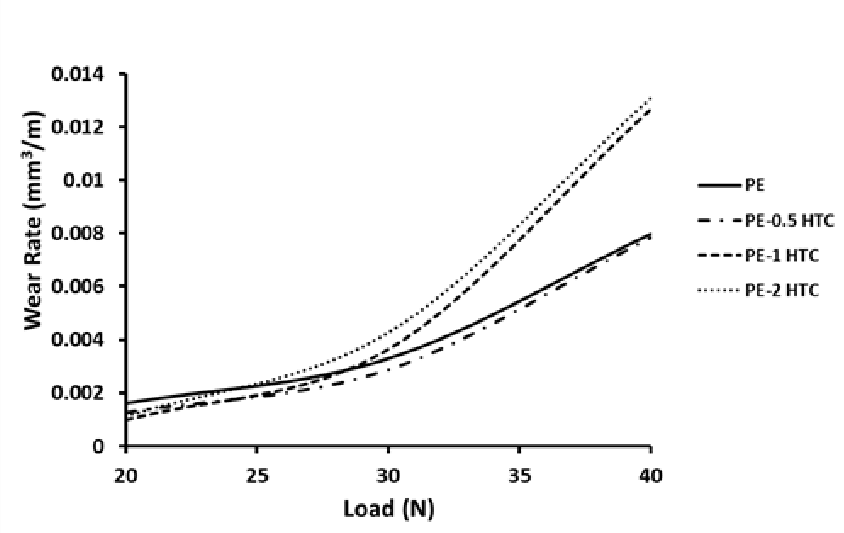

Figure 6. Wear rates of samples

Up to 20 N applied load, the addition of HTCs led to the enhancement of wear resistance of pure PE. Wear rates of PE, PE-0.5HTC, PE-1HTC and PE-2HTC were $1.61*10^{-3}$ mm^3/m, $1.26*10^{-3}$ mm^3/m, $0.98*10^{-3}$ mm^3/m and $1.12*10^{-3}$ mm^3/m, respectively. PE-1HTC had the lowest wear rate at this load. According to Archard's wear law, harder materials exhibit a lower wear rate [26]. Thus, it may be argued that the results were coherent with the mechanical properties of samples. Also, Yetgin and Colak observed similar findings in graphite filled polypropylene composites [27].

However, the wear rates of PE-1HTC and PE-2HTC were higher than PE under 40 N applied load. When the applied load was increased from 20 N to 40N, wear resistance of the PE-1HTC and PE-2HTC decreased 58 % and 64 % respectively. This can be attributed to poor interfacial bonding between HTCs and PE because much more wear debris can be occurred at higher applied loads during the wear test for samples which have agglomerated HTCs [5].

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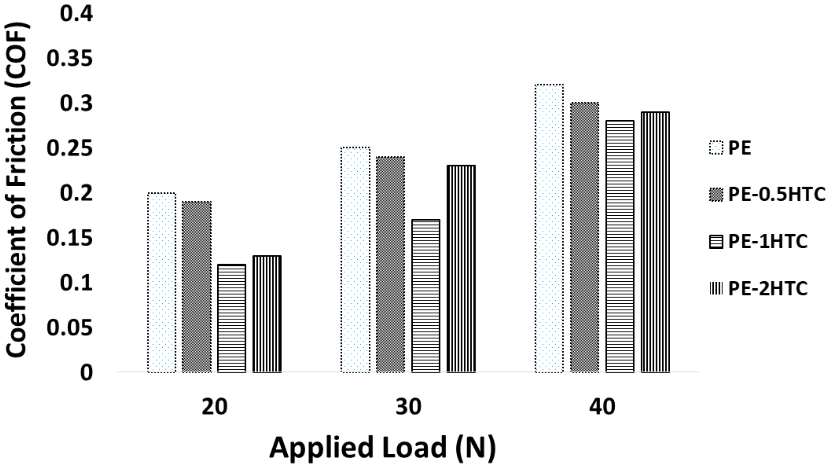

Figure 7. The coefficient of friction values of samples

Figure 7 presents the coefficient of friction (COF) values of samples. Carbonaceous reinforcements including HTCs have a lubricant effect [11] so the coefficient of friction values of samples were decreased with the addition of HTCs. On the other hand, COF values were increased when the applied load increased due to non-uniform friction at higher reapplied loads.

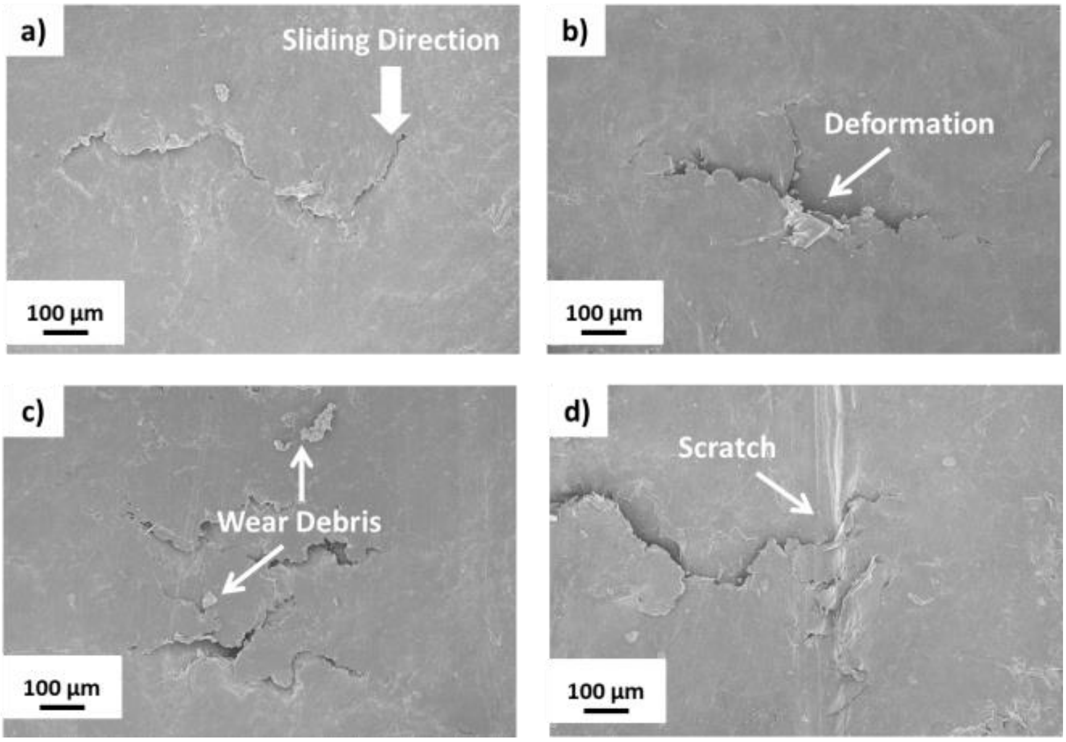

Figure 8. Worn surfaces of samples a) PE, b) PE-0.5HTC, c) PE-1HTC, d) PE-2HTC

Figure 8 shows the SEM images of the worn surfaces of samples. It was seen that wear debris occurred for both HTC reinforced composites and pure PE. This indicated the formation of an abrasive wear mechanism. Parallel to the sliding direction, scratches can be seen for PE-2HTC. This result also confirmed the formation of an abrasive wear mechanism.

4. CONCLUSIONS

In this study, PE/HTCs composites were produced via 3-D mixing and injection molding processes. The effect of HTCs on the tribological properties of polymer matrix composites was investigated for the first time. It was found that there is no chemical bonding between HTCs and PE matrix. The tensile and impact properties of pure PE were improved by nearly 18% and 31% with 1 wt.% HTCs addition, respectively. Wear test results showed the same trend as mechanical test results at lower applied loads and PE-1HTC showed 39% better wear properties than pure PE. Also, HTCs reinforced composites had lower COF values than pure PE due to the lubricant effect of HTCs. However, when an applied load was increased, PE-1HTC and PE-2HTC had lower wear resistance than PE due to the poor interfacial bonding between matrix and reinforcement. To sum up, the usage of HTCs as reinforcement material showed a positive effect on the wear properties of PE matrix composites. Therefore, it can be taught that HTCs may be promising reinforcement material for polymer matrix composites.

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CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

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