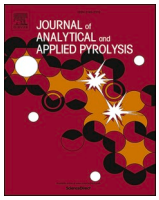
Journal of Analytical and Applied Pyrolysis 181 (2024) 106625

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



A study of the efficacy and structural performance of modified coal tar and dimethylpolysiloxane as binders for coal-carbon composites

Mhlawakhe Vatsha, Orevaoghene Eterigho-Ikelegbe *, Samson Bada *

Clean Coal Technology Research Group, School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag X3, Wits 2050, Johannesburg, South Africa

ARTICLE INFO

Keywords:
Binder
Coal fines
Coal tar pitch
Circular economy
Mechanical property
Resource efficiency
Sustainability

ABSTRACT

Amidst global resource depletion and population growth, repurposing carbon-containing waste as raw materials into products offers promise for a more resource-efficient, circular economy. This research examines the efficacy of using coal tar modified through air-blowing as a binder for producing coal composite, alongside exploring dimethylpolysiloxane as an alternative binder. The effects of the binder type, mixing ratios, and coal fine composition on the properties of the composites were systematically studied. Microscopic analysis revealed anisotropic spherules in pitch formed at 400 °C/9 h and 450 °C/6 h possess favorable chemical properties like low H/C ratios (0.24–0.25) and high carbon content (96–97 %). Pyrolyzed coal fines and modified pitch-based composites exhibited moderate weight loss (11–17 %), notable compressive strength (106.58–344.71 MPa), and flexural strength (49–160 MPa). However, composites produced from coal tar pitch (400 °C/9 h) blended with 50 % GG1 and further pyrolyzed at 600 °C for 5 h exhibited a high water absorption (19 %). Also, composites with inferior flexural strength were produced using dimethylpolysiloxane as a binder, rendering them unsuitable for structural applications. This straightforward approach offers a viable means to repurpose significant quantities of coal fines and coal tar destined for landfills. This research is intended as a reference for researchers seeking to tranform coal waste into structural composites, thereby promoting circularity, and mitigating associated environmental risks.

1. Introduction

Coal fine residues are produced during automated mining and beneficiation of coal and their composition varies depending on the mineralogy of the coal deposit and how it was processed. Over 30 billion metric tons of coal fines or tailings are spread over the top ten coal-producing countries [8]. This highlights the enormity of this problem. An estimated 58 gigatons of these resources were left behind in tailings dumps, slurry impoundments, and surface dams worldwide as of 2011 [24]. In South Africa, mining companies report that roughly 4–6 % of the coal mined annually falls within the −0.20 mm (-200 μm) fraction, amounting to over 8 million tons being discarded in dams or dumps [3, 29]. These low-market-value coal fines are difficult to handle, store, or utilize, and are expensive to treat. Untreated and unused coal fines present serious environmental risks such as acid mine drainage, dust emissions, carbon and sulfur dioxide releases, and the possibility of spontaneous combustion-related fires [28,30]. Diverse techniques have been employed to extract value and beneficiate coal fines as low-smoke fuel, for power generation, methane production, and polymer manufacturing [24,29,38]. However, these approaches are not without difficulties. It is insufficient to rely only on these applications to reduce the amount of coal fines and their associated environmental effects.

On the other hand, the carbonization of coking coal, a crucial process in producing coke as a "reductant" for the metallurgical industry, generates coal tar as a by-product ([40]; X. [27]). In 2013, ArcelorMittal South Africa alone produced an estimated 109,000 tonnes of tar, raising environmental concerns [2]. The disposal and hazardous nature of this waste, which is also a resource, has led to numerous investigations into how it can be utilized. Coal tar has found applications in road construction in China and India, which is expected to continue to grow [17]. The same is true in the automobile industry, where coal tar is used to obtain coal tar pitch, for producing carbon-based products [9]. Liu et al. [27] and Yuan et al. [40] investigated the alternative uses of coal tar as feedstock for carbon fibers and the hydrogenation of coal tar to produce different chemical substances for various applications. However, coal tar necessitates pretreatment before utilization to remove impurities and

* Corresponding authors.
E-mail addresses: eterighoo@gmail.com (O. Eterigho-Ikelegbe), Samson.Bada@wits.ac.za (S. Bada).

https://doi.org/10.1016/j.jaap.2024.106625
Received 10 April 2024; Received in revised form 13 June 2024; Accepted 2 July 2024
Available online 3 July 2024

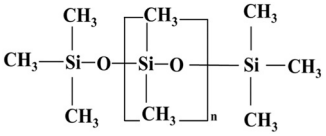


Fig. 1. Chemical structure of pure DMPS.

achieve a uniform composition [32]. This process also adjusts its plastic properties and transforms it into mesophase pitch, a precursor for high-performance carbon materials [5]. Various methods, including toluene extraction, vacuum distillation, cross-linking, and air blowing are employed to modify or pretreat coal tar to produce coal tar pitch (CTP). Among these, air blowing stands out as a simple, cost-effective, and versatile method that yields CTP with a wide range of properties [16,34,39]. The air-blowing method can yield CTPs with a desirable softening point by subjecting coal tar to temperatures between 250 °C and 300 °C, [7,16,39]. Prauchner et al. [35] demonstrated using Fourier transform infrared (FTIR) spectra that the air blowing reduces the aliphatic stretching absorbance in the resultant pitch.

The building and construction sector stands out as a major consumer of natural resources, contributing significantly to greenhouse gas emissions [31]. Developing strategies to harness waste materials in these sectors reduces reliance on conventional raw materials and natural resources while conserving energy. In addition, minimizing greenhouse gas emissions. The building sector is a natural vehicle for recycling waste and has great potential to absorb coal or carbon-containing waste. Some studies have explored coal and coal-derived wastes to produce coal composites with properties similar to architectural parts (ceramic bricks and tiles) [12,14,15,19,20,37]. In a study by Eterigho-Ikelegbe et al. [14], high-ash coals were blended with a laboratory-formulated polysiloxane preceramic polymer resin and then pyrolyzed to produce coal/ceramic composites. The composites demonstrated flexural strength up to 36.46 MPa and water absorption as low as 1.94 %. Another investigation was undertaken by Eterigho-Ikelegbe et al. [13] using commercial polysiloxane polymer (SPR-212) as a binder for coal wastes. Composites of low water absorption at 8.9 % were obtained. In addition, the composites showed good thermal stability, comparable to ceramic and structural clay building materials. Although these promising results suggest the potential of using coal waste as raw materials for coal composite production for these applications, ceramic-forming binders are quite expensive.

The abundant reserves of economic raw materials such as coal tar present a persistent challenge, yet also represent economic opportunities if efficiently utilized. Despite the reported methods to modify pitch, the conditions used to produce a coal tar pitch with low volatile matter, high aromaticity, and excellent thermal and fusibility properties vary for different coal tar sources. The primary aim of this research was to modify coal tar by thermal pretreatment under various conditions to ensure adequate polymerization of the tars, leading to large molecules composed of mesophase formation. The second objective of the study was to investigate the derived CTP as a binder for high ash coal fines to produce structural composites. In parallel, dimethylpolysiloxane (DMPS) was investigated as an alternative binder for the coal fines to produce coal composites. The prepared composites were subsequently subjected to surface imaging, functional group analysis (Fourier-transform infrared spectroscopy) and mineral phase analysis (X-ray diffraction). Finally, the physico-mechanical properties of the composites (pyrolysis shrinkage, density, porosity, water absorption tests, flexural strength, and compressive strength) were evaluated.

2. Materials and method

2.1. Preparation and analysis of coal fines, coal tar, and coal tar pitch

The coal fines designated GG1 and GS were used for this investigation while coal tar, coal tar pitch, and dimethylpolysiloxane are denoted as CT, CTP, and DMPS, respectively. Characterized by its low cost and excellent chemical and thermal stability, DMPS is a silicone polymer which features a chemical structure depicted in Fig. 1. It comprises repeating units of dimethylsiloxane (-[-Si$(CH_3)_2$O-]-) and -Si-O- backbone, expressed as $CH_3[Si\ (CH_3)_2\ O]_n\ Si\ (CH_3)_3$. CT was subjected to air-blowing pre-treatment at varying temperatures and residence times to produce CTP, the binder for the composites. Initially, the coal fines underwent sun-drying to eliminate excess moisture. Subsequently, they were milled, screened, and divided using a rotary divider to obtain representative samples with particle sizes of −212 and −53 micrometers (μm). The coal samples (-212 μm), tar and pitches were analyzed for physicochemical properties, functional groups, and mineralogical compositions. Proximate analysis was carried out on coal fines, CT, and CTP using a thermogravimetric analyzer (TGA 701, LECO Corp. USA) following the ASTM D-5142 standard. The ultimate analysis (C, H, O, and N) was conducted using the Leco CHN 628 with a 0.25 g sample, adhering to ASTM D 5373–14:2015 standards. Total sulfur was determined according to ISO 19579:2006. The Spectrum Two™ FTIR spectrometer (Perkin Elmer Corp., USA) equipped with an attenuated total reflectance accessory was used to probe spectra information (functional groups and chemical bond configuration) present in the coal fines, coal tar, CTP, DMPS, and coal composites. The pulverised samples were scanned from 450 to 4000 cm^{-1}. A Bruker D2 phaser diffractometer (Bruker Corp., USA) equipped with Cu-Kα radiation (λ = 1.54184 Å), operating at 50 kV and 23 mA in the 2-theta scanning range of 10–90 ºC was used to obtain diffraction patterns of the samples. Data obtained from XRD analysis were processed using X'Pert HighScore Plus software

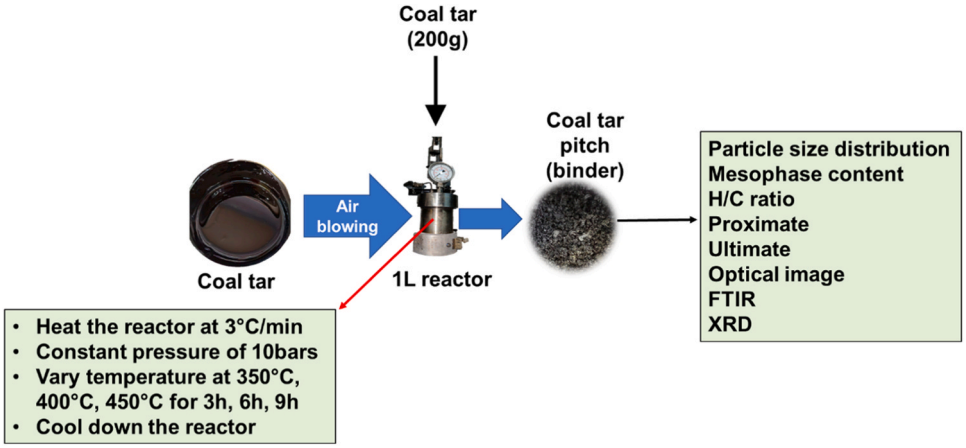


Fig. 2. Coal tar air-blowing method.

Table 1
The proposed blending ratio of coal fines to CTP and DMPS.

Coal fines (%)	CTP (%)	DMPS (%)
80	-	20
90	10	-
70	30	-
50	50	-

for mineral phase identification.

2.2. Modification of the coal tar by air-blowing

The coal tar underwent modification in a 1 L cylindrical stainless-steel reactor using the air-blowing method. The reactor is equipped with inlet and outlet valves, a heating jacket, and a pressure gauge for monitoring vessel pressure, ensuring controlled conditions. An air-blowing pretreatment process was used to pretreat the coal tar in a temperature window of 350–500 °C, following the temperature range used by Banerjee et al. [4]. In each experiment, 200 g of coal tar was charged into the vessel and 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 steadily blown into the reactor at 16 ml/s for residence times of 6 h, 3 h, and 9 h. The pressure inside the vessel was maintained at a constant pressure of 10 bars. During air-blowing, the inlet and outlet valves were opened to allow air into the reactor and discharge volatile matter. The reactor vessel was then removed from the heating jacket at the end of the experiment and allowed to cool to room temperature. Once cooled, the product was chipped from the reactor, weighed to determine weight loss, and transferred to a clean container. Fig. 2 provides an overview of the coal tar air-blowing method employed to produce coal tar pitch (CTP). The CTPs obtained were characterised to identify the conditions that would enhance the bonding and fusibility of the coal fines. The CTP sample of superior chemical properties was selected as the binder for producing coal composites.

All modified CTP samples were characterized using polarised light optical microscopy to determine the growth and content of the bulk liquid crystalline mesophase following ASTM D4616–95. Coal tar pitch samples were first reduced to −1.0 mm fine size, then placed in epoxy resin in 30 mm silicon molds and vacuum-cured for 24 hours. The surface of the hardened blocks was subsequently polished, as per ISO 7404, using a Struers Tegraforce polisher. The polished blocks were assessed petrographically using a Zeiss AxioImager M2M petrographic microscope fitted with a Fossil Hilgers system at a magnification of 100 X using an air lens and 500 X under oil immersion. Microphotographs were captured to illustrate the optical textures observed in each sample, employing white light and polarised light with crossed nicols (crossed polars, with lambda plate) rotated by 45 ºC to visualise anisotropy.

2.3. Fabrication of the composite specimens

The second objective of the research was to investigate the properties of the coal composites formed through the thermal conversion of the blend of varying ratios of coal fines and CTP/DPMS (Table 1). An 80 % and 20 % weight ratio of coal fines and dimethylpolysiloxane (DMPS) was used. A DMPS weight percentage exceeding 20 % in the mixture turns into a slurry, posing difficulties in molding and shaping. The obtained pitch particles were crushed into smaller particles to facilitate effective blending with the coal fines. A total blend of 2.0 g of coal fines (-53 μm) and coal tar pitch (-53 μm) was molded and compacted into square and circular green composites using a hydraulic press (cold compression) at 25 MPa pressure. Subsequently, the green composites underwent thermal stability testing to ascertain the pyrolysis temperature of the composites. The test indicated that the residual mass of all the composites at 600 °C was more than 75 %. Hence, 600 °C was chosen as the pyrolysis temperature. The DMPS mixture was cured in an oven at 150 °C for 1 h to crosslink or stabilize the green composites before pyrolysis. Pyrolysis process transforms the green body into an organic/inorganic composite. Pyrolysis was conducted in an airtight furnace under an argon atmosphere, with a heating rate of 5 °C/min from 25 °C to 600 °C, maintained for 5 hours. Fig. 3 displays an overview of the coal composites manufacturing process.

2.4. Assessment of the composites

The composites were rigorously assessed to check if they met essential standard properties of construction or building materials. To guarantee result accuracy, all analyses were conducted in triplicate. The weight loss and the linear shrinkage of the coal composites after pyrolysis were determined according to the following equations.

$$\%Weight\ loss = \frac{M_G - M_P}{M_G} \times 100 \quad (2\text{-}1)$$

$$\%Linear\ Shrinkage = \frac{L_G - L_P}{L_G} \times 100 \quad (2\text{-}2)$$

where M_G is the mass (g) of the green composite, M_P is the mass (g) of the pyrolyzed composites, L_G is the length (mm) of the green composite, and L_P is the length (mm) of the pyrolyzed composite.

The relative density, apparent porosity, apparent specific gravity, bulk density, and water absorption were measured following the ASTM C373 standard test method for ceramic tiles. Composite specimens, sized

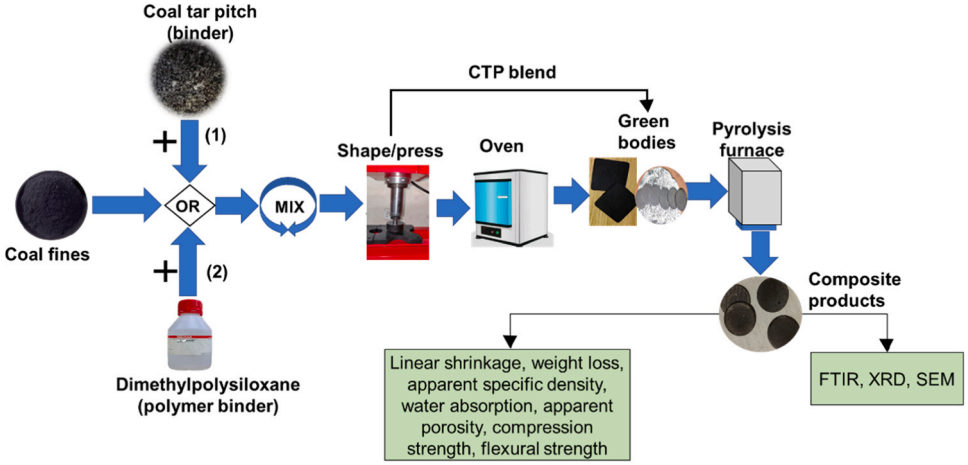


Fig. 3. Fabrication procedure for the coal composites.

Table 2
Proximate and ultimate analysis of coal fines, coal tar, and the produced coal tar pitch samples.

Sample	Proximate analysis			Elemental compositions (%)								
	Dry basis (%)											
	VM (%)	Ash (%)	FC (%)	N	C	H	S	O	H/C	C/H	f_a	$(R/C)_u$
GG1	10.34	84.02	5.62	0.18	8.79	1.44	0.21	4.84	1.95	0.51	0.60	-
GS	20.72	62.73	16.55	0.63	23.77	1.744	2.48	8.02	0.87	1.15	0.66	0.23
CT	64.50	0.28	35.23	-	-	-	-	-	-	-	-	-
CTP 350°C/3 h	28.80	0.28	70.92	0.91	77.42	3.54	0.00	18.13	0.54	1.85	0.88	0.29
CTP 350°C/6 h	26.10	0.24	73.66	1.18	88.05	3.48	0.00	7.30	0.47	2.13	0.81	0.36
CTP 350°C/9 h	22.74	0.33	76.93	1.00	89.78	3.33	1.02	4.87	0.44	2.27	0.83	0.37
CTP 400°C/3 h	22.34	0.29	77.36	0.83	95.06	3.51	0.50	0.11	0.44	2.27	0.79	0.39
CTP 400°C/6 h	16.74	0.84	82.42	0.88	73.74	3.11	1.03	1.26	0.50	2.00	1.07	0.21
CTP 400°C/9 h	**11.33**	**0.49**	**88.17**	**0.94**	**96.01**	**2.05**	**0.00**	**1.00**	**0.25**	**4.00**	**0.88**	**0.43**
CTP 450°C/3 h	12.11	0.55	87.33	0.90	88.58	3.01	0.96	6.56	0.40	2.50	0.95	0.32
CTP 450°C/6 h	**11.19**	**0.49**	**88.31**	**1.05**	**96.92**	**2.02**	**0.00**	**0.01**	**0.24**	**4.17**	**0.88**	**0.44**

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; N: nitrogen; S: total Sulphur; VM: volatile matter

ø 20 × 4 mm, were subjected to compressive strength testing to evaluate their resistance to crushing loads. A constant load was applied at the rate of 1.0 mm/min until the composite fractured. The compression strength was calculated using equation (2−3) and following the ASTM C67 standard test method.

$$C = W/A \tag{2-3}$$

where C is the compression strength in MPa; W is the maximum compression load; A is the average of the lower and upper bearing surface in mm.

Flexural strength was assessed using a flexural test machine, applying a constant load at 1.0 mm/min to the composite specimens (30 × 30 × 4 mm) in a 3-point loading configuration until failure. The flexural strength was calculated using equation (2−4) based on the ASTM C67 standard.

$$F = \frac{P \times L}{b.d^2} \tag{2-4}$$

where F(MPa) is the flexural strength, $P(N)$ is the maximum breaking load, $L(mm)$ is the distance between the supports, $b(mm)$ and $d(mm)$ is the breadth and thickness of the composite specimen.

The microstructure and surface morphology of coal composite specimens were visualized using a ZEISS Sigma 300 VP scanning electron microscope. Before scanning, specimens were coated with at least two layers of gold to enhance conductivity and achieve high-resolution images.

3. Results and discussions

3.1. Evaluation of the raw materials

The particle size distributions (PSD) for the pulverized CTP, GG1, and GS coal fines contained 49.73 %, 92.73 %, and 76.67 % passing −75 μm. Table 2 summarizes the results of the physiochemical analysis, including proximate and ultimate analyses, for the coal fines, coal tar, and CTP produced at various temperatures. Equations (3−1) and (3−2) were used to obtain f_a and $(R/C)_u$ recorded in Table 2

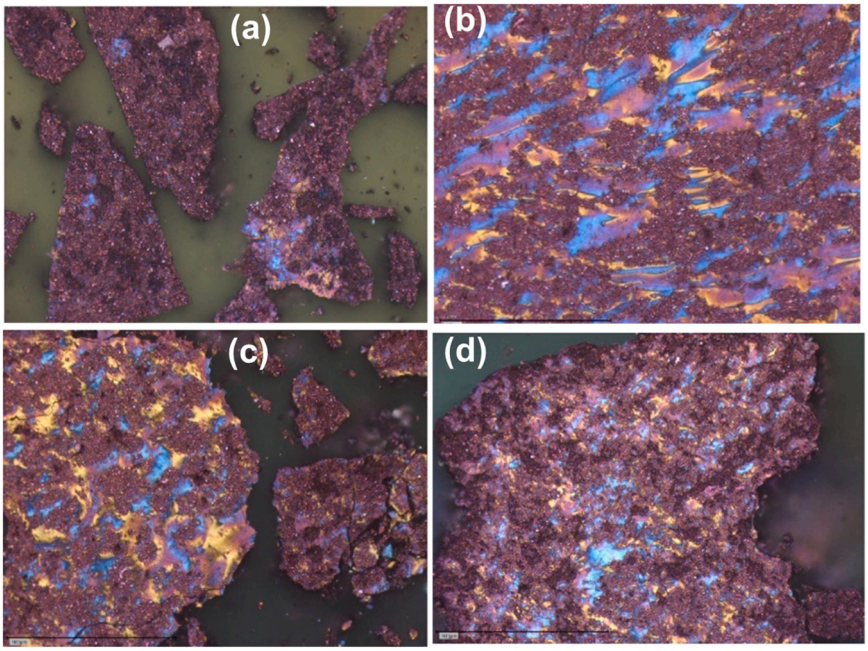


Fig. 4. Optical microscopy images of CTPs produced at (a) 350 °C/9 h, (b) 400 °C/6 h, (c) 400 °C/9 h coarse circular, (d) 450 °C/6 h.

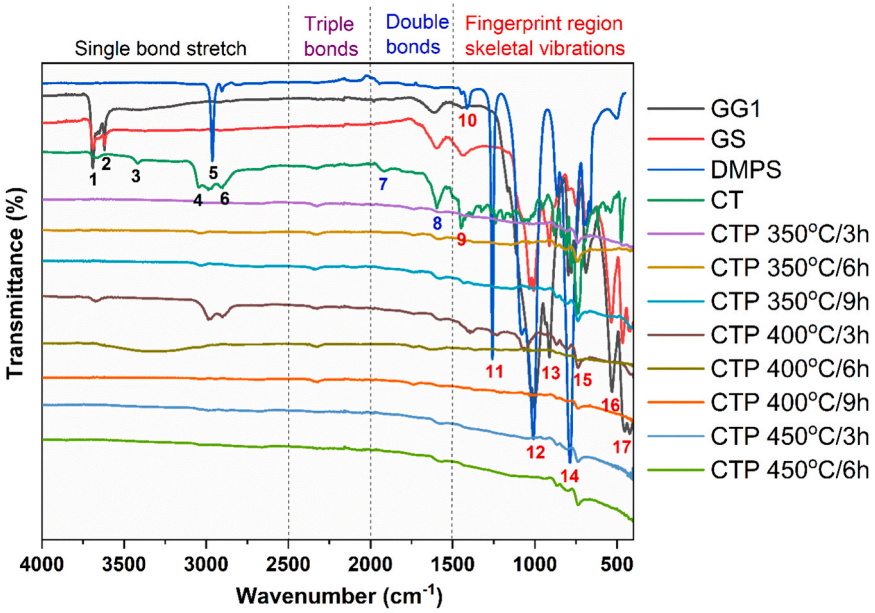


Fig. 5. Comparison of FTIR spectra of GG1, GS, DMPS, CT, and CTP produced at different conditions.

$$f_a = \left(100 - V_{d.a.f}\right) \times \frac{0.9677}{C} \quad (3\text{-}1)$$

$$(R/C)_u = 1 - \frac{f_a}{2} - \frac{\left(\frac{H}{C}\right)}{2} \quad (3\text{-}2)$$

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

Notably, GG1 and GS coal fines exhibited higher ash content (84.02 % and 62.27 %) than coal tar and CTP samples (0.28–0.84 %). Air-blowing of the coal tar at 450 °C for a residence time of 6 hours reduced the volatile matter content from 64.50 % to 11.19 %. Whereas the fixed carbon content of the CTP increased as the temperature and residence time of pretreatment increased. This signifies the conversion of short-chain hydrocarbons into long-chain hydrocarbons [5]. The pitches produced at 400 °C/9 h and 450 °C/6 h displayed the highest total carbon content due to increased aromaticity and polymerization [16,36]. The H/C atomic ratio of the produced CTP (ranging from 0.24–0.54) in this study was lower than the typical value for fossil pitches (0.5–0.9) [35]. Specifically, the CTPs produced at 400 °C/9 h and 450 °C/6 h had the lowest H/C ratio (0.25 and 0.24) and the highest rings of atomic C $(R/C)_u$ value (Table 2). A low H/C ratio CTP suggests loss of aliphatic hydrogen or hydrogen atoms from the structure and formation of large condensed aromatic rings through dehydrogenative polymerization of the tar components [5,34].

Table 3
Bond assignment and the corresponding wavenumber observed from FTIR spectra of GG1, GS, DMPS, CT, and CTP produced at different conditions [23,25].

Band no.	Wavenumber (cm^{-1})	Bond assignment
#1, #2	3688, 3619	O-H stretch, free hydroxyl
#3	3418	O-H stretch
#4	3047	C-H stretching vibration on the aromatic ring
#5 (DMPS)	2963	Methyl C-H
#6	2907	Aliphatic C-H stretch
#7	1916	C-C═C-CH (aromatic rings)
#8	1697, 1597	C═O stretching vibration of aromatic COOH (shoulder), C═C aromatic ring stretching structure
#9	1443	CH_2, CH_3 bending vibrations
#10 (DMPS)	1412	CH_3 asymmetric deform
#11 (DMPS)	1259	CH_3 symmetric deform
#12 (DMPS)	1005	Si-O-Si
#12	1005	C-O-C stretch
#13	906	Si-O-Si and Al-O-Al vibrations associated with aluminates and silicates such as kaolinite and quartz
#14 (DMPS)	866	Si-C
#15 (DMPS)	780	Si-$(CH_3)_2$
#15, #16	797, 741	Bending vibrations associated with quartz, calcite, dolomite, kaolinite
#17, #18	529, 463	Si-O and Si-O-Si deformation associated with kaolinite and quartz

3.2. Optical image analysis of the produced coal tar pitch

The optical image analysis was crucial for understanding the development of anisotropic (mesophase) spherules in the coal tar pitches, arising from pretreatment. High anisotropic phase content in pitch, composed of more aromatic compounds and carbon atoms might make it suitable as a binder [6,10] for coal fines. Fig. 4 illustrates mesophase development in CTPs produced at various temperatures and durations (350 °C/9 h, 400 °C/6 h, 400 °C/9 h, and 450 °C/6 h). At 350 °C/9 h, CTP exhibits an incipient anisotropic binder phase with filler fragments. Coarse circular anisotropic phases are observed at 400 °C/6 h, while coarser circular anisotropic textures develop at 400 °C/9 h. CTP produced at 450 °C/6 h displays variable textures with evidence of circular anisotropic phases. These findings align with Liu et al. [26] observations, indicating spherule merging or compacting with increased temperature and residence time. CTP with more anisotropic spherules (produced at 400 °C/9 h and 450 °C /6 h) correlates with the lowest H/C ratio (0.25 and 0.24) and highest carbon content. The mesophase in these pitches appears more uniform than those produced at lower temperatures and shorter reaction times.

According to the findings from optical microscopy, proximate analysis and elemental composition, the pretreatment conducted at 400 °C/

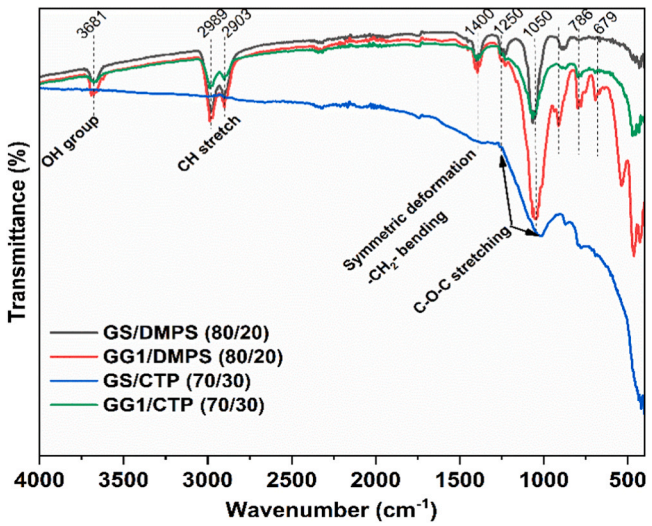


Fig. 6. Comparison of FTIR spectra of coal/CTP composites and coal/DMPS composites.

9 h was identified as the optimal condition for obtaining a suitable pitch binder from coal tar for composite production. This condition was chosen because the CTP had low volatile matter, high total carbon, low H/C atomic ratio, and high aromaticity. Although CTP obtained at 450 °C/6 h had identical properties as those obtained at 400 °C/9 h. The trend suggests that air-blowing of coal tar at temperatures higher than 400 °C did not significantly change the properties of the resultant pitch.

3.3. Fourier transform infrared spectroscopy (FTIR)

Coal and coal-related materials possess a complex structure with diverse functional groups, analyzed using Fourier transform infrared (FTIR) spectroscopy [11,40]. FTIR results of GG1, GS, DMPS, CT, and CTPs produced at various temperatures and reaction times are shown in Fig. 5. The bond assignment and the corresponding wavenumber observed from FTIR spectra are listed in Table 3. The absence of the O-H (hydroxyl) group in the modified CTPs, observed between 3500 and 4000 cm^{-1} in coal tar (band no. #1, #2 and #3), indicates moisture loss. Pretreatment of CT at various heat treatment conditions led to the disappearance of the aliphatic C-H stretch at 2895 cm^{-1} (band no. #6) with the rise in reaction temperature. This observation is in agreement with the low H/C atomic ratios recorded for CTPs in Table 2 and could be ascribed to the dehydrogenative polymerization and crossing-linking of oligomers [39]. It was also observed that the peak intensity at

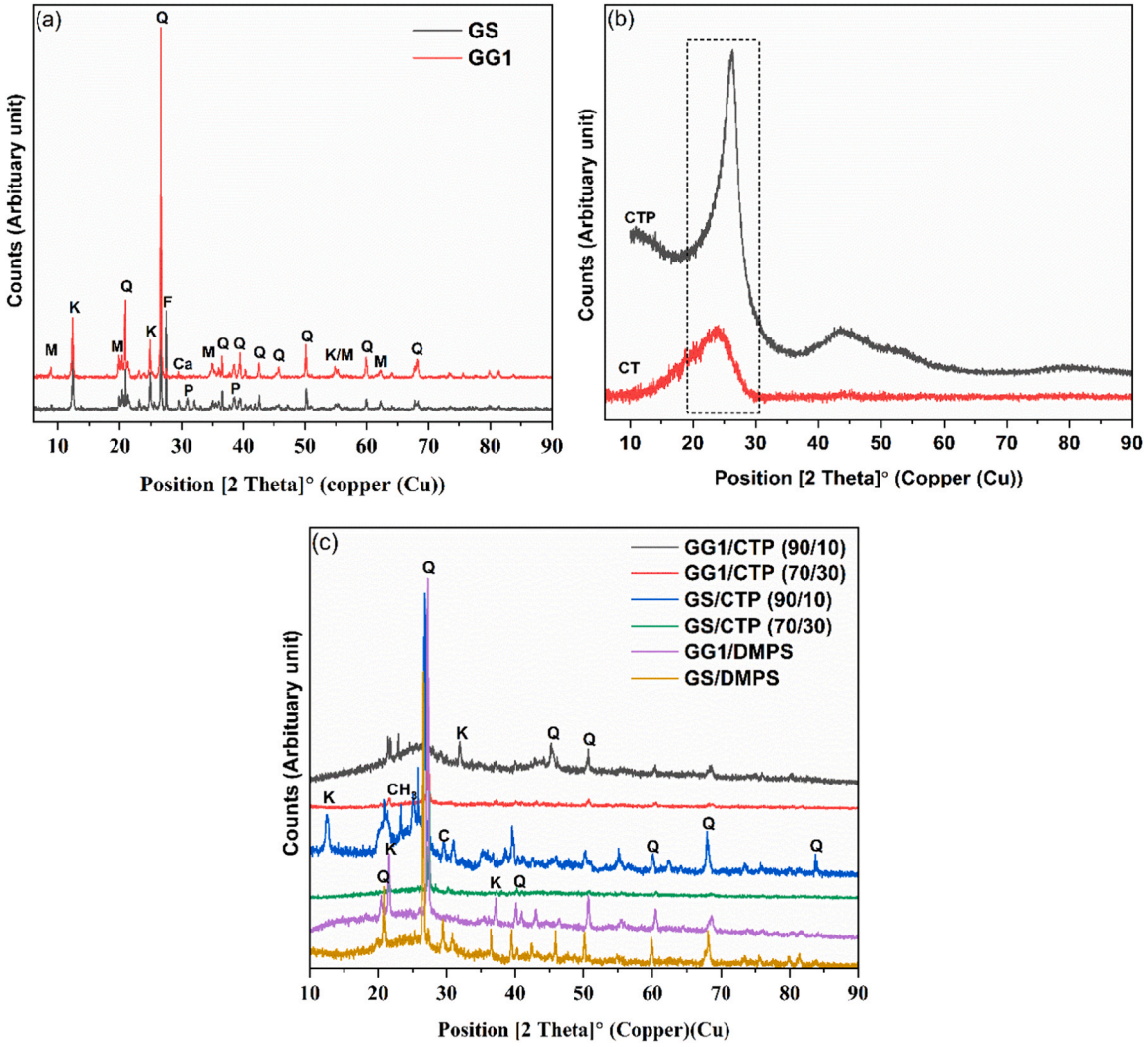


Fig. 7. Comparison of the powder XRD patterns (a) coal fines, (b) coal tar and coal tar pitch, (c) coal composites [K: kaolinite-1A ($Al_2Si_2O_5(OH)_4$); Q: quartz (SiO_2); M: muscovite ($KSi_3Al_3O_{12}H_2$); F: feldspar (K, Na)$AlSi_3O_8$; P: pyrite (FeS_2); Ca: calcite ($CaCO_3$)].

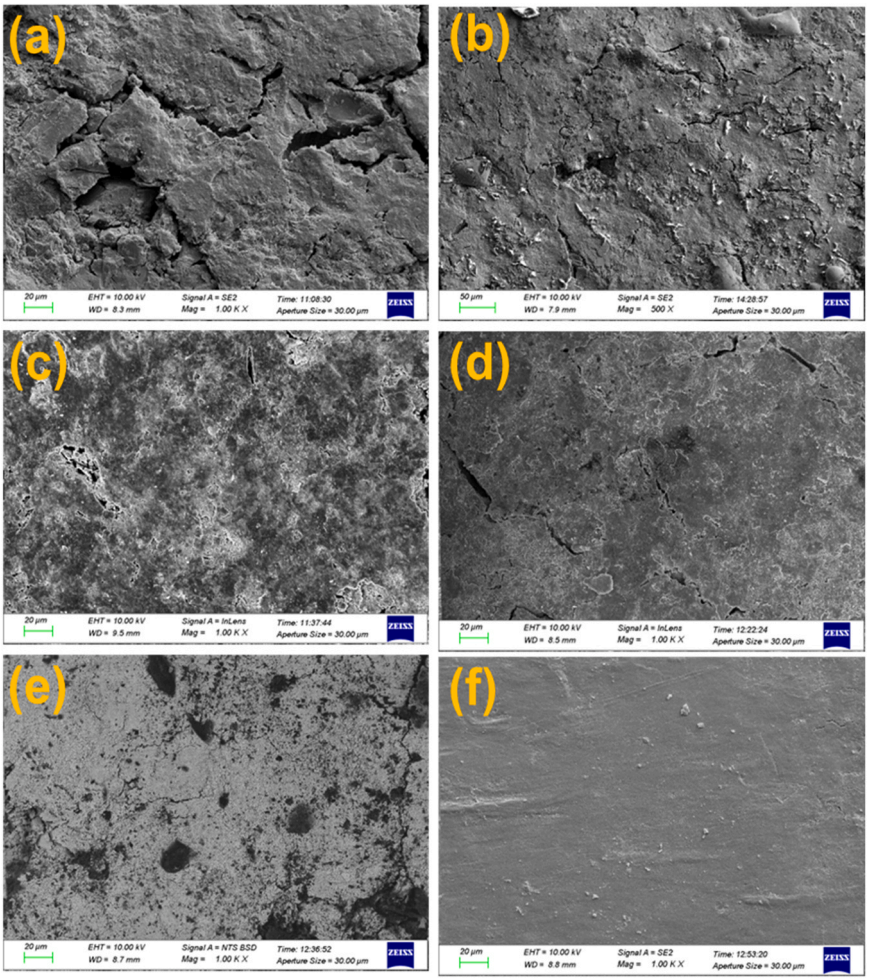


Fig. 8. SEM micrographs of (a) GS/CTP (90/10), (b) GS/CTP (70/30), (c) GG1/CTP (90/10), (d) GG1/CTP (70/30), (e) GS/DMPS (80/20), (f) GG1/DMPS (80/20).

1600 cm^{-1} (band no. #8) decreased significantly in the CTP. This indicates that the thermal modification reduced the relative content of aromatic rings in the CTP as pyrolysis temperature increased. On the other hand, DMPS is characterized by predominant C-H stretching peaks attributed to methyl (CH_3) groups (band no. #5, #10 and #11). Alkyl (C-H) and ether groups (C-O-C) were observed in the ATR-FTIR spectra of coal/CTP and coal/DMPS composites (Fig. 6). Their presence and changes in band intensities may be due to the breakdown of volatiles, unreacted small molecule mixtures, and macromolecular aromatic compounds during composite pyrolysis.

3.4. X-ray diffraction analysis

XRD analysis was conducted to assess crystallinity and identify mineral phases in the coal fines, coal tar, CTP, and produced coal composites as shown in Fig. 7(a), (b) and (c). Identified minerals in the coal samples include kaolinite, quartz, muscovite, feldspar, pyrite, and calcite (Fig. 8a). All the peaks could not be matched because of the high number of peaks and/or the presence of multiple minerals with overlapping peaks. GG1 fines exhibited higher intensity peaks when compared to GS fines, indicating a higher inorganic mineral content, consistent with GG1's higher ash content (Table 2). Heat treatment of coal tar led to a more graphitic structure or graphite-like carbon material, evident in peaks around 2 theta = 24° and 45°, resulting from polycondensation in the binder pitch. The air-blowing treatment produced CTP mainly composed of organic compounds (amorphous carbons), evidenced by a low crystallinity peak at 43°. Regarding the coal composite mineral compositions, mixture blends containing up to 30 % CTP yielded composites with fewer mineral phases or impurities. This suggests the blend of coal fines with up to 30 % CTP shows a high degree of vitrification, causing features of kaolinite and quartz to nearly disappear. This further indicates that intimate consolidation between the different crystalline phases in the mixture had occurred.

3.5. Scanning electron microscopy analysis

The morphologies of fractured composites produced from coal fines, CTP, and DMPS blends at different ratios are depicted in Fig. 8(a)-(f). Comparing GS composites of 10 % and 30 % CTP (Fig. 8(a) and (b)), surface undulations and cracks were observed, with crack sizes decreasing as the CTP percentage increased. This trend was similarly observed in GG1 composites with 10 % and 30 % CTP (Fig. 8(c) and (d)), indicating crack filling with increased CTP content. The results show that increasing the amount of CTP in the composite materials enhances their fusibility, compaction, and homogeneity. In contrast, composites produced using DMPS as a binder (Fig. 8(e) and (f)) exhibited smoother, crack-free surfaces. This can be attributed to DMPS's solubility and fluidity, which facilitated homogeneous wetting and fusion of the coal surface. Additionally, GG1 composites displayed a more uniform and smoother surface when compared to composites produced using GS coal fines. Surface irregularities and lack of fusibility observed in GS composites suggest poor compatibility between the coal fines and binder.

3.6. Linear shrinkage and weight loss of the composites

Pyrolysis is a pivotal step in converting green bodies into stabilized

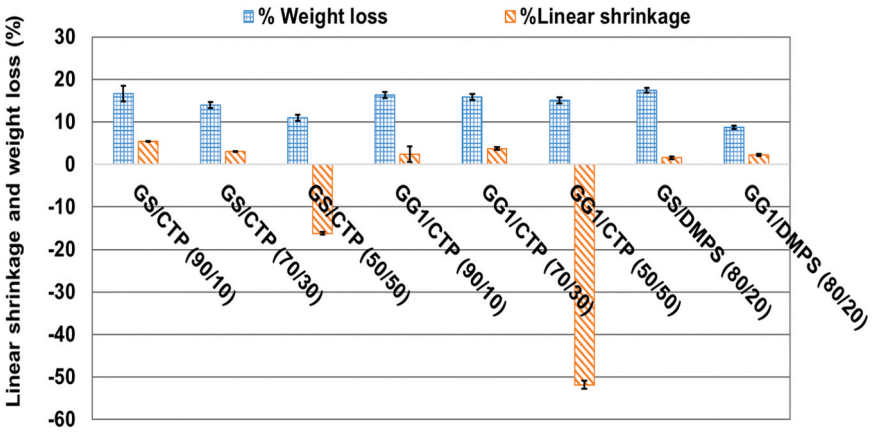


Fig. 9. Weight loss and linear shrinkage of the composites (CTP obtained at 400 °C).

Table 4
Bulk density, apparent specific density and apparent porosity of the composites (CTP obtained at 400 °C).

Composites	Bulk density (g/cm^3)			Apparent specific gravity			Apparent porosity (%)		
	5-h cold	24-h cold	5-h boil	5-h cold	24-h cold	5-h boil	5-h cold	24-h cold	5-h boil
GS/CTP (90/10)	1.637	1.681	1.675	1.898	2.046	2.047	13.724	17.341	18.176
GS/CTP (70/30)	1.588	1.628	1.619	1.715	1.846	1.874	7.428	11.532	13.620
GS/CTP (50/50)	1.456	1.449	1.460	1.493	1.527	1.709	2.482	5.188	14.570
GG1/CTP (90/10)	2.013	1.900	1.890	2.354	2.241	2.296	14.467	16.311	17.678
GG1/CTP (70/30)	1.778	1.812	1.775	1.857	1.989	2.049	4.258	8.697	13.399
GG1/CTP (50/50)	1.343	1.365	1.322	1.365	1.430	1.744	1.590	4.507	24.236
GS/DMPS (80/20)	1.568	1.556	1.557	2.116	2.115	2.151	25.902	26.634	27.643
GG1/DMPS (80/20)	2.044	2.062	2.038	2.090	2.150	2.127	2.228	4.050	4.200

CTP: coal tar pitch; DMPS: dimethylpolysiloxane

coal composites and is crucial for establishing the final ordering structure. During pyrolysis, the particles in the mixture rearrange and stick tightly, leading to weight loss and shrinkage of the composites. It can be deduced from Fig. 9 that the linear shrinkage of CTP-produced composites decreased with increasing binder content. As seen from the graph, composites containing 50 % CTP underwent a process of expansion, hence the negative values of linear shrinkage. The expansion might be due to the release of a considerable amount of gaseous products during pyrolysis. Furthermore, GS composites with 10 %, 30 %, and 50 % CTP exhibited decreasing weight loss trends (16.61 %, 13.92 %, and 10.96 %, respectively). Conversely, GS composites of 20 % DMPS recorded the highest weight loss at 17.43 %, potentially attributed to DMPS's high C-H/aliphatic side chain content released during pyrolysis. Polymer network degradation and release of unreacted monomers during pyrolysis could also be responsible for the high weight loss [22]. High shrinkage loss during pyrolysis is detrimental in that it can lead to cracking, deformation, or warping of composites [12,13].

3.7. Water absorption, bulk density, apparent specific density, and porosity of the composites

Physical properties such as apparent porosity, apparent specific

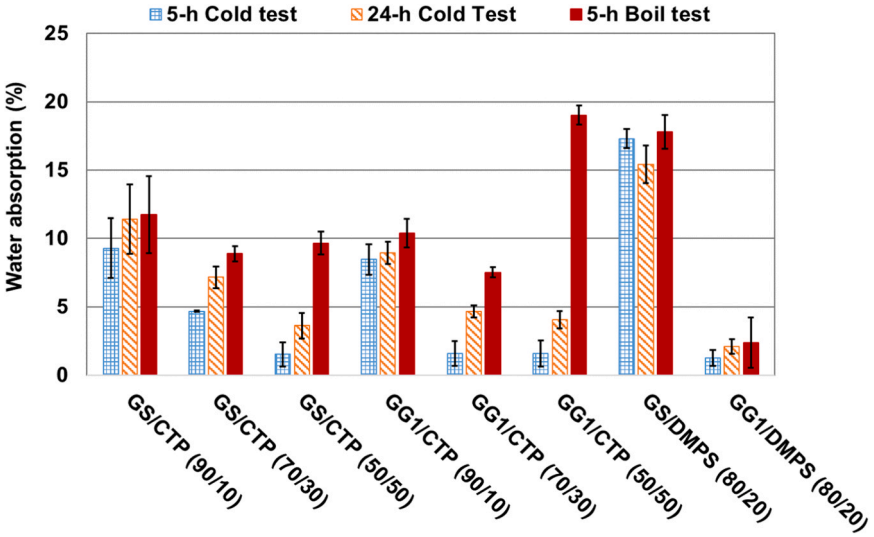


Fig. 10. Comparison of water absorption of the composites (CTP obtained at 400 °C).

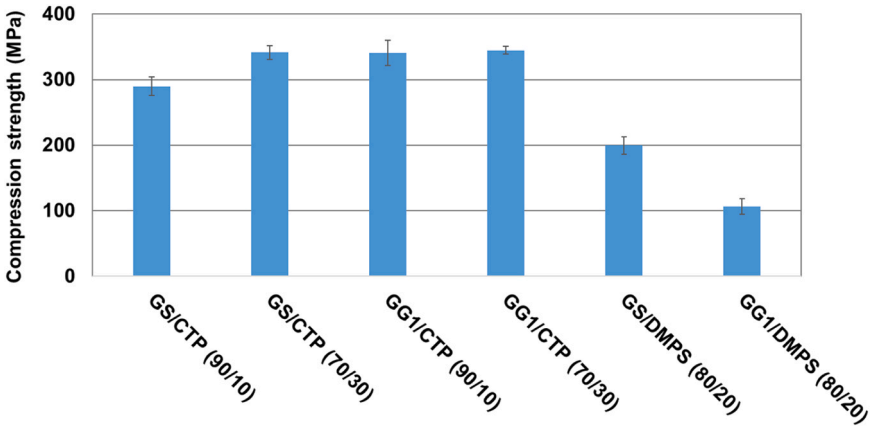


Fig. 11. Compressive strength of the coal composites.

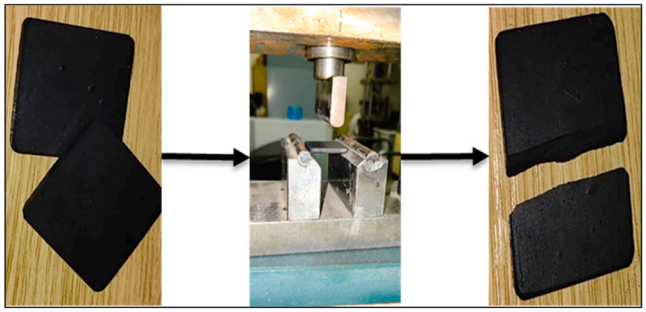


Fig. 12. Procedure used to test flexural strength.

gravity, bulk density, and water absorption were conducted to evaluate the quality and durability of the composites. The composite mixture pyrolyzed in an inert atmosphere to temperatures higher than 500 °C, evolves gases resulting in weight loss. Table 4 presents results for apparent porosity, apparent specific gravity, and bulk density under various water immersion conditions (5-h and 24-h cold water tests, and a 5-h boil water test). As anticipated, GG1 composites exhibited higher bulk and apparent densities when compared to GS composites due to higher inorganic mineral and ash content. Increasing CTP proportion yielded decreased bulk density across immersion tests, with values ranging from 1.32 to 2.044 g/cm^3 - lower than standard ceramic construction materials (2.05–2.17 g/cm^3) [33]. Elevated CTP ratios correlated with reduced composite porosity, indicating enhanced binding during pyrolysis and decreased pore size.

The water absorption test (Fig. 10) provided insights into composite water resistance crucial for composite building materials. All composites exhibited water absorption below 20 %, falling within the typical range for building materials (0–25 %) [12,13]. Notably, increasing the CTP content correlated with reduced water absorption and showed a direct relationship with porosity. Overall, composites utilizing coal fines (GG1/CTP (70/30)) with low volatile matter content and high H/C ratio showcased superior performance. The result aligns with findings from Eterigho-Ikelegbe et al. [14], where coal waste with a higher H/C atomic ratio yielded lower water absorption composites.

3.8. Compressive and flexural strength of the composites

Compressive strength is an essential parameter for structural composites as it determines the ability of the composites to withstand crushing loads. The composites' compressive strength ranged from 106.58 to 344.71 MPa (Fig. 11). Notably, the GG1/CTP (70/30) composite exhibits superior compressive resistance compared to the DMPS binder composites such as GG1/DMPS (80/20). Flexural strength testing

Table 5
Flexural strength of the coal composites (CTP obtained at 400 °C).

Composites	FS (MPa)	FM (GPa)	Yield Force (N)	Yield stress (MPa)
GS/CTP (90/10)	48.75 ± 0.361	1030 ± 0.5	97.5 ± 0.721	85.2 ± 0.681
GS/CTP (70/30)	159.3 ± 0.764	1270 ± 0.26	318.7 ± 1.528	284.3 ± 6.429
GG1/CTP (90/10)	-	-	-	-
GG1/CTP (70/30	63.8 ± 0.25	1408 ± 0.29	127.5 ± 0.5	113 ± 2
GS/DMPS (80/20)	-	-	-	-
GG1/DMPS (80/20)	-	-	-	-

CTP: coal tar pitch; DMPS: dimethylpolysiloxane; FS: flexural strength; FM: flexural modulus; MPa: Megapascals; N: Newtons; -: unavailable data

(Fig. 12) revealed GS/CTP (90/10), GS/CTP (70/30), and GG1/CTP (70/30) composites were able to withstand bending loads, with flexural strengths of 48.75, 159.30, and 63.80 MPa, respectively (Table 5). These values surpassed typical concrete roof tile flexural strengths (14–41 MPa) [1]. GG1/CTP (70/30) also exhibited the highest flexural modulus at 1408 GPa, indicating exceptional resistance to deformation under bending loads. This is attributed to the improved interfacial bonding between the mixture compositions [18,21]. These results suggest the potential of GS/CTP (90/10), GS/CTP (70/30), and GG1/CTP (70/30) composites in applications that require high mechanical performance.

4. Conclusion

The efficacy of using coal tar modified through air-blowing as a binder for coal fines composite production, alongside exploring the feasibility of dimethylpolysiloxane as an alternative binder was studied. The effects of binder quantity and coal fine quality on the physicomechanical properties and chemical structure of the composites were evaluated. Heat treatment of coal tar at 400 °C/9 h using the air-blowing method yielded a high-quality binder pitch composed of mesophase. Increasing the amount of CTP enhances the fusibility, compaction, and homogeneity of the CTP and coal fines during pyrolysis. GS-based composites recorded the worst weight loss (17.43 %) during pyrolysis. The produced composites possess acceptable water absorption levels (0–25 %) and most exceeded the minimum compressive strength requirement of 35 MPa for typical building materials. Notably, certain mixture ratios (GG1/CTP (90/10), GS/CTP (70/30), and GG1/CTP (70/30)) yielded composites of excellent flexural strength of up to 150 MPa.

These promising findings suggest the feasibility of modifying coal tar as a binder for coal fines via the pyrolysis technique to achieve cost-effective and desirable architectural composites. Continuous evaluations such as flammability assessment, environmental impact, and thermal stability are being conducted to verify further the suitability of these composites.

CRediT authorship contribution statement

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

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.

Acknowledgements

The first author received funding from Coaltech Research Association (Grant number: P2022-2) and this article forms part of his M.Sc. dissertation. The authors acknowledge the Helmut and Babs Amos Scholarship from the DAAD-Stiftung – DAAD South Africa and National Research Foundation (NRF) South Africa's SARChI Clean Coal Technology Grant (Grant number: 86421) for assisting with additional financial support. The authors' perspectives, research, and conclusions are entirely their own.

References

[1] S. Al-Thasneem, B.M. Reddy, A study on strength and durability of cement concrete made with industrial waste water containing iron heavy metal, Int. J. Res. Appl. Sci. Eng. Technol. *6* (2) (2018) 604–612. ⟨https://www.cabdirect.org/cabdirect/abstract/20183391452⟩.

[2] ArcelorMittal South Africa, Parliament colloquium on beneficiation, 27 August 2014. https://static.pmg.org.za/140827amsa.pdf. Accessed 11 February 2024.

[3] S.O. Bada, R.M.S. Falcon, L.M. Falcon, C.P. Bergmann, Co-firing potential of raw and thermally treated Phyllostachys aurea bamboo with coal, Energy Sources, Part A: Recovery, Util., Environ. Eff. *38* (10) (2016) 1345–1354, https://doi.org/10.1080/15567036.2014.921739.

[4] C. Banerjee, V.K. Chandaliya, P.S. Dash, Recent advancement in coal tar pitch-based carbon fiber precursor development and fiber manufacturing process, J. Anal. Appl. Pyrolysis *158* (2021) 105272, https://doi.org/10.1016/j.jaap.2021.105272.

[5] C. Banerjee, V.K. Chandaliya, P.S. Dash, B.C. Meikap, Effect of different parameters on porosity and compressive strength of coal tar pitch derived carbon foam, Diam. Relat. Mater. *95* (2019) 83–90, https://doi.org/10.1016/j.diamond.2019.04.009.

[6] D. Choi, H.-S. Kil, S. Lee, Fabrication of low-cost carbon fibers using economical precursors and advanced processing technologies, Carbon *142* (2019) 610–649, https://doi.org/10.1016/j.carbon.2018.10.028.

[7] K.H. Choi, S.-Y. Lee, I. Hong, S. Son, J.-C. An, S. Kim, Molecular-level investigation of coal-tar pitch treated by air blowing: revealing the restructure of aromatic compounds via radical reactions, Carbon *203* (2023) 377–385, https://doi.org/10.1016/j.carbon.2022.11.022.

[8] CoalTech (2024). https://www.coaltechenergy.com/market-overview/. Accessed 6 February 2024.

[9] The Coaltech Research Association (2023). https://coaltech.co.za/coal-processing/alternative-uses-of-coal-in-the-production-of-advanced-materials-and-lightweight-products-for-the-sustainability-of-the-south-african-coal-industry/. Accessed 14 June 2024.

[10] C. Daulbayev, B. Kaidar, F. Sultanov, B. Bakbolat, G. Smagulova, Z. Mansurov, The recent progress in pitch derived carbon fibers applications. A Review, South Afr. J. Chem. Eng. *38* (2021) 9–20, https://doi.org/10.1016/j.sajce.2021.07.001.

[11] W. Dun, L. Guijian, S. Ruoyu, F. Xiang, Investigation of structural characteristics of thermally metamorphosed coal by FTIR spectroscopy and X-ray diffraction, Energy Fuels *27* (10) (2013) 5823–5830, https://doi.org/10.1021/ef401276h.

[12] O. Eterigho-Ikelegbe, R. Trammell, E. Ricohermoso, S. Bada, Mechanism of bonding, surface property, electrical behaviour, and environmental friendliness of carbon/ceramic composites produced via the pyrolysis of coal waste with polysiloxane polymer, Environ. Sci. Pollut. Res. *30* (41) (2023) 93786–93799, https://doi.org/10.1007/s11356-023-28661-z.

[13] O. Eterigho-Ikelegbe, E. Ricohermoso, H. Harrar, R. Riedel, S. Bada, Strong, lightweight, thermally stable, and hydrophobic sustainable structural composites produced from coal-based waste and polymer-derived SiOC ceramics, Clean. Technol. Environ. Policy *25* (9) (2023) 2865–2884, https://doi.org/10.1007/s10098-023-02589-x.

[14] O. Eterigho-Ikelegbe, R. Trammell, S. Bada, Preparation and characterization of ceramic composites from South Africa coal discard, Constr. Build. Mater. *302* (2021) 124164, https://doi.org/10.1016/j.conbuildmat.2021.124164.

[15] O. Eterigho-Ikelegbe, R. Trammell, S.O. Bada, Novel ceramic composites produced from coal discards with potential application in the building and construction sectors, J. South. Afr. Inst. Min. Metall. *122* (8) (2022) 421–428, https://doi.org/10.17159/2411-9717/2001/2022.

[16] J.J. Fernández, A. Figueiras, M. Granda, J. Bermejo, R. Menéndez, Modification of coal-tar pitch by air-blowing - I. Variation of pitch composition and properties, Carbon *33* (3) (1995) 295–307. ⟨https://www.sciencedirect.com/science/article/pii/000862239400130R⟩.

[17] Future market insight (2024). ⟨https://www.futuremarketinsights.com/reports/coal-tar-pitch-market⟩. Accessed 14 June 2024.

[18] W. Guang-Heng, Z. An-ning, H. Xiao-Bing, Effect of coal filler on the properties of soy protein plastics, J. Appl. Polym. Sci. *102* (4) (2006) 3134–3143, https://doi.org/10.1002/app.24277.

[19] Hill, A., & Easter, W. (2021). Carbon ceramic composites and methods (United States Patent US10988680B2). https://patents.google.com/patent/US10988680B2/en.

[20] Hill, A., Sherwood, W., Trammell, R., & Easter, W. (2022). High strength, tough, coal and coal by-product based composite ceramics (United States Patent US20220144706A1). https://patents.google.com/patent/US20220144706A1/en.

[21] G. Hu, Z. Bian, R. Xue, W. Huang, S. Komarneni, Polymer-coal composite as a novel plastic material, Mater. Lett. *197* (2017) 31–34, https://doi.org/10.1016/j.matlet.2017.03.148.

[22] Y. Huang, H. Zhang, X. Zhang, L. Yan, Y. Ling, H. Zou, Y. Chen, M. Liang, Effect of mesophase pitch incorporation on the ablation behavior and mechanism of phenolic composites, Ind. Eng. Chem. Res. *61* (13) (2022) 4612–4624, https://doi.org/10.1021/acs.iecr.2c00367.

[23] J. Jiang, W. Yang, Y. Cheng, Z. Liu, Q. Zhang, K. Zhao, Molecular structure characterization of middle-high rank coal via XRD, Raman and FTIR spectroscopy: implications for coalification, Fuel *239* (2019) 559–572, https://doi.org/10.1016/j.fuel.2018.11.057.

[24] Lewitt, M. (2011). Opportunities for fine coal utilisation. IEA Clean Coal Centre. https://usea.org/sites/default/files/082011_Opportunities%20for%20fine%20coal%20utilisation_ccc185.pdf.

[25] K. Li, R. Khanna, J. Zhang, M. Barati, Z. Liu, T. Xu, T. Yang, V. Sahajwalla, Comprehensive investigation of various structural features of bituminous coals using advanced analytical techniques, Energy Fuels *29* (11) (2015) 7178–7189, https://doi.org/10.1021/acs.energyfuels.5b02064.

[26] H. Liu, T. Li, X. Wang, W. Zhang, T. Zhao, Preparation and characterization of carbon foams with high mechanical strength using modified coal tar pitches, J. Anal. Appl. Pyrolysis *110* (2014) 442–447, https://doi.org/10.1016/j.jaap.2014.10.015.

[27] X. Liu, Y. Wang, L. Zhan, Carbon foams prepared from coal tar pitch for building thermal insulation material with low cost, Chin. J. Chem. Eng. *26* (2) (2018) 415–420, https://doi.org/10.1016/j.cjche.2017.04.012.

[28] S. Mills, Combining solar power with coal-fired power plants, or cofiring natural gas, Clean. Energy *2* (1) (2018) 1–9. ⟨https://academic.oup.com/ce/article-abstract/2/1/1/4924632⟩.

[29] Muzenda, E. (2014). *Potential uses of South African coal fines: A review.* ⟨https://ujcontent.uj.ac.za/esploro/outputs/journalArticle/Potential-uses-of-South-African-coal/9911465307691?skipUsageReporting=true&skipUsageReporting=true&recordUsage=false&recordUsage=false&institution=27UOJ_INST⟩.

[30] M. Onifade, B. Genc, Spontaneous combustion of coals and coal-shales, Int. J. Min. Sci. Technol. *28* (6) (2018) 933–940. ⟨https://www.sciencedirect.com/science/article/pii/S2095268617307929⟩.

[31] F. Pacheco-Torgal, J.A. Labrincha, The future of construction materials research and the seventh UN Millennium Development Goal: a few insights, Constr. Build. Mater. *40* (2013) 729–737, https://doi.org/10.1016/j.conbuildmat.2012.11.007.

[32] R.H. Patel, S. Sharma, K.K. Prajapati, M.M. Vyas, N.M. Batra, Studies on non-oxide coating on carbon fibers using plasma enhanced chemical vapor deposition technique, AIP Conf. Proc. *1728* (1) (2016) 020480, https://doi.org/10.1063/1.4946531.

[33] I.A. Pavlova, S.S. Kutasheva, E.P. Farafontova, Production technology of ceramic roof tiles based on raw materials of Ural region, IOP Conf. Ser.: Mater. Sci. Eng. *687* (2) (2019) 022022, https://doi.org/10.1088/1757-899X/687/2/022022.

[34] V. Prada, M. Granda, J. Bermejo, R. Menéndez, Preparation of novel pitches by tar air-blowing, Carbon *37* (1) (1999) 97–106, https://doi.org/10.1016/S0008-6223(98)00191-2.

[35] M.J. Prauchner, V.M.D. Pasa, C. Otani, S. Otani, Characterization and thermal polymerization of eucalyptus tar pitches, Energy Fuels *15* (2) (2001) 449–454, https://doi.org/10.1021/ef000196o.

[36] S. Sharma, R.H. Patel, B.K. Patel, Comparative study on the carbon–carbon composites developed from petroleum pitch, coal tar pitch, and their mixture, J. Compos. Mater. *54* (23) (2020) 3395–3404, https://doi.org/10.1177/0021998320914068.
[37] W. Sherwood, A. Hill, G. Nameni, W. Easter, Composite tile and method of manufacture, Google Pat. (2021).
[38] R.C. Uwaoma, C.N. Henning, J.R. Bunt, N.T. Leokaoke, H. Neomagus, Comparison of industrial wastes as a binder in the agglomeration of coal fines, Results Eng. *16* (2022) 100729. ⟨https://www.sciencedirect.com/science/article/pii/S2590123022003991⟩.
[39] Y.-G. Wang, Z.-S. Niu, J. Shen, P. Li, Y.-X. Niu, W. Zhao, X.-Y. Wei, Formation of benzene polycarboxylic acids using alkali-oxygen oxidation of coal-tar pitch pre-treated by extraction and air-blowing, Fuel Process. Technol. *185* (2019) 100–105, https://doi.org/10.1016/j.fuproc.2018.12.001.
[40] Y. Yuan, D. Li, L. Zhang, Y. Zhu, L. Wang, W. Li, Development, status, and prospects of coal tar hydrogenation technology, Energy Technol. *4* (11) (2016) 1338–1348, https://doi.org/10.1002/ente.201600184.