

Preparation and structure evolution of coal-based needle coke by co-carbonization of coal direct liquefaction pitch and waste engine oil

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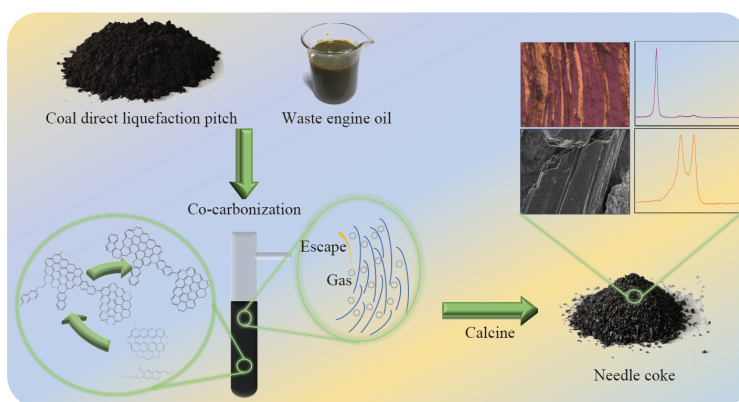
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Abstract: Needle coke, a high-performance artificial carbon material, requires precise composition control of its raw materials as this critically determines the structural characteristics and performance of the final product. In this study, needle coke samples were prepared from coal direct liquefaction pitch (CDLP) and waste engine oil (WEO) through component optimization and a co-carbonization process. The microstructure and properties were investigated using the following characterization techniques:

Fourier Transform Infrared Spectroscopy (FT-IR), Polarized Light Microscopy (PLM), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Raman Spectroscopy, Thermogravimetric Analysis (TGA), Micro-Strength (MS) and Powder Resistivity (PR). The co-carbonization mechanism of CDLP and WEO was systematically investigated. The results indicated that the incorporation of WEO significantly reduced the viscosity of the co-carbonization system, and its abundant aliphatic structures provided alkyl radicals and active sites. The synergistic interaction of aromatic components between the CDLP and WEO effectively promoted the growth and order accumulation of aromatic carbon layers. When 50% WEO was introduced, the prepared needle coke exhibited an excellent microstructure and properties. The fibrous and leaflet structure content reached 76.2%, the ideal graphite lattice content reached 89.7%. These results demonstrated remarkable oxidation resistance and electrical conductivity, with a powder resistivity of 605.1 mΩ·mm. This work establishes a process with cost advantages for the production of needle coke.

Key words: needle coke; co-carbonization; coal direct liquefaction pitch; waste engine oil



Needle coke, a synthetic carbon material with an ordered structure and facile graphitization, exhibits characteristics such as high thermal and electrical conductivity, low thermal expansion coefficient, and high mechanical strength^[1–3]. Its outstanding comprehensive properties are extensively utilized in the fabrication of artificial graphite, anode materials for lithium-ion batteries, high-power and ultra-high-power electrodes^[4–6]. The industrial production of

needle coke is categorized into three processes: (i) raw material pretreatment, (ii) delayed coking, and (iii) calcination^[7]. Specifically, the raw material pretreatment stage determines the formation and development of the carbonaceous structure during the carbonization process^[8]. In other words, precisely regulating the component structure of the raw materials is the key to prepare high-performance needle coke. In recent years, with the advancements in the

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fields of clean energy and advanced materials, the demand for low-cost and high-performance needle coke has significantly increased. Many researchers have employed pretreatment strategies of the raw material through solvent extraction^[9–11], co-carbonization^[12–13], high-pressure thermal polymerization^[14], or a combination of one or more methods^[15–16], to achieve the regulation of raw material components and prepare high-performance needle coke.

The co-carbonization method has emerged as a highly effective approach for optimizing the structural characteristics and performance properties of needle coke. This technique involves the simultaneous carbonization of two or more raw materials with distinct chemical compositions and properties. Compared to the other methods, the co-carbonization method offers several substantial advantages, including (i) the utilization of a broader range of raw material sources, (ii) reduced production costs, and (iii) simplified operational procedures with enhanced process controllability. Zhang et al.^[17] fabricated needle coke through the co-carbonization of heavy oil and modified low-temperature coal tar pitch. By adjusting the proportion of the modified low-temperature coal tar pitch, they controlled the composition distribution in the co-carbonization system and discovered that a sufficient amount of alkyl radicals could facilitate the ordered growth of aromatic molecules during the polycondensation process, yielding needle coke with a fibrous structure content of 60%. Xu et al.^[12] prepared needle coke by co-carbonization of refined medium and low temperature coal tar pitch and refined high temperature coal tar pitch. They found that reducing the content of heterocyclic compounds in the raw materials was conducive to the ordered polycondensation of aromatic molecules and the accumulation of carbonaceous layers. He et al.^[18] added refined high temperature coal tar pitch to refined medium and low temperature coal tar pitch for the preparation of needle coke. They discovered that the refined high temperature coal tar pitch significantly increased the aromatic hydrocarbon content in the mixed pitch. Adding 25% of the refined high temperature coal tar pitch and maintaining a stable and continuous vacuum reduction (1.5–1.0 MPa) during the liquid-phase carbonization process was beneficial for the production of high-quality needle coke with a fibrous structure content of 76.84%. Lim et al.^[19] prepared needle coke by co-carbonization of fluid catalytic cracking (FCC) decant oil and perfluoropolyether. They found that adding 10% of perfluoropolyether at a reaction temperature of 440 °C and 1 bar, the fluorine and oxygen radicals released during the thermal decomposition of perfluoropolyether induced dehydrogenation and cross-linking reactions, successfully fabricating needle coke. Evidently, the co-carbonization method demonstrates significant potential for needle coke production, enhancing material performance through synergistic interactions among multi-component raw materials while simultaneously expanding feedstock diversity and reducing production costs.

In this paper, needle coke was prepared through the co-

carbonization process. The aliphatic hydrocarbon content in the mixed pitch was precisely controlled by systematically adjusting the mass ratio between CDLP containing condensed arenes^[20–21] and WEO containing aliphatic components. The effect of WEO addition ratio on the microstructure of needle coke was investigated, and the correlation between the composition of raw materials and its microstructure and macroscopic properties was established. Furthermore, the co-carbonization mechanism of CDLP and WEO was explored.

1 Experimental

1.1 Experimental material

The coal direct liquefaction pitch (CDLP, softening point 160 °C) was extracted by the extraction-distillation method from the coal direct liquefaction residue. The extraction-distillation procedure was followed our previous work^[22–23]. The coal direct liquefaction residue obtained from China Shenhua Coal To Liquid and Chemical Co., Ltd. Waste engine oil (WEO) was provided by a machinery company in Anshan, China. Toluene (T, analytical pure) and quinoline (Q, analytical pure) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

1.2 Preparation of needle coke

The CDLP and WEO were blended and homogenized at varying mass ratios to prepare the mixed pitch, denoted as CDLP-O_{x%}, where *x* represents the weight percentage of WEO added based on the weight of CDLP. For example, the mixed pitch obtained by mixing 20 g of CDLP with 20 g of WEO was denoted as CDLP-O_{100%}. About 25 g of the mixed pitch was co-carbonized in a pit resistance furnace by heating to 500 °C at 1 °C/min followed by a 4 h holding period to obtain green needle coke. The green needle coke was then calcined in a tube furnace under a N₂ atmosphere. The temperature was increased from ambient to 1400 °C at 5 °C/min and held for 1 h. Finally, the furnace was cooled naturally to room temperature, yielding the final needle coke product labeled as CDLP-O_{x%}-C. The yields of green needle coke and needle coke were calculated by formula (1) and (2), respectively.

$$Y_{GC} = \frac{m_2 - m_1}{m_0} \times 100\% \quad (1)$$

$$Y_{NC} = \frac{m_5 - m_4}{m_3} \times 100\% \quad (2)$$

where Y_{GC} is the yield of green needle coke, m_0 is the mass of the mixed pitch, m_1 is the mass of the glass tube, m_2 is the mass of green needle coke and the glass tube. Y_{NC} is the yield of needle coke, m_3 is the mass of green needle coke, m_4 is the mass of the crucible, m_5 is the mass of needle coke and the crucible.

1.3 Characterization

1.3.1 Basic properties characterization of raw materials

The proximate analysis of CDLP and mixed pitch was performed with reference to the corresponding standards, including coking value (CV, GB/T8727—2008), volatile matter (V, YS/T63.17—2019), toluene insoluble (TI, GB/T2292—2018), quinoline insoluble (QI, GB/T2293—2019). The elemental contents of C, H, N, S were determined by the Vario EL III elemental analyzer (Elementar, German), while the O content was calculated using the difference method.

The Fourier Transform Infrared Spectra (FT-IR) of CDLP and WEO were determined using a Nicolet IS-10 Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific, USA). The FT-IR spectra were fitted and the relative contents of the functional groups and chemical bonds were calculated to obtain the molecular structure information of the feedstocks^[13]. The aromatic index (I_{ar}), branch index (CH_3/CH_2), C-H substitution index (I_{CH_3}), alkyl index (I_A), ortho-substitution index (I_{OS}), and condensation index (H_{AC}/C_A) of the raw materials were calculated by the methods described in references^[7,24–25].

The thermogravimetric analysis (TGA) of CDLP and WEO was performed on a TA-Q500 thermogravimeter (TA Instruments, USA). About 4 mg sample was heated to 750 °C at a heating rate of 5 °C/min under dynamic heating conditions in a nitrogen atmosphere.

1.3.2 Structural characterization of needle coke

The optical microstructures of the needle coke were characterized using an Axio Scope A1 polarized microscope (Carl Zeiss, Germany) equipped with an adjustable eyepiece (10×) and an oil immersion objective (50×). According to the feature size of the optically anisotropic structures in the needle coke^[11,26–27], they were classified into fine mosaic structures (Mf, feature size $\leq 1 \mu m$), medium mosaic structures (Mm, $1 \mu m < \text{feature size} \leq 5 \mu m$), coarse mosaic structures (Mc, $5 \mu m < \text{feature size} \leq 10 \mu m$), fine fibrous structures (Ff, length size $> 10 \mu m$, width size $< 10 \mu m$), coarse fibrous structures (Fc, length size $> 30 \mu m$, width size $< 10 \mu m$), and leaflet structures (L, feature size $\geq 10 \mu m$).

The surface morphology of the needle coke was observed using a SIGMA-HD type Scanning Electron Microscope (Carl Zeiss, Germany). X-ray Diffraction (XRD) analysis was conducted using the D8 ADVANCE X-ray diffractometer equipped (BRUCKER, German) with Cu K α radiation ($\lambda=0.15418 \text{ nm}$). Raman spectroscopy was performed using the LabRAM HR Evolution Raman spectrometer (JOBIN YVON, France) with excitation light wavelength of 532 nm.

1.3.3 Performance test of needle coke

The combustion characteristics of needle coke were analyzed by using STA449 F3 thermogravimeter (Netesch, German). The experiment involved approximate 10 mg of needle coke to 850 °C at a heating rate of 10 °C/min. During the heating process, pure oxygen was introduced, with the gas flow rate maintained at 30 mL/min. The combustion characteristic parameters of needle coke were calculated according to the method described in GB/T33304—2016. This included the initial mass loss temperature (t_i), the maximum mass loss rate temperature (t_{max}), the burnout temperature (t_f), the maximum specific combustion rate (R_{max}) and the average specific combustion rate (R_{mean}).

The micro-strength (MS) of the needle coke was determined according to the method described by Ragan & Marsh^[28], and the powder resistivity (PR) was determined according to the method of GB/T24521—2018 on the HM-500A powder resistivity measuring instrument (HengMei, China).

2 Results and discussion

2.1 Basic properties of raw materials

As shown in Figure 1, the infrared spectra of coal direct liquefaction pitch (CDLP) and waste engine oil (WEO) are presented. The FT-IR of WEO displays strong absorption peaks at near 3000–2800, 1450 and 1375 cm^{-1} , which correspond to methyl and methylene C–H stretching vibrations, asymmetric deformation vibrations, and methyl symmetric deformation vibrations, respectively^[12–15,18,20–21]. These absorption peaks indicate that WEO is rich in aliphatic hydrocarbon components. The shoulder peak noted between 3100 and 3000 cm^{-1} can be attributed to the overlapping of =C–H stretching vibrations from olefins ($\sim 3020 \text{ cm}^{-1}$) and aromatic hydrocarbons ($\sim 3050 \text{ cm}^{-1}$)^[21,25]. The detection of aromatic C=C stretching vibration peaks^[13,18,20] near 1600 cm^{-1} further confirms the existence of aromatic hydrocarbons in the WEO. The absorption peaks in the range of 900–700 cm^{-1} caused by aromatic C–H out-of-plane bending vibrations^[12], indicating that WEO contains a minor proportion of aromatic components besides its predominant aliphatic constituents. Notably, the characteristic absorption peaks at 840 and 740 cm^{-1} demonstrate that the substitution pattern of aromatic hydrogens in WEO is primarily ortho- and para-substituted. The position of the infrared absorption peaks for CDLP closely aligns with those of WEO, but the intensity of these peaks in CDLP is considerably weaker. This is particularly evident in the aliphatic C–H absorption peaks at 3000–2800 and 1450 cm^{-1} , which are significantly less intense than those observed in WEO, indicating a lower content of aliphatic hydrocarbons in CDLP. Conversely, CDLP demonstrates pronounced aromatic characteristics, as evidenced by the aromatic C–H stretching vibration peak at

3050 cm^{-1} , the aromatic C=C stretching vibration peak at 1600 cm^{-1} , and the aromatic =C–H out-of-plane bending vibration peaks at 870, 810 and 740 cm^{-1} . These findings suggest that CDLP is predominantly rich in aromatic components, with alkyl groups primarily occurring as substituents on aromatic hydrocarbons.

In order to further clarify the structural information of WEO and CDLP, we fitted the absorption peaks^[13,21] in the regions of I (3100–2800 cm^{-1}), II (1700–1000 cm^{-1}) and III (900–700 cm^{-1}) in Figure 1(a), as shown in Figure 1(b) and calculated the molecular structure parameter. The results are presented in Table 1.

As shown in Table 1, the aromaticity index and condensation index of WEO are 0.03 and 0.5, respectively, which are lower than those of CDLP. The CH_3/CH_2 , I_{CH_3} , I_{A} , and I_{Os} values are higher compared to CDLP. This indicates

that WEO contains fewer aromatic hydrocarbons and exhibits a lower aromatic ring condensation degree, but it has a higher content of aliphatic hydrocarbons and is rich in long-chain alkyl branches^[21,24–25]. In contrast, CDLP is characterized by abundant aromatic hydrocarbon structures and a higher aromatic ring condensation degree, accompanied by a relatively lower content of aliphatic hydrocarbons and shorter alkyl branches.

2.2 Proximate and ultimate analysis of mixed pitch

CDLP and WEO were blended in various mass ratios to produce mixed pitch. Table 2 displays the results of proximate analysis and ultimate analysis for the mixed pitch.

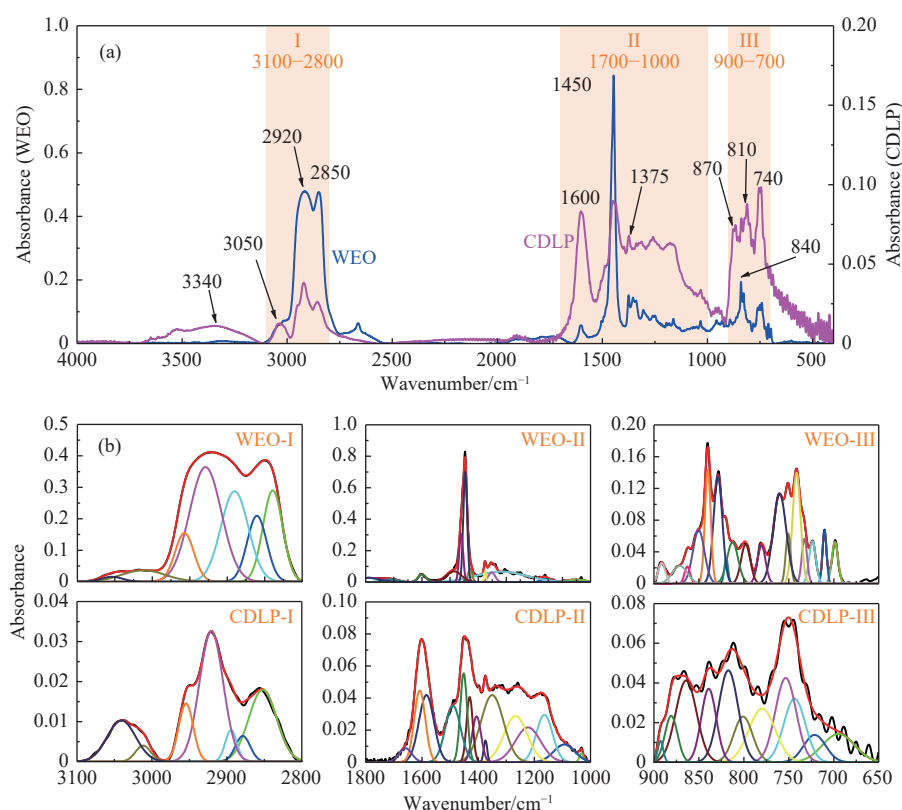


Fig. 1 The FT-IR of WEO and CDLP (a) and fitting diagrams of regions I, II and III (b)

Table 1 Molecular structure parameters of WEO and CDLP

Sample	I_{ar}	CH_3/CH_2	I_{CH_3}	I_{A}	$H_{\text{AU}}/C_{\text{A}}$	I_{Os}
WEO	0.03	0.25	0.80	0.9	0.5	0.4
CDLP	0.27	0.27	0.79	0.4	0.8	0.3

Table 2 The proximate and ultimate analysis of mixed pitch

Sample	Proximate analysis/%				Ultimate analysis/%					C/H
	CV	V	QI	TI	C	H	N	S	O	
CDLP-O _{0%}	69.0	45.3	0.9	24.8	91.4	5.4	1.1	0.1	2.0	1.4
CDLP-O _{25%}	56.5	55.1	0.5	22.0	90.6	6.4	0.8	0.2	2.0	1.2
CDLP-O _{50%}	46.7	62.1	0.5	15.7	90.3	7.5	0.8	0.1	1.3	1.0
CDLP-O _{75%}	40.5	69.2	0.2	15.2	89.9	7.9	0.6	0.2	1.4	1.0
CDLP-O _{100%}	35.6	71.7	0.2	14.0	87.8	8.2	0.6	0.1	3.3	0.9

Given that WEO is a light oil enriched in aliphatic structures, the inclusion of WEO increases the volatile light component content in the mixed pitch, resulting in greater mass loss at high temperatures.

With the increasing proportion of WEO, there is a notable decrease in the values of CV, QI and TI in the mixed pitch, while the V value increases. Simultaneously, the incorporation of WEO significantly elevates the H content in the mixed pitch, which consequently lowers the value of C/H. Compared with CDLP-O_{0%} (without WEO), the value of V in CDLP-O_{100%} rises to 71.7%, while the value of CV and C/H decreases to 35.6% and 0.9, respectively.

2.3 Co-carbonization process analysis of mixed pitch

The TGA curves of CDLP and WEO are shown in Figure 2 (a), (b) and the analysis results of the curves are presented in Table 3. The pyrolysis interval of WEO is significantly wider than that of CDLP. The initial mass loss temperatures

(t_i) of the two samples are 102.0 and 241.9 °C, respectively. When the pyrolysis temperature reaches 500 °C, the TG curves of both CDLP and WEO stabilize, with residual carbon ratios (W_{500}) of 54.0% and 4.9%, respectively, indicating that the pyrolysis reaction is essentially complete. The CDLP exhibits a single mass loss peak at 456.3 °C with a maximum mass loss rate (R_{max}) of 0.27% °C⁻¹, while WEO shows two mass loss peaks at 276.6 and 456.3 °C, with R_{max} values of 0.44% and 0.14% °C⁻¹, respectively. Due to its high content of aliphatic hydrocarbons, WEO exhibits significantly lower thermal stability than CDLP. As shown in Figure 2(b), the slope of the DTG curve of CDLP decreases, and the pyrolysis reaction rate slows when the pyrolysis rate of WEO reaches its maximum. In addition, the DTG curve of WEO displays a shoulder peak when the pyrolysis rate of CDLP reaches the maximum value. These pyrolysis parameters demonstrate that CDLP and WEO share characteristic temperature points during pyrolysis, and their pyrolysis rate variations are complementary, resulting in a synergistic effect during co-carbonization.

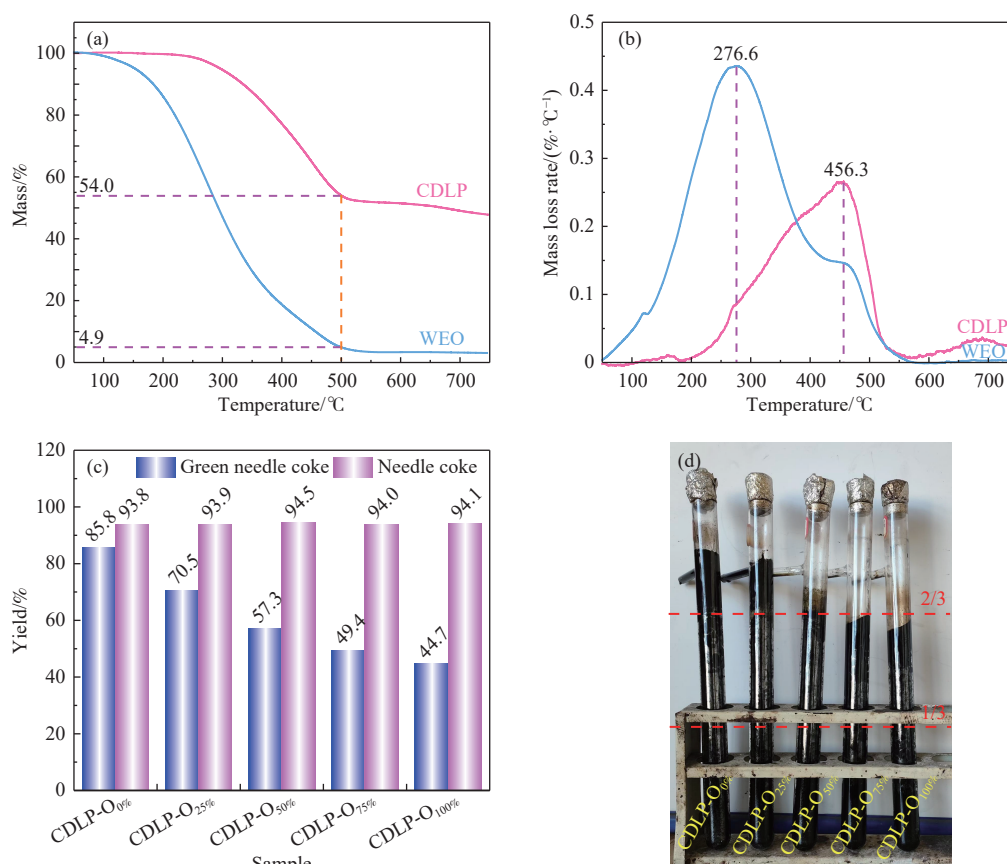


Fig. 2 The TGA curves of CDLP and WEO: (a) TG, (b) DTG and the yield of the green needle coke and the needle coke (c) and the morphology of the green needle coke (d)

Table 3 Pyrolysis characteristic parameters of raw materials.

Sample	$t_i/^\circ\text{C}$	$t_{max}/^\circ\text{C}$	$R_{max}/(\% \cdot ^\circ\text{C}^{-1})$	$W_{500}/\%$
CDLP	241.9	456.3	0.27	54.0
WEO	102.0	276.6	0.44	4.9

Figure 2(c) demonstrates the yield of green needle coke and needle coke. The yield of green needle coke significantly decreased with the increasing WEO addition. When the WEO addition exceeded 75%, the coke yield declined to below 50%. Figure 2(d) shows the reaction product after thermal transformation. The height of the black portion in the tube reflects both the expansion of the liquid level during thermal transformation and the rheological properties of the reaction system. During thermal transformation, as temperature increases, the pitch transitions from solid to liquid, and pyrolytic polymerization occurs. Small molecules generated from the cleavage of alkyl side chains escape as gas. In systems with poor rheological properties, the high viscosity of the liquid phase causes the liquid level to rise due to shear forces generated by escaping gas, resulting in an “expansion” phenomenon. The greatest expansion is observed in CLP-O_{0%}, which is attributed to the high viscosity of the reaction system during CDLP thermal conversion. However, as the WEO content increased, the degree of “expansion” in the liquid level of reaction system decreased markedly. When the WEO content exceeded 75%, the liquid level dropping to less than two-thirds of the branch tube. This demonstrates that WEO addition significantly improves the rheological properties of the co-carbonization system during thermal transformation, maintains a low system viscosity, and reduces the resistance encountered by the escaping gaseous products. Macroscopically, this results in a reduction of the reaction system’s liquid-level “expansion” height during the co-carbonization process.

2.4 Analysis of needle coke

2.4.1 Optical microstructure analysis of needle coke

The typical optical microstructures in the needle coke samples are shown in Figure 3. As shown in Figure 3, the optical microstructure of all five needle cokes exhibits optical anisotropy, primarily characterized by leaflet and fibrous structures. The addition of WEO further promotes the alignment of these fibrous structures. Notably, the addition of WEO exceeding 50% leads to a substantial improvement in the alignment of needle coke optical microstructure, resulting in clearly defined fibrous structures emerging.

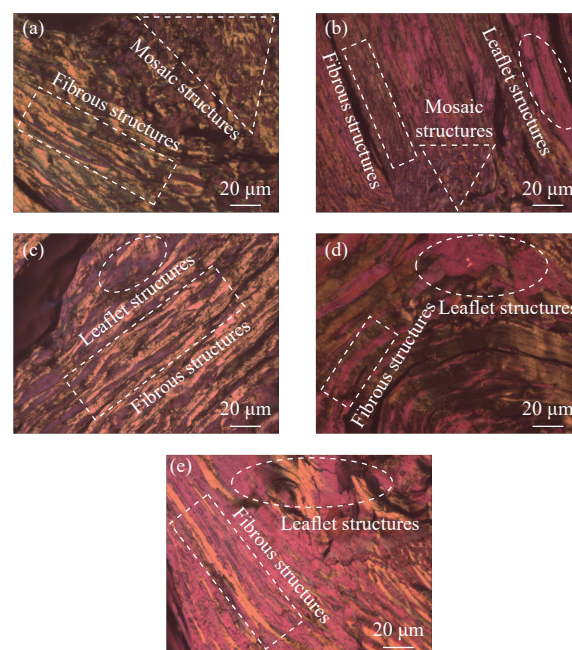


Fig. 3 Polarizing microstructure of (a) CDLP-O_{0%}-C, (b) CDLP-O_{25%}-C, (c) CDLP-O_{50%}-C, (d) CDLP-O_{75%}-C and (e) CDLP-O_{100%}-C

To further elucidate the impact of WEO addition on the optical microstructure of needle coke, a statistical analysis was conducted. For ensure data accuracy, more than 200 optically valid points were collected from each sample. The resulting optical microstructure distributions of the needle coke samples are presented in Table 4.

As shown in Table 4, the incorporation of WEO results in a tendency for the total content of fibrous and leaflet structures in needle coke to exhibit an initial increase then decrease. Notably, the fibrous and leaflet structures in CDLP-O_{50%}-C exhibit a maximal content reaching 76.2%. In fact, the formation of the optical microstructure in needle coke is closely related to the composition of the raw materials. The CDLP has a high aromatic condensation degree and a low content of alkyl side chains. This deficiency in alkyl side chains results in fewer alkyl radicals and active sites, thereby hindering the orderly condensation of aromatic macromolecules and restricting the planar growth of the carbonaceous structure. WEO has been shown to be rich in aliphatic hydrocarbons and relatively low in aromatic hydrocarbons; thus, its addition increases the aliphatic hydrocarbon content of the mixed pitch.

Table 4 Optical microstructure distribution of needle coke

Sample	Optical microstructure/%						
	Mf	Mm	Mc	Ff	Fc	L	Ff+Fc+L
CDLP-O _{0%} -C	6.7	13.5	13.5	20.8	21.3	24.2	66.3
CDLP-O _{25%} -C	2.2	13.1	13.2	19.2	30.6	21.7	71.5
CDLP-O _{50%} -C	5.1	9.1	9.6	25.2	28.6	22.4	76.2
CDLP-O _{75%} -C	8.1	8.1	7.6	26.2	25.8	24.2	76.2
CDLP-O _{100%} -C	7.8	14.6	7.3	26.9	22.8	20.6	70.3

The addition of WEO provided ample reaction sites for aromatic molecular polymerization during the co-carbonization process, promoting the accumulation of carbonaceous structures during the mesophase development stage. This enhancement consequently increased the content of fibrous and leaflet structures within the needle coke. The content of fibrous and leaflet structures in CDLP-O_{100%}-C decreased to 70.3%, indicating that the excessive addition of WEO negatively impacts the polymerization of aromatic hydrocarbon structures during the co-carbonization process. Consequently, this results in a reduced content of large-sized leaflet and coarse fibrous structures, accompanied by an increase in smaller fine fibrous and medium-sized mosaic structures.

2.4.2 SEM analysis of needle coke

SEM is a powerful tool for characterizing the surface morphology of needle coke, and the SEM images of the prepared needle cokes are shown in Figure 4.

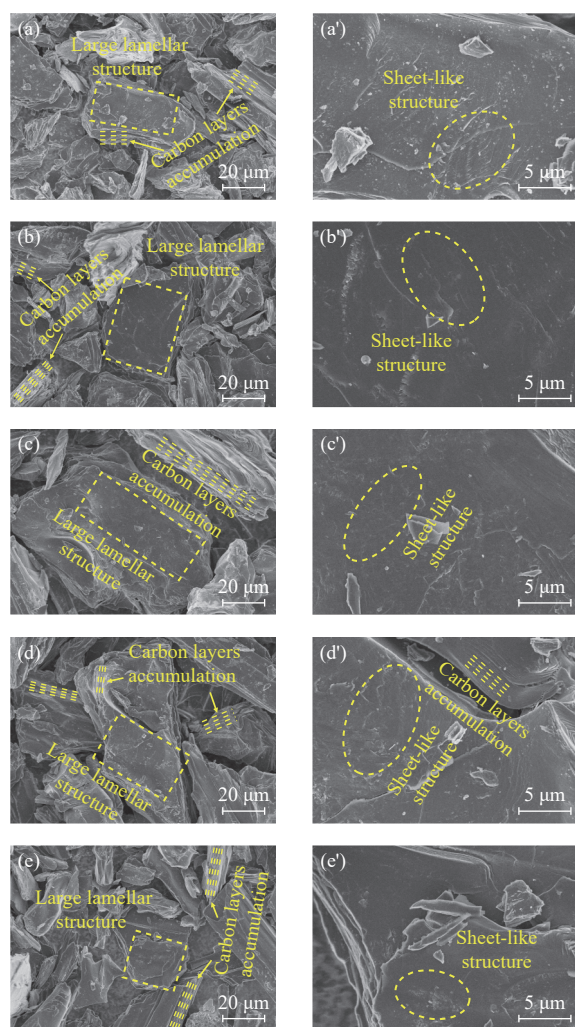


Fig. 4 The SEM images of needle coke: (a)–(e) 1000×; (a')–(e') 5000×; (a), (a') CDLP-O_{0%}-C; (b), (b') CDLP-O_{25%}-C; (c), (c') CDLP-O_{50%}-C; (d), (d') CDLP-O_{75%}-C; (e), (e') CDLP-O_{100%}-C

As shown in Figure 4(a)–(e), the surface morphology of needle coke is dominated by large lamellar structures, with a compact accumulation of carbon layers observable in the cross-sections of needle coke particles.

In addition, as shown in Figure 4(a')–(e'), the surfaces of needle coke particles exhibit a distinct sheet-like structure. With the addition of WEO, the accumulation of carbon layers in the needle coke becomes more regular. The surfaces of the large lamellar structure appear smoother and better oriented, while the sheet-like structures are reduced.

2.4.3 XRD analysis of needle coke

XRD is an effective method for characterizing the crystal structure of carbon materials. Figure 5(a) shows the XRD spectra of the needle coke. It can be observed that all five needle coke samples exhibit three distinct characteristic peaks at approximate 2θ 26°, 43° and 53°, corresponding respectively to the (002), (100) and (004) crystal planes^[29]. Furthermore, as the proportion of WEO in the raw material increases, the intensity of the (002) diffraction peak in the needle coke is significantly enhanced. The peak intensity of CDLP-O_{50%}-C is significantly higher than that of other needle coke samples, indicating a higher degree of graphitization. This suggests that the aromatic lamellae is more parallel and better oriented spatially.

As shown in Figure 5(b)–(f), the diffraction peak (002) was deconvoluted into the π band, representing regular carbon microcrystals, and the γ band, representing amorphous carbon, at approximately 23° and 26°, respectively. The crystallite structure parameters of the needle coke were calculated based on the peak fitting information, utilizing the calculation methods described in the literatures^[18,27]. These parameters include the average interlayer spacing (d_{002}) of the carbon layers, the average stacking height (L_c), the content of regular carbon crystallites (I_g), the average number of parallel carbon layers (N) and average number of aromatic rings per layer (n). The calculation results are presented in Table 5.

As shown in Table 5, the I_g values of the needle coke samples ranged from 81.8% to 89.7%, initially increasing and then decreasing. Among them, CDLP-O_{50%}-C exhibited the highest I_g value at 89.7%, indicating a more ordered arrangement of carbon microcrystalline structures and a higher degree of graphitization. Meanwhile, CDLP-O_{50%}-C exhibited higher values of L_c (4.1 nm), N (12.7), and n (51.8), along with a smaller d_{002} value of 3.464 Å. This phenomenon can be attributed to the ample supply of free radicals provided by WEO, which promotes the directional arrangement of CDLP molecules and the stacking of aromatic lamellae during the carbonization process. Consequently, this compensates for defects in the carbonaceous structure and increases the content of ordered carbon microcrystals in the calcined needle coke. As a result, a more regular carbon crystal structure is achieved. As the proportion of WEO addition in the raw materials exceeds 75%, there is a corresponding decrease in the L_c , N , and n values of the needle coke.

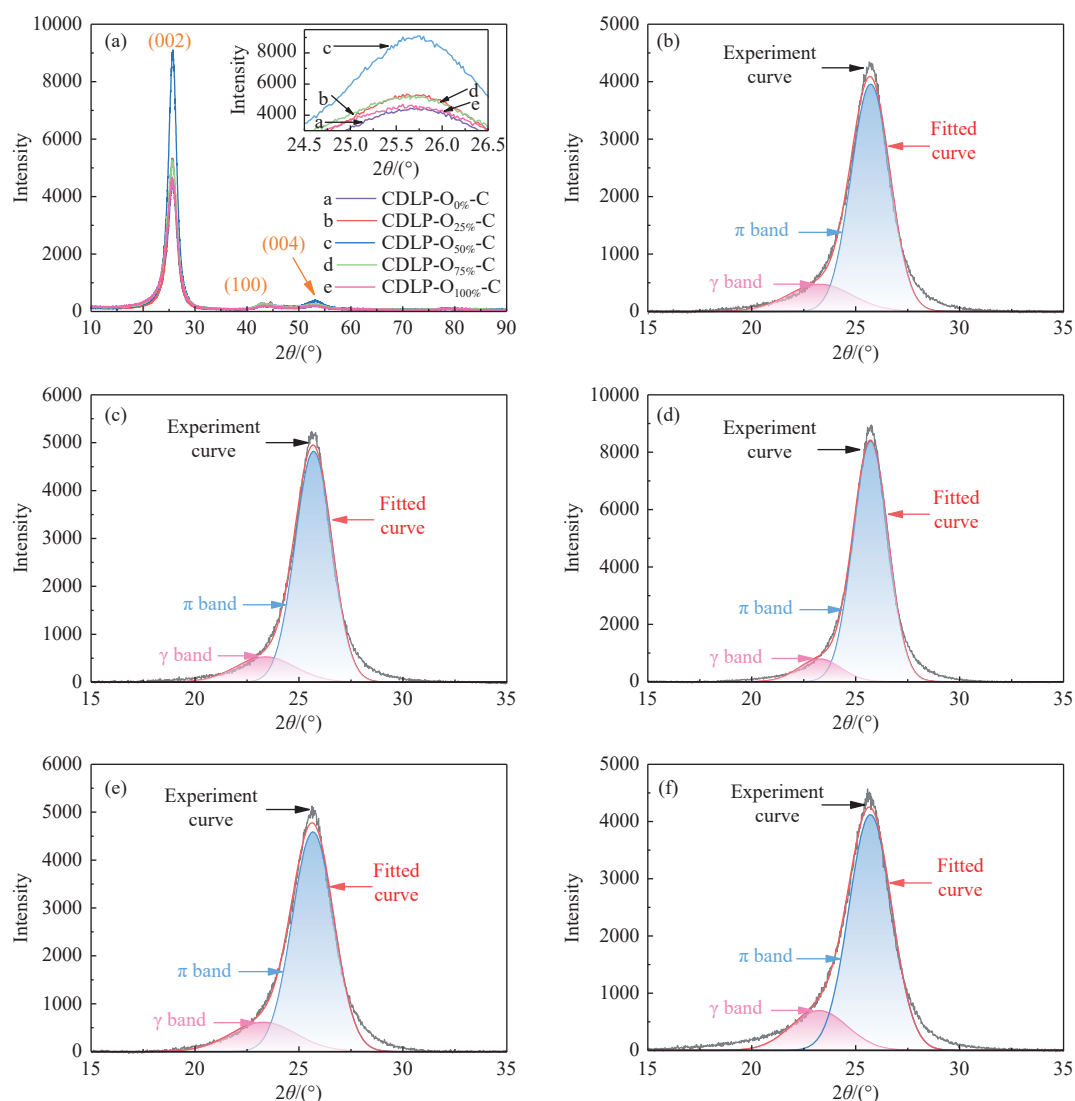


Fig. 5 The XRD spectra of needle coke (a) and the XRD curve-fittings of CDLP-O_{0%}-C (b), CDLP-O_{25%}-C (c), CDLP-O_{50%}-C (d), CDLP-O_{75%}-C (e), CDLP-O_{100%}-C (f)

Table 5 The crystallite structure parameters of needle coke

Sample	$2\theta_{\gamma}/(^{\circ})$	$2\theta_{\pi}/(^{\circ})$	A_{γ}	A_{π}	$d_{002}/\text{\AA}$	$I_g/\%$	L_c/nm	N	n
CDLP-O _{0%} -C	23.29	25.72	1820.5	9231.5	3.464	83.5	3.7	11.6	43.2
CDLP-O _{25%} -C	23.39	25.70	1868.0	10690.7	3.466	85.1	3.9	12.2	47.3
CDLP-O _{50%} -C	23.28	25.72	2031.9	17729.2	3.464	89.7	4.1	12.7	51.8
CDLP-O _{75%} -C	23.29	25.68	2414.2	11460.7	3.470	82.6	3.4	10.9	38.0
CDLP-O _{100%} -C	23.24	25.70	2367.8	10621.2	3.466	81.8	3.3	10.6	36.0

This phenomenon is due to that excessive WEO addition leads to the generation of excess free radicals and reactive sites within the co-carbonization system. Additionally, there is competition between alkyl radicals and thick cyclic aromatic hydrocarbons during the polycondensation process.

Simultaneously, out-plane crosslinking^[30] between the excess alkyl radicals and the aromatic layers occurs, which in turn impacts the planar size and stacking height of the aromatic lamellae.

2.4.4 Raman analysis of needle coke

Raman spectroscopy is an effective method for analyzing the graphitization degree of carbon materials. Figure 6(a) presents the Raman spectra of needle coke samples, displaying the characteristic D and G peaks typically observed in graphitizable carbon materials at approximately 1350 and 1580 cm^{-1} , respectively. These peaks correspond to the disordered carbon lattice structure (D peak) and the ideal graphite lattice structure (G peak)^[15,26–27]. The G and D

peaks were deconvoluted into five distinct peaks: D1, D2, D3, D4 and G^[13,18]. The area of each peak represents the proportion of different crystal structures within the needle coke. Among them, the content of ideal graphite lattice structure (I_G) directly influences the properties of needle coke. In addition, the ratio of defective lattice structure content to ideal graphite lattice structure content (I_{D1}/I_G) utilized to assess the graphitization degree of the material. Typically, a lower I_{D1}/I_G value indicates a higher degree of graphitization^[30].

The composition of various carbon crystal structures in the needle coke is presented in Table 6. With increasing

incorporation of WEO, the I_G value of needle coke initially rises and then declines, while the I_{D1}/I_G ratio initially decreases and subsequently increases. Among them, CDLP-O_{50%}-C exhibits a higher ideal graphite lattice content, a lower disordered graphite lattice content at the edge of the graphite layer, and a greater degree of graphitization, which are 16.8%, 46.7% and 2.8, respectively. This phenomenon can be attributed to the abundant aliphatic hydrocarbons in WEO, which provide sufficient active sites and an appropriate concentration of alkyl radicals for polymerization among aromatic compounds during pyrolysis.

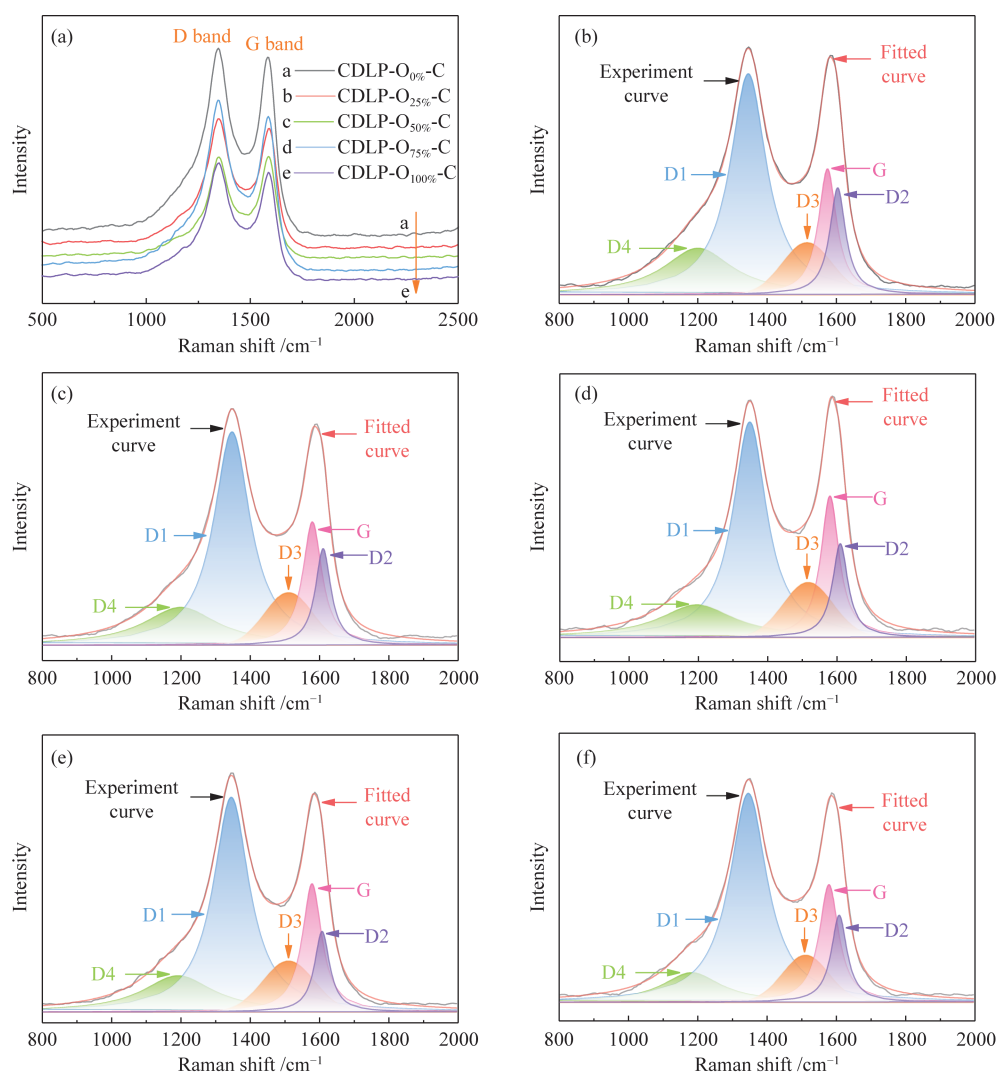


Fig. 6 Raman spectra of needle coke (a) and the Raman curve-fittings of CDLP-O_{0%}-C (b), CDLP-O_{25%}-C (c), CDLP-O_{50%}-C (d), CDLP-O_{75%}-C (e), CDLP-O_{100%}-C (f)

Table 6 Content of different carbon crystal structures in needle coke

Sample	$I_{D1}/\%$	$I_{D2}/\%$	$I_{D3}/\%$	$I_{D4}/\%$	$I_G/\%$	I_{D1}/I_G
CDLP-O _{0%} -C	47.6	10.5	10.8	17.3	13.8	3.4
CDLP-O _{25%} -C	48.3	9.7	11.2	15.8	15.1	3.2
CDLP-O _{50%} -C	46.7	9.7	12.6	14.2	16.8	2.8
CDLP-O _{75%} -C	49.1	8.1	11.7	14.9	16.2	3.0
CDLP-O _{100%} -C	53.0	9.7	10.5	11.0	15.8	3.3

This facilitates the growth of aromatic char lamellae. Meanwhile, the enhancement of the co-carbonization system's rheological properties by WEO significantly reduced the stacking resistance between the aromatic carbon lamellae. This leads to a more ordered structure in the needle coke and a higher degree of graphitization.

2.5 Performance analysis of needle coke

2.5.1 Antioxidant performance analysis of needle coke

The TGA curves of the needle coke under oxygen atmosphere are shown in Figure 7. As indicated in Figure 7, the needle coke experiences a weight loss of approximately 5% below 550 °C, corresponding to the preheating stage during which moisture evaporation and the release of small molecular substances primarily occur. It is noteworthy that the rate of decrease in the TG curve slows after approximately 300 °C during the preheating stage. This phenomenon occurs due to the thermal expansion of the sample and the weight gain resulting from chemisorption reactions between oxygen and the coke surface^[31], which partially compensates for the weight loss caused by the volatilization of small molecules. The rapid combustion stage of the needle coke occurs between 550 and 790 °C, during which the coke matrix rapidly reacts with oxygen, and combustion of fixed carbon primarily takes place. At this stage, distinct differences emerge in the TG and DTG curves of the needle coke. The TG curve of CDLP-O_{50%}-C exhibits a steeper decline, and the combustion peak in its

DTG curve is sharper, more intense, and shifts toward higher temperatures. Beyond 790 °C, the TG curves stabilize as the fixed carbon is fully consumed, marking the end of the reaction.

The antioxidant performance of needle coke is closely related to the arrangement of its carbon crystal structure. Specifically, a more ordered structural arrangement corresponds to a higher degree of graphitization, resulting in reduced reactivity with oxygen. As shown in Table 7, the t_i , t_{max} , R_{max} , R_{mean} values of the needle coke initially increase and subsequently decrease, which aligns well with the observed changes in the degree of graphitization. Meanwhile, the t_f values, primarily concentrated between 770 and 790 °C, exhibit a gradual upward trend. Compared with other needle coke samples, CDLP-O_{50%}-C exhibits the highest t_i and t_{max} values, at 648.3 and 715.4 °C, respectively, along with a t_f value of 780.3 °C. These results indicate its lower reactivity with oxygen and superior antioxidant performance.

2.5.2 Macroscopic performance analysis of needle coke

The micro-strength and powder resistivity of the needle coke are shown in Figure 8. As indicated in Figure 8, the MS and PR of the needle coke exhibit a trend of initially decreasing and then increasing. Among them, CDLP-O_{50%}-C has the smallest MS and PR, which are 74.5% and 605.1 mΩ·mm, respectively. This is attributed to the microstructure and crystal type of the needle coke.

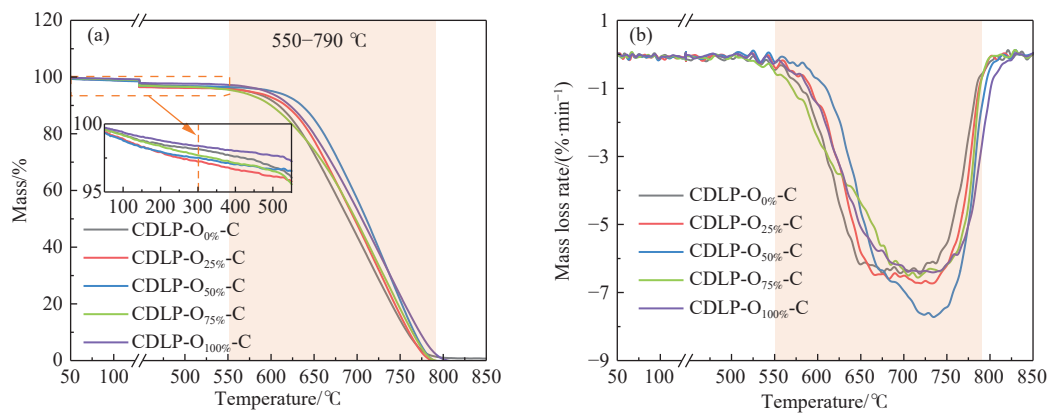


Fig. 7 Combustion characteristics curves of needle coke

Table 7 Combustion characteristic parameters of needle coke

Sample	$t_i/^\circ\text{C}$	$t_{max}/^\circ\text{C}$	$t_f/^\circ\text{C}$	$R_{max}/(\% \cdot \text{min}^{-1})$	$R_{mean}/(\% \cdot \text{min}^{-1})$
CDLP-O _{0%} -C	613.2	718.6	771.0	6.5	5.3
CDLP-O _{25%} -C	623.1	732.2	776.7	6.7	5.6
CDLP-O _{50%} -C	648.3	734.4	780.3	7.7	6.3
CDLP-O _{75%} -C	621.1	715.4	782.0	6.6	5.1
CDLP-O _{100%} -C	626.1	732.8	789.1	6.4	5.3

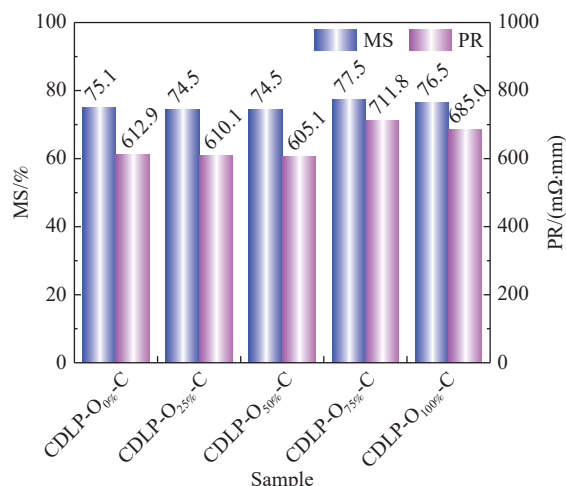


Fig. 8 Micro-strength and powder resistivity of needle coke

The higher the content of fibrous and leaflet structures in the needle coke, the lower its MS and PR. The total content of fibrous and leaflet structures in CDLP-O_{50%}-C reaches 76.2%. The higher the degree of orientation, the more pronounced the anisotropy in the macroscopic properties of the needle coke. Consequently, CDLP-O_{50%}-C is more susceptible to breaking when subjected to external forces perpendicular to the direction of the lamellar structure. Meanwhile, the ideal graphite crystal content in CDLP-O_{50%}-C is as high as 89.7%. This high content of graphite-like lamellar structures contributes to lower powder resistivity and enhanced electrical conductivity in the needle coke.

2.6 Analysis of co-carbonization mechanism of needle coke

Figure 9 illustrates the promotion effect of WEO on the growth and stacking of carbonaceous lamellar structures in CDLP during the co-carbonization process. The pyrolysis of CDLP and WEO leads to the generation of free radicals and reactive sites. The small molecular weight aromatic hydrocarbons in WEO serve as the links for the directional alignment between the CDLP aromatic hydrocarbon structures. Following multistage radical polymerization, larger aromatic hydrocarbon structures linked by aliphatic chains are formed. Subsequently, with the participation of alkyl radicals, the aromatic hydrocarbon structures undergo polycondensation and aromatization reactions, leading to the formation of a molecular structure with an enlarged aromatic core. During pyrolysis, the alkyl active structures generated in WEO contribute free radicals, while preserving the low viscosity of the co-carbonization system. This low viscosity facilitates the physical stacking and orientation of aromatic molecules through π - π intermolecular forces among large-sized aromatic molecules, thereby increasing the stacking height of the lamellae. Furthermore, the incorporation of WEO into the mixed pitch leads to an increased concentration of aliphatic hydrocarbons, thereby enhancing the rheological properties of the reaction system. The small molecule gases generated during the pyrolysis process exert a degree of shear force while escaping, thereby effecting further adjustments in the arrangement of the carbonaceous structure. This ultimately resulted in the formation of a long-range ordered arrangement of the fibrous structure in the later stages of the carbonization process.

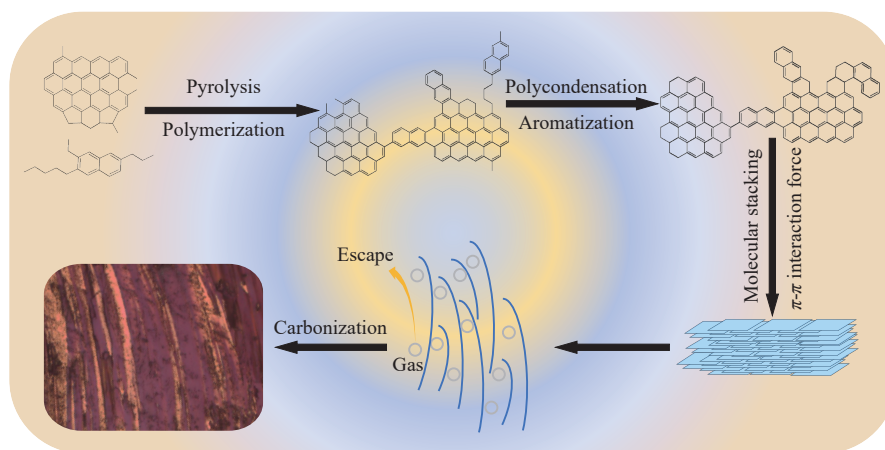


Fig. 9 The co-carbonization mechanism of CDLP and WEO

3 Conclusion

In this paper, WEO and CDLP were utilized as raw materials for the production of needle coke through a co-carbonization process. The impact of WEO addition on the structure and properties of coal direct liquefaction pitch-based needle coke was thoroughly investigated. The content of aliphatic hydrocarbons in the mixed pitch can be

controlled by adjusting the WEO addition ratio. The findings revealed that the aromatic hydrocarbon structure in WEO facilitated the polymerization of CDLP molecules, thereby promoting the growth of aromatic carbon layers. Concurrently, the aliphatic hydrocarbon structure in WEO compensated for the defects in the carbon crystal structure of the needle coke to a certain extent, as indicated by the I_{D1}/I_G value of 2.8. In addition, the addition of WEO

improved the rheological properties of the co-carbonization system, enhancing the mobility during the reaction and facilitating the orderly arrangement and stacking of the carbon layers, with a L_c of 4.1 nm and N of 12.7. The needle coke prepared by adding 50% WEO to CDLP exhibited a more regular structure and demonstrated good antioxidant performance. It contained an increased content of fibrous and leaflet structures at 76.2%, 89.7% ideal graphite crystals, and gave a micro-strength of 74.5% and a powder resistivity of 605.1 mΩ·mm.

Declaration of Competing Interest

The authors declare no conflict of interest.

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煤直接液化沥青与废机油共炭化制备煤基针状焦及其结构演变研究

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摘 要: 针状焦作为一种高性能的人造炭材料, 其原料的组分调控对材料的结构性能具有决定性影响。本研究以煤直接液化沥青(CDLP)和废机油(WEO)为原料, 通过组分优化和共炭化工艺, 制备了一系列针状焦。采用红外光谱(FT-IR)、偏光显微镜(PLM)、扫描电子显微镜(SEM)、X射线衍射(XRD)、拉曼光谱(Raman)、热重分析(TGA)、显微强度(MS)和粉末电阻率(PR)等多种表征手段, 研究了针状焦的微观结构和性能特征, 并探讨了CDLP和WEO的共炭化机理。实验结果表明, WEO的加入显著降低了共炭化体系的粘度, WEO丰富的脂肪结构提供了烷基自由基和活性位点。CDLP与WEO芳香组分间的协同作用有效促进了芳香碳层的生长和有序堆积。当WEO添加量为50%时, 制备的针状焦表现出优异的微观结构和性能: 纤维状和片状结构含量达到76.2%, 理想石墨晶格含量高达89.7%, 且具有良好的抗氧化性和导电性能, 粉末电阻率达605.1 mΩ·mm。本研究通过协同利用工业副产品, 为针焦炭生产提供了一个具有成本优势的工艺路线。

关键词: 针状焦; 共炭化; 煤直接液化沥青; 废机油

中图分类号: TQ529

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