Utilization of polyethylene terephthalate waste as a carbon filler in polypropylene matrix: Investigation of mechanical, rheological, and thermal properties

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Abstract
Polyethylene terephthalate (PET) waste was converted into carbon and the feasibility of utilizing it as a reinforcing filler material in a polypropylene (PP) matrix was investigated. The carbon produced by the pyrolysis of waste PET at 900°C in nitrogen atmosphere contains high carbon content (>70 wt%). PP/carbon composites were produced by melt blending process at varying loading concentrations. Scanning electron microscopy images at the fractured surface revealed that the carbon filler has better compatibility with the PP matrix. The mechanical, thermal, and rheological properties and surface morphology of the prepared composites were studied. The thermogravimetric analysis studies showed that the thermal stability of the PP/carbon composites was enhanced from 300 to 370°C with 20 wt% of carbon. At lower angular frequency (0.01 rad/s), the storage modulus (G') of PP was 0.27 Pa and those of PP with 10 and 20 wt% carbon was 4.06 and 7.25 Pa, respectively. Among the PP/carbon composite prepared, PP with 5 wt% carbon showed the highest tensile strength of 38 MPa, greater than that of neat PP (35 MPa). The tensile modulus was enhanced from 0.9 to 1.2 GPa when the carbon content was increased from 0 to 20 wt%.

KEYWORDS
composites, mechanical properties, microscopy, rheology, thermal properties

1 | INTRODUCTION

Environmental pollution is growing at an alarming rate owing to injudicious disposal of solid waste into land and water, particularly in developing countries. The fastest-growing contributor to such pollution is the accumulation of nondegradable plastic waste. Plastic has become an inevitable part of human life because of its low cost, lightweight, moldability, thermal, and chemical stability. The most commonly used plastics, such as polyolefins, polyesters, polystyrene, and polyamides, are nonbiodegradable and fragmented due to weathering into particulate plastics, contaminating the ocean, land and atmosphere. These micro and macrosized waste particles can accumulate in living organisms and adversely affect them.1 These plastic wastes are persistent environmental pollutant and need to convert such plastic waste into value-added materials that are not harmful to the
economy. In a recent study; the temperature, reaction time, and catalyst amount was optimized for the production of oil from the pyrolysis of polystyrene waste,2–4 polypropylene (PP) waste5 and was found to be a great promise for replacing the fuel oil. The byproduct of pyrolysis of polymeric waste is gas, which can also be utilized as a fuel.6 Apart from these, there are many methods reported such as mechanical–chemical recycling,7 thermomechanical degradation,8 biological,9 and so forth. for the plastic waste disposal treatment. These methods often require a special apparatus as well as catalysts for the conversion process.

Polyethylene terephthalate (PET) get much attention owing to its broad range of applications in packaging, manufacturing bottles, fibers, and films; and as an engineering thermoplastic.10 PET bottles are the second-most popular type of consumer packaging in the global market, and its market share is expected to grow by 3.9% over the coming years.11 Worldwide production of PET was reported to be 41.56 million metric tons (MMT) in 2014 and is estimated to reach 73.39 MMT by 2020. Owing to the lack of proper waste management systems in many countries, alarming amounts of solid waste are directed to landfills and incineration. According to a survey conducted in 2015, out of 6300 million tons (Mt) of plastic waste, only 9% was recycled; 12% and 79% were incinerated and landfilled, respectively. If the current trends continue, by 2050, 12,000 Mt of plastic will pile up in landfills.12 The incineration of plastic waste releases large amounts of toxic greenhouse gases such as CO₂ and CO, which may accelerate global warming and climatic changes.13–16 This motivated us to develop an efficient and ecofriendly method to recycle plastic waste or convert it into value-added products that would mitigate the accumulation of waste and reduce the toxic gas emissions to the environment. The recycling process is one of the effective methods to control plastic waste accumulation.10,17,18 Among the different recycling methods, the chemical recycling process can break the polymers into their respective monomers via depolymerization. The decomposition of PET into its monomers in the presence of reagents such as acids (acidolysis)19 or methanol (alcoholysis),20,21 or by glycols (glycolysis)22 is an established process. The starting monomers of PET can be recovered and reused.23 Additionally, the polymer waste has been converted into valuable products, such as carbon nanotubes,24–26 polymer carbon dots with photoluminescence,27,28 and plastic-derived oils.29 Numerous processes have been reported for the synthesis of carbon, such as arc discharge,30 chemical vapor deposition,25 and thermal oxidation to obtain graphitic carbon.31 The easiest and sustainable method of utilizing PET waste is converting it into carbon via pyrolysis process under an inert atmosphere. In contrast to recycling, the pyrolysis process can be considered as a green technology, even though it generates gaseous products that can be used for satisfying the energy needs for the pyrolysis plant.14,32,33 Since pyrolysis is performed in an inert atmosphere, it produces less gaseous pollutants than incineration. Furthermore, the pyrolysis process does not require the sorting of polymers; hence, it is less labor-intensive than incineration. Hence, these pyrolysis processes have many advantages such as ease of operation with no pretreatment, cost-effective way to reduce environmental waste and is counted as an energy efficient process for the conversion of waste to carbon.33

The PET has more carbon in the molecular chain (above 60%), and its pyrolysis yields a higher amount of carbon as a residue.34 It is reported that the activated carbon from waste PET finds application as an adsorbent in natural gas storage,35 CO₂ capture,36,37 and so forth. The carbon procured after pyrolysis has various characteristics, such as a large surface area, less functional groups and low concentration of impurities than the carbon collected from biomass pyrolysis. Thus, PET waste is a suitable precursor for the carbon production, which can be effectively utilized as a filler material to enrich the thermal and mechanical characteristics of a polymer matrix. Accordingly, the main objective of this study was to utilize PET waste collected from a recycling firm in Riyadh, Saudi Arabia to produce carbon through pyrolysis under controlled atmospheric conditions. The carbon produced via pyrolysis was characterized using various techniques and its feasibility as a reinforcing filler material in a PP matrix was investigated.

2 | EXPERIMENTS

2.1 | Materials and characterization

2.1.1 | Synthesis of carbon from PET waste via pyrolysis

PET waste (raw material) was collected from the Saudi Plastic Factory Co. Riyadh, Saudi Arabia. The chopped (10 mm) PET collected directly from the company was cleaned with distilled water to remove any dust and kept in an oven for drying at 110°C for 5–7 h. The PET waste was pyrolyzed at 900°C with a heating ramp of 10°C/min. Using a tube furnace under an inert atmosphere for a residence time of 2 h. After the 2 h holding time, the heater was switched off allowed it to cool down by natural convection. The carbon collected was weighed and ground using a ball-milling apparatus (Fritsch Pulverisette 7 model with zirconia ceramic balls) at 250 rpm
for 6 h. The ground carbon collected from the ball mill was used directly without a sieving process.

2.1.2 Scanning electron microscopy

Morphological and elemental analyses were performed with the aid of scanning electron microscope (SEM) (JEOL JSM-6360A Japan, with energy-dispersive X-ray spectroscopy (EDS) facility. The gold coating for the samples was done in JFC/1600 auto fine coater for 40s. The sputter gold coating was conducted to avoid the charging effect leading to better image quality.

2.1.3 Raman spectroscopy

The Raman spectrum of the carbon was examined using an NRS-4500 Laser Raman spectrometer (1000–3000 cm$^{-1}$). The excitation beam was tuned to a wavelength of 532 nm. The measurement was carried out by the objective lens with 20× magnification. A 6 mW beam power and an exposure time of 3 min. Were used for the experiment.

2.1.4 Elemental analysis

An elemental examination (C, H, N, and O) was executed in PerkinElmer 2400 Series II CHNS/O machine (Norwalk) employing acetanilide standard. Roughly, 3 mg of carbon was utilized for the analysis and the test was performed twice.

2.1.5 Brunauer–Emmett–Teller

The Brunauer–Emmett–Teller (BET) specific surface area of the carbon was measured by obtaining nitrogen adsorption isotherms using a Tristar-II 3020 (Micromeritics) instrument at −196°C. For the BET measurements, 0.2–0.3 g of the samples were taken and were subjected to degassing at 200°C for about 3 h prior to the testing.

2.1.6 Preparation of PP/carbon composites

The PP homopolymer (TASNEE PP H4120) was supplied by TASNEE, Saudi Arabia. It had a melt flow index of 12 g/10 min. (ISO 1133) and a density of 0.9 g/cm$^3$. Different formulations (2.5, 5, 7.5, 10, 12.5, 15, and 20 wt % wt/wt) of PP/carbon composites were prepared via the melt-mixing process in a micro Compounding (DSM Xplore) at a temperature of 220°C with a screw rotation of 100 rpm. The mixing process was carried out for 3 min. and after the stipulated blending time, the PP/carbon composites were subjected to microinjection molding (DSM Xplore 12 cm$^3$, Netherlands). Dumb-bell shaped standard tensile testing specimen was prepared keeping the mold at 35°C and 6 bar pressure. Tensile testing was done in UTM (Hounsfield H100 KS model) by the ASTM D638 method. The average of four test results was plotted.

2.1.7 Differential scanning calorimetry

Differential scanning calorimetry (DSC, Shimadzu DSC-60 model) was performed on the composites. The heating and cooling program was set from 30 to 220°C, with a ramp of 10°C/min. and 4 min. Holding time by taking 6–10 mg sample in an aluminum pan.

2.1.8 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60H in the temperature span of 30–600°C. 10 ± 1.5 mg of the sample was kept in an aluminum pan where it is heated to 600°C (air atmosphere) with a ramp of 20°C and the weight loss was recorded.

2.1.9 Fourier transform infrared spectroscopy

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) test was performed in a Thermo-Scientific Nicolet iN10 FTIR model with germanium microtip attachment (400–4000 cm$^{-1}$).

2.1.10 Rheology

The melt flow behavior of the prepared samples was monitored using TA instruments AR G2 model having a parallel-plate geometry (25 mm diameter). The samples were set at an experimental temperature of 190°C where the PP composites melt and the plates gap was retained at 1000 µm for the measurements. The angular frequency sweep measurements were carried out from 0.01 to 628.3 rad/s under oscillatory stress of 3.259 Pa.
3 | RESULTS AND DISCUSSION

3.1 | Scanning electron microscopy, elemental composition, and BET analyses of carbon collected from pyrolysis

SEM images of carbon before and after the ball-milling process are shown in Figure 1(a,b), respectively. The carbon collected directly from the furnace was porous and lightweight, with a sheet-like structure, as shown in Figure 1(a). After the ball milling, the carbon particles had an angular shape with a nonuniform size (<30 μm), as shown in Figure 1(b). According to the SEM-EDS results, the carbon content was 77 wt% (Figure 2). The EDS data matched the C, H, N, O analysis data shown in Table 1. The BET analysis shows that the average surface area of the carbon particles was 214.5 m²/g (Table 1). It can be observed, from Table 1, that the mass percentage of oxygen is relatively high. This is due to the fact that the PET repeating unit (C₁₀H₈O₄) consist of 33.3 wt% of oxygen, compared to 62.5 wt% of carbon content.

3.2 | Raman spectrum analysis of waste-derived carbon

Raman spectrum of carbon collected from the pyrolysis of PET waste is shown in Figure 3. The spectrum exhibited G and D bands with excitation in the visible region. The peak at 1593 cm⁻¹ is due to the sp² hybridized carbon which corresponds to the G band. The G band is attributed to the bond stretching of sp² carbon. The peak at 1341 cm⁻¹ relates to the D band associated with the breathing mode of the aromatic ring. In the case of crystalline graphite, the G mode of vibrations appears at 1589 cm⁻¹ and can be shifted to the higher or lower frequencies when the nanostructures are disordered. According to the position of the G band in the spectrum, the graphene stacking in the carbon had a less strained geometry. The second prominent band of the carbon was the D band at 1341 cm⁻¹, which is due to the lattice breathing mode. The D band is not present for a graphitic crystal and is very weak for graphene sheets but appears for disordered graphitic structures. The ratio of intensities of D and G band provide the amount of disorder in the carbon. The I_D/I_G is the ratio of the disordered to ordered carbon (disorder density). The I_D/I_G ratio of the PET waste carbon is ~0.88, which is lower than carbon produced at lower pyrolysis temperatures but similar to KOH activated graphene aerogel. Since the I_D/I_G is low, the quantity of sp² hybridized carbon in the PET waste carbon is high. The increase in the graphitic carbon in the PET waste is due to the pyrolysis of waste at elevated temperature, which removes all volatile components and leaving behind porous carbon.

3.3 | Thermal characterization of PP/carbon composites

The DSC results indicated that the PP homopolymer had a temperature of melting (T_m) at 166°C and...
crystallization temperature ($T_c$) of 121°C. The DSC analysis of the composites revealed that the incorporated carbon, has no influence on the temperature of melting of PP. This is due to the fact that the PP has no chemical modification due to carbon filler as the mixing process is purely physical and the melting point of the studied composites remains the same as that of PP. However, the crystallization temperature was found to increase with the carbon addition; in other words; the incorporation of carbon shifted the crystallization temperature slightly toward higher values. This is an indication of enhanced nucleation efficiency due to the addition of the carbon filler such nucleation efficiency is observed for other types of carbon-based fillers. On the other hand; the enthalpy of melting ($\Delta H_m$) for the PP-carbon composites and this reduction is proportional to the carbon loading percentage, reaching its lowest value of (67 J/g) in PP filled with 20 wt% compared (89 J/g) for neat PP, as shown in Table 2. This is due to the reduction in the PP weight percentage with increased loading of carbon.

The overall crystallinity ($X_c$) of the prepared samples was determined as follows:

$$X_c(\%) = \frac{\Delta H_m}{(1-\Phi)\Delta H^0_m} \times 100$$  \hspace{1cm} (1)

where ($\Phi$) represents the weight fraction of carbon in the composites, $\Delta H_m$ represents the melting enthalpy, and $\Delta H^0_m$ represents melting enthalpy of fully crystalline PP (207 J/g).44

It can be seen from Table 2 that the overall crystallinity ($X_c$) of the PP-carbon composites is decreased when compared to PP. When only 2.5 wt% of carbon is added to PP, the overall crystallinity of the composite was found to be reduced from 43 (for neat PP) to 35.8 (for 2.5 wt%). Although the incorporation of carbon into PP developed the formation of a greater number of nuclei, as indicated previously by the shifted crystallization temperature, however; the crystallization rate of the PP the crystal growth rate is decreased due to the restricted motion of the PP chain in the presence of the carbon particles. The carbon particles occupied the interstitial positions of the PP chains, which hindered the orderly packing of the PP chains and reduced the total crystallinity of the PP/carbon system.45

Figure 4(a,b) present the TGA and DTG results for PP and PP/carbon composites, respectively. The TGA results, Figure 4(a), reveals that the degradation process of neat the PP and the PP/carbon composites occurs in a single step pattern and that thermal steadiness of the PP/carbon composites is greater than that of neat PP as indicated by the shift in the onset of degradation temperature toward higher temperatures. This enhancement of PP thermal steadiness is due to the higher thermal stability of the carbon incorporated, which is produced at high temperatures with no volatiles to escape.46 When the carbon content is raised from 0 to 20 wt%, the onset of degradation moved gradually toward the higher temperatures and reaches its highest value, which is shifted by 70°C for PP matrix filled with 20 wt% carbon. A similar trend of
enhanced thermal stability has been observed in the literature with other types of carbon-based fillers when added to the PP matrix.\textsuperscript{47,48} According to the thermogram (Figure 4), while comparing the residual weight at the end of the curve, it can be noticed that the weight of residuals is directly proportional to loading percentage of PET carbon into PP. The thermal stability of the polymer composite was improved owing to the dissipation of thermal energy by the carbon, which prevented the accumulation of energy and the degradation of PP chains.\textsuperscript{49}

### 3.4 | ATR-FTIR study of PP composites

Figure 5 shows the ATR-FTIR spectra of the PP and PP/carbon composites. The FTIR spectra of the PP and PP/carbon composites had peaks at the same frequencies with the same intensities, indicating that the melt blending was a purely physical process; that is, the carbon filler was not chemically connected to the PP matrix and there was no possibility of a copolymerization reaction. The peaks at 2900, 1400, and 1350 cm\(^{-1}\) were assigned to CH\(_2\) bending (asymmetrical), CH\(_3\) bending (symmetrical, and asymmetrical) in PP, respectively.\textsuperscript{50,51}

### 3.5 | Rheological properties of PP/carbon composites

Figure 6 shows the storage moduli (G’) of the PP and PP/carbon composites. For the PP/carbon composites, the storage modulus improved with the carbon content because of the possible PP/carbon network formation.\textsuperscript{52} At lower angular frequency (0.01 rad/s), G’ of PP was 0.27 Pa, and those of PP with 10 and 20 wt% carbon was 4.06 and 7.25 Pa, respectively. As shown in Figure 6, with the highest carbon loading (20 wt%), there was a two-order of magnitude increment in the G’ matched with pure PP. The storage modulus was higher than that reported for PP/biochar composites\textsuperscript{53} and lower than that reported for PP/carbon black composites.\textsuperscript{38,45} These results denote that the interaction between the carbon from the PET waste and the PP matrix was better than that for biochar/PP composites.

Figure 7 shows the tan δ (G”/G’) versus frequency data for the studied composites. At low frequencies, the PP displayed liquid-like behavior, with G’’ > G’. At
higher frequencies, it exhibited solid-like behavior and the PP and PP/carbon composites had similar tan δ values. With the increasing carbon content in the PP matrix, the storage modulus was increased and the tan δ values at lower frequencies became equal to those at higher frequencies. The carbon filler concentration at which the tan δ versus frequency slope becomes close to 0 is the rheological threshold; this was not achieved for the present system even with a carbon content of 20 wt%.54,55

3.6 Mechanical behavior of PP/carbon composites

Figure 8 shows the dependence of the tensile strength and tensile modulus (secondary axis) of the PP/carbon composites on the loading percentage of carbon. The incorporation of carbon improved the tensile strength of the PP/carbon composites compared with the PP sample. Among the samples prepared, the composite sample with 5 wt% carbon loading exhibited the peak tensile strength (37.94 MPa), which was approximately 7.8% elevated than that of PP (35.2 MPa). Further increase in the carbon content, slightly decreases the tensile strength of the composites due to the brittleness imparted by the carbon. The brittleness was indicated by SEM images of the tensile fracture surfaces, as shown in Figure 9(a–d). The tensile modulus of the PP/carbon composites increased with the carbon content owing to the PP/carbon network formation, which restricted the movement of the PP chains.56 Although the addition of carbon increases the tensile properties with low concentrations, at high carbon loading, the tensile strength has reduced. The maximum amount of carbon that can be added to the PP matrix without diminishing the tensile properties has not studied.

Figure 10 shows the elongation percentage at the break and elongation percentage at yield for the PP and PP/carbon composites. The addition of carbon to the PP matrix imparted a sudden decrease in the elongation at break related to PP. However, the elongation at the yield of the PP/carbon composites decreased linearly with the increasing carbon loading. The substantial reduction in the composite ductility was due to the constrained movement of the PP chains in the presence of carbon particles.
CONCLUSION

The plastics are inevitable in daily life, and accordingly, the plastic waste will grow and need to find out sustainable methods to convert such wastes into valuable products. The researchers are in search of various methods to convert such plastic waste into useful products. The pyrolysis of waste plastic under controlled atmospheric conditions is economical and safe for the environment.

In this article, we demonstrated the feasibility of utilizing plastic waste-derived carbon as a reinforcing filler in polymer composites. PET waste-derived carbon with high carbon content was produced and utilized as a filler material in a PP matrix. ATR-FTIR characterization revealed that the melt-blending process was purely physical and Raman spectra indicated that the graphene stacking in the carbon led to a less strained geometry with disordered graphitic structures. The thermal stability, the tensile modulus and tensile strength of the resultant composites were further improved with a decrease in elongation at break. Future work can be oriented toward the surface functionalization of collected carbon for better filler-matrix interaction and hence enhancement of mechanical properties. The effect of carbon particle size and different pyrolysis temperatures on the properties of carbon and the composites can be done in future.

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