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Article

Mechanical and Thermal Properties of Extrudates Produced from Discarded Coal Fines and Recycled Plastics as Binders

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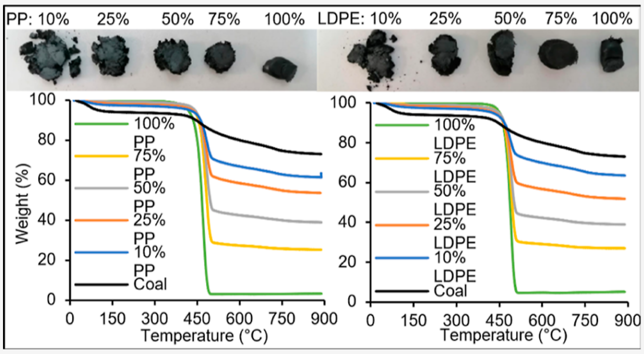

ABSTRACT: This study focuses on the extrusion of discarded coal fines from the Highveld coalfield together with recycled low-density polyethylene (LDPE) and polypropylene (PP) which are used as binders to produce agglomerates with better handling properties than the coal fines for industrial use. The binder content varied between 5 and 100 wt %. The barrels of the twin screw extruder were kept at a temperature of 220 °C to melt the binders while forcing the mixture through a 10 mm die. The extrudates containing 10% or more binder were strong and homogeneous, while a 5% binder addition proved to be too low to produce homogeneous extrudates. The extrudates containing 10% LDPE and 10% PP showed compressive strengths of 17.5 and 7.9 MPa before breaking, respectively. The rest of the extrudates (>10% plastic addition) did not break but merely flattened as the plastic load increased. The compressive strength of all the extrudates showed no significant difference after being exposed to water. Furthermore, the extrudates absorbed less than 5% water after being submerged for 24 h. Thermogravimetric analysis of the extrudates was conducted under a nitrogen atmosphere up to 900 °C. Three iso-conversional methods, Kissinger−Akahira−Sunose, Starink, and Flynn−Wall−Ozawa, were used to determine the activation energy of the extrudates and raw materials. The lower activation energy and conversion temperatures found for the extrudates indicate a synergy between plastic and coal fines when the extrudates are pyrolyzed. Results from this study suggest that the co-extrusion of recycled plastic with coal fines will produce solid carbonaceous fuels with high hydrophobicity, heating value, and high mechanical strength compared to coal fines.

1. INTRODUCTION

Coal is crucial for the socio-economic development in South Africa, and the resource is widely used across the country.[1] Approximately 77% of the country's energy needs are supplied by coal,[2] which includes 83%[3] of the electricity generated and 30% of the country's produced fuels.[4] Globally, South Africa is the sixth largest coal producer[2] and mines approximately 250 Mt of coal per annum.[4] During mining and operation, coal fines (coal particles with a <1 mm diameter) are formed[5] and account for approximately 12% of the total South African mined coal.[6] The South African coal mining industry currently discards 60 Mt of coal fines per annum.[7] Discarding coal fines causes environmental problems since acid mine drainage occurs when stored in slime dams[1] and improper storage can result in spontaneous combustion.[7] Industrial processes do not readily use coal fines due to handling and transportation difficulties[5] as well as high ash yield, sulfur,[7] and moisture content.[6] From a financial incentive,[6] the use of coal fines would positively affect the environment and provide an additional source of coal available for utilization.[8] To extend the life of the remaining coalfields, the utilization of discarded coal fines is beneficial and aligned with government policy.[9]

To be used in industrial processes, coal fines need to be agglomerated to improve the handling of the material.[5] These agglomerates need to adhere to mechanical strength standards[10] and must have water resistance properties.[10] In order to improve the mechanical strength of the agglomerates, binders are often added. These binders should be environmentally friendly; binders can often be the most expensive aspect of agglomeration.[11] To overcome this problem, the binding properties of municipal wastes are continually being investigated.[12]

South Africa has a complicated global standing in terms of waste management. Even though the country is one of the

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front runners in waste plastic recovery by recycling 46.3% of its 1.1 Mt of plastic waste annually,[13] the country is still however ranked the 11th most mismanaged plastic waste practice globally (630 000 tons per annum).[14] Plastic waste is continuously increasing and is an enormous environmental threat. Traditional plastics are not biodegradable and cause problems decades after the initial pollution.[15] The problem presented by plastic waste is further complicated because plastics are significantly cost-effective to produce.[15] Globally, the most popular and economical waste management method is via landfilling; however, landfilling produces secondary pollutants such as releasing toxic gases, acid leachate, and spontaneous combustion.[16] When waste, including plastic waste, is incinerated, more poisonous gases are released, which cause damage to the environment and human health.[17] Polymers like polyethylene (PE) and polypropylene (PP) experience decreasing quality during recycling and are unsuitable for monomer recovery. The lack of recyclability leads to the exploration of blending plastics with other feedstock materials for application as a fuel source which can produce high-energy pyrolysis products or liquid fuels.[18]

Plastics have many good binder attributes, such as high heating values and no discernible sulfur or mineral content. From all the plastic types, low-density polyethylene (LDPE) and PP have the highest heating values (~46.5 MJ/kg) and do not contain toxic compounds like chlorine.[19] These plastics consist almost completely of carbon and hydrogen, making plastics ideal candidates for producing syngas.[20] Furthermore, plastics contain mostly volatile matter, that is, LDPE contains approximately 99.8%, and PP contains 97.7% volatile matter.[19] When combining plastics with other feed materials, the amount of plastic can be varied to produce the required amount of volatile matter necessitated for the industrial application.[21]

Both LDPE and PP have shown that when used as binders, strong agglomerates can be produced.[12,22] The authors are not aware of previous studies conducted on the extrusion of fine coal and plastic. Only one study has reported on the extrusion of plastics (LDPE and PP) together with a woodchip feedstock.[23] The study used extrusion as a mixing method and indicated that none of the previous studies used sufficient agglomeration techniques that allowed for the simultaneous mixing and heating of the plastics with the respective feedstock, including coal, biomass, and woodchips.[23] Furthermore, Peng et al.[22] investigated the pelletization of biochar and plastic, while Massaro et al.[12] investigated the briquetting of LDPE and coal fines. These studies all indicated that plastic usage as binders have significant industrial applications since plastics mostly have high energy densities, are hydrophobic, and produce durable agglomerates.[12,22,23] Furthermore, Peng et al.[22] found that waste plastics could be an economically feasible binder solution. Song et al.[23] increased the energy density of woodchips by extruding them with thermoplastics like LDPE and PP. Hence, this study is considered a novel study to understand the behavior of discarded South African coal fines when blended with these plastics and extruded.[18] By improving the understanding of the co-pyrolysis of extruded coal and plastic mixtures, the possible applications of this new fuel source in processes such as pyrolysis or gasification can be better evaluated.

Studies have reported on the thermogravimetric analysis (TGA) pyrolysis of plastic and coal mixtures by only mixing the raw powders.[24,25] Furthermore, most available literature investigates the addition of low percentages of plastics (0 to 15%) to coal blends.[12,24,25] The low addition of plastic to the coal blends were investigated in order to find a suitable replacement for traditional fossil fuels without drastically changing current industrial processes.[12,24,25] Sharypov et al.[26] and Sharma et al.[18] both reported synergy between coal and plastics during pyrolysis as larger plastic to coal addition ratios (1:1, 3:1, and 1:3) were investigated. Sharypov et al.[26] investigated the effect of PP on brown coal in an autoclave in an argon atmosphere and reported that the blends' maximum degradation temperature remains close to that of the PP. Sharma et al.[18] investigated mixtures of LDPE and Indian ledo coal. The ledo coal has lower activation energy than LDPE, and the blends reported higher activation energy than for both individual materials. These studies included larger ratios of plastic addition so that the fuel source can be applied to both waste management and energy production.

All the available studies in the literature use Northern hemisphere coal,[12,18,25−27] and the thermal behavior of South African (inertinite-rich) discarded coal fines and plastic blends have not yet been reported. Furthermore, no direct comparison was found in the literature between the synergic effect of coal and PP and that of coal and LDPE pyrolysis over a wide range of plastic concentrations, as has been conducted in this study. Multiple simultaneous reactions need to be accounted for when investigating the pyrolysis kinetics and thermodynamic parameters of carbonaceous material. It is difficult to obtain the mechanism for each reaction; therefore, iso-conversional methods are used to estimate these parameters.[28] Multiple iso-conversional methods have been used to determine kinetic parameters for both coal and plastics;[29,30] however, the use of these methods have not been reported on the pyrolysis of mixtures of coal and plastics.

This study investigates the extrusion of Highveld discarded coal fines with different ratios of recycled waste LDPE and PP as binders to produce extrudates suitable for industrial processes. The mechanical strength, as well as the thermal properties, were investigated, and three iso-conversional methods [Kissinger−Akahira−Sunose (KAS), Flynn−Wall−Ozawa (FWO), and Starink] were utilized to determine the kinetic and thermodynamic properties of the extrudates during co-pyrolysis.

2. METHODS

2.1. Materials. *2.1.1. Coal Fines.* Inertinite-rich discarded coal fines were sourced directly from the Highveld coalfield in South Africa. These fines were dried for a week, and all lumps were crushed using a manual roller and a ball mill. The moisture content of the coal fines after air drying was determined to be 4.8% wt. The fines were screened, and particles <1 mm were used in this study.[31]

2.1.2. Plastic. Recycled LDPE and PP cylindrical pellets were obtained from Potch Plastic (Potchefstroom, South Africa) with a particle size of approximately 5 mm. Where fines are required for analyses of the plastic, a FRITSCH variable speed rotor mill PULVERISETTE 14 classic line was used to reduce the plastic particle size, and the particles were also sieved to <1 mm.

2.2. Extrusion. Before attempting extrusion, the melt flow index (MFI) of the plastics was determined. The MFI can be related to viscosity, shear strength, and the shear rate of the material.[32] The MFI indicated that the plastic melt would flow evenly with fine coal particles acting as obstructions. However, as the coal fines content increased, the mass flow decreased, and eventually, blockages occurred. The MFI results obtained are further discussed in the Supporting Information.

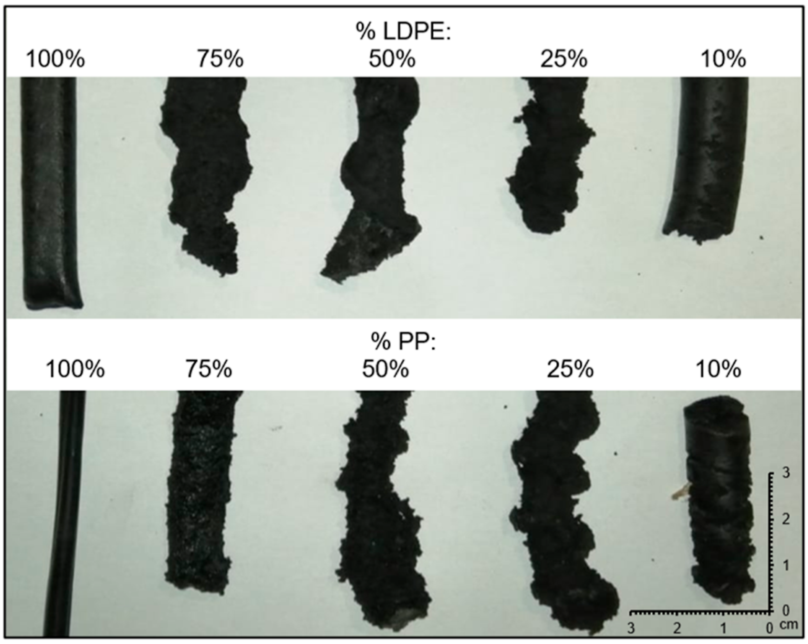

Figure 1. Extrudates containing various percentages of LDPE and PP.

The extrudates were produced using a TX 32 laboratory-scale extruder supplied by CFAM Technologies (Pty) Ltd. Since the increase in coal particles decreased the mass flow during the MFI test, the pure plastics were extruded first, and then, the coal content was only increased if a stable run was obtained at the previous set concentration. The run was considered stable if a homogeneous product could be produced and no blockages occurred. The samples contained 100, 75, 50, 25, 10, and 5% wt of plastic pellets (5 mm) mixed with discarded coal fines (<1 mm). A screw feeder fed the mixture into the co-rotating twin screw extruder at a feed rate of 22.5 kg/h. The screws rotated at a constant speed of 250 rpm, while the extruder barrels were kept at 220 °C. The hot extrudates were pressed through a 10 mm die and quenched in a water bath to cool the extrudates.

As the coal concentration of the blends increased during extrusion, the flow became more restricted. A 5% plastic content no longer produced homogeneous products and caused blockages in the extruder. Only the homogeneous extrudates produced (100 to 10% plastic) are illustrated in Figure 1 and were used for the remainder of the experiments.

The extrudate strands were collected, dried, and then manually cut into 2 cm lengths using a table saw.

2.3. Chemical Composition. *2.3.1. Characterization.* The discarded coal fines, LDPE, PP, and extrudates were characterized using proximate, ultimate, and calorific value analysis. The proximate analyses and calorific value analysis were conducted at the North-West University along with the percentage carbon, hydrogen, and nitrogen. Bureau Veritas determined the percentage sulfur, and the percentage oxygen was determined by difference. The operating procedures used for these analyses are summarized in Table 1.

2.4. Mechanical Strength. *2.4.1. Compressive Strength.* Compressive strength tests were conducted using a Lloyd LRX Plus Press. A single extrudate was placed between the two flat plates of the press, and the top plate applied a load onto the extrudate by extending downward at a rate of 5 mm/s. The maximum load at which the extrudate breaks or is permanently deformed is considered the maximum load. The LRX press provides two different graphs when the extrudate breaks and deforms (Figure 2a,b).

When the extrudate breaks, a clear maximum peak can be recognized by the LRX press, and a breaking point is identified (Figure 2a); however, when the extrudate is deformed, a clear breaking point is not identified because the extrudate is slowly flattened and does not have a defined breaking point. The LRX press will thus show a slightly lower load when the deformation starts, and then, the load will increase until the press reaches its maximum load

Table 1. Characterization Operating Procedures

description	operating procedure
proximate analyses	
moisture (M)	ISO 11722:2008
volatile matter (VM)	ISO 1171:2010a
ash (A)	ISO 562:2010b[a]
fixed carbon (FC)	by difference
ultimate analyses	
carbon, hydrogen, nitrogen	ISO 29541:2010
sulfur	ISO 19579:2006
oxygen	by difference
calorific value	ISO 1928:2009b

[a] The ash yields of the coal and extrudates were determined using ISO 562:2010b; the ash yields of the plastics were determined using the operating procedure described in Wong et al.[33]

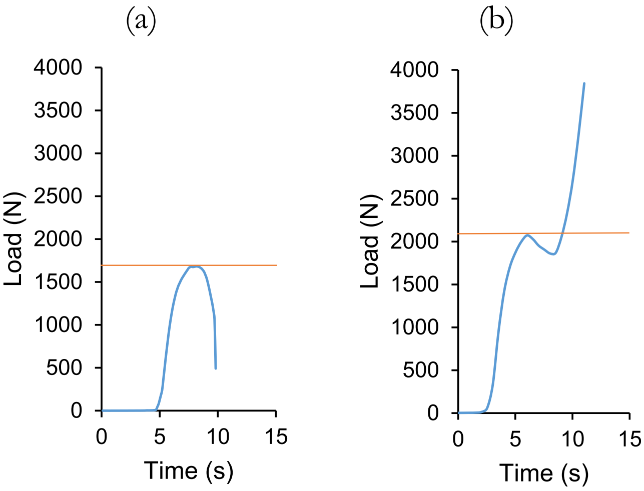

Figure 2. Compressive strength curves of (a) breaking extrudates and (b) deforming extrudates.

Table 2. Proximate Analyses, Ultimate Analyses, and Calorific Value of the Feed Materials and Extrudates (Air-Dry Basis)

	proximate analyses				ultimate analyses						calorific value
	% M	% VM	% A	% FC (by difference)	% C	% H	% N	% S	% O	molar ratio C/H	(MJ/kg)
feed materials											
recycled LDPE	0.3	97.7	0.3	1.6	83.4	14.6	0.1	0.1	1.5	2:1	46.2
recycled PP	0.3	98.5	0.0	1.2	84.0	14.7	0.0	0.1	1.2	2:1	46.7
coal fines	4.8	24.9	40.8	29.6	50.3	2.8	1.3	1.0	3.9	6:1	19.5
extrudates											
10% LDPE	2.2	35.1	32.5	30.3	56.4	5.4	1.1	0.7	3.9	4:1	24.0
25% LDPE	1.7	45.5	25.8	26.9	62.0	7.4	0.9	0.6	3.3	3:1	28.6
50% LDPE	1.3	64.2	17.5	17.0	69.1	9.6	0.7	0.4	2.7	3:1	33.6
75% LDPE	0.9	75.1	13.9	10.1	73.5	11.2	0.5	0.4	0.7	2:1	39.8
100% LDPE	0.1	96.8	1.4	1.6	83.6	13.8	0.5	0.2	0.4	2:1	45.9
10% PP	2.5	36.7	31.4	29.4	57.0	5.3	1.1	0.6	4.6	4:1	24.7
25% PP	2.1	45.9	28.4	23.7	60.9	6.9	0.9	0.6	2.4	3:1	28.6
50% PP	1.3	64.0	19.0	15.7	68.6	9.4	0.7	0.4	2.0	3:1	33.9
75% PP	0.8	76.7	12.6	9.9	73.5	10.9	0.5	0.4	2.23	2:1	41.2
100% PP	0.1	98.6	0.0	1.3	83.9	14.5	0.1	0.1	1.5	2:1	46.6

since a breaking point was not identified (Figure 2b). The red line indicates the maximum load before breaking or deformation. The compressive strength of the extrudate was then calculated using eq 1.

$$\mathrm{CS} = \frac{L}{\mathrm{Ac} \times 1000} \tag{1}$$

where compressive strength is represented by CS (MPa), the maximum load applied by L (N), and the cross-sectional area is represented by Ac (cm^2).[34]

2.4.2. Water Resistance. The water resistance properties of the extrudates were evaluated by two methods: (1) the extrudates were submerged in water for 2 h, and directly afterward the compressive strength of the extrudates was measured using the operating procedure, as discussed in Section 2.4.1;[6] (2) the water absorbance of the extrudate provides a quantitative measure of its water resistance. Extrudates were submerged in water for 30 min, and the mass difference between the sample before and after being submerged was measured. The water resistance index (WRI) was determined using eq 2.

$$\mathrm{WRI} = 100 - \%\ \text{water absorbed after 30 minutes immersion} \tag{2}$$

Extrudates need to obtain a WRI >95% after 30 min of submersion to be deemed water-resistant.[10] This process was then repeated, and the samples' mass was recorded hourly until the extrudates achieved maximum water absorption.

2.4.3. Impact Resistance. Each extrudate was dropped from a 2 m height onto a flat concrete floor. The extrudates were dropped for a maximum of six times or until the extrudate shattered into several small fractions. By counting the number of fractions (n) that the extrudate breaks into and the amount of drops necessary (N), the impact resistance index (IRI) was calculated using eq 3. The IRI value of the extrudates should be higher than 50 to withstand the strains of industrial processes.[10]

$$\mathrm{IRI} = \frac{100 \times N}{n} \tag{3}$$

2.5. Pyrolysis. *2.5.1. Thermogravimetric Analysis.* Before the samples were pyrolyzed, the extrudates were pulverized using a FRITSCH variable speed rotor mill PULVERISETTE 14 classic line, and all the samples were screened to <1 mm. The raw materials and extrudates were pyrolyzed using an SDT Q600 TGA. The samples were weighed, and ±15 mg was placed into a cylindrical alumina crucible. Each sample was kept under a constant nitrogen flow rate of 100 mL/min, while the temperature increased from 25 to 900 °C. The heating rate was varied between 10, 20, 30, and 40 °C/min.

2.5.2. Kinetic Analysis. Non-isothermal conditions were used at a constant heating rate for each experiment. The decomposition rate (dX/dt) was defined using eq 4.

$$\frac{\mathrm{d}X}{\mathrm{d}t} = f(X)k(T) \tag{4}$$

where $f(x)$ is the conversion function and $k(T)$ is the temperature-dependent rate function.[29,30] The degree of conversion (X) was determined using eq 5.

$$X = \frac{m_0 - m_\mathrm{T}}{m_0 - m_\infty} \tag{5}$$

where m_0 and m_∞ are the initial and final sample mass, respectively. m_T represents the mass of a sample at a specific temperature. $k(T)$ is described by the Arrhenius equation.[29,30]

$$k = A\ \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{6}$$

where A (s^{-1}), E_a (J mol^{-1}), and R (J K^{-1} mol^{-1}) are the pre-exponential factor, activation energy, and ideal gas constant, respectively. By substituting the Arrhenius equation into eq 4 and dividing by the heating rate β (β = dT/dt), eq 7 is obtained.[30]

$$\frac{\mathrm{d}X}{\mathrm{d}T} = \frac{A}{\beta}\ \exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(X) \tag{7}$$

When integrating eq 7, eq 8 is obtained.

$$g(X) = \int_0^X \frac{\mathrm{d}X}{f(X)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_\mathrm{a}}{RT}\right)\mathrm{d}T \tag{8}$$

where

$$T = T_0 + \beta t \tag{9}$$

and T_0 is the initial experimental temperature.[30]

The thermal degradation of carbonaceous material is complex since multiple reactions occur simultaneously and need to be accounted for. It is difficult to obtain the reaction mechanism for each individual reaction.[28] Therefore, iso-conversional methods, including FWO, KAS, and Starink, were used to estimate the activation energy without knowledge of the reaction mechanisms. The integral in eq 8 has no specific solution; therefore, the iso-conversional methods simplify the equation using linearization and approximate the solution using the constants S and B, as seen in eq 10.[28]

$$\ln\left(\frac{\beta}{T_\mathrm{X}{}^{S}}\right) = C_\mathrm{s} - \left(\frac{BE_\mathrm{a}}{RT_\mathrm{X}}\right) \tag{10}$$

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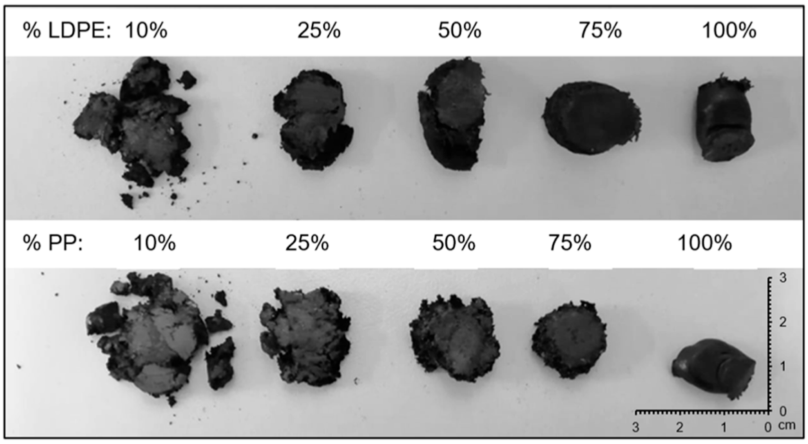


Figure 3. Extrudates after compressive strength analyses.

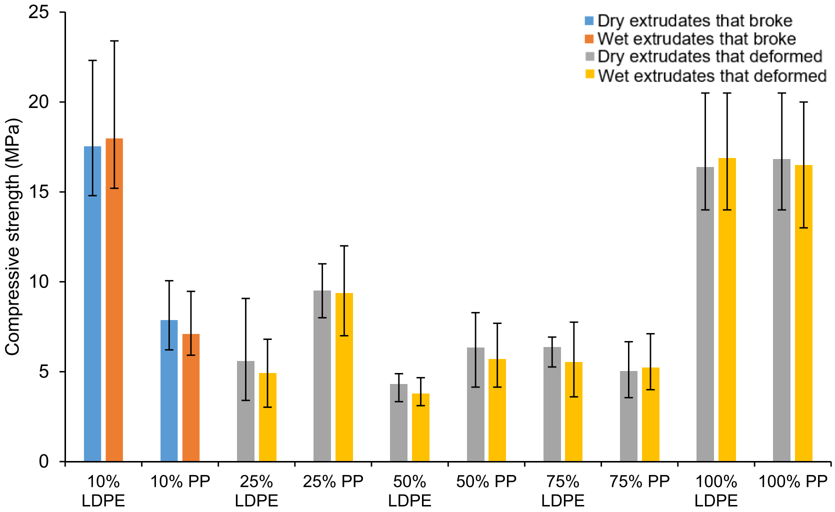


Figure 4. Compressive strength of breaking and deforming extrudates.

where the value of S and B varies for each method. $S = 0$ and $B = 0.457$ for FWO; for KAS, $S = 2$ and $B = 1$; and for Starink, $S = 1.8$ and $B = 1.0037$. The activation energy can be determined by plotting $\ln\left(\frac{\beta}{T^s}\right)$ versus $1/T$ and varying the heating rate. The slope of the straight line is equal to the activation energy.[28−30]

3. RESULTS AND DISCUSSION

3.1. Chemical Composition. The proximate analyses, ultimate analyses, and calorific value results obtained in this study are reported in Table 2.

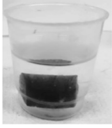
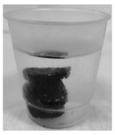
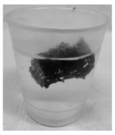
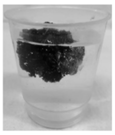
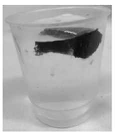
3.1.1. Proximate Analysis. It can be observed from Table 2 that the discarded coal fines have moisture and volatile matter contents within the range of bituminous coal[35] typically mined in the Highveld coalfield.[36] Compared to run of mine (ROM) coal mined from the Highveld coalfield, the discarded coal fines used in this study have a lower volatile matter content and higher ash yield and moisture content than reported in previous studies. Matjie et al.[36] showed that ROM Highveld coals typically contain 30−34% volatile matter, 22.1−29.7% ash, and 2.9−3.8% moisture.

LDPE and PP consist almost exclusively of volatile matter. Similar to the results obtained in this study, Diaz Silvarrey and Phan[19] reported that pure LDPE and PP had 99.8 and 97.7% volatile matter content, respectively, with the remainder being fixed carbon. Furthermore, the plastics contain almost no moisture or mineral matter. As expected, when the plastic concentration in the extrudates increased, the volatile matter content increased and the moisture, ash yield, and fixed carbon content decreased. All the extrudates showed a moisture content of less than 3%. Furthermore, the moisture content remained low and did not increase linearly toward the moisture content of fine discarded coal as the plastic content decreased.

3.1.2. Ultimate Analysis. LDPE and PP have a lower molar carbon to hydrogen ratio than coal fines. From Table 2, it can be observed that as the plastic content increased in the extrudates, the ratio of carbon to hydrogen decreased. Since plastic has a higher hydrogen content, the calorific value of the extrudates increased as the plastic content increased. Furthermore, the coal fines have a sulfur content below the maximum limit of export coal. The highest grade of Richard Bay (RB) export coal accepts a maximum sulfur content of 1%, while the lowest grade accepts coal with a sulfur content of 1.2%.[37] Both LDPE and PP have sulfur contents of less than 0.2%. Therefore, as the plastic content increased in the blends, the sulfur content within the extrudates decreased even lower, further improving the extrudates' quality.

3.1.3. Calorific Value. The recycled LDPE and PP calorific values agree with a study by Diaz Silvarrey and Phan,[19] who reported that both LDPE and PP had a calorific value of 46.5 MJ/kg. The calorific values of LDPE and PP are more than

Table 3. Visual Effect of Water Submersion on Extrudates

	LDPE extrudates		PP extrudates	
Plastic content	**0 hours**	**24 hours**	**0 hours**	**24 hours**
10%wt				
25%wt				
50%wt				
75%wt				
100%wt				

double that of the discarded coal fines, which is due to the high hydrogen to carbon ratio,[38] along with the low ash yield, low moisture, and high volatile matter content of the plastics compared to that of the coal fines.[39] With this significant difference in calorific value between coal fines and plastics, the calorific value of the extrudates increased linearly with the increase in plastic content.

3.2. Mechanical Strength.

3.2.1. Compressive Strength and Water Resistance. Both the dry and wet compressive strength results are discussed. Figure 3 illustrates the effect of the compressive strength test on the extrudates.

Only the dry extrudates are depicted in Figure 3; however, both the dry and wet extrudates behaved the same when subjected to a large load. Thus, water exposure did not affect whether an extrudate was broken or deformed. As the plastic content increases, the extrudates start to deform instead of breaking when subjected to large loads. It can be observed that the 10% plastic bound extrudates were the only extrudates that broke when a large load was exerted on them. Thus, there is a distinct difference between an extrudate that breaks and one that deforms. When an extrudate breaks into smaller particles, the particles generally present problems in industrial processes. On the other hand, extrudates which deform (flattened in the case of >10% plastic bound extrudates) do not break into smaller particles and can still be used in industrial processes. Massaro et al.[12] reported similar plastic deformation when the LDPE content of the fine coal briquettes was increased to 15%. The measured compressive strength results of the extrudates are indicated in Figure 4.

The wet extrudates have a compressive strength that has no noticeable difference from that of the dry extrudates (Figure 4). The wet and dry extrudates containing 10% plastic had an average compressive strength far exceeding the 350 kPa minimum proposed by Richards.[10] This can be attributed to the good water-resistant characteristics of both LDPE and PP. It can also be seen that the average extrudate containing 10% LDPE had greater compressive strength than that of the extrudates containing 10% PP. The average extrudate containing 10% LDPE had a compressive strength that exceeded the 14 MPa compressive strength of ROM coal of the same dimension (10 mm), as reported by Leokaoke et al.[40] The higher compressive strength of the extrudates containing LDPE when compared to PP can be attributed to the Barus effect during extrusion, which results in additional swelling of plastics due to the remaining elastic energy when heated.[41] LDPE has more elastic energy, and the swelling could increase pressure during the extrudate formation within the die. Once the LDPE leaves the die, it swells more than the PP illustrating the Barus effect (Figure 1).

To compare the compressive strength of the deformed extrudates to that of the minimum acceptable strength proposed by Richards[10] or to that of the ROM coal reported by Leokaoke et al.[40] would not be an adequate comparison since the deformed extrudates never broke under the load to form smaller pieces. Because these extrudates remained in one piece while being compressed, all these extrudates possess more than sufficient compressive strength to be used in industrial applications as feedstock. Furthermore, the deformation points for extrudates containing 100% plastic are much higher than that of the extrudates comprising of coal and plastic mixtures. This is due to the physical structure of the extrudates, that is, as the coal and plastic mixtures produce a much more rugged extrudate than the smooth extrudate produced by only plastic (Figure 1).

3.2.2. Water Absorbance. All the extrudates showed excellent water resistance by maintaining their integrity and

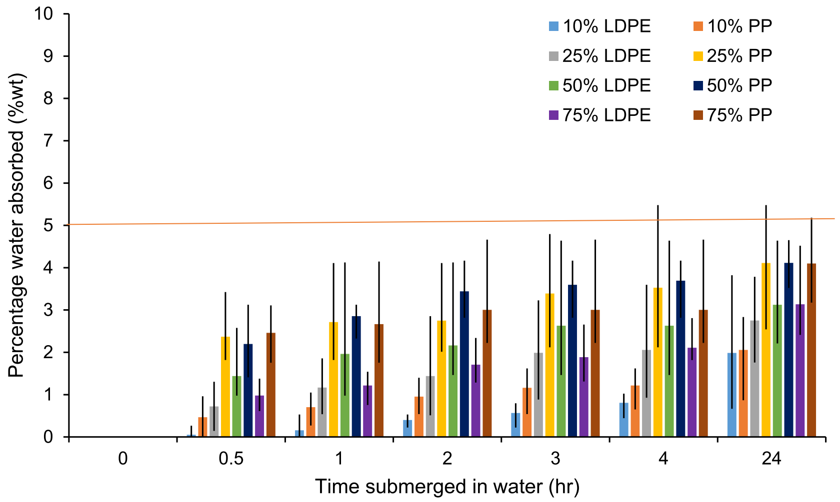


Figure 5. Water absorbance of extrudates.

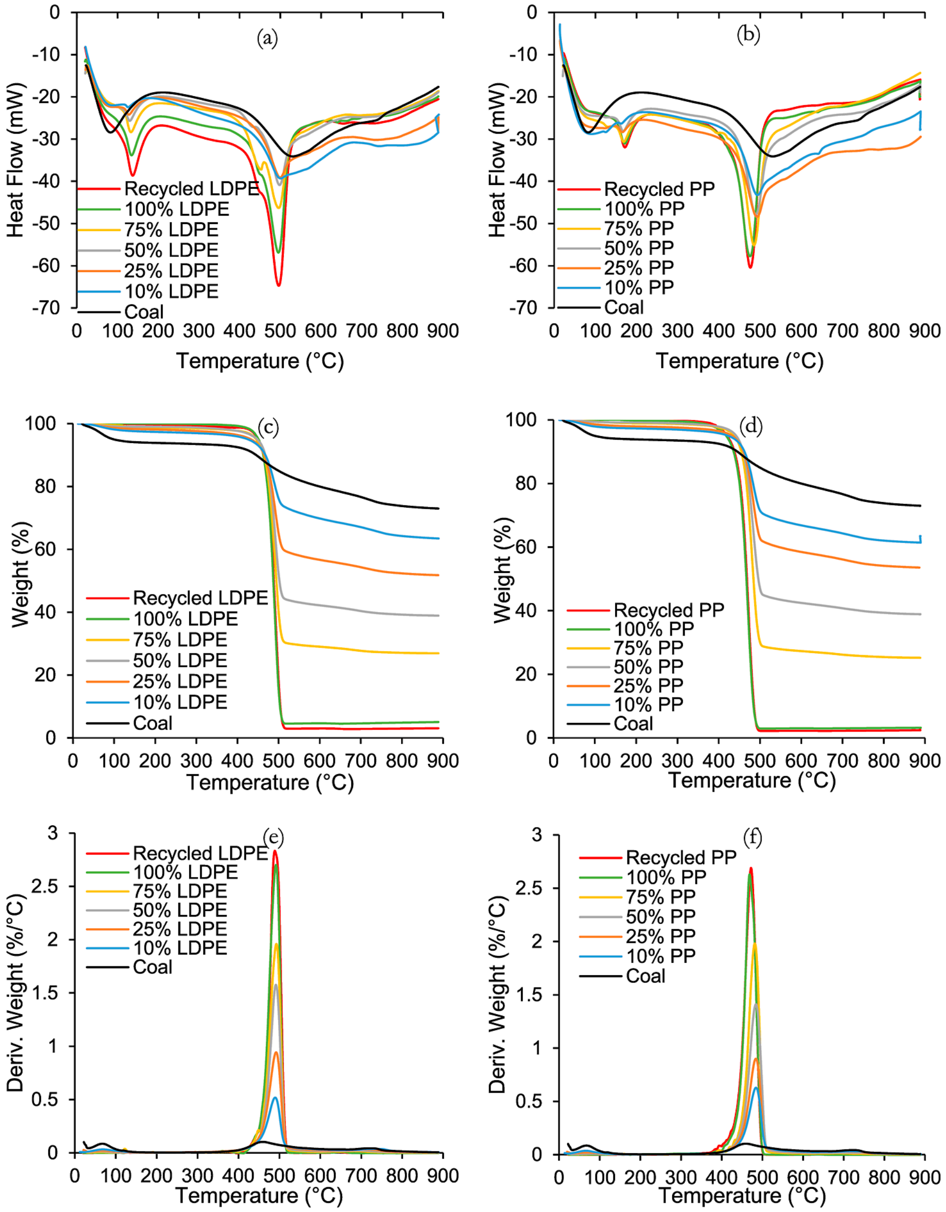


Figure 6. Heat flow (a,b), TGA (c,d), and DTG (e,f) of the LDPE and PP extrudates and the respective raw materials.

not disintegrating after 24 h of submersion (Table 3). The extrudates containing 25% and higher PP remained floating in water for 24 h, while only the extrudates containing 75 and 100% LDPE remained floating for the entire 24 h period. This is explained by the higher specific gravity of LDPE (0.94 g/cm^3) compared to PP (0.91 g/cm^3). The specific gravity was measured at Potch Plastic, and the values obtained correspond to previously reported values in literature.[42]

Figure 5 illustrates the percentage of water the submerged extrudates absorbed over 24 h.

Even after 24 h, the average water absorbance of all the extrudates tested remained under the absorbance limit of 5% wt specified for 30 min of submersion,[10] as indicated by the red line in Figure 5. The 100% plastic containing extrudates are not shown in Figure 5 since these extrudates absorbed no significant water as expected. For the remainder of the extrudates, the extrudates containing 10% LDPE absorbed the least amount of water (2.0% wt after 24 h) and was closely followed by the extrudate containing 10% PP (2.1% wt after 24 h). Generally, the 50% plastic-containing extrudates absorbed the most water due to the rugged surface of these extrudates, allowing more moisture to seep into cervices. The extrudate containing 50% PP had the highest absorbance of 4.1% wt water after 24 h. The extrudates having a smoother surface (100 and 10% plastic) absorbed the least amount of water. The LDPE extrudates absorbed slightly less water at all the various plastic concentrations when compared to PP.

3.2.3. Impact Resistance. None of the extrudates broke or shattered when dropped; therefore, all extrudates obtained a maximum IRI value of 600 and far surpassed the minimum IRI value of 50.[10] All the extrudates have a more than sufficient impact resistance to stay intact during conveyor belt transfers and other drops during handling.[10] The extrudates containing high concentrations of plastic (100, 75, and 50% plastic) did not even break when the extrudates were forcefully thrown onto the floor; however, the extrudates containing lower plastic concentrations (25 and 10% plastic) yielded very minor breakage as only small fractions broke off when forcefully thrown.

3.3. Pyrolysis. *3.3.1. Thermogravimetric Analysis.* Variation in heating rate influences the temperature at which decomposition occurs. As described in Uwaoma et al.,[30] a higher heating rate causes the initial, maximum, and final decomposition temperatures to slightly increase. Even though the decomposition temperatures are affected by the change in heating rate, the residual mass remains constant. This is expected when using a non-isothermal approach.[30] The DTG−TGA results using a heating rate of 20 °C/min is exemplary of the behavior of the results obtained at all the heating rates used in this study (10, 20, 30, and 40 °C/min). The mass loss and heat flow results of the samples using a heating rate of 20 °C/min are shown in Figure 6.

The first heat flow peak at 100 °C indicates the moisture within the samples being driven off (Figure 6a,b). The proximate analysis indicated that LDPE, PP, and the extrudates have a lower moisture content than the coal fines; therefore, the increase in weight loss observed at 100 °C as the plastic content decreases is expected (Figure 6c,d). The onset of degradation occurred around 325 °C for coal, whereas LDPE and PP had later onset temperatures but degraded within a narrower temperature range (Figure 6e,f). Since both plastics consist mostly of volatile matter, the total conversion increases as the weight concentration of plastic in the extrudates increases (Figure 6c,d). Therefore, the properties of fuel can be adapted to be used in various existing pyrolysis processes by altering the plastic content. The average pyrolysis parameters across the four different heating rates are illustrated in Table 4. Details of the influence of heating rate on the pyrolysis parameters is illustrated further in the Supporting Information.

Table 4. Pyrolysis Parameters[a]

	T_i (°C)	T_{max} (°C)	T_f (°C)	Rp (%/min)	Rv (%/min)	mass residue (%)
coal	327.7	457.7	765.3	0.10	0.04	78.29
LDPE	386.4	489.3	519.5	2.88	0.19	3.25
PP	353.9	468.9	505.0	2.66	0.22	1.88
10% LDPE	343.8	488.3	774.6	0.59	0.06	63.37
10% PP	331.4	483.4	777.9	0.50	0.07	66.45
25% LDPE	357.6	490.6	775.3	0.95	0.09	53.16
25% PP	345.1	481.9	772.7	0.88	0.09	55.21
50% LDPE	353.8	490.2	730.2	1.69	0.12	36.47
50% PP	348.8	479.8	777.6	1.58	0.11	37.66
75% LDPE	352.5	490.6	754.3	2.02	0.13	27.00
75% PP	347.6	478.7	771.7	1.95	0.13	27.94

[a] Table 4 presents the average onset temperature (T_i), maximum degradation temperature (T_{max}), final degradation temperature (T_f), maximum decomposition rate (Rp), and average decomposition rate (Rv).

It can be observed from Table 4 that the final degradation temperature of fine discarded coal occurs above 760 °C, whereas LDPE and PP have final degradation temperatures below 520 °C. This is in accordance with Zhou et al.,[25] who determined that 99% of LDPE decomposed between 426 and 526 °C and that 98% of PP decomposes between 399 and 507 °C. Das and Tiwari[29] found that the degradation onset and peak degradation temperatures of LDPE is higher than that of PP. The extrudates have a final degradation temperature c.a. 770 °C which can be attributed to the final degradation temperature of coal where mineral matter decomposition (carbonates)[43] and hydrogen abstraction occurs[44] since the plastics have decomposed at much lower temperatures.

The degradation of the coal and the plastics overlap, resulting in interactions between the degradation reactions of the coal and plastics within the extrudates. Synergy during the pyrolysis of blends of coal and plastic has been observed by various researchers[18,24,26,27,45,46] and is attributed to the free radicals from the coal that participate during the degradation reactions of plastics which then results in an acceleration in the degradation of coal.[27,45] The coal fines have a maximum degradation temperature (T_{max}) of 458 °C, and the LDPE had a T_{max} of 489 °C. The remaining extrudates containing LDPE had similar maximum degradation temperatures than for the pure LDPE. LDPE decomposes in a narrow temperature range (386−520 °C) and provides a much larger derivative mass loss peak than for coal; therefore, even a low LDPE content will cause the maximum decomposition temperature to be the same as that of LDPE (Figure 6e). Sharma et al.[18] found that the T_{max} of mixtures of coal and LDPE was slightly higher than that of the individual products; however, the study used ledo coal and LDPE with similar maximum degradation temperatures. In this study, Highveld medium rank C bituminous

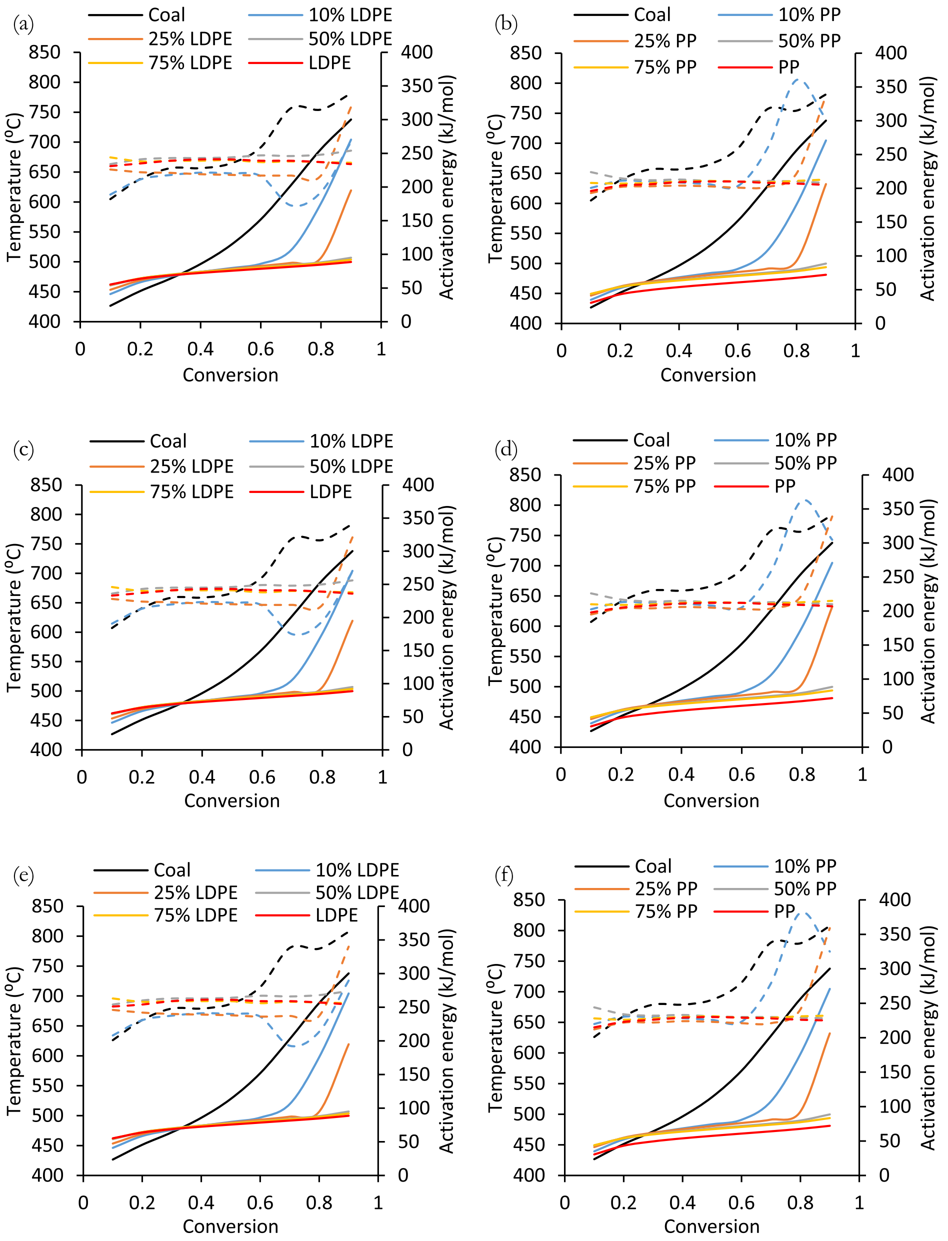


Figure 7. Temperature of conversion (solid line) and determined activation energy (dotted line) using the KAS (a,b), Starink (c,d), and FWO (e,f) methods.

discarded coal reported a lower maximum degradation temperature than for the LDPE (Table 4) which could explain why the resulting maximum degradation temperature of the mixture is similar to that of the LDPE and not higher.

Sharypov et al.[26] found that powder mixtures of coal and PP have maximum degradation temperatures close to that of PP. This study found that the extrudates have a maximum degradation temperature closer to PP than coal but is still higher than that obtained for both raw samples. The maximum degradation temperature of the 10% PP extrudate is the highest for the extrudates containing PP, and the maximum degradation temperature slightly decreases as the plastic content of the extrudates increases. The maximum degradation temperature of the extrudates is higher than that of the PP and coal samples separately; the right shift is visible in Figure 6f. This is an indication of synergy between coal and PP during the degradation of the extrudates.

As expected, coal has the highest residual mass, whereas plastics are almost completely devolatilized. This results in the coal having the lowest average decomposition rate (Rv) and lowest maximum decomposition rate (Rp). Therefore, the extrudates have increasing decomposition rates as the plastic concentration increases.

3.3.2. Kinetic Analysis. 3.3.2.1. Iso-Conversional Methods and Activation Energy. The KAS, Starink, and FWO methods were used to plot ln (β/T^2) against $1/T$, and the slope of the linear graph was used to calculate the activation energy. The activation energy at various degrees of conversion and the temperatures at which the conversion occurs for each of the samples are illustrated in Figure 7.

The tabled values for the conversion temperature, showing activation energy and the corresponding R^2 values can be found in the supporting document. All of the predicted activation energies had an R^2 value above 0.86. All three models showed similar values for the activation energies of all the samples with only slight deviation. The KAS method was found to predict the lowest activation energy values, whereas the FWO method predicted the highest values. Coal has the highest activation energy variance across all three modes (182−362 kJ/mol), whereas LDPE (231−261 kJ/mol) and PP (196−230 kJ/mol) have small variances as conversion increases. Using the same iso-conversional methods, Uwaoma et al.[30] reported a similar activation energy range for the float fraction of bituminous discarded Highveld coal that ranged from 182 to 316 kJ/mol for a conversion range between 20 and 90%. These methods were also used by Das and Tiwari,[29] confirming that both plastics have only a slight increase in activation energy and that PP (136−173 kJ/mol) has a lower activation energy than LDPE (148−242 kJ/mol). Selecting the best model from the three used in this study is difficult since complex reaction mechanisms occur simultaneously during degradation.[29]

As the conversion increases, the activation energy required for the coal sample increases, Uwaoma et al.[30] also observed an increase in activation energy as conversion increased. The activation energy for the plastics remains relatively constant and only slightly increases as conversion increases are observed (not significant). The extrudates containing both LDPE and PP exhibit similar activation energies to that of their respective plastics; however, at higher conversions the activation energy of the extrudates containing a lower plastic content starts to vary. The 10 and 25% PP bound extrudates deviate from the almost constant activation energy found for the PP, that is, around 60 and 80% conversion, respectively. Both of these extrudates show an increase in activation energy which shifts closer to that of the coal. This also includes an increase in the conversion temperature above the final degradation temperature of the PP (505 °C). Therefore, the increase in activation energy can possibly be attributed to the remaining fine coal fraction of the extrudates once the PP has completely decomposed. The 50 and 75% PP containing extrudates do not show an increase in activation energy up to 90% conversion since the decreasing coal content results in the coal only having a negligible effect on the overall conversion. This is especially prominent since the coal only has 27% weight loss during degradation, while LDPE and PP have 97 and 98% weight loss, respectively (Figure 6c,d). An increase in activation energy for the 50 and 75% PP-containing extrudates would, therefore, only be observed between 90 and 100% conversion. The lack of an increase in the activation energy at higher concentrations of PP further confirms that the increase is caused by the remaining coal char fraction.

The 10 and 25% LDPE containing extrudates also deviate from the almost constant activation energy reported for LDPE; however, the activation energy of the 10% LDPE bound extrudates does not directly increase as for the 25% LDPE containing extrudates. The multiple complex reactions in which chemical bonds are broken during pyrolysis can cause the activation energy to fluctuate as different reaction mechanisms are used.[18] The deviance also occurs around 60 and 80% conversion, respectively, and happens between 490 and 520 °C, once again at the final degradation temperature of the LDPE (520 °C). The rest of the extrudates follow the same trend as the 25% PP containing extrudate, but due to the low coal content, the increase in activation energy only occurs above 90% conversion.

In the temperature ranges where the degradation of the coal and the plastics overlap, the activation energy of the extrudates resembles that of the plastic and is not as high as that of the coal. This occurs for all the extrudates indicating that even a low plastic content can decrease activation energy and conversion temperature that would not occur if there was no synergy between the coal and the plastics. This results in the average activation energy of the extrudates being similar to that of the plastics, and it remains similar to the plastics even when the coal content increases. Miranda et al.[47] and Melendi-Espina et al.[24] reported that a blend of polymers would cause a decrease in the activation energy of the more stable polymers due to a transfer of hydrogen (free radicals) from the more stable polymers to the less stable polymers. The transfer of free radicals from the coal to the plastic during degradation has been reported as the reason for the observed synergy between the coal and plastics.[27,45,48] Therefore, since coal has a higher activation energy, it can fulfil the role of the more stable component when mixed with plastics. Thus, during degradation, the transfer of free radicals from the coal to the plastics can cause the activation energy to be lower than expected and similar to that of the plastics rather than that of the coal. The lower activation energy results in a lower conversion temperature for the extrudates. Therefore, the synergy between the coal and plastic results in a degradation reaction that requires less activation energy than it would require if the coal and plastics were individually degraded. Hong et al.[45] also concluded that coal and PE blends have a lower activation energy than the individual materials.

4. CONCLUDING REMARKS

In this study, recycled waste plastics (LDPE and PP) were used as binders together with discarded coal fines in producing extrudates having high mechanical strength, hydrophobicity, and high heating value. Both LDPE and PP served as excellent binders to extrude coal fines. Moisture, ash, and sulfur content increased as the plastic content decreased. The increase in plastic content led to an increase in properties such as the ratio of hydrogen to carbon, volatile matter, and calorific value. The 10% LDPE extrudate had the highest average compressive strength (dry = 17.5 MPa and wet = 18.0 MPa). All extrudates having a plastic content higher than 10% did not break but were merely deformed. All the extrudates maintained their integrity after being submerged in water for 24 h. After 24 h, the 50% PP bound extrudates absorbed the most water (4.1% wt), and the extrudates containing 10% LDPE absorbed the least (2.0% wt). All the produced extrudates have sufficient mechanical strength and water resistance to be used industrially. Depending on which properties are required during utilization of the extrudates, the binder addition can be varied to significantly alter properties such as calorific value and volatile matter content. By incorporating recycled plastics, the coal fines were valorized into valuable extrudates. If the recycled plastics could be replaced with waste plastics, two waste streams would be reduced simultaneously to produce a new valuable fuel source.

The TGA results further demonstrated that both LDPE and PP have synergic interactions when pyrolyzed with fine discarded coal. In addition, the synergy between coal fines and plastics was found to be prevalent across all ratios of mixtures. The extrudates containing PP had an increase in maximum degradation temperature compared to the PP and coal, respectively, indicating synergy between the two materials. Even with this increase in maximum degradation temperature, the iso-conversional methods found that the activation energies of all the extrudates were similar to that of the plastics, and only increased when above the final degradation temperature of the plastics. Furthermore, the average activation energy of the extrudates resembled that of the plastics and is lower than that of the coal. The decrease in activation energy and conversion temperature demonstrates the synergy obtained between coal and LDPE and coal and PP and could be attributed to free radical transfer from the coal. Since the decomposition of both LDPE and PP overlap with that of the coal fines, the use of waste plastics to improve the calorific value of coal during pyrolysis can be considered based on the findings reported in this study. The extrudate pyrolysis product yield and composition as well as the steam gasification reactivity of the derived chars will be reported in future papers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c00514.

> MFI, influence of heating rate on pyrolysis parameters, conversion temperatures, activation energies, and R^2 values (PDF)

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Notes

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