

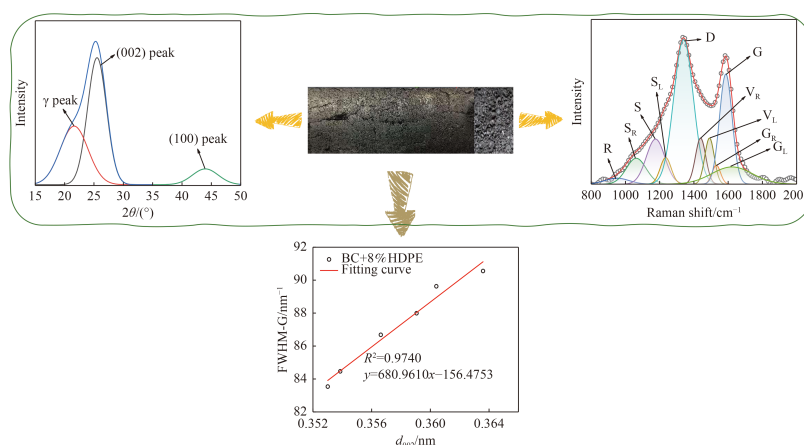
Mechanism of microstructural evolution in coke during the co-pyrolysis of coking coal with organic additives

ZHAO Xinni¹, TIAN Lu¹, YU Peng¹, XU Xiuli², DOU Jinxiao^{1,*}, YU Jianglong¹

¹ Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, College of Chemical Engineering, Liaoning University of Science and Technology, Anshan 114051, China;

² Sinosteel Anshan Research Institute of Thermo-Energy Co., Ltd., Anshan 114044, China

Abstract: To deepen understanding of the evolution of coal char microstructural properties of coal char during the co-pyrolysis of coking coal with additives, this study incorporated two typical additives, coal tar pitch (CTP) and waste plastic (HDPE), into a blended coal sample and carried out pyrolysis experiments. The pyrolysis process and the microstructure of char were systematically characterized using various analytical techniques,



including thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Raman spectroscopy. Data correlation analysis was performed to reveal the mechanism of carbon structural ordering evolution within the critical temperature range (350–600 °C) from colloidal layer formation to semi-coke conversion in coking coal, and to elucidate the regulatory effects of different additives on coal pyrolysis pathways. The results indicate that HDPE releases free radicals during high-temperature pyrolysis, accelerating the pyrolysis reaction and increase the yield of volatile components. Conversely, CTP facilitates pyrolysis at low temperatures through its light components, thereby delaying high-temperature reactions due to the colloidal layer's effect. XRD results indicate that during the process of pyrolysis, there is a progressive decrease in the interlayer spacing of aromatic layers (d_{002}), while the aromatic ring stacking height (L_c) and lateral size (L_a) undergo significant of carbon skeleton ordering. Further comparative reveals that CTP partially suppresses structural ordering at low temperatures, whereas HDPE promotes the condensation and alignment of aromatic clusters via a free radical mechanism. Raman spectroscopy reveals a two-stage reorganization mechanism in the microstructure of the coal char: the decrease in the I_D/I_G ratio between 350 and 550 °C is primarily attributed to the cleavage of aliphatic side chains and cross-linking bonds, leading to a reduction in defective structures; whereas the increase in I_D/I_G between 550 and 600 °C is closely associated with enhanced condensation reactions of aromatic structures. Correlation analysis further demonstrates progressive graphitization during pyrolysis, with a significant positive correlation ($R^2 > 0.85$) observed between d_{002} and the full width at half maximum of the G-band (FWHM-G).

Key words: coking coal; organic additives; co-pyrolysis; colloidal layer; carbon structure

The steel industry, which is responsible for nearly 15% of China's total carbon emissions, faces urgent pressure to reduce its carbon footprint through technological

innovation^[1–3]. Limited resources and mounting environmental constraints are accelerating the sector's transition toward “low-consumption, high-efficiency”

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* Corresponding author. Tel: 18841262185, E-mail: doujx123@163.com.

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production pathways, where coking coal blending technology plays a pivotal role^[4]. Coking, a core process in metallurgy and carbon material production, fundamentally involves the pyrolysis and polycondensation of coal at high temperatures. During this transformation process, the carbon structure of coal undergoes profound changes that determine the quality of the resulting coke. The microstructure of coke, particularly its degree of graphitization, directly influences its electrical conductivity, mechanical strength, and high-temperature stability. Recent studies have increasingly focused on structural evolution during coal pyrolysis by introducing exogenous additives. Bitumen and waste plastics, in particular, have attracted attention because of their availability and capability to modify carbon structures. Within the coking process, the gel phase (350–600 °C) defines the crucial reaction window for coal transformation and governs the formation and distribution of major products such as tar, gaseous products, and semi-coke. Compared to the drying stage, which primarily involves moisture removal, and the polycondensation stage, which is dominated by secondary reactions, the gel phase is the stage in which coal macromolecular break down, volatiles are released, and product selectivity is determined. This makes the gel phase the decisive interval for steering outputs toward high-value chemicals or clean fuels. Moreover, the initial structure of semi-coke is established during this phase, thereby shaping its subsequent performance. Furthermore, the core temperature range for industrial processes like coal pyrolysis and coking precisely corresponds to this stage, making research findings directly applicable for process optimization. In contrast, other stages involve either overly simple (drying) or overly complex (polycondensation) reactions, whereas the main stage simultaneously reveals the fundamental mechanisms of coal conversion and possesses clear practical value.

X-ray diffraction (XRD) and Raman spectroscopy serve as analytical tools. XRD enables quantitative characterization of crystalline phases^[5] and assesses the aggregation state of macromolecular structures, proving effective for obtaining microcrystalline parameters such as the size of coal aromatic nuclei and stacking height^[6]. Raman spectroscopy captures variations, including amorphous domains, aromatic configurations, and crosslinking density, which has made it a standard tool in coal research^[7]. Together, these techniques detect carbon structural changes at the microscopic level with high precision, offering robust support for elucidating additive mechanisms. Grint et al.^[8] proposed that the mixing process of non-caking coal, caking coal, and coking coal involves interactions among mixture components to form intermediate phases and optical textures. When used as an additive, petroleum pitch can effectively modify carbonization by participating in hydrogen transfer reactions. Li et al.^[9] concluded that XRD and Raman spectroscopy can characterize the phase evolution and structural differences during the graphitization trajectory of

high-rank coal. Xiang et al.^[10–11] thoroughly investigated the mechanisms of particle size adjustment for gas coal and lean coal, along with key technologies to increase blending ratios. Their work enabled blending of weakly caking coking coal above 30% without the need for briquetting or compaction, while maintaining coke quality. Viwero et al.^[12], Suresh et al.^[13], and others demonstrated that co-pyrolysis of high-density polyethylene (HDPE) with coal could both mitigate environmental pressures and reduce coal fluidity during pyrolysis. However, most existing research has focused on the distribution of final products from coal-additive co-pyrolysis^[14–15], such as tar yield, gas composition, and semi-coke properties, while neglecting dynamic characterization of the colloidal layer, a critical stage that governs mass and heat transfer efficiency. The core of coal-to-coke conversion lies in the formation of the plastic state (colloidal layer), during which changes in gel structure directly shape the development of coke's three-dimensional architecture and overall quality. In particular, when additives such as HDPE and coal tar pitch (CTP) are co-pyrolyzed with coal, the interaction mechanisms between these additives and coal macromolecules during the gel phase remain poorly understood. Current understanding of how additives influence carbon-structure evolution within the gel phase and regulate the formation and transformation of intermediate phases remains limited, constraining deeper insights into the co-pyrolysis mechanisms.

Therefore, this study aims to employ analytical characterization techniques, including XRD and Raman spectroscopy, to systematically investigate chemical structural changes and carbon-structure formation processes during the gel-formation stage (350–600 °C) of mixed coal with added asphalt and waste plastics. The objective is to clarify the mechanisms through which these additives affect the degree of coke graphitization during the coking of mixed coal. This research provides a theoretical basis for rationally selecting additives and optimizing coal blending strategies in coking production, thereby supporting the industry's pursuit of efficient, green development and the realization of China's "dual carbon" strategic goals.

1 Experimental

1.1 Materials

Two kinds of coal with differing degrees of metamorphism were utilized in the experiment, Kunpeng Fat Coal (FM) and Yonghesheng Lean Coal (SM), procured from Shanxi province, China. The raw materials utilized in this study included medium-temperature CTP from a coking plant in Anshan, Liaoning, and high-density polyethylene HDPE was purchased from Jiangsu Yaoyi Plasticization Co., Ltd. The proximate and ultimate analyses of the samples are shown in Table 1.

Table 1 Proximate and ultimate analysis of the samples

Sample	Proximate analysis $w_{ad}/\%$				Ultimate analysis $w_{daf}/\%$				
	<i>M</i>	<i>A</i>	<i>V</i>	FC*	C	H	O*	N	S
SM	1.03	11.23	19.05	68.69	80.11	4.32	14.24	0.83	0.49
FM	1.17	14.88	26.69	57.26	77.69	2.82	17.31	1.07	1.11
CTP	0.10	0.50	58.20	41.20	91.20	3.28	3.80	1.20	0.52
HDPE	0.00	0.08	99.92	0.00	85.24	14.76	0.00	0.00	0.00

ad-air dried basis; daf-dry ash free basis; *: calculation by difference.

The coal samples BC (Kunpeng fat coal: Yonghesheng lean coal = 9:1) were thoroughly mixed according to the specified ratio. The mixture was sieved using standard 12 mesh and 200 mesh screens, and the intermediate-sized fraction was collected to obtain coal samples with a particle size range of 0.074 to 1.500 mm. The pulverized sample was then dried in a vacuum oven for 8 h.

1.2 Experimental method

A program-controlled temperature coking apparatus was employed in this study to investigate the co-carbonization characteristics of coal and additives. Experimental samples were prepared by precisely blending coal sample BC (Kunpeng fat coal: Yonghesheng lean coal = 9:1) with two additives, CTP and HDPE, at mass percentages of 0, 2%, 4%, 6% and 8%. Subsequent to thorough mixing, the blends were loaded into quartz reactors designed for specific purposes. To ensure precise control over experimental variables, a manual pressure compensation device was employed to adjust the bulk density of samples to $790 \pm 10 \text{ kg/m}^3$. The compaction of coal to this specific density range was a deliberate choice, as the packing density of coal and the subsequent structure that emerges during the coking process. It was observed that all samples exhibited uniform density.

In this experiment, a staged gradient heating strategy was employed, the sample was heated at a rate of $10 \text{ }^\circ\text{C/min}$ to the critical temperature node at $300 \text{ }^\circ\text{C}$. Thereafter, a slow heating mode was implemented at rate of $5 \text{ }^\circ\text{C/min}$ to reach the final temperature of $1000 \text{ }^\circ\text{C}$. The isothermal process was sustained for a duration of 150 min within the designated coke maturation temperature zone. The experimental system utilized thermocouples for real-time monitoring of temperature distribution within the coal samples during heating. The use of calibrated temperature

probes ensured measurement accuracy within $\pm 1.5 \text{ }^\circ\text{C}$. To establish unidirectional heat transfer boundary conditions, the reactor featured a three-sided insulation design, with thermal insulation materials covering the bottom, top and side walls to effectively suppress radial heat dissipation.

This laboratory-scale directed heat transfer coking reaction system comprises core modules: an airtight quartz reaction tube ($\Phi 34 \text{ mm} \times 174 \text{ mm}$); a three-sided insulated jacket; an axially movable temperature measurement/sampling probe. A programmed temperature tracking system enables targeted sampling at different carbonization stages (plastic zone, semi-coke formation zone, coke shrinkage zone). After argon quenching, coke samples undergo structural characterization and performance testing per ISO standards. Figure 1 shows the schematic diagram of the coking experimental device.

The temperature gradient profile of the coal sample is shown in Figure 2. Three thermocouples are equidistantly arranged on the reactor to measure the central temperature variation of the coal seam with distance from the heating end. Thermocouple 1 measures temperatures between $300\text{--}500 \text{ }^\circ\text{C}$, Thermocouple 2 measures temperatures between 500 and $700 \text{ }^\circ\text{C}$ and Thermocouple 3 measures temperatures between 800 and $950 \text{ }^\circ\text{C}$. Samples were cut at equal intervals based on the actual temperatures detected by the thermocouples, yielding specimens from the gel-semi-coke stage. Since the reactor length was fixed and heating was applied via single-sided heat transfer, the temperature gradient was distributed continuously along the axial direction. Thus, equidistant cutting yielded samples corresponding to different temperature zones. Within the critical gel-semicoal temperature range ($350\text{--}600 \text{ }^\circ\text{C}$), six temperature points (e.g., $350, 400, 450, 500, 550, 600 \text{ }^\circ\text{C}$) were selected based on the temperature-distance correlation, ensuring each sample represented the maximum temperature experienced at that position.

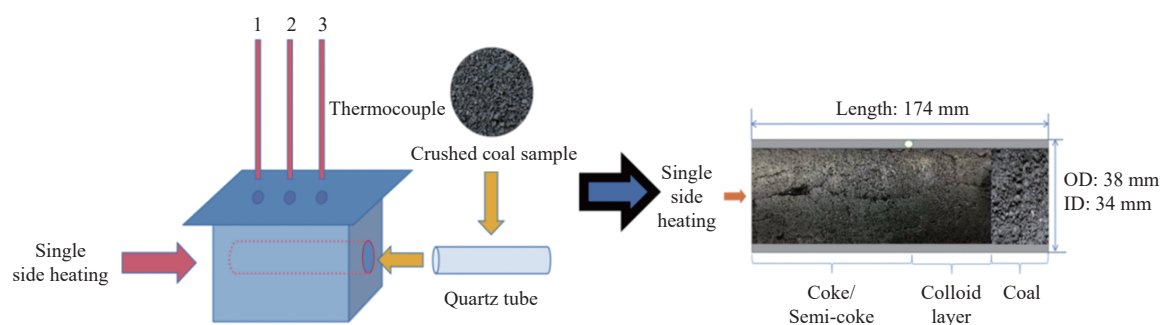


Fig. 1 Schematic diagram of the coking experimental device

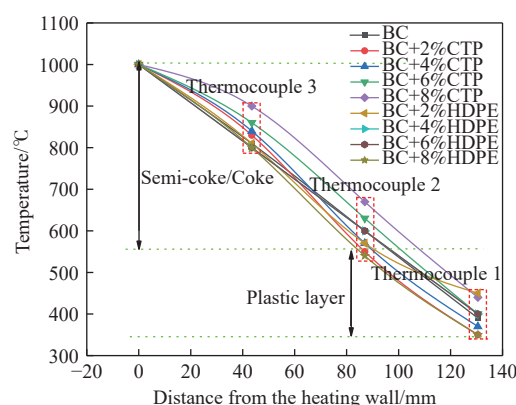


Fig. 2 Variation of central temperature in the coal seam with distance from the heating end

1.3 Experimental characterization

The coal coke samples were obtained at different pyrolysis temperatures and underwent relevant analytical testing. Weight loss analysis of the coal sample was performed using STA449 F3 TGA (Netesch, Germany) to generate the sample's weight loss/weight loss rate (TG/DTG) curve.

The crystalline structure of the samples was characterized using X-ray diffraction (XRD, Kuraray Co., Ltd., Japan) with a copper target radiation wavelength $\lambda = 0.15405$ nm, tube voltage 40 kV, current 100 mA, scanning range $2\theta = 10^\circ$ – 90° , scanning speed $\omega = 3^\circ/\text{min}$ and instrument step size 0.02° , $D_s = 1^\circ$, $S_s = 1^\circ$.

Raman spectroscopy was primarily applied to examine the crystal structure and molecular structure of coal samples. Raman analysis of a coal coke sample was conducted on the Raman microscopy (Raman, HORIBA Jobin Yvon S.A.S., France) with a single-crystal silicon substrate, laser wavelength 532 nm, laser power 5 mW, spectral resolution 1.5 cm^{-1} , integration time 1 s, accumulation count 10, with a scanning range of 100 – 4000 cm^{-1} .

2 Results and discussion

2.1 Thermogravimetric analysis of pyrolysis process

Pyrolysis experiments on nine coal samples yielded the thermogravimetric curves of coking coal, as shown in Figures 3(a), (c). The derivative of mass versus time from the TG curves produced the DTG curves depicted in Figures 3(b), (d). The DTG curve reflects changes in the thermal weight loss rate of the coal samples. Distinct weight loss rate peaks are observed on the DTG curves of all nine samples. The peak apex corresponds to the maximum weight loss rate of the coking coal, and the temperature at the peak apex is the maximum weight loss rate temperature (T_p), also known as the maximum pyrolysis temperature of the coal. The pyrolysis behavior of coal samples can be divided into three stages through TG-DTG curve analysis

(Figure 3): Before 300°C , both the TG curve and DTG curve show insignificant changes. Around 200°C , adsorbed gases in the coal, such as CO_2 and CH_4 , are primarily desorbed. Between 300 and 600°C , coking coal undergoes the most intense pyrolysis reactions. Aliphatic side chains undergo extensive cleavage, and oxygen-containing functional groups react extensively to produce gases such as CO , CO_2 and CH_4 . A gel-like substance containing gas, liquid, and solid phases is also formed. As the temperature rises, this gel undergoes further polycondensation reactions to form semi-coke. During this stage, a significant decrease in the TG curve and a distinct peak in the DTG curve are observed. When pyrolysis proceeds beyond 600°C , the semi-coke undergoes polymerization to form coke, releasing substantial amounts of H_2 . At this point, the TG curve decline flattens, while the DTG curve gradually rises, albeit with a minimal increase. This process reveals the multiscale evolution mechanism in coal pyrolysis, progressing from physical desorption to chemical bond breaking, gel phase transformation, and solid-state polymerization.

As shown in Figure 4, the pyrolysis conversion rate curve of coking coal dynamically characterizes its pyrolysis process through weight loss. The conversion rate x was defined as the proportion of weight loss at a given time relative to the total weight loss during pyrolysis^[16], which was calculated by Equation (1):

$$x = \frac{m - m_t}{m - m_f} = \frac{\Delta m}{\Delta m_t} \times 100\% \quad (1)$$

$$T_f = 2T_p - T_s \quad (2)$$

where m is the initial mass, m_t is the mass at a given time, m_f is the final pyrolysis mass; $\Delta m = m - m_t$ represents the instantaneous weight loss, and $\Delta m_t = m - m_f$ denotes the total weight loss^[17].

On the conversion curve, the point corresponding to $x = 50\%$ is designated as point A, and the point corresponding to $x = 5\%$ is designated as point B. By linearly fitting points A and B and extrapolating to $x=0$, the intersection temperature corresponds to the pyrolysis onset temperature T_s . The pyrolysis termination temperature T_f is calculated using equation (2). Additionally, characteristic parameters include the maximum weight loss rate temperature T_p , reflecting the intensity of the pyrolysis reaction^[18]. The measured values of the above parameters (T_s , T_p , T_f) are summarized in Table 2, providing key references for pyrolysis stage classification and subsequent analysis.

TG data indicate that when HDPE is blended with BC, the pyrolysis onset temperature (T_s) increases from 320°C to 378°C as the HDPE content rises from 2% to 8%. The peak pyrolysis rate temperature (T_p) approaches that of pure HDPE at 466°C , while total weight loss increases from 31.99% to 35.15%. This indicates that HDPE releases heat and free radicals through rapid high-temperature decomposition, significantly accelerating coal cracking and enhancing volatile matter yield.

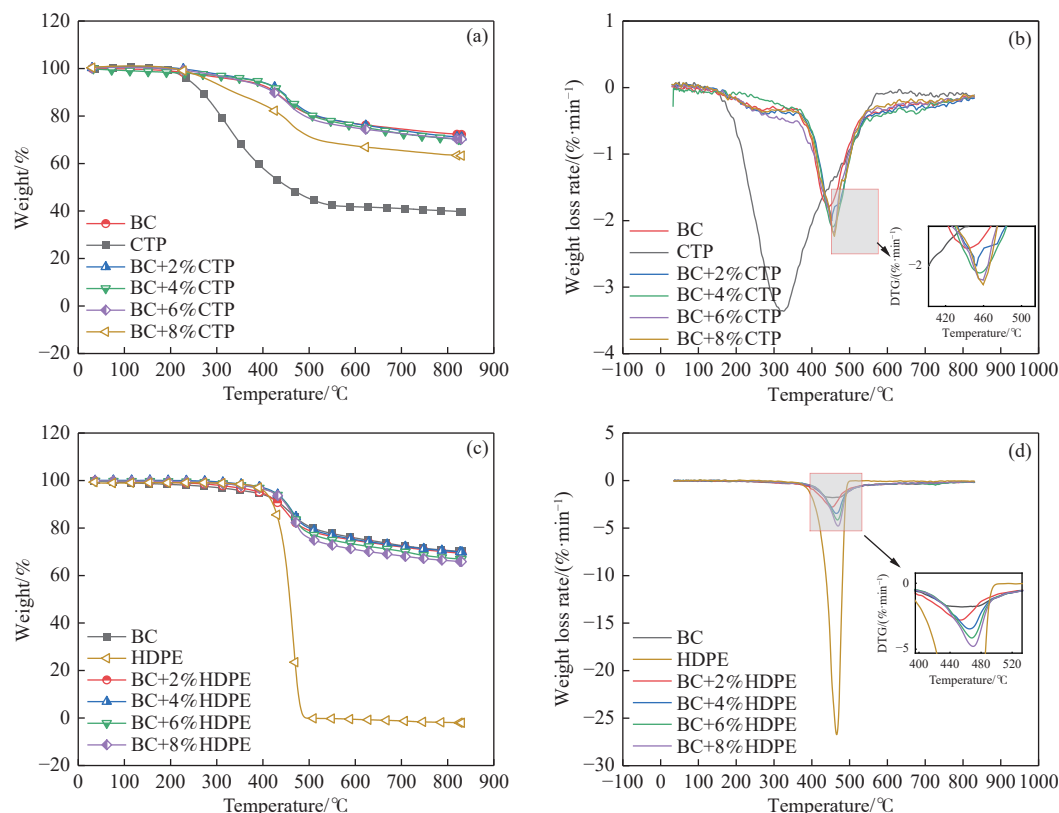


Fig. 3 Thermogravimetric profiles of the samples: (a), (c) TG curves; (b), (d) DTG curves

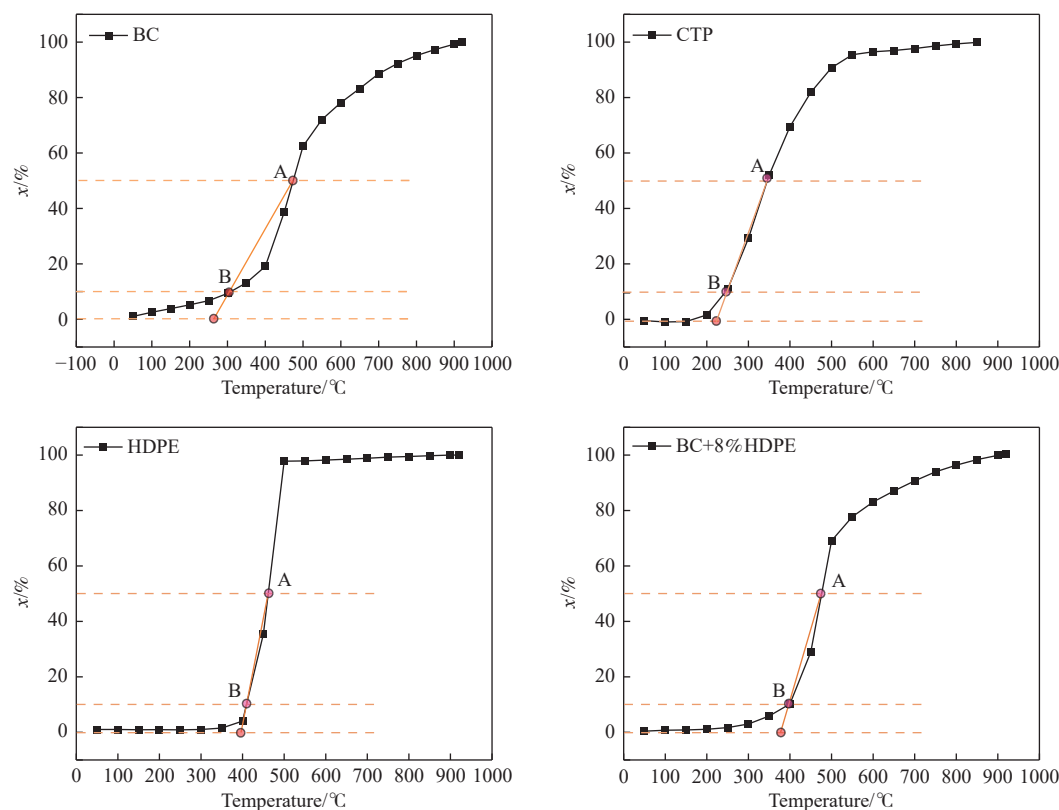


Fig. 4 Conversion rate curves

Table 2 TG-DTG parameters

Sample	T_s	T_p	T_f	DTG _{max} /(%·min ⁻¹)	Weight loss/%
HDPE	395.81	466.30	536.79	26.62	102.41
BC	264.25	454.85	645.45	1.80	30.91
BC+2%HDPE	320.11	452.51	584.91	2.81	31.99
BC+4%HDPE	375.97	466.05	556.13	3.44	31.16
BC+6%HDPE	375.28	468.81	562.34	4.14	34.39
BC+8%HDPE	377.79	469.56	561.33	4.77	35.15
CTP	219.79	322.25	442.29	3.36	60.23
BC+2%CTP	268.67	452.44	636.22	2.00	29.18
BC+4%CTP	264.71	455.40	646.10	2.08	29.79
BC+6%CTP	258.32	458.60	658.87	2.18	29.80
BC+8%CTP	217.28	459.44	701.59	2.24	36.91

T_s is the pyrolysis start temperature, T_p is the temperature corresponding to the maximum rate of pyrolysis, T_f is the pyrolysis end temperature.

It is suitable for high-efficiency gas or liquid fuel production processes. When CTP is blended with coal, adding 8% CTP reduces T_s from 264.25 to 217 °C (approaching the low-temperature decomposition characteristics of pure CTP). Concurrently, the pyrolysis completion temperature (T_f) extends to 701.59 °C, with total loss increasing to 36.91%. This indicates CTP initiates coal pyrolysis at low temperatures via light components while retarding high-temperature reactions through its colloidal fraction, making it suitable for staged product recovery (e.g., co-production of low-temperature light oil and high-temperature coke). The additive's influence on radical generation and bond energy distribution causes the peak temperature difference. HDPE undergoes chain cleavage at higher temperatures, generating an abundance of alkyl radicals. These radicals facilitate the breakage of coal-based macromolecules via hydrogen extraction and chain propagation mechanisms. This significantly accelerates pyrolysis and increases the yield of volatile matter in the high-temperature zone. This results in elevated DTG peaks and a shift of T_p toward the cracking temperature of HDPE. Conversely, CTP contains light components with low boiling points that participate in hydrogen transfer at lower temperatures, prematurely inducing weak bond breakage in coal and lowering T_s . Its polymer/resin components form a high-viscosity liquid phase or coating layer during the gel phase. This physically inhibits volatile diffusion and restricts radical migration. These factors impede high temperature reactions, prolong T_f , and broaden the DTG peak shape. Overall, both additives optimize coal pyrolysis behavior through synergistic effects, but HDPE emphasizes rate and yield enhancement while CTP focuses on stage regulation. Practical application requires selecting the appropriate scheme based on target products.

2.2 X-ray diffraction analysis

Taking BC as an example, its XRD patterns are shown in Figure 5. As depicted in Figure 5, coal contains a significant proportion of highly disordered material composed of

amorphous carbon^[19]. As the pyrolysis temperature increases, the coal sample enters the gel phase. At this stage, low-molecular-weight components generated by covalent bond cleavage significantly influence softening and fluidity^[20], causing the γ peak to gradually flatten and broaden. By the semi-coke phase, the γ peak nearly disappears, indicating near-complete decomposition of the coal's fat structure. The full width at half maximum (FWHM) of the (002) peak gradually narrows, the characteristic peak shifts toward higher angles, and peak intensity continuously increases. This result indicated that as pyrolysis continued, the order of the coal sample steadily increases. The FWHM of the (100) peak gradually narrows, the characteristic peak shifts toward lower angles, and peak intensity continues to increase. This result indicated that as pyrolysis continued, the microcrystalline structure of the coal sample tended toward stability. During the colloidal layer-semi-coke stage, the highly disordered structure dominated by amorphous carbon in the coal undergoes significant transformation with increasing temperature.

Peak fitting was performed on the γ peak and (002) peak within the 15°–35° range using Origin 2024 software, as well as the (100) peak within the 35°–50° range of the XRD patterns, achieving an $R^2 \geq 0.99$ for the fitting results. BC 450 °C was selected as the template here. The fitting results for its (002) peak and (100) peak are shown in Figure 6.

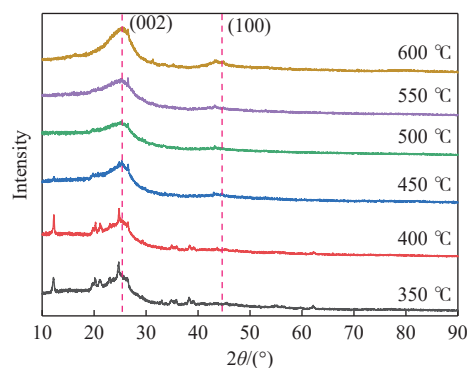


Fig. 5 XRD patterns of BC at different temperatures

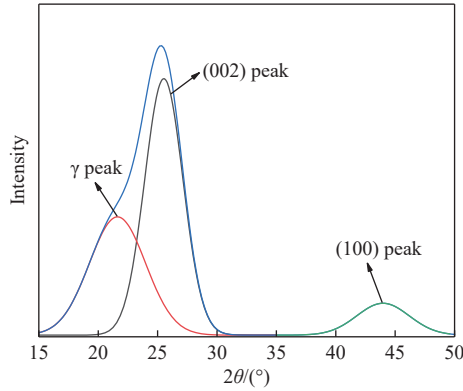


Fig. 6 XRD fitting map

Based on the fitting results, the aromatic interlayer spacing (d_{002}) and aromatic cluster sizes (L_c , L_a) were calculated using the Bragg formula (Equation (3)) and the Scherrer formula (Equations (4) and (5)). Peak (100) represents the number of aliphatic carbon atoms (C_{al}); thus, the aromaticity (f_a) was calculated using Equation (6)^[21]. Figure 6 shows the temperature-dependent variations in XRD microcrystalline carbon structure parameters for each coal sample during the gel phase.

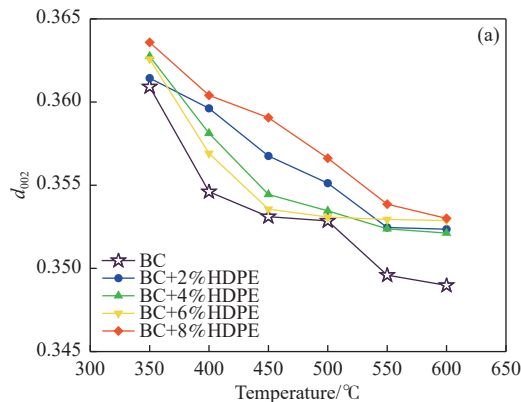
$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (3)$$

$$L_c = \frac{0.94\lambda}{\beta_{002}\cos\theta_{002}} \quad (4)$$

$$L_a = \frac{1.84\lambda}{\beta_{100}\cos\theta_{100}} \quad (5)$$

$$f_a = \frac{A_{002}}{A_{002} + A_\gamma} \quad (6)$$

In the equation, d_{002} represents the aromatic interlayer spacing, L_c denotes the planar extension, L_a indicates the aromatic stacking height, f_a signifies the aromaticity, λ is the X-ray wavelength (constant $\lambda = 0.15406$ nm), θ is the peak position of the diffraction peak, β is the half-width at half-maximum of the diffraction peak, and A is the peak area of the diffraction peak.



As shown in Figure 7, d_{002} exhibits a continuous decrease with increasing pyrolysis temperature, indicating a gradual reduction in the interplanar spacing of aromatic layers. This is attributed to the coal sample melting into a gelatinous state, where the aromatic layers within the sample undergo polycondensation reactions. Chemical bonds begin to break and reform, increasing molecular structural activity. This leads to a tighter arrangement of carbon atoms, enhancing the interlayer interactions between aromatic layers while reducing interlayer voids and disordered arrangements^[22].

Comparative analysis of samples incorporating varying proportions of CTP and HDPE. XRD analysis indicates that CTP and HDPE exert significantly different effects on the ordering of carbon structures during BC pyrolysis. At low temperatures (300–450 °C), CTP addition inhibits interlayer spacing (d_{002}) contraction through gelation (e.g., BC+8%CTP exhibits d_{002} =0.358 nm at 450 °C, higher than pure BC's 0.355 nm), delaying the ordered stacking of aromatic layers. At high temperatures (>500 °C), light hydrocarbons generated from CTP decomposition participate in polycondensation reactions, ultimately yielding a d_{002} value (approximately 0.350 nm at 600 °C) close to that of pure coal. This demonstrates synergistic coking properties consistent with thermogravimetric analysis results. HDPE addition accelerates macromolecular coal fragmentation via free radicals generated during high-temperature cracking, significantly promoting interlayer spacing contraction even in the low-temperature stage (e.g., BC+8% HDPE exhibits d_{002} =0.348 nm at 450 °C, lower than pure BC). During the high-temperature stage, its short-chain hydrocarbons further intensify aromatic ring condensation, resulting in a d_{002} value (0.342 nm at 600 °C) significantly lower than pure coal, indicating a marked increase in graphitization.

As shown in Figure 8, CTP and HDPE have opposite effects on the evolution of the lateral dimension (L_a) of aromatic rings during BC pyrolysis. At low temperatures (300–450 °C), CTP addition inhibits planar expansion of aromatic rings through gummatization (e.g., $L_a = 1.5$ nm at 450 °C for BC+8%CTP, lower than the 1.8 nm of pure BC).

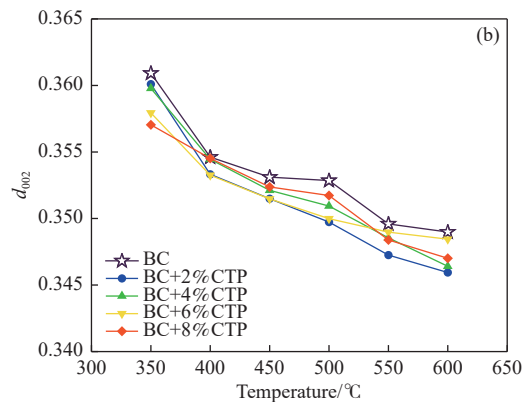


Fig. 7 Variation of microcrystalline structural parameters with temperature: (a) d_{002} of the sample with HDPE added; (b) d_{002} of the sample with CTP added

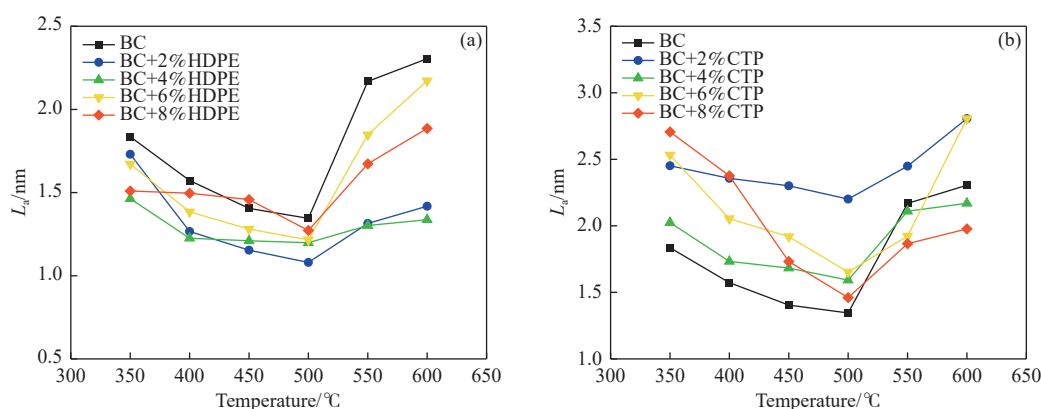


Fig. 8 Variation of microcrystalline structural parameters with temperature: (a) L_a of the sample with HDPE added; (b) L_a of the sample with CTP added

While its adhesive properties further restrict microcrystalline growth in the high-temperature stage (500–650 °C) ($L_a = 2.2$ nm at 650 °C, significantly lower than the 3.5 nm of pure BC), indicating that CTP delays polycondensation reactions through physical hindrance. Adding HDPE catalyzes coal macromolecular fragmentation via free radicals generated during high-temperature pyrolysis. This accelerates aromatic ring expansion during the low-temperature stage ($L_a = 2.5$ nm at 450 °C for BC+8%HDPE, exceeding pure BC). During the high-temperature stage, short-chain hydrocarbons produced by HDPE decomposition serve as carbon sources, significantly promoting aromatic

ring condensation (L_a reaches 2.8 nm at 600 °C), resulting in markedly larger microcrystalline dimensions.

As shown in Figure 9, the result indicates that as pyrolysis temperature increases, the L_c value begins to rise rapidly while the L_a value decreases sharply, signaling entry into a more active pyrolysis stage. The rates of chemical bond breaking and recombination significantly accelerate, generating a large number of free radicals. Some of these radicals participate in cross-linking condensation reactions within the coal sample, promoting the formation of its internal ordered structure.

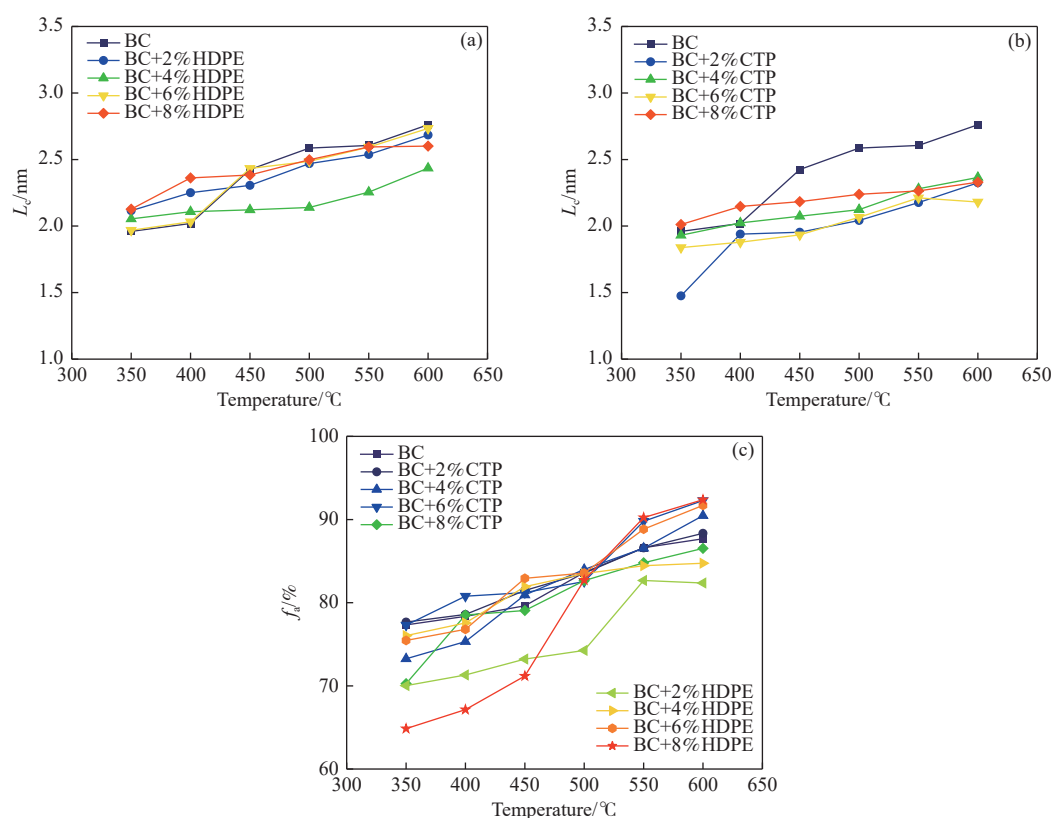


Fig. 9 Structural parameter variations of carbon microcrystals with temperature: (a) L_c of the sample with HDPE added; (b) L_c of the sample with CTP added; (c) f_a of the sample

At this stage, small molecules generated between aromatic layers during pyrolysis act as lubricants, facilitating relative sliding along the layered direction. Adjacent aromatic layers rapidly connect, stack, and arrange themselves tightly, undergoing polycondensation and rearrangement to form large-area, ordered aromatic layers. Notably, CTP and HDPE exhibit distinct regulatory mechanisms for carbon structural parameters during BC pyrolysis. Regarding L_c (aromatic ring stacking height), CTP delays stacking via gelation at low temperatures (300–450 °C) (e.g., BC+8%CTP exhibits $L_c=2.2$ nm at 450 °C, lower than pure BC's 2.5 nm). While HDPE significantly promotes stacking through radical catalysis (BC+8%HDPE exhibits $L_c=3.8$ nm at 650 °C, higher than pure BC's 3.5 nm). Regarding f_a (aromaticity), CTP delays aromatization in the low-temperature range, whereas HDPE catalyzes graphitization throughout the process. In summary, CTP's staged regulation (low-temperature suppression and high-temperature synergy) makes it suitable for functional carbon material preparation (e.g., adsorbents), while HDPE's enhanced cracking and polycondensation reactions favor high-graphitization coke production (e.g., electrode materials). Their synergy effect provides a multiscale regulation strategy for the targeted design of coal-based carbon materials.

2.3 Raman analysis

Taking BC as an example, the Raman spectra of coking products between 350–600 °C are shown in Figure 10. Raman peak intensities decrease overall with increasing temperature, with significantly greater changes observed between 450–600 °C. This indicates more intense coal-coke reactions and more pronounced structural changes in the coke during this temperature range. The Raman peak intensity of coal and coke is determined by their Raman scattering capability and optical absorption capacity.

To investigate changes in carbon structural order during the gel phase, this study employed Peak Fit v4.12 software to perform peak-by-peak fitting of Raman spectra using a 10-peak method, requiring $R^2 \geq 0.99$. Here, BC-350 °C is selected as an example, with the Raman fitting spectrum shown in Figure 11.

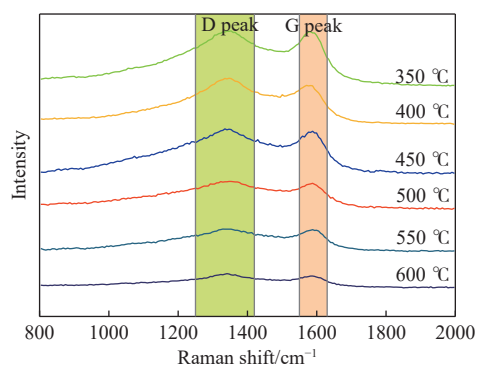


Fig. 10 The Raman fitting spectra of coking products of BC at different temperatures

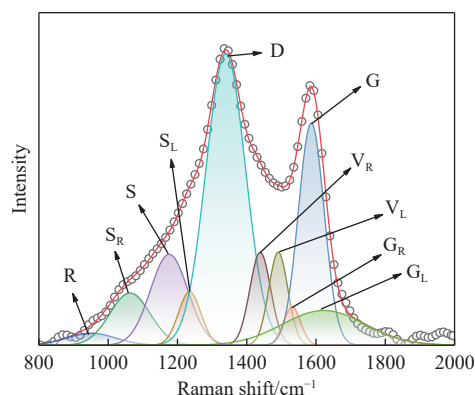


Fig. 11 Raman fitting spectrum

The full width at half maximum of the G-band FWHM-G represents the full width at half maximum of the G peak, indicating the order of the carbon structure^[23–24].

Raman spectral fitting results of nine coal blending systems during the colloidal layer-semi-coke stage (350–600 °C) are shown in Figure 12. The evolution patterns of structural parameters reveal key pyrolysis mechanisms. The intensity of the D peak positively correlates with the disorder of carbonaceous materials (defects, sp^3 hybridized structures), while the G peak intensity reflects the graphitization degree of sp^2 carbon ordered domains. The core parameter I_D/I_G serves a dual indicative role: it characterizes the relative abundance of large polycyclic aromatic structures in coal while also functioning as an order index (higher ratios correspond to reduced graphitization). This ratio exhibits a distinct two-stage evolution pattern (Figure 12(a)): a continuous decline between 350–550 °C followed by a sharp increase at 550–600 °C. Specifically, the gradual decrease of I_D/I_G between 350–400 °C stems from the dissociation of large polycyclic aromatic structures into smaller aromatic units due to crosslink bond breakage. Deposition of small aromatic molecules forms surface defects and amorphous regions. Concurrently, active sites generated by aliphatic chain removal promote aromatic rearrangement, partially enhancing local order. The deceleration rate of I_D/I_G between 400–500 °C exhibits coal-type dependency. During this stage, accelerated crosslink bond breakage drives enhanced polycondensation and aromatization reactions, forming smaller, thermally more stable aromatic clusters. Concurrent volatilization of CH_4 , CO and other volatiles further reduces the relative abundance of large polycyclic aromatic structures. Notably, the content of large polycyclic aromatic structures is closely related to the potential for gel formation. Comparing the I_D/I_G of benchmark coal (BC) shows that adding CTP or HDPE ($\geq 6\%$) significantly disrupts the pyrolysis pathway, affecting semi-coke formation and final coke quality. The rapid increase in I_D/I_G after 550 °C corresponds to the vitreous transition of the gel phase and a sharp drop in radical concentration.

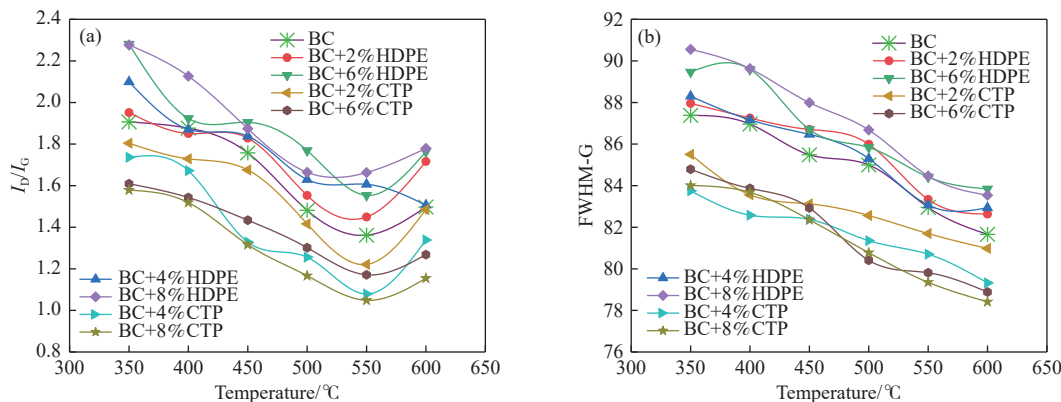


Fig. 12 Raman structural parameters of coal samples: (a) variation of I_D/I_G with temperature; (b) variation of FWHM-G with temperature

The removal of amorphous carbon phases promotes the polycondensation of macromolecular networks into highly condensed aromatic units. Comparing I_D/I_G values at 350 and 600 °C reveals an overall decrease in large polycyclic aromatic structures after the gel phase, indicating incomplete condensation of small aromatic rings.

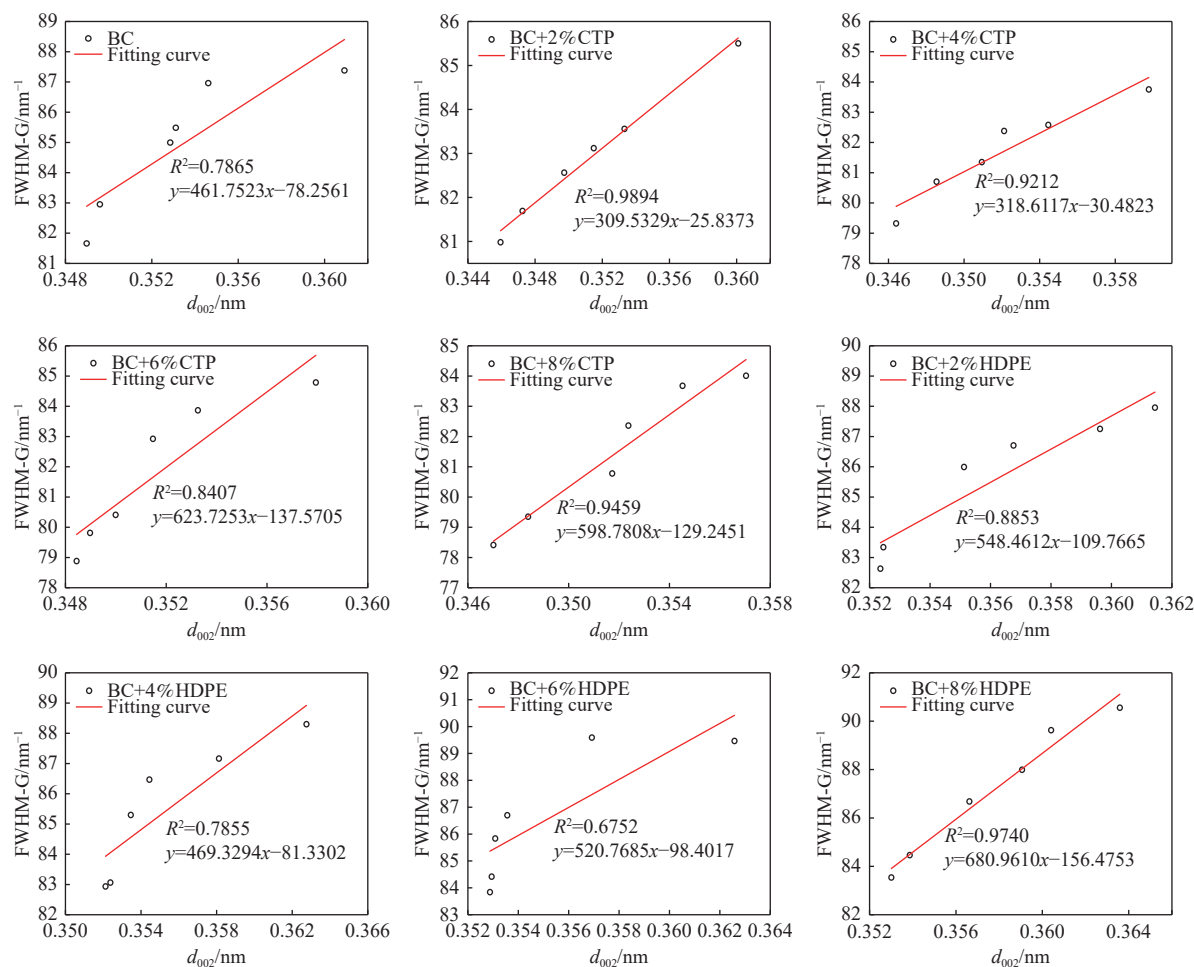
This phenomenon corroborates Qi Yuexin's findings that large polycyclic aromatic content in semi-coke to coke stages (>600 °C) continues to rise until reaching an inflection point at 900 °C. Additive effect analysis (Figure 12(b)) further reveals: Compared to BC, the HDPE-added system exhibits enhanced G peaks and significantly increased I_D/I_G ratios, indicating its suppression of graphitization in the coal matrix and enhancement of system disorder. Conversely, the CTP system shows weakened G peaks and reduced I_D/I_G ratios, confirming its promotion of ordered development. These two systems thus exhibit opposed regulatory mechanisms.

2.4 XRD and Raman correlation analysis

In XRD analysis, it was observed that as coal pyrolysis progressed, the stacking height of carbon microcrystalline layers increased while their lateral dimensions first decreased and then increased. The rise in aromaticity also indicated a deepening graphitization of the coal sample. Raman analysis revealed a two-stage change in both the large aromatic ring content and amorphous carbon content of the coal sample. Concurrently, the decrease in FWHM-G indicates an increase in the sample's order. Raman spectroscopy (I_D/I_G , FWHM-G) reflects the size of local sp^2 clusters and defect density. XRD (d_{002} , L_c , L_a) characterizes interlayer stacking and crystal size. As pyrolysis progresses from the gel phase to semi-coke, improvement in local order promotes interlayer stacking and long-range order of the crystal, showing significant statistical coupling. To

correlate structural features with lattice parameters, this study constructed a cross-scale correlation model of XRD-Raman. By integrating XRD and Raman results, we further investigate the behavior and evolution mechanisms during coal pyrolysis.

Figure 13 shows the correlation analysis between d_{002} and FWHM-G for nine sample groups. It can be observed that d_{002} and FWHM-G exhibit an overall positive linear correlation. As d_{002} increases, the FWHM-G value continues to rise, indicating that the interplanar spacing generally shows a negative correlation with order. As coal pyrolysis progresses, the interplanar spacing of aromatic layers decreases, bringing aromatic layers closer together and reducing the distance between molecular bonds. At this stage, intermolecular van der Waals forces cause the aromatic layers to bind tightly, resulting in a more ordered arrangement. This reduces relative sliding and disordered distribution between layers, thereby increasing order. Order exhibits multifaceted effects on the interplanar spacing of aromatic layers. Initially, during the early stages of coal pyrolysis, order is relatively low, and the interplanar spacing is large. As pyrolysis progresses and the temperature gradually increases, the organic matter in coal undergoes thermal decomposition and polycondensation reactions. Some side chains and functional groups detach from the aromatic structures, releasing volatiles. However, the overall increase in orders is not yet significant at this stage. Although the interplanar spacing decreases, the change is relatively slow. As pyrolysis temperatures further increase, the order of coal pyrolysis rapidly rises. Polycondensation reactions within aromatic structures intensify, leading to continuous growth and stacking of aromatic layers. Carbon atoms arrange themselves more regularly, forming numerous graphite-like microcrystalline structures. At this stage, the interplanar spacing reaches its maximum limit, with the d_{002} value approaching that of graphite's crystal plane spacing.

Fig. 13 Correlation analysis of nine samples FWHM-G and d_{002}

3 Conclusions

This study systematically revealed the evolution of carbon structures in coking coal during the colloidal layer-semi-coke stage (300–600 °C) through combined XRD and Raman spectroscopy techniques. It elucidated the differential regulatory mechanisms of CTP and HDPE additives on coal pyrolysis pathways. Key conclusions are as follows:

(1) TGA indicates that HDPE rapidly decomposes at high temperatures, releasing heat and free radicals to significantly accelerate coal cracking and enhance volatile matter yield. This renders it suitable for high-efficiency gas or liquid fuel production processes.

In contrast, CTP mixed with coal initiates pyrolysis at low temperatures via its light components while retarding high-temperature reactions through its gelatinous phase. This renders it suitable for staged product recovery, such as the co-production of low-temperature light oil and high-temperature coke. Both additives synergistically optimize coal pyrolysis behavior, but HDPE emphasizes rate and yield enhancement while CTP focuses on stage regulation. Practical application requires selecting the appropriate scheme based on target products.

(2) XRD analysis indicates that during coal pyrolysis, there is a continuous decrease in aromatic interlayer spacing, while the stacking height and lateral dimensions of aromatic rings significantly increase. These findings confirm the transformation of carbon microcrystals from a disordered to highly ordered graphitic structures.

(3) The two-stage evolution of Raman parameters (I_D/I_G , FWHM-G) (a decrease at 350–550 °C followed by an increase at 550–600 °C) reveals a multiscale reorganization mechanism: crosslink bond breakage triggers dissociation of large polyaromatic structures, which then leads to the condensation of small aromatic units and the formation of highly condensed aromatic networks.

(4) During the co-pyrolysis of CTP and coal, the low-temperature range (300–450 °C) has been shown to inhibit interlayer spacing contraction and aromatic ring extension through gelatinous encapsulation, thereby delaying ordering. The high-temperature range (>500 °C) facilitates synergistic condensation involving light hydrocarbons, thereby enabling the controlled synthesis of functional carbon materials (e.g., adsorbents). HDPE: Radical catalysis accelerates low-temperature cracking, while the presence of short-chain hydrocarbons at high temperatures enhance aromatic ring condensation, thereby significantly increasing

graphitization. This facilitates the targeted production of high-value graphite coke (e.g., electrode materials).

(5) The XRD-Raman cross-scale correlation I_D/I_G shows significant positive correlation with FWHM-G, thereby confirming the synergistic evolution of reduced interlayer spacing and enhanced order. This correlation provides validation for the “disorder-to-order” transformation in coal pyrolysis.

Declaration of Competing Interest

The authors declare no conflict of interest.

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炼焦煤与有机添加剂共热解过程中煤焦微观结构演变机制

赵馨妮¹, 田 露¹, 于 鹏¹, 徐秀丽², 窦金孝^{1,*}, 余江龙¹

(1. 辽宁科技大学化学工程学院 辽宁省先进煤焦化重点实验室, 辽宁 鞍山 114051;
2. 中钢集团鞍山热能研究院有限公司, 辽宁 鞍山 114044)

摘 要: 本研究在混合煤样中分别引入两种典型添加剂—煤沥青(CTP)和废塑料(HDPE)并进行热解实验。采用热重分析(TGA)、X射线衍射(XRD)和拉曼光谱(Raman)等分析手段,对热解过程及所得煤焦的微观结构进行表征,并通过数据关联分析,旨在揭示炼焦煤在胶质体形成至半焦转化关键温度区间(350–600 °C)内炭结构有序化演变机制,阐明不同添加剂对煤热解路径的调控作用。结果表明,HDPE在高温裂解释放自由基,加速热解反应并提高挥发分产率;CTP则通过轻质组分在低温促进热解,并因胶质层作用延缓高温反应。XRD结果表明,热解过程中芳香层片间距(d_{002})逐渐减小,芳环堆叠高度(L_c)与横向尺寸(L_a)显著增加,表明炭骨架有序化程度不断提升。进一步对比表明,CTP在低温阶段一定程度抑制结构有序化,而HDPE通过自由基机制芳香簇的缩合与排列。Raman分析揭示了两阶段煤焦微观结构重组特征:在350–550 °C, I_D/I_G 值的下降主要归因于脂肪侧链和交联键的断裂,导致缺陷结构减少;而在550–600 °C, I_D/I_G 值的上升则与芳香结构的缩聚反应密切相关。关联分析结果表明,热解过程中样品石墨化程度增加, d_{002} 与 FWHM-G 呈显著正相关 ($R^2>0.85$)。

关键词: 炼焦煤; 有机添加剂; 共热解; 胶质层; 炭结构

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作者简介:



赵馨妮(2000), 硕士研究生, 研究方向为煤焦化与焦炭质量评价, 1443877642@qq.com。



窦金孝(1986), 博士, 副教授, 研究方向为煤炭和生物质清洁高效热转化、气体净化技术与反应过程、煤基固体废弃物资源化利用、煤基碳材料, doujx123@163.com。