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Insights into the carbon structure, thermal properties and environmental friendliness of composites produced using coal tar pitch and dimethylpolysiloxane as binders for coal waste

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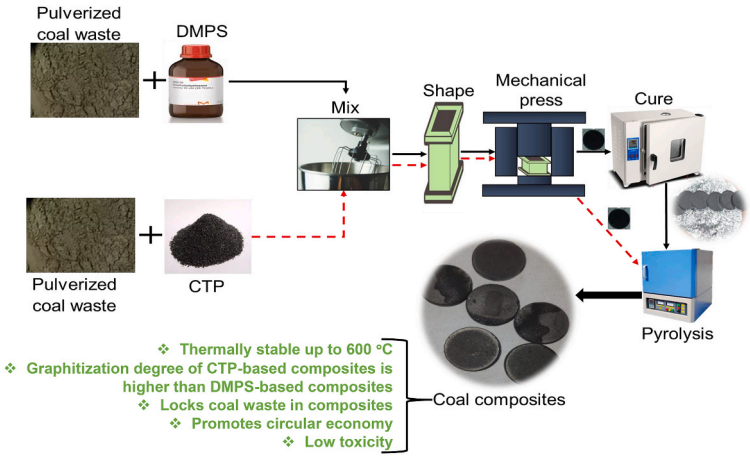
HIGHLIGHTS

- The composites are thermally stable up to 600 °C, beyond which they degrade rapidly.
- Metal ion contaminants in the composites were below the low-risk threshold, except for manganese.
- Dimethylpolysiloxane (DMPS) composites exhibited higher corrosion rates compared to coal tar pitch (CTP) composites.
- CTP is a more effective binder than DMPS for producing composite building materials that may serve as sinks for coal waste.

GRAPHICAL ABSTRACT



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ABSTRACT

This study introduces modified coal tar pitch (CTP) and dimethylpolysiloxane (DMPS) polymer as resins for the fixation of carbon-containing wastes into value-added composites. Secondary heat treatment of coal tar at 400 °C with a residence time of 9 h using the air-blowing pretreatment method yielded CTP with a hydrogen-to-carbon ratio of 0.4 and total carbon content (77 %–95 %). The effects of blending coal tar pitch to coal waste regarding the carbon structure, thermal stability, flame ablation rates, corrosion resistance, and leaching potential of coal composites were systematically investigated. The CTP-based composites have more ordered carbon structures compared to the DMPS-based composites. The composites are thermally stable up to 600 °C, beyond which they degrade rapidly. Composites containing 10 % CTP recorded the lowest linear and mass ablation rates. Interestingly, DMPS-based composites recorded higher corrosion rates compared to CTP-based composites. Finally, metal ion contaminants in the composites were below the low-risk threshold, suggesting these wastes can be

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bound in the composites in that they pose minimal environmental risks. Overall, the CTP binder is better than DMPS for producing composite materials that may serve as carbon sinks for coal waste. The combination of high thermal stability, low resistance to corrosion, low ablation rates, and low susceptibility to leaching suggests that the composites could be shaped into building materials such as tiles or pavers.

1. Introduction

Coal tar pitch (CTP), a by-product of the coke oven, is a locally available and low-cost carbonaceous precursor that attracts the attention of researchers for developing products such as carbon foams, carbon composites, carbon fibers, and other novel applications [1–4]. CTP has been used to prepare graphite anodes for lithium-ion battery [5] and porous carbon materials for supercapacitor electrode (Y. [6]). Due to its high volatile matter content and non-carbonaceous organic impurities, CTP is modified using different techniques to meet requirements. For example, Yu et al. [4] used the gradient selectivity separation technique under optimal conditions of 420 °C/1 h to obtain CTPs with suitable chemical compositions to produce carbon foams with good thermal insulation and oxidation resistance. Liu et al. [3] initially oxidized CTP into a high softening point pitch (HSPP) then regulated the HSPP by vacuuming at 380–420 °C/10 kPa/2 h to produce carbon foam with excellent performance. Huang et al. [7] preoxidized the pitch to suppress the violent expansion of synthetic mesophase pitch and to transform it from a thermoplastic material to a thermosetting material while achieving the formation of crosslinking sites consisting of oxygen functional groups. The results demonstrated that the pre-oxidized pitch reduced the ablation rates of the modified polymer-based matrix and their fiber-reinforced composites compared to their counterparts.

One of the largest markets for functional composite is building materials. These materials can serve as carbon sinks if produced from coal waste rather than virgin resources. Raw coal combined with preceramic polymer, was utilized to produce composite building materials [8]. The composites were produced via curing and pyrolysis of the coal/-preceramic polymer blend under an inert atmosphere, yielding products characterized as lightweight, sufficient strength, thermally stable, fire resistant, and chemical resistant, among others. Coal/polymer composites utilizing coal particulates and polymer materials have been studied and targeted for building applications, thus generating value-added products from coal-related materials [9–15]. Polydimethylsiloxane (DMPS), a silicone-containing organic polymeric widely explored in functional materials and composites, has many interesting properties [16,17]: flame retardance, water repellency, and oxidation resistance. However, only one study has explored its potential as a binder for coal waste in the fabrication of ceramic composites, which demonstrated mechanical and physical properties suitable for building applications [18]. The authors recommended conducting flame ablation tests, metal ion leaching, and thermal stability to verify the suitability of these composites.

Leveraging CTP or DMPS as a binder for carbon waste particles is a resource-recovery opportunity. Also, given the abundance of CTP and coal waste, developing a strategy for their transformation into a new material with substantial market demand is highly significant. Coal/CTP composites are compared to coal/DMPS composites to assess the effect of each binder on the final structure and properties of the coal composites. Therefore, the first objective of this paper was to prepare CTP from coal tar modified using air-blown treatment under these conditions: 1 MPa, 350–450 °C, and airflow of 16 ml/s for 3, 6, and 9 h. The effects of air-blowing on the CTP composition and structure were monitored by proximate analysis, elemental analysis, aromatic ratio, H:C ratio, and the number of atomic C rings. The second objective was to systematically study the effects of pyrolyzing CTP/coal waste and DMPS/coal waste blend to coal waste loading on the composites' carbon structure, thermal stability, and ablation properties. Also, some reuse and recycling measures may cause new and serious environmental problems. Hence, the composites' environmental friendliness (leaching behavior) was performed on the crushed pyrolyzed composites to provide a comprehensive understanding of a material's leaching characteristics. The leaching test is performed considering a second-life scenario where shaped composites are discarded or recycled as granulates (non-shaped composites). Exploring ways to increase the valorization potential of coal-related wastes into products with the desired properties rather than energy mitigates their long-term environmental impact. And achieves decarbonization goals since the process traps the fixed carbon in the products. Consequently, coal waste volume footprint will be significantly diminished, crucial resources will be conserved, energy demand will be minimized and fewer greenhouse gases will be emitted.

2. Materials and method

2.1. Raw materials and processing of coal tar to coal tar pitch

GG1 and GS coal waste with ash content of 81.26 % and 61.65 % were utilized alongside coal tar pitch (CTP) and dimethylpolysiloxane (DMPS) as binders. DMPS (molecular weight ~9430 g/mol) (Sigma Aldrich South Africa (Pty) Ltd) is a type of silicone polymer that contains a silicon atom bonded to two oxygen atoms in its backbone including two methyl groups attached to the silicon atoms (Fig. 1). The crude tar used in this study is a by-product of a metallurgical coking coal plant in South Africa. Coal tar was modified in a 2-L cylindrical stainless-steel reactor using the air-blowing pretreatment method to produce CTP. The reactor is equipped with inlet and outlet valves, a controller, a heating jacket, and a pressure gauge for monitoring. 200 g of coal tar was heated at a constant rate of 3 °C/min to predetermined temperatures of 350 °C, 400 °C, and 450 °C. Upon reaching the target temperature, air was blown into the reactor at a constant flow rate of 16 ml/s for 3, 6, and 9 h, maintaining a constant pressure of 1 MPa. Inlet and outlet valves were operated to allow air into the reactor and discharge volatile matter during air-blowing. After cooling to room temperature, the reactor vessel was emptied, and the product (CTP) was weighed for mass loss and placed in a clean container. Proximate analysis, elemental analysis, aromatic ratio, H:C ratio, and the number of atomic C rings were used as key structural indicators to assess changes caused by the pretreatment and polymerization of coal tar.

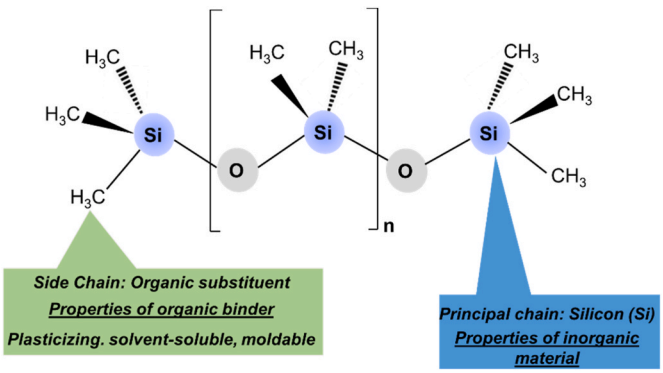

Fig. 1. Chemical structure of polydimethylsiloxane.

2.2. Preparation of composite test specimens

To explore the application of the prepared CTP and DMPS binders, formulations were made for each composite with a range of weight loadings of coal waste and binders as illustrated in Fig. 2. The blend ratio of DMPS and coal waste was kept constant at 20 and 80 wt%, as this ratio maintained a moldable mixture with the coal waste. Above the reported amount of DMPS (20 %) resulted in a watery and fluid mixture with unmoldable properties (difficulty in shaping). On the other hand, CTP is a solid binder and its ratio to coal waste was varied to study the effect on the composite properties. A total blend of 2.0 g of coal waste and CTP (−53 μm) were homogeneously mixed mechanically and compacted into square and circular molds with a hydraulic press to obtain green composites. Subsequently, the thermal stability of the molded composites was evaluated to provide crucial information regarding the temperature necessary for pyrolysis. The DMPS-based composites underwent curing in an oven at 150 °C for 1 h. The main purpose of this step is to crosslink/stabilize DPMS chains to a structure that can withstand high-temperature heating processing. The green body composites were then subjected to pyrolysis in an airtight furnace under an argon environment, using a heating rate of 5 °C/min from 25 °C to 600 °C, and held for 5 h. Fig. 3 illustrates the production process showing the digital images of the produced coal composites.

2.3. Raw materials and composites characterization

The produced CTP samples were exposed to an open atmosphere to remove excess moisture, crushed, screened, and divided using a rotary divider to obtain representative samples of sizes −53 and −212 μm (μm). Proximate analysis was conducted using a Leco thermogravimetric analyzer 701 following ASTM D-5142 standard and a 1.0 g sample was placed in a crucible for this analysis. Fixed carbon content was determined as the difference between the sum of other parameters (ash content + inherent moisture content + volatile matter) and 100 %. Ultimate analysis was carried out using the Leco CHN 628 with a 0.25 g sample analyzed for carbon, hydrogen, and nitrogen according to ASTM D 5373–14:2015 standards. Total sulfur was determined following ISO 19579:2006. Raman spectroscopy (Horiba LabRAM HR Raman spectrometer equipped with an Olympus BX41 microscope) was employed to study the microcrystalline carbon structure, including the degree of disordering and graphitization. Raman spectra were excited by a linear polarized Ar^{+} laser at λ = 514.5 nm of the Lexel™ 95 SHG laser system and data were collected using LabSpec v.5 software. The thermogravimetric analyzer was used to analyze the weight loss, thermal stability, and optimal pyrolysis temperature. Approximately 1.0 g of coal composite sample was heated under nitrogen and air atmospheres for the above thermal analyses from 25 to 950 °C, with a heating rate of 10 °C/min and a residence time of 5 h. A butane oxyacetylene torch was utilized as the heat source to generate a high-temperature flame to assess the burning/ablation performance of the composites [19]. The torch was kept at a distance of 2 cm far from the surface of the composites. Three

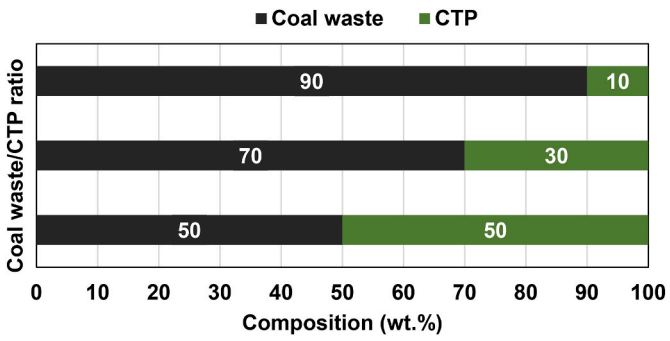

Fig. 2. Blending ratios of coal waste with different CTP loadings.

specimens (ø30 × 10 mm) each were exposed to the flames for varying durations (10, 20, 30, and 40 s) at their centers to increase the statistical confidence in the results. Subsequently, common metrics for ablative performance measurement such as the mass loss, the linear ablation rate (LAR, mm/s), mass ablation rate (MAR, g/s), and percentage mass loss (PML, %) were calculated using standard mathematical equations Equations (1)–(3).

$$LAR = \frac{d_1 - d_2}{t} \quad \text{Equation 1}$$

$$MAR = \frac{m_1 - m_2}{t} \quad \text{Equation 2}$$

$$PML = \frac{(m_1 - m_2) \times 100}{m_1} \quad \text{Equation 3}$$

where d_1, d_2 are the thickness (mm) and m_1, m_2 are the mass (g) of the specimens before and after flame exposure, and t is the duration (s) of the flame ablation process. To estimate the corrosion rate of the samples, hydrochloric acid was added dropwise to a beaker containing a mixture of 3.5 % concentration sodium chloride solution, hydrochloric acid, and distilled water, to obtain a pH of 3.7. Subsequently, the composites were immersed but suspended in the solution, with the beakers securely covered in glad wrap to prevent evaporation. Allowing ample time for the samples to interact with the solution, they were left undisturbed in the beakers for seven days. After which, the coal composite samples were gently removed from the beakers. The weight of each specimen was recorded before and after immersion to obtain weight loss and the corrosion rate was calculated using Equation (4).

$$C_{pr} = \frac{87.6\Delta W}{\rho A t} \quad \text{Equation 4}$$

where C_{pr} is the corrosion rate (micrometer per year: μmy^{-1} or μmpy), Δ W is the weight loss (mg), ρ is the density of the composite ($g.cm^{-3}$), A is the surface area (cm^2), and t is the time (year).

Considering a second-life scenario, the environmental performance tests of the pyrolyzed composites (ground particles) were performed to evaluate their environmental friendliness, wherein the shaped composites are demolished or recycled as granulates (non-shaped composites). Extraction fluids of pH 2.9, 5.0, and 9.2 were prepared according to Ref. [20], Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1992) and Kurmus & Mohajerani [21]. The extraction fluid was added to grounded composites to the required solid-to-liquid ratio of 1:20, equivalent to 10 g composite and 200 mL liquid. Screw bottles containing the mixture were then placed on a roller mixer rotating at 30 rpm for 18 h. Upon completion of the leaching process, the slurry was filtered using a 0.45 μm syringe to separate solids from the solution. Subsequently, the extracts containing the cumulative release of metal ions were then analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) to determine their concentration - chromium (Cr), copper (Cu), silver (Ag), barium (Ba), mercury (Hg), selenium (Se), nickel (Ni), cadmium (Cd), arsenic (As), lead (Pb), and zinc (Zn). The obtained results were compared to the regulatory limits of the leachable concentration threshold (LCT) outlined in the South African National Environmental Management: Waste Act NEMWA 59 of 2008 [22].

3. Results and discussions

3.1. Analysis of the composition of coal tar coal wastes and tailored CTPs

The particle size distribution analysis revealed that the pulverized CTP, GG1, and GS coal wastes contain 49.73 %, 92.73 %, and 76.67 % respectively, passing through a −75 μm sieve. Table 1 summarizes the proximate and ultimate results of the coal wastes, coal tar, and CTP produced at various temperatures. GG1 and GS exhibited the highest ash content at 81.26 % and 61.65 %, respectively, in contrast to the lower

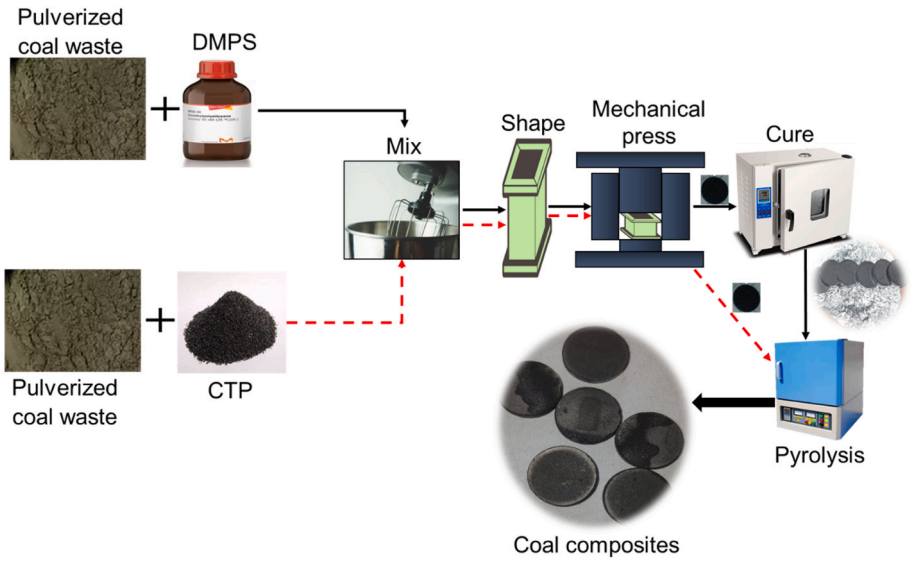

Fig. 3. Schematic showing the production of coal composites.

Table 1
Proximate and ultimate analysis of the coal wastes, coal tar, and coal tar pitches.

Parameters	GG1	GS	CT	CTP							
				350 °C 3h	350 °C 6h	350 °C 9h	400 °C 3h	400 °C 6h	400 °C 9h	450 °C 3h	450 °C 6h
Proximate analysis (%); ad											
Inherent moisture	3.28	1.71	25.3	0.4	0.24	0.33	0.33	1.07	0.56	0.72	0.58
Volatile matter	10	20.37	48.2	28.68	26.04	22.66	22.27	16.56	11.27	12.02	11.13
Ash	81.26	61.65	0.21	0.28	0.24	0.33	0.29	0.83	0.49	0.55	0.49
Fixed carbon	5.44	16.27	26.3	70.64	73.48	76.68	77.1	81.54	87.68	86.71	87.8
Ultimate analysis (%)											
Nitrogen (N)	0.18	0.63	-	0.91	1.17	1	0.83	0.88	0.94	0.9	1.05
Total carbon (C)	8.79	23.77	-	77.41	88	89.78	95.06	73.74	96.01	88.58	96.92
Hydrogen (H)	1.44	1.74	-	3.54	3.48	3.33	3.5	3.11	2.05	3.01	2.02
Total sulfur (S)	0.21	2.48	-	0	0	1.02	1	1.03	0.01	0.96	0.01
Oxygen (O)	4.84	8.02	-	18.14	7.35	4.87	0.11	21.24	1.95	5.96	0.01
Ratio											
H:C	1.95	0.87	-	0.54	0.47	0.44	0.44	0.50	0.25	0.40	0.24
f_a	0.6	0.66	-	0.88	0.81	0.83	0.78	1.07	0.88	0.95	0.88
$(R/C)_u$	-	0.23	-	0.29	0.36	0.37	0.39	0.21	0.43	0.32	0.44

ad: air-dried; CT: as received coal tar; CTP: coal tar pitch; f_a: aromatic ratio; FC: fixed carbon; $(R/C)_u$: Kasttners' equation to represent the number of rings of atomic C in the monomer; H:C: hydrogen to total carbon ratio.

ash content in coal tar (0.21 %) and the CTP samples (0.24 %–0.83 %). The volatile matter of the as-received coal tar at 48.20 % diminished to 11.13 % at heat treatment of 450 °C/6 h, reflecting the removal of low boiling points and low molecular weight components. The fixed carbon content of the raw coal tar (26.3 %) increased at heat treatment of 400 °C (6 h and 9 h) and 450 °C (3 h and 6 h) to yield CTP of fixed carbon in the range of 81.54 %–87.8 %. This increase is due to the removal of volatile components coupled with condensation and polymerization reactions to form larger, carbon-rich aromatic compounds [1,4]. The H:C ratio of the samples, aromatic ratio (f_a), and the number of atomic C rings $(R/C)_u$ were calculated using Equations (5) and (6). Notably, the pitch produced at 400 °C/9 h and 450 °C/6 h, displayed the lowest H:C ratio among all samples, accompanied by the highest $(R/C)_u$ value. This decline in the H:C ratio signifies the release of aliphatic hydrogen from the structure via the dehydrogenative polymerization reaction of tar components [1,23]. Considering their high carbon yield, mesophase structures may have developed in pitches produced by tar air-blowing at 400 °C/9 h and 450 °C/6 h, respectively [24,25]. Hence, are favored as binders for composite fabrication. However, high temperature has a direct impact on composite processing cost, therefore, the optimal conditions for obtaining appropriate pitch precursor for coal composite development were determined to be 400 °C with a residence time of 9 h.

$$f_a = (100 - V_{d.a.f}) \times \frac{0.9677}{C} \quad \text{Equation 5}$$

$$(R/C)_u = 1 - \frac{f_a}{2} - \frac{\left(\frac{H}{C}\right)}{2} \quad \text{Equation 6}$$

where f_a is the aromatic ratio, C is the total carbon content, $V_{d.a.f}$ is the volatile matters on a dry ash-free basis; $(R/C)_u$ is Kasttners' equation to represent the number of rings of atomic C in the monomer, and $H:C$ is the hydrogen to total carbon ratio.

3.2. Raman spectroscopy analysis/graphitization of coal wastes, CTP, and composites

Pyrolysis decomposes the coal wastes, pitch, and DMPS to form a rigid composite, thereby inducing a new carbon structure. On this basis, Raman spectroscopy was used to examine the graphitization degree of the carbon structure of the composites based on their intensity ratio i.e. the ratio of the disordered to graphitized peaks (I_D/I_G). The crystallite size (L_a) representing the in-plane crystallite size of graphitic carbon (nm) was calculated using Equation (7). The Raman spectra in Fig. 4 show the presence of the D band (a structural disorder in the graphitic structure, 1340-1350 cm^{-1}), G band (crystalline graphite, 1580-1590 cm^{-1}), and D + G band consistent with other scientific reports of carbon-based materials. Although GS has a higher total carbon content than GG1 (Table 1), the spectra (Fig. 4) show that GS is less graphitized than GG1.

$$L_a = 4.4\left(\frac{I_D}{I_G}\right)^{-1} \quad \text{Equation 7}$$

I_D/I_G ratios of DMPS-based composites were higher than CTP-based composites (Fig. 5). The lower I_D/I_G ratios of CTP-based composites suggest a low level of defects or a high degree of graphitization of the carbon phase i.e., bigger sp^2 carbon clusters. A liquid crystalline phase (mesophase) with a pre-graphitic structure may have been formed during the coal tar modification process. Therefore, the growth and coalescence of the mesophase upon heat treatment of the composites at elevated temperatures would further facilitate the graphitization of the composite [26]. The DMPS resin, on the other hand, does not undergo such a fluid phase upon pyrolysis with the coal waste. Consequently, the composites displayed a more disordered, less graphitizable microstructure.

3.3. Thermogravimetric analysis of CTP, green bodies, and pyrolyzed composites

Thermogravimetric analysis (TGA) was performed to identify the suitable temperature for pyrolyzing green composites in an inert atmosphere by estimating the temperature at which a rapid decrease in weight occurs. As seen in Fig. 6a, there is no significant weight loss up to 500 °C and the residual mass around 600 °C is more than 75 %. Hence, 600 °C was selected as the pyrolysis temperature for all the composites to conserve energy. Notably, the pure CTP (100 %) binder lacks thermal stability beyond 600 °C due to the release of light gases and the elimination of low molecular components above this temperature, thereby causing a rapid decrease in weight loss. Also, the incorporation of CTP did not delay the onset of degradation of the green bodies, except for the amount of the final residue. Generally, GG1/CTP and GG1/DMPS green composites exhibit better stability than GS/CTP and GS/DMPS green composites. This suggests a stronger chemical interaction between GG1 particles and the binders during pyrolysis.

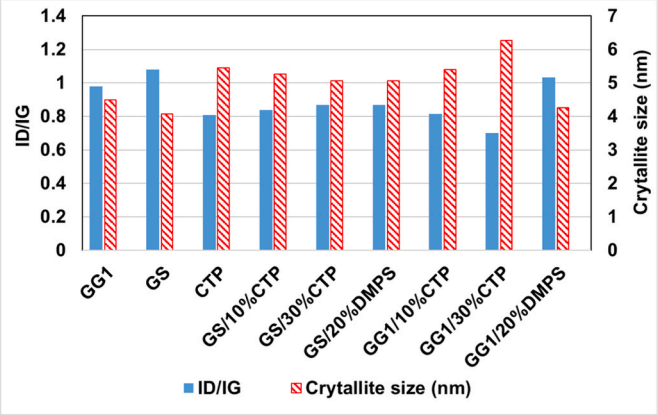

Fig. 5. The I_D/I_G ratio and crystallite size for GG1 and GS coal waste, CTP, and the composites.

Subsequently, the thermal decomposition of the pyrolyzed coal composites in air atmospheres (thermal oxidation) employing a heating rate of 10 °C/min from 25 to 950 °C is depicted in Fig. 6b. Notably, GS/10 % CTP composite degraded rapidly above 600 °C. This means that the carbon layer strength is weak and oxygen molecules can easily penetrate the composite matrix. The residual mass data of the green bodies and the coal composites following heating in nitrogen (green composites) and air atmospheres (produced composites) is presented in Table 2. In particular, the DMPS-based composite (GG1/20%DMPS) emerged as the most thermally stable composite, with a residual mass of 92.53 %. This composite recorded low fixed carbon content (4.68 %) available for combustion reactions and may contain stable Si–O and Si–C chemical bonds in contrast to the C–C bond in the CTP-based composites[27,28]. Thermally stable composites imply efficient thermal endurance and are generally more desirable since they inhibit heat transfer into the composite matrix. This property is advantageous for the performance of the composite as a building material. However, investigations into the burning characteristics and physical properties after exposure to an oxidizing thermal environment would be necessary to provide more information.

3.4. Flame ablation performance

The composites' ablation performance (linear and mass ablation rates) was measured using the butane blow torch (Fig. 7). The linear ablation rate (LAR) provided insight into the change in thickness (mm) of the composites over exposure time (Fig. 8). The LARs of GS and GG1/

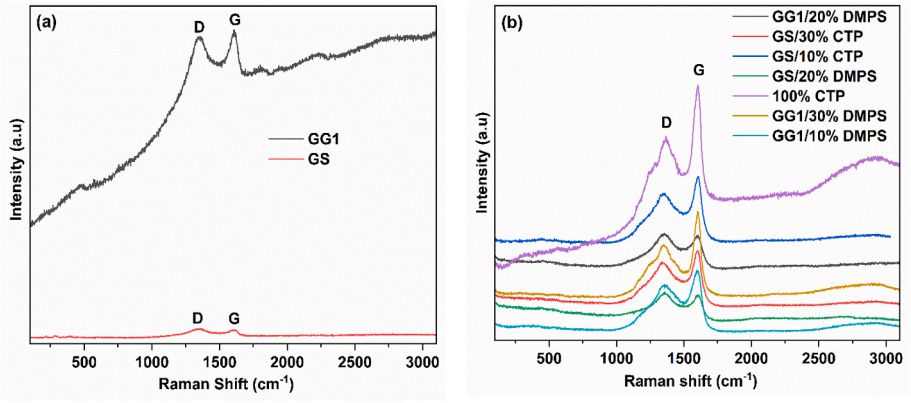

Fig. 4. Raman spectroscopy for (a) GG1 and GS coal waste (b) coal tar pitch and coal composites.

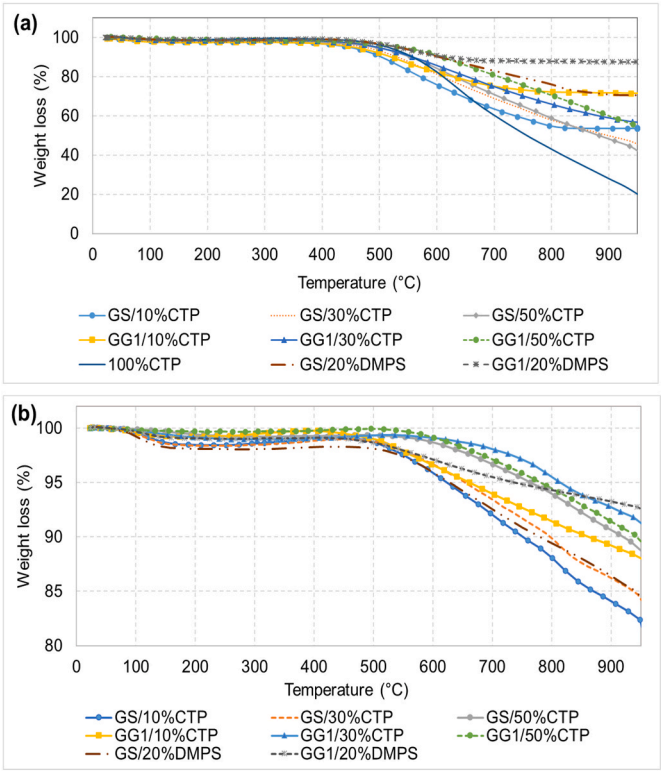

Fig. 6. Thermogravimetric analysis of (a) green bodies in a nitrogen atmosphere and (b) composites in an air atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Residual mass after thermogravimetric analysis.

Samples	Residual mass (%)	
	Green bodies	Composites
100 % CTP	4.00	–
GS/10%CTP	53.66	70.06
GS/30%CTP	42.58	84.19
GS/50%CTP	32.26	88.74
GG1/10%CTP	71.39	88.01
GG1/30%CTP	56.66	91.23
GG1/50%CTP	42.57	89.51
GS/20%DMPS	70.42	84.29
GG1/20%DMPS	87.39	92.53

CTP: coal tar pitch; GS, GG1: coal waste; DMPS: dimethylpolysiloxane.

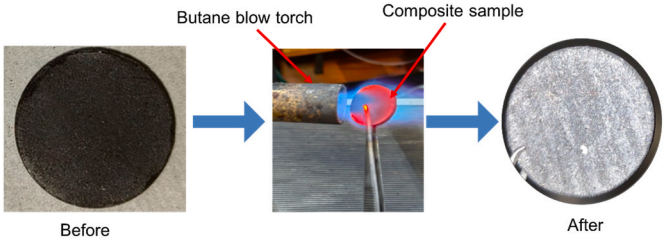

Fig. 7. Flame resistance demonstration of the composite showing surface morphology before and after ablation showing no dripping or shape deformation.

CTP-based composites increased significantly from 10 to 20 s as the content of CTP increased, then decreased critically post-20 s exposure time. Subsequently, the ablative process tends to reach a steady state

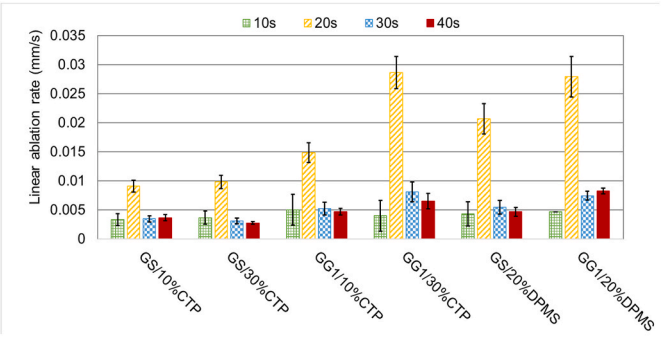

Fig. 8. Linear ablation rate of the coal composites under different duration times.

with a constant linear ablation rate. GS/CTP composites exhibited better resistance to substantial thickness changes when attacked by heat and oxygen compared with the GG1/CTP composites.

The results further show GS/30%CTP and GG1/20%DPMS composites present the worst mass loss (%) during ablation testing (Table 3). Fig. 9 presents the mass ablation rate (MAR) of all the composites, indicating MARs increase as the content of CTP increases, with GS/20% DPMS displaying the least MARs. A low MAR suggests a slower rate of mass change of the composites over time. It is noteworthy that the MARs for all produced composites remained below 0.008 g/s and are comparable to carbon-bonded composites reported in the literature [19]. GS/10%CTP composite recorded the least MAR and LAR, implying this composite can withstand the influx of high heat and would not easily ignite or burn out.

The decline in ablation rates after 20 s of exposure time to the invasion of heat and oxygen suggests that a char-like layer/film could have formed during the first 20 s of the test. It can be inferred that the molecular chains of the carbon layer on the surface at this period rapidly decompose and carbonized to form a passivating carbon layer or closed carbon layer structure resistant to the butane acetylene torch flame. The appearance of a whitish ablated/eroded surface of the post-ablating specimen (Fig. 7) may be related to the thermal decomposition of the binder or the oxidation reaction of carbonaceous compounds. The structural integrity of the composites after burning at higher temperatures and longer time should be checked to ensure they are safe during fire hazards.

3.5. Corrosion resistance evaluation

A key attribute of composites is their ability to withstand conditions of chemical attacks through corrosion as this could contribute to composite failure, either directly or indirectly. The corrosion resistance and durability of the composites were measured based on their corrosion rates. These rates reflect how swiftly composite degradation could occur due to chemical reactions upon exposure to corrosive environments. For this study, the composites were subjected to short-term laboratory tests by exposing them to an acid solution for seven days. As depicted in Fig. 10, GS-based composites corroded faster than GG1-based composites. An increase in CTP content increased the corrosion rate of the

Table 3
Mass loss (%) results for composite under different duration times of ablation testing.

Composite	10 s	20 s	30 s	40 s
GS/10%CTP	0.367	1.149	2.137	2.807
GS/30%CTP	3.856	4.026	4.037	7.306
GG1/10%CTP	0.993	1.546	1.942	3.102
GG1/30%CTP	0.928	1.554	2.191	2.789
GS/20%DPMS	0.893	1.637	1.999	2.804
GG1/20%DPMS	5.861	6.469	6.892	13.922

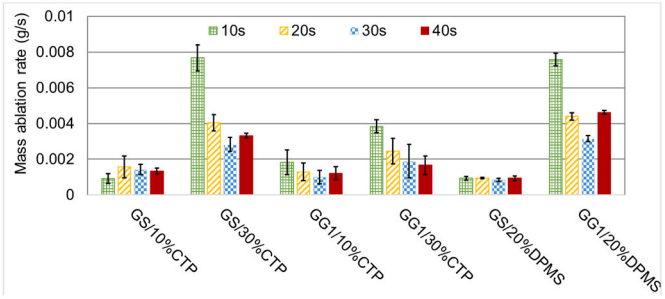

Fig. 9. Mass ablation rate of the coal composites under different duration times.

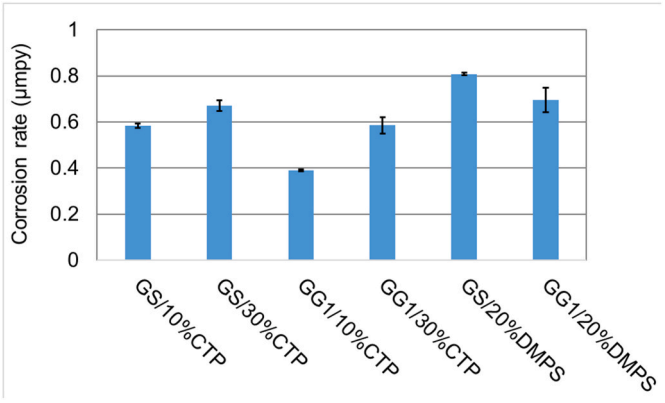

Fig. 10. Corrosion rate of the coal composites.

composites. On the other hand, DMPS composites presented higher corrosion rates compared to the CTP-based composites. The higher corrosion rates of GS composites may be attributed to their elevated carbon content. Remarkably, GG1/10%CTP composites recorded the lowest corrosion rate (<0.39 μmpy) and may be an ideal material for building applications requiring robust resistance to corrosion. Nevertheless, it is essential to investigate their corrosion resistance in solvents, alkalis, and notably alternating acidic and alkaline solutions and their corresponding compositional, physical, and microstructural characteristics.

3.6. Leaching analysis

Shaped composites could be demolished, landfilled, or recycled at their end-of-life or second-life phase. Internal and external environmental factors may cause the composite matrix to degrade. Therefore, environmental safety is considered when recycling these wastes. Leaching analyses were conducted to assess the potential release of metal ions from the composites when they come into contact with various liquids. The concentrations of metal ion contaminants in the leached solutions under three pH conditions (Table 4) are compared against four levels of leachable concentration threshold (LCT) waste management risk assessment data outlined in the waste management standard [22]. The leaching of metal ions tends to be least mobile at higher pH levels (9.2). At a pH of 9.2, concentrations of metal ion contaminants remained below the low-risk threshold for all composites, except for Se, which was moderate. Mercury (Hg) leaching was negligible given that the boiling point of Hg is approximately 360 °C and the composites were pyrolyzed at 600 °C. Thus, leading to the volatilization of Hg at the pyrolysis temperature. In general, the release concentration of As, Cr, Cu, Zn, Se, Cd, and Pb from the composites posed low to moderate risks. Notably, Mn mobility in GG1/30%CTP and GS/20% DMPS exhibited high risk at pH 2.9 and 4.9 respectively, which could be due to its high susceptibility to leaching under acidic conditions. For the GS/20 % DMPS composites at a pH of 4.9, the type of bonding that occurs when coal containing manganese is blended and pyrolyzed with the DMPS may be responsible for Mn degradation and leaching from the composite. It should be noted that metal ion leaching is influenced by factors such as the solution's pH, the element's ionic strength, redox potential and the physical properties of the particles.

4. Conclusion

The production of valuable composites from coal waste offers a sustainable and resource-efficient approach to waste management. The carbon structure, thermal stability, flame ablation rates, corrosion resistance, and leaching potential of coal composites produced from coal waste and coal tar pitch (CTP) or dimethylpolysiloxane (DMPS) as binder were evaluated in this study. The results revealed that pretreating coal tar at 400 °C for 9 h resulted in favorable chemical properties, of CTP including a low H:C ratio and increased carbon content. Raman spectroscopic data revealed that the graphitization level of the carbon structure in CTP-based composites was higher than in DMPS-based composites, as evidenced in the I_D/I_G ratio variations. Moreover, the thermal stability of the composites in an air environment displayed a direct relationship with the increasing proportion of CTP in the blend. GG1/20%DMPS emerged as the most thermally stable composite with a residual mass of 92.53 % at 950 °C, possibly due to stable Si–O and Si–C chemical bonds present. Notably, composites with higher CTP content displayed higher ablation rates, with GS/10 % CTP composites demonstrating the best resistance to flame ablation. Regarding corrosion resistance, GG1-based composites were better than their GS-based counterparts, and with a slight increase in corrosion rate when CTP loading is increased. Finally, the concentration of metal ion contaminants in all composites remained below the moderate environmental

Table 4
The leaching of metal ions contaminants from the composites.

Metal ion contaminants	pH = 2.9 / mg/l				pH = 4.9 / mg/l				pH = 9.2 / mg/l			
	GG1/30% CTP	GG1/20% DMPS	GS/20% DMPS	GS/30% CTP	GG1/30% CTP	GG1/20% DMPS	GS/20% DMPS	GS/30% CTP	GG1/30% CTP	GG1/20% DMPS	GS/20% DMPS	GS/30% CTP
As	0.0085	0.161	0.0702	0.156	0.211	0.0168	0.0243	0.233	0.0026	0.0031	0.0033	0.0016
Cr	0.0416	0.105	0.144	0.418	0.353	0.0286	0.0292	0.725	0.0260	0.0052	0.0084	0.0228
Cu	0.0859	0.0856	0.195	0.0822	0.312	0.0948	0.255	0.144	0.0257	0.0474	0.0324	0.0513
Hg	<0.00 1	<0.00 1	<0.00 1	<0.00 1	0.0015	<0.00 1	<0.00 1	<0.00 1	<0.00 1	<0.00 1	0.0014	<0.00 1
Se	0.0178	0.0378	0.0233	0.0275	0.0256	0.0284	0.0223	0.0467	0.0108	0.0104	0.0085	0.0209
Cd	0.00434	0.00213	0.00165	0.00093	0.00077	0.00086	0.00076	0.00175	0.00040	0.00081	0.00052	0.00046
Zn	0.0574	1.068	0.514	1.352	1.923	0.646	1.276	1.808	0.0163	0.309	0.0285	0.0163
Pb	0.0123	0.0851	0.0349	0.119	0.0125	0.088	0.005	0.122	0.001	0.0029	0.0014	0.0011
Mn	25.2	13.0	17.3	19.8	9.4	2.6	45.2	17.4	< 0.1	1.1	< 0.1	< 0.1

LCT – Leachable concentration threshold; Green – LCT 0 (low risk); Blue – LCT 1 (moderate risk); Yellow – LCT 2 (high risk); Red – LCT 3 (extreme risk); GG1: GG1 coal discard; GS: Greenside coal waste; CTP: coal tar pitch; DMPS: dimethylpolysiloxane; As: arsenic; Cr: chromium; Cu: copper; Hg: mercury; Se: selenium; Cd: caladium; Zn: zinc; Pb: lead; Mn: manganese
A slurry ratio of 1:20 (composites (10 g of -212):solution (200 mL))
LCT 0 limits (mg/l): As (0.01), Cr (0.1), Cu (2), Hg (0.006), Se (0.01), Cd (0.003), Zn (5), Pb (0.01) and Mn (0.5)
LCT 1 limits (mg/l): As (0.5), Cr (5), Cu (100), Hg (0.3), Se (0.5), Cd (0.15), Zn (250), Pb (0.5) and Mn (25)
LCT 2 limits (mg/l): As (1), Cr (10), Cu (200), Hg (0.6), Se (2.0), Cd (0.3), Zn (500), Pb (1) and Mn (50)
LCT 3 limits (mg/l): As (4), Cr (40), Cu (800), Hg (2.4), Se (8), Cd (1.2), Zn (2000), Pb (4) and Mn (200)

risk threshold except magnesium. As such, metal ion leaching from these composites may be deemed satisfactory and would not pose a significant environmental threat. With a high degree of graphitization, excellent thermal stability, low corrosion rates, and minimal susceptibility to leaching, these composites show promising applications for roof tiles, blocks, or pavers. Exploring the incorporation of nanomaterial additives to enhance their performance and the concentration of heavy metal elements leached from the composites over a long period are promising areas for future investigations.

CRediT authorship contribution statement

Mhlawakhe Vatsha: Writing – original draft, Validation, Methodology, Formal analysis. **Orevaoghene Eterigho-Ikelegbe:** Writing – review & editing, Visualization, Validation, Formal analysis. **Samson Bada:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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