



Original Research

Synthesis and graphitization of resole resins by ferrocene

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ABSTRACT

Commercial (Rs) and laboratory synthesized resoles (LSRs) containing 3–5 wt% ferrocene have been used to study the development of thermosetting resin compositions as binder materials for carbon-containing refractories (CCRs) production. The LSRs were developed based on formaldehyde to phenol 1.5 mol.% (1.5Rs) and 2.0 mol.% (2Rs). Microstructure and oxidation resistance of carbons derived from plain and modified resins have been compared. Chemical structure of the resins was studied using Fourier Transform InfraRed-Attenuated Total Reflection (FTIR-ATR) spectroscopy. X-ray Photoelectron spectroscopy was used to examine chemical changes during heat treatment of the modified products. Flow behavior of plain and formulated resins has been measured under isothermal condition. Rheology measurement results show that the selected amount of ferrocene did not affect the resin near-Newtonian fluid behavior and processability during refractory production. X-ray diffraction (XRD) analysis and transmission Electron Microscope (TEM) were used to characterize the derived carbon samples after thermal treatment of the resins. The results demonstrate that ferrocene is an excellent additive for crystallizing resole carbon. The presence of fringes in TEM images indicates the graphitized carbon microstructure. The carbon reactivity in an oxidizing environment was also determined via thermogravimetric analyzer (TGA). Several factors, such as bond strength and atoms arrangement, have been found to control the carbonized modified-resin oxidation resistance.

1. Introduction

The recent technology used in steel production demands for refractories with improved performance and life cycles. A new class of carbon-containing refractories (CCRs), which contains carbon in addition to the refractory oxide aggregates such as MgO and Al₂O₃ has emerged. They have gained approval in steel making applications, especially for converters, electric arc furnace and steel treatment ladles. CCRs performance is highly dependent on the presence of carbon with features close to graphite [1–3]. In this sense, it is desired to find alternative binders or additives to induce an additional in-situ formation of crystalline carbons with favor microstructure to enhance their thermomechanical properties [2].

Graphite induces the excellent thermal shock resistance, low thermal expansion, and good toughness of CCRs at elevated temperatures [4]. Similarly, its non-wetting characteristics allows the bricks to have better resistance to slag attack. The advantages provided by graphite addition are due to its crystallinity and anisotropic behavior.

Pitch is a good binder for the development of refractory bricks

susceptible to hydration reactions. However, because of environmental and health concerns associated with its use (release of toxic substances), this material has been replaced by thermosetting resins. Phenolic resins (novolac and resole) offer the advantage of minimal emissions of polycyclic aromatic hydrocarbons and other toxic substances during their pyrolysis [5,6]. They usually enhance the green strength and reduce the porosity level of CCRs [7,8]. Nevertheless, the unaided pyrolysis of these resins is exclusively a solid-state process without the formation of liquid or semi-liquid components, which leads to the generation of glassy or non-graphitic carbons. As a consequence, the “hard carbons” derived from these type of resins usually keep their disordered atomic arrangement at temperatures up to 3000 °C [9]. Moreover, this amorphous structure presents inferior oxidation resistance, low fracture energy and are highly sensitive to thermo-mechanical stresses and impact loads [1]. Therefore, their usefulness as a binder in refractory products for high-temperature applications is still limited [10]. Due to these drawbacks, there is increasing interest to induce graphitization of phenolic resin carbon using processing parameters that are adaptable for CCRs production. It is expected that the

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product from the binder carbonization could be another source of crystalline carbon, which would improve the thermomechanical properties of such bricks. Jansen et al. [2] and Grosse et al. reported the advantages arising from the crystallization of CCRs binder carbons [11].

Several methods based on the application of compressive force, magnetic field and radiation, have been employed to induce the conversion of disordered-hard-carbons into crystalline ones [12–15]. However, the most successful technique that is suitable for CCRs development may involve the use of agents through a process referred to as catalytic graphitization [16]. This approach can lead to the transformation of glassy carbons from phenolic resin to graphitic products during their carbonization in the presence of some elements or compounds. Compounds such as organometallics (e.g., metallocenes, benzoates, octoates and naphthenates, ferrocene) and metal oxides are useful for inducing crystallinity in disordered carbons. These additives can accelerate graphite generation during phenolic resin carbonization at low temperatures of 1000 °C [16–22].

Based on these observations, this study investigated the effects of ferrocene addition on the structure and oxidation resistance of carbons derived from commercial and laboratory synthesized resoles (LSRs). The resins were carbonized using designed heat treatment procedures that can be used to produce CCRs. The role of this additive in the graphitization of carbonized novolac resins has been evaluated in previous studies by some of the present authors using X-ray diffraction technique [16,23]. In this experiment, however, resole-type phenolic resins were selected to investigate the influence of chemistry and structure on catalytic graphitization of the prepared formulations containing 3–5 wt% ferrocene. Moreover, X-ray Photoelectron Spectroscopy (XPS) and rheology measurements were employed to understand the reaction mechanism during the system pyrolysis and the effect of ferrocene addition on flow characteristic of the binder material, respectively. In addition, Transmission Electron Microscope (TEM) was used to characterize the microstructure of the produced carbon.

2. Experimental procedures

The investigated binder formulations were prepared by mixing commercial resole (Rs, Prefere® 88 5000R, Dynea, Brazil) or laboratory synthesized ones with 3–5 wt% of ferrocene (Fc). All the as-received reagents are described in Table 1. The quantity of additive used as a graphitizing agent was based on previous studies, which involved commercial novolac resin (a different type of phenolic resin) [16].

The LSRs were produced based on formaldehyde to phenol molar ratio of 1.5 and 2.0. The apparatus used for this synthesis comprised a three-neck round bottom flask, thermometer, Dean-Stark system, reflux condenser and hot plate magnetic stirrer. To enhance the Dean-stark effectiveness for water removal (condensation reaction product), the arm connected to the round bottom flask was covered with aluminum foil to prevent heat loss. The mixture was stirred under reflux throughout the synthesis and the flask heated via an oil bath. The production was carried out by firstly heating the solution of phenol, water, and NH₄OH to the maximum temperature of around 60 ± 5 °C for 30 min. NH₄OH was selected as a catalyst to eliminate the formation of sodium-related compounds, which were detected in the carbon

composition when NaOH was used to catalyze the reaction. The presence of such impurities may not be favorable in CCRs, as it can lead to the formation of low-melting phases during CCRs sintering [24,25]. After that, formaldehyde (37 wt%) was added to the mixture and the reaction continued at 80 ± 5 °C for 105 min.

The binder components (commercial or synthesized ones) were mixed with the aid of a mechanical mixer (rotation speed of 300 rpm) for 10 min to achieve a dispersion of the additive (3–5 wt% Fc) within the resins. The prepared compositions were poured into alumina crucibles, covered with disk, embedded in a refractory box filled with coke and carbonized inside a muffle furnace. The step-wise pyrolysis procedure involved heating the samples from 30 °C to 100 °C and holding it at that temperature for 4 h, followed by increasing the temperature to 500 °C for 1 h, before finally heating them to 1000 °C and keeping at that temperature for 5 h. Firstly, the commercial resin formulation was used to investigate the best heating rate for the pyrolysis operation by varying it from 3° to 5°C/min. After that, the heating rate of 3 °C/min (that promoted maximum graphite generation) was selected for the pyrolysis of the LSR formulations. After carbonization, the samples were cooled to room temperature (~30 °C) inside the muffle furnace. The commercial and laboratory synthesized resole carbons (without any additive) were used as reference samples.

The samples and heating procedures were designated according to the description in Table 2.

2.1. XRD analysis

Shimadzu X-ray diffraction equipment (LabX XRD-6000) under CuK α radiation [$\lambda = 1.5418 \text{ \AA}$, scanning step = 0.032°] was used to characterize the derived carbons and to determine the amount of generated graphite in the fired samples. The diffractogram was analyzed with OriginPro 9 software according to the description of Bitencourt et al., 2015 [16]. The graphitization level (GL) value for each carbon samples was determined using Eq. (1). The calculation involved dividing the total area related to graphitic peaks by the sum of the peaks associated with graphitic and non-graphitic carbons.

$$GL = \frac{\text{Graphitic carbon area}}{\text{Total area (graphitic carbon + non-graphitic carbon)}} \quad (1)$$

2.2. X-ray photoelectron spectroscopy (XPS) analysis

The XPS analysis was carried out with a Thermo Scientific™ K-alpha X-ray Photoelectron Spectroscopy (Al K α radiation), which is a fully integrated, monochromated (using quartz crystal) small-spot system with a detection limit > 0.05%. Avantage software was used for data analysis, peak deconvolution and curves fitting to quantify chemical states from overlapping peaks. The analysis was conducted to study the structural evolution that occurred during the pyrolysis operation (curing and carbonization stages) of resole resin containing ferrocene. The analyzed samples were prepared using stepwise heat treatment procedures. 1.5Rs-5Fc formulation was subjected to sequent heat treatment up to 300 °C, 500 °C, 800 °C and 1000 °C at 3 °C/min, inside a muffle furnace and under reducing environment, as described earlier. The equipment measured the compositional and chemical state of

Table 1
General information about the used materials.

Raw materials		Supplier
Binder	Commercial Resole resin (Rs, Prefere 88 5000 R) LSRs, i.e., the laboratory synthesized resin (1.5Rs, 2Rs) based on: Phenol, C ₆ H ₅ OH, solid, molecular weight = 94.11 g/mol Formaldehyde (37 wt.%), CH ₂ O, liquid, molecular weight = 30.03 g/mol	Dynea (Brazil) Synth Chemical Co., SP-Brazil
Catalyst	NH ₄ OH, aqueous, molecular weight = 35.04 g/mol	Synth Chemical Co., SP-Brazil
Additive	Ferrocene (150 < d < 70 μm, 98% purity)	Aldrich, USA

Table 2

Designation of samples and heating procedures used during the binders carbonization.

Sample designation	Description
Rs	Commercial resole resin
1.5Rs	LSR with Formaldehyde: Phenol equal to 1.5
2Rs	LSR with Formaldehyde: Phenol equal to 2.0
1.5Rs-3Fc	1.5Rs + 3 wt% ferrocene
1.5Rs-4Fc	1.5Rs + 4 wt% ferrocene
1.5Rs-5Fc	1.5Rs + 5 wt% ferrocene
2Rs-3Fc	2Rs + 3 wt% ferrocene
2Rs-4Fc	2Rs + 4 wt% ferrocene
2Rs-5Fc	2Rs + 5 wt% ferrocene
Heating procedures	
A3	100 °C/4 h + 500 °C/1 h + 1000 °C/5 h at 3 °C/min heating rate
A4	100 °C/4 h + 500 °C/1 h + 1000 °C/5 h at 4 °C/min heating rate
A5	100 °C/4 h + 500 °C/1 h + 1000 °C/5 h at 5 °C/min heating rate

samples produced at the different reaction stages.

2.3. Microstructural analysis

FEI Tecnai G2 F20 transmission electron microscope (TEM) was used to obtain microstructural information, lattice resolution imaging (HRTEM) and Selected Area Electron Diffraction (SAED) patterns of the amorphous and graphitized carbon samples derived from the plain and modified resin formulation at 200 kV. Philips XL-30 FEG Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) detector was used to determine the chemical composition of the carbon samples. The images and SAED patterns were evaluated with GATAN DigitalMicrograph software.

2.4. Oxidation resistance measurement

NETZSCH STA 449F3 analyzer was used to measure the carbon samples oxidation resistance. The equipment can detect mass loss with a resolution of 0.001 g as a function of temperature and time. Synthetic air (80% N₂, 20% O₂) at a flow rate of 50 cm³/min was used as the oxidizing environment and each sample was heated from 30 °C to 1000 °C ± 10 °C using 10 °C/min heating rate. The thermogravimetric (TG) curves were normalized to eliminate the effect of non-carbon material described by the initial mass loss between 30 °C to ~150 °C. From the non-isothermal profile, the inflection point temperature, which represents the onset of carbons oxidation (T_i), mass at the onset of carbon oxidation (MO_i) and the final residual mass (RM_f) was determined as depicted in Fig. 1. To obtain the actual carbon loss (designated as “X” in Fig. 1), RM_f was subtracted from MO_i.

2.5. FTIR-ATR and Viscosity measurement

FTIR-ATR spectroscopy was used to study the structure of the commercial and laboratory synthesized resins. The FTIR spectra were recorded via a Nicolet 6700 spectrometer between 400 and 4000 cm⁻¹, 32 accumulations at 2 cm resolution. The resins shear viscosity with and without the additive was measured with a ThermoHaake Rheostress 300 equipment under different shear rates. The measurement was obtained with a 41 mm cylindrical plate, at a constant gap of 3 mm under an isothermal condition at 30 °C.

3. Results and discussion

3.1. Viscosity of the plain and modified resole resins

The viscosity-shear rate curves at 30 °C of the Rs and 1.5Rs resoles

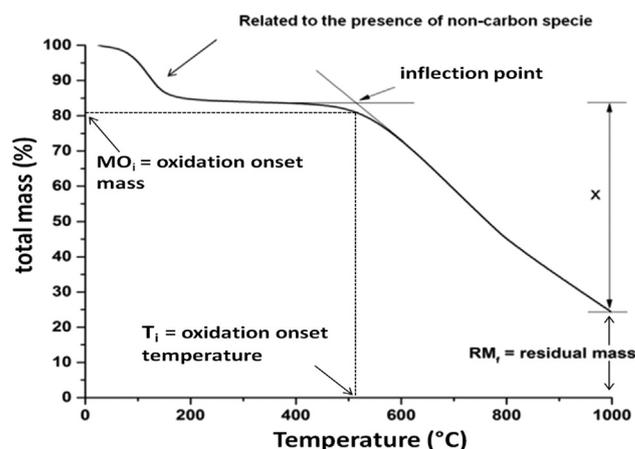


Fig. 1. TG profile pointing out parameters used to determine the actual carbon loss of the prepared samples.

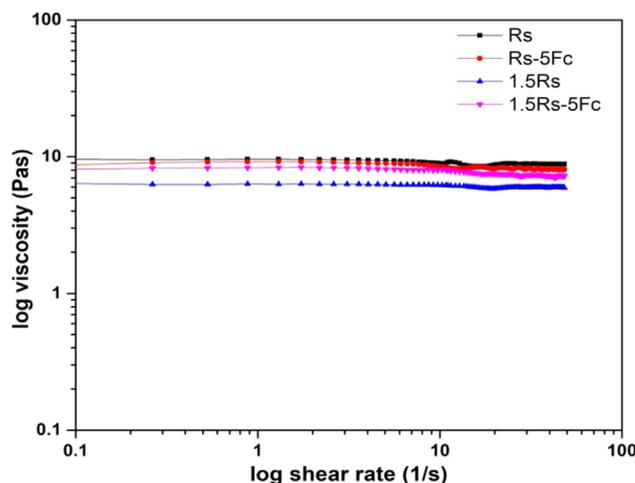


Fig. 2. Viscosity of commercial and LSR resin with and without ferrocene at 30 °C.

with and without ferrocene are shown in Fig. 2. The commercial and LSR resins present near Newtonian fluid feature (i.e., the stress rate to shear rate was constant and independent of the shear load duration) under the test conditions. Moreover, this behavior was not affected by the incorporation of the additive to the resins. Compared to 1.5Rs, the commercial product (Rs) has a higher viscosity. However, with the addition of 5 wt% ferrocene, the LSR product became more viscous and attained a status close to the commercial one. This information assures that the inclusion of ferrocene by mechanical mixing will not limit its processability during the refractory production. The formulations viscosity is expected to provide ease of processing and penetration into the refractory materials.

3.2. FTIR-ATR analysis of commercial and laboratory synthesized resole resins

Fig. 3 shows the spectra in the wavenumber range from 400 to 4000 cm⁻¹ of the commercial and LSRs. The peaks at 511 cm⁻¹, 691 cm⁻¹, 754 cm⁻¹, 826 cm⁻¹, and 888 cm⁻¹ were assigned to C–H vibrations [26]. The peak at 754 cm⁻¹ and 826 cm⁻¹ correspond to CH out-of-plane, ortho-substituted and para-substituted positions, respectively [27]. The proportion of the ortho and para linkages was determined from the absorbance intensities of these peaks, which were measured with the aid of spectragraphy 1.1.1 software. The peaks finding threshold was set at 5.0% of visible spectrum ordinate and the

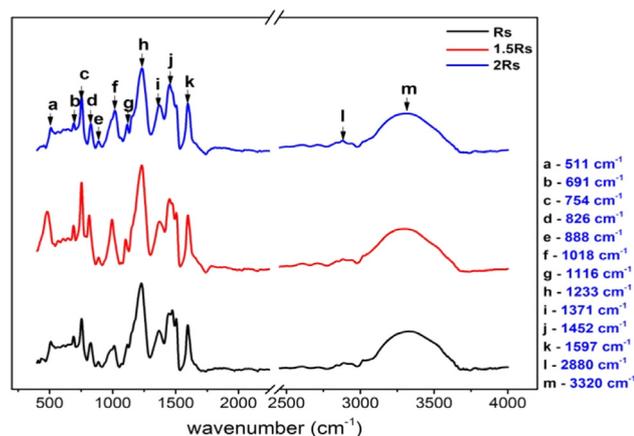


Fig. 3. FTIR-ATR spectra of commercial and the laboratory synthesized resole resins.

Table 3
Peaks absorbance intensity of ortho and para linkages.

Peaks position (cm ⁻¹)	Rs Absorbance	1.5Rs Absorbance	2Rs Absorbance
754	0.19011	0.28527	0.20185
826	0.09996	0.18064	0.10378
Para links proportion (%)	34	39	33

obtained results are presented in Table 3. The analysis shows that 1.5Rs has the highest percentage of para links (39%), whereas values for the commercial and 2Rs resins are 34% and 33%, respectively. This observation was later related to the attained graphitization level after pyrolysis of the respective resin formulations. The peaks at 1018 cm⁻¹ and 1116 cm⁻¹ were assigned to the C–O vibrations of CH₂OH group. The band that corresponds to the asymmetric stretch of phenol was detected at 1233 cm⁻¹. The width of the band at 1371 cm⁻¹ and 3320 cm⁻¹ indicated that these peaks were due to OH bond vibration related to the aromatic ring [27]. The peak at 1452 cm⁻¹ and 1597 cm⁻¹ correspond to C=C aromatic ring vibration [26,27]. Besides, the peak at 2880 cm⁻¹ was due to aliphatic CH₂ in-phase stretch [27]. All the functional groups were the same for both the commercial resole and laboratory synthesized ones. However, the integration by area of the OH band represents 45.8 cm², 48.9 cm², and 45.0 cm² for the Rs, 1.5Rs, and 2Rs resins, respectively (based on individual baseline), which may be related to the amount of phenol used for the synthesis. Moreover, the peak intensity of each resin differs, especially the one at 511 cm⁻¹, which has the highest value in 1.5Rs sample. This difference (in peak intensity) can be related to the concentration of the functional groups in the resins, which could affect the graphitization process.

3.3. XRD profiles of the phenol formaldehyde resins carbons

The diffractograms of the resulting carbons from unmodified resole resin (both commercial and laboratory synthesized ones) show a low-intensity hump between 20° and 30° and ~43° (Fig. 4a). The profiles indicate a disordered atomic arrangement after pyrolysis at 1000 °C. This XRD pattern is peculiar to sp³-hybridized carbons associated with an amorphous structural arrangement without a long range of carbon layer orientation [22]. Resole resins are non-graphitizable organic precursors as the process leading to carbon formation is mainly a solid-state reaction that does not include semi-liquid phase formation during their pyrolysis. The resins produced glassy carbons in which the randomly spaced regions of 6 members sp² bonded cyclic structures of the resulting carbons are held tightly within a network of sp³ crosslink, as shown in Fig. 4b [28]. This type of rigid structure does not allow the

reorganization needed for carbons graphitization. The presence of π-bonds inhibits the required atoms rotation for graphite generation [22]. Generally, the disordered organization of carbons derived from plain phenolic resin does not change when heated up to 3000 °C due to their highly cross-linked nature [9]. Consequently, the carbonization product is usually isotropic and possesses distinct properties when compared to graphite.

3.4. Graphitization of commercial and laboratory synthesized resoles containing ferrocene

Fig. 5 shows the effect of ferrocene addition (3–5 wt%) to resoles on the crystallization of carbons derived from these formulations after heat treatment up to 1000 °C. The diffraction peak at ~26° and 54° represent an asymmetric 002 and 004 plane, which corresponds to graphene layers. The intensity, sharpness and integrated area value of these peaks relative to the non-graphitic ones in XRD pattern of carbon samples have been used to describe graphitization degree [16,22,29,30]. Firstly, the commercial resin containing 3 wt% Fc was selected to investigate the most suitable heating rate (3–5 °C/min) for the pyrolysis operation. Regardless of the heating rates used, the presence of ferrocene led to the carbonized resole graphitization (Fig. 5a). However, the best GL value (61%) was attained for 3 °C/min (Rs-3Fc-A3). This heating rate appears to provide sufficient time for ferrocene to act, as well as the carbon atoms bond disruption and rearrangement necessary for graphite generation during the carbonization process. 1.5Rs and 2Rs were formulated in the laboratory to have control over the resin chemistry and find other factors that can influence the amount of generated graphite. These resins were subjected to the same stepwise heat treatment procedure using the heating rate that presented the best result with the commercial resin (i.e., 3 °C/min). Furthermore, 3, 4 and 5 wt% of ferrocene (content related to the resin) were added to the synthesized products. 1.5Rs resin (formaldehyde to phenol ratio = 1.5) generated the highest amount of crystalline carbons during pyrolysis and the carbonized products prepared with 3–5 wt% Fc presented 64%, 66% and 71% graphitization level, respectively (Fig. 5b). These values were higher than those attained with pyrolytic carbon from 2Rs formulations containing the same amount of additive, under similar experimental conditions (Fig. 5c). The higher formaldehyde ratio with more methyl functional group and a corresponding methylene bridge implied higher cross-linking during the curing stage [31]. Consequently, the high degree of bonding at the initial stage of pyrolysis limit the graphitization of the resulting carbon [22]. This observation explained why 1.5Rs formulations were more susceptible to graphitization. Besides, the FTIR analysis suggested that para linkages during the curing stage may be beneficial to graphitization (as observed with 1.5Rs). Moreover, the peak corresponding to Fe₃C phase indicates that this compound may have acted as a site for graphite generation during the pyrolysis operation. The results also agree with previous research studies involving the use of ferrocene as a graphitizing agent [2,32].

3.5. Microstructural analysis

Microstructural analysis was conducted to compare the structural arrangement of disordered carbon atoms from the unmodified resin (Rs-A3) and the graphitic ones from 1.5Rs-5Fc-A3 with the highest GL (Fig. 6). The high-resolution transmission electron microscope (HRTEM) images show a distinct structural difference between both carbon samples. The image obtained for Rs-A3 indicates an irregular structural arrangement (Fig. 6a), whereas the presence of fringes attested to the crystalline nature of 1.5Rs-5Fc-A3 carbon (Fig. 6b). Lattice lines corresponding to 002 plane were more pronounced in the sample derived from resole formulation containing ferrocene, although there was evidence of different orientation as well (Fig. 6b). This ordered arrangement covers a significant portion of the sample microstructure. From the HRTEM image, interplaner spacing (i.e., the spacing between

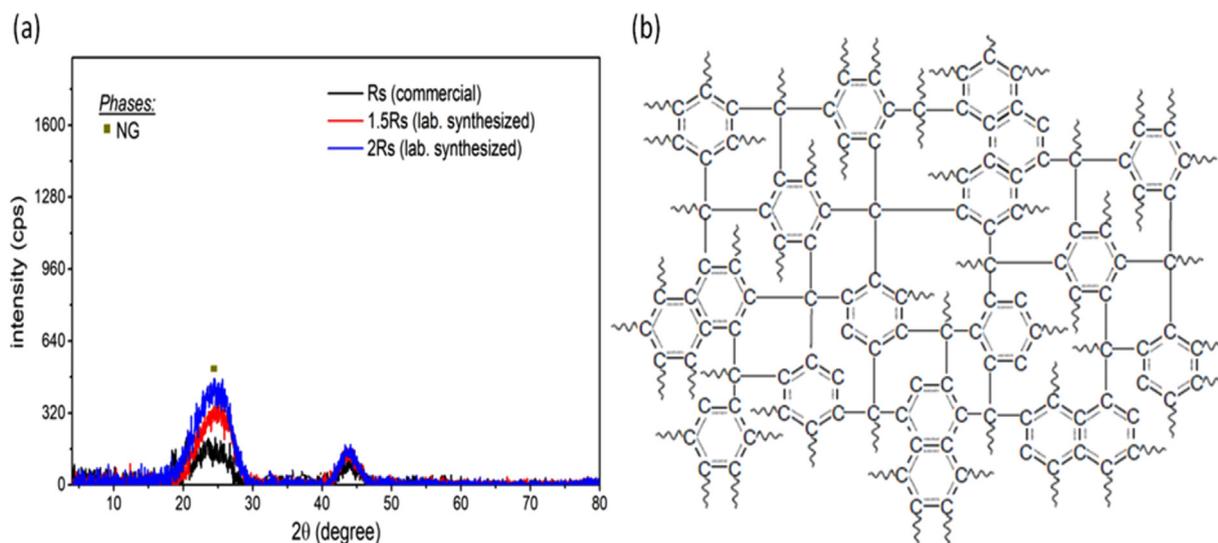


Fig. 4. (a) X-ray Diffraction pattern of uncatalyzed resole resin after carbonization at 1000 °C, (b) schematic structure of fully carbonized phenolic resin [28].

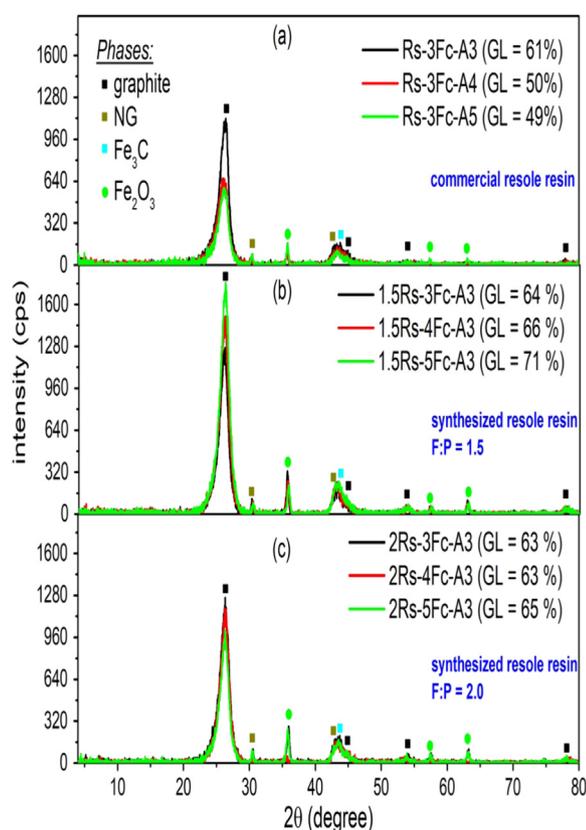


Fig. 5. XRD profiles showing the effect of ferrocene additions on the graphitization of carbonized resole resins after thermal treatment up to 1000 °C for 5 h under reducing atmosphere. NG = non-graphitic; A3, A4 and A5 = heating procedure at 3 °C/min, 4 °C/min and 5 °C/min, respectively.

the fringes) corresponding to 002 lattice plane orientation was determined to be ~ 0.341 nm and this value is close to graphite d_{002} (0.335 nm). The stacked plane thickness was 0.2235 ± 0.001 nm. The crystalline carbon HRTEM image also shows evidence of partial graphitization (as seen by the indicated amorphous region, Fig. 6b). Some further information was obtained from the selected area electron diffraction (SAED) analysis. The Rs carbon has two diffraction circles at 0.2132 nm and 0.1154 nm (Fig. 6c). Regarding the graphitized sample (1.5Rs-5Fc-A3), the individual spots, which represent the lattice plane

distance corresponding to the 2θ values of the XRD were barely visible in the diffraction circles. This characteristic is peculiar to polycrystalline materials without preferred stacking orientations and indicates a short-range order close to that of graphite. The d_{002} value determined for 1.5Rs-5Fc-A3 was 0.3384 nm (Fig. 6d) and compared to Rs-A3, this sample showed stacked graphene sheet layers and the presence of Fe_2O_3 phase (Fig. 6e and f). These carbon features should improve the thermomechanical performance of CCRs bricks developed based on ferrocene addition to the resin binder.

The EDS analysis of Rs-A3 and 1.5Rs-5Fc-A3 shows that a significant amount of oxygen was still present in the fired specimens after carbonization at 1000 °C (Fig. 6g and h). This observation matches those of other researchers regarding the composition of carbon derived from pyrolyzed phenolic resins [30,33,34]. Under such testing conditions, up to 12% and 10%, oxygen was detected in the carbon samples derived from the plain and modified resin respectively. Fig. 6h also shows the presence of about 4.31% Fe in the ferrocene-containing carbon composition after pyrolysis at 1000 °C. This information agrees with the XRD results and the statement that Fe and Fe_3C may have acted as active sites for structural rearrangement that led to the attained graphitization [16]. Other authors have suggested that this carbide compound (formed at 900 °C) may be responsible for the rearrangement of amorphous carbon to graphene sheets during the pyrolysis operation [1,16,35]. It implied that the reactions that led to graphite generation started at a later stage of carbonization.

3.6. Chemical structure changes during the pyrolysis of resole containing ferrocene

The high-resolution C1s profiles of 1.5Rs-5Fc formulation subjected to heat treatment at temperatures up to 300 °C, 500 °C, 800 °C and 1000 °C (based on A3-heat treatment procedure) are shown in Fig. 7a-e. The spectra indicate the presence of different types of carbon functional groups, i.e., C–C, C–O–C, C=O. The peaks at ~ 284.6 eV were assigned to C–C, at ~ 286.2 eV, C–O–C, at ~ 287.9 , C=O (carbonyl) and ~ 289.2 eV to O–C=O (carboxyl) functionalities [36,37]. The relative percentage changes in the functional groups during the heating process were also presented. The degradation and dehydration reaction during the pyrolysis operation led to the formation of compounds such as CO_2 , methanol, phenol, and water [28]. The release of these substances was responsible for the shift and evolution of the C1s spectra. The percentage area of C–C bond increased at 500 °C, which indicated that significant carbonization reaction started around that temperature.

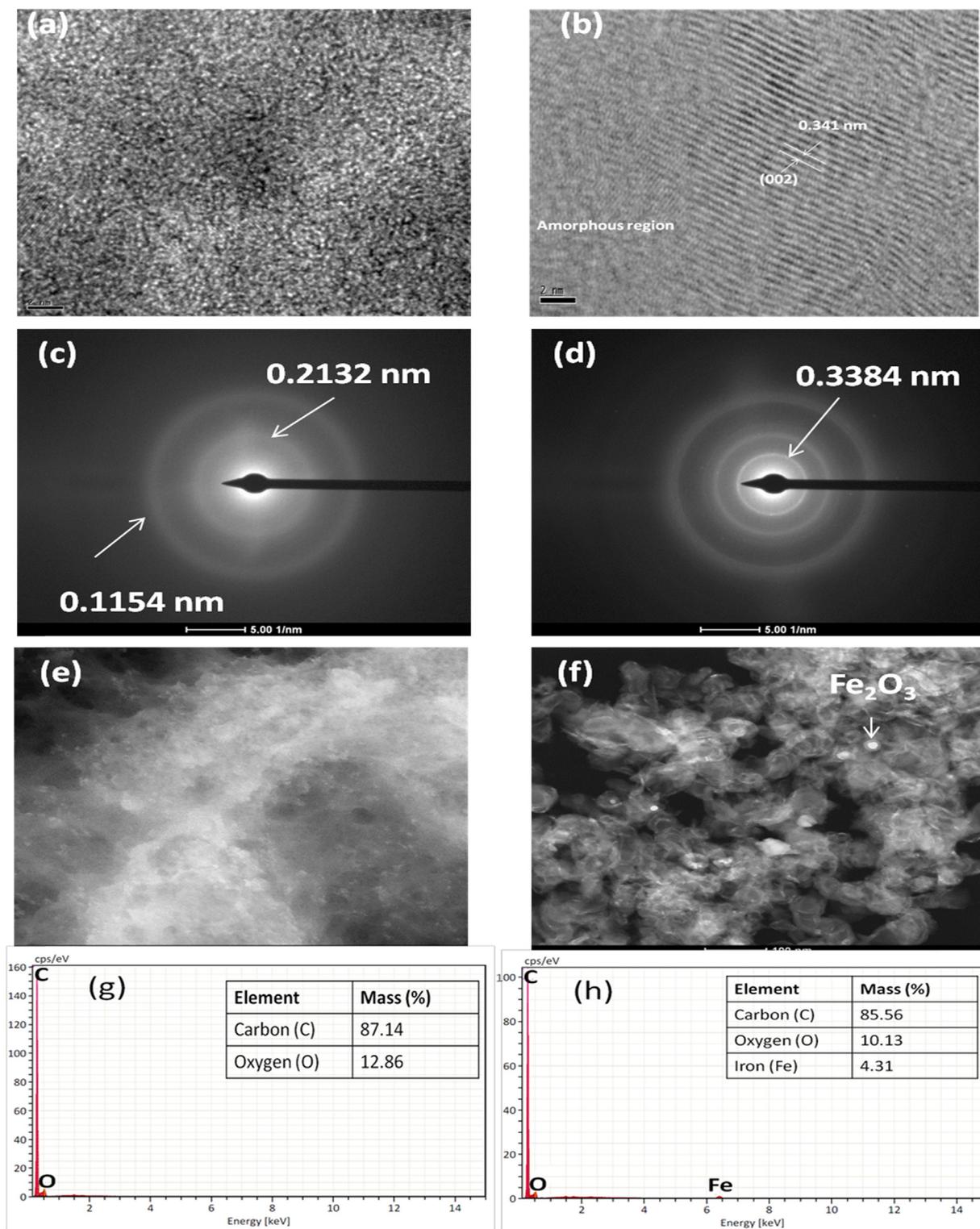


Fig. 6. Microstructural and chemical information of carbons derived from Rs and 1.5Rs-5Fc formulations after thermal treatment at 1000 °C for 5 h under reducing atmosphere: HRTEM images of (a) Rs-A3 and (b) 1.5Rs-5Fc-A3. SAED images of (c) Rs-A3 and (d) 1.5Rs-5Fc-A3. TEM images of (e) Rs-A3 and (f) 1.5Rs-5Fc-A3. Chemical composition of (g) Rs-A3, and (h) Rs-A3 1.5Rs-5Fc-A3. A3 = heating procedure at 3 °C/min.

Nevertheless, some amount of oxygen was still present in the carbonized structure after pyrolysis at 1000 °C. The large full width at half maximum (FWHM) values in Fig. 7a-d, which are 1.53 eV, 1.44 eV, 1.36 eV, and 1.35 eV, respectively, suggested that the peak assigned to C-C bonds is the combination of C-C/C=C signal.

Moreover, the binding energy of the C-C bonds slightly shifted towards a lower binding energy value (284.3 eV) with a more narrowed

width (0.96 eV), indicating the graphitization of these carbon samples after pyrolysis at 1000 °C for 5 h (Fig. 7e).

The fitted Fe2p spectra of 1.5Rs-5Fc heat-treated samples are presented in Fig. 8a-e. The profiles were characterized with a doublet of Fe²⁺ and Fe³⁺ oxides (Fe2p_{3/2} and Fe2p_{1/2}), as well as the oxides shake-up satellites. The presence of Fe₃C was also detected at temperatures of 800 °C and 1000 °C/5 h. The binding energy values were

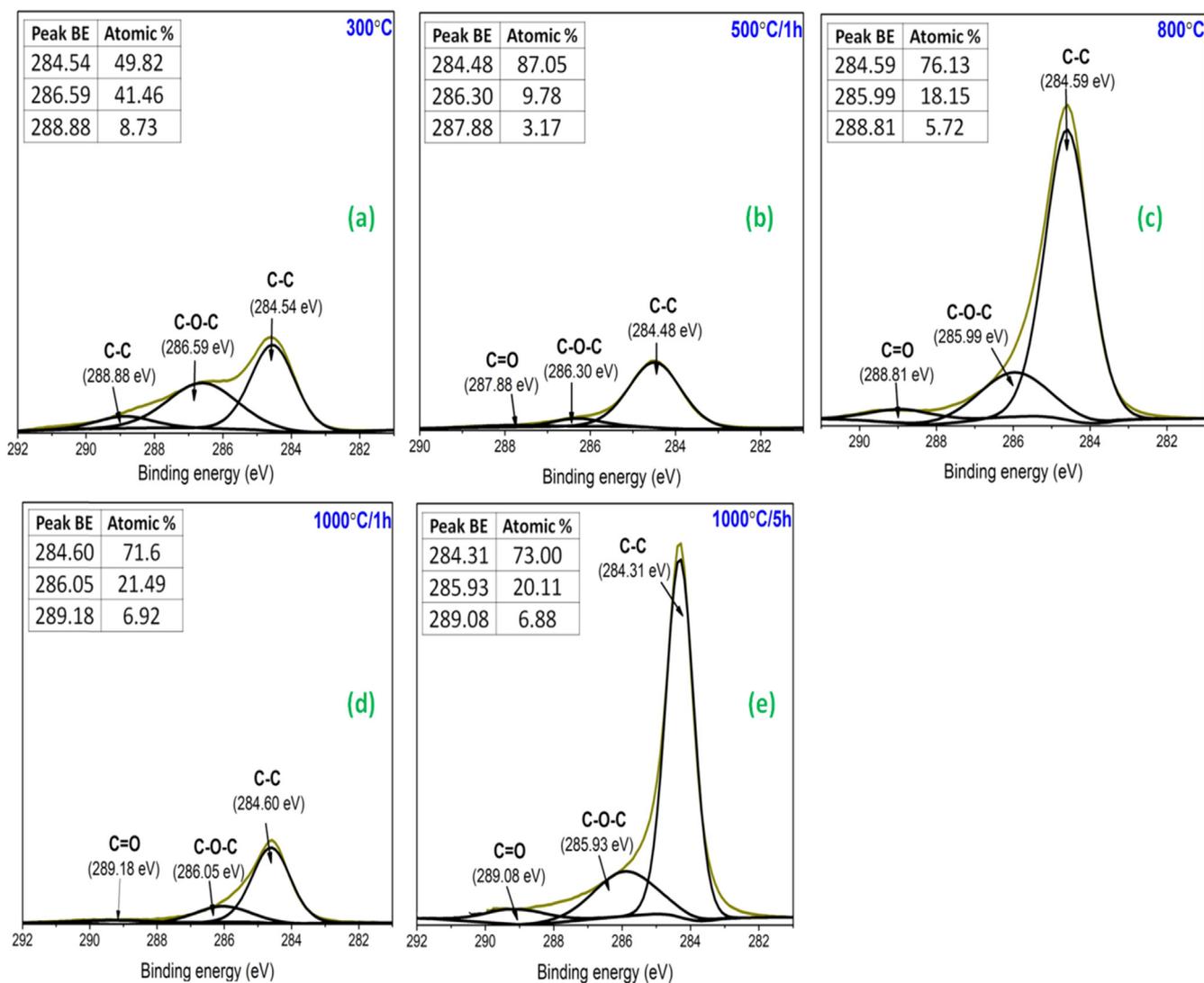


Fig. 7. The XPS C1s spectra of 1.5Rs-5Fc formulation as a function of heat treatment temperatures. BE = Binding Energy.

assigned in line with studies, which involved Fe2p profile deconvolution [38–40]. Based on the transition of Fe2p profile, it is not clear whether there was a chemical reaction between the resin and ferrocene during the heat treatment process or if the various oxide species were due to the additive decomposition. The lack of clarity on the issue is because ferrocene is an organometallic material. Nevertheless, the solubility of carbon in iron may have consequently led to graphite generation with Fe_3C acting as active sites. Moreover, Fe_2O_3 appears to be the predominant oxide after the pyrolysis operation at 1000 °C. This observation agrees with the XRD results.

3.7. Oxidation resistance of carbon derived from modified and unmodified phenol formaldehyde resin

The TG curves in Fig. 9 described the carbon samples (obtained after the plain and ferrocene-containing resin were thermally treated up to 1000 °C at 3 °C/min) reactivity in an oxidizing environment and at temperatures up to 1000 °C.

From these curves, the carbon oxidation onset temperature (T_i) and mass loss were determined as described in Section 3.3 and the results presented in Table 4.

An attempt was made to ascertain the relationship between the attained graphitization level (GL) to the formulations starting composition and oxidation resistance of the derived carbon samples. Regarding

this comparison, the carbon samples were grouped into different categories according to the several factors that seem to control their reactivity in synthetic air.

- Carbon derived from the commercial resin without the additions of any additive (Rs) has the lowest oxidation initiation temperature (Fig. 9a), 0% graphitization level and possesses the least oxidation resistance with 81% mass loss up to 1000 °C. Generally, the isotropic nature, high surface area and high amount of edge carbon atoms in their structure promoted high oxidation rate in air. The lack of detailed information regarding the resin chemistry does not allow a thorough understanding of why the carbon exhibited the smallest thermal stability in air. However, the disordered arrangement of its atom, as depicted by the TEM image, will reduce its thermal stability in an oxidizing environment. This characteristic will limit CCRs service life and performance [41].
- 1.5Rs-A3 and 2Rs-A3 (derived from the unmodified LSR resins) show improved oxidation resistance than that of the commercial one (Fig. 9b). The carbon derived from these resins has non-crystalline features, under the testing conditions, but also higher T_i than the commercial resin carbon and those containing ferrocene. Interestingly, their overall performance in the oxidizing environment was similar to the graphitized ones. These observations suggest that other factors, such as bond strength play a significant role in the

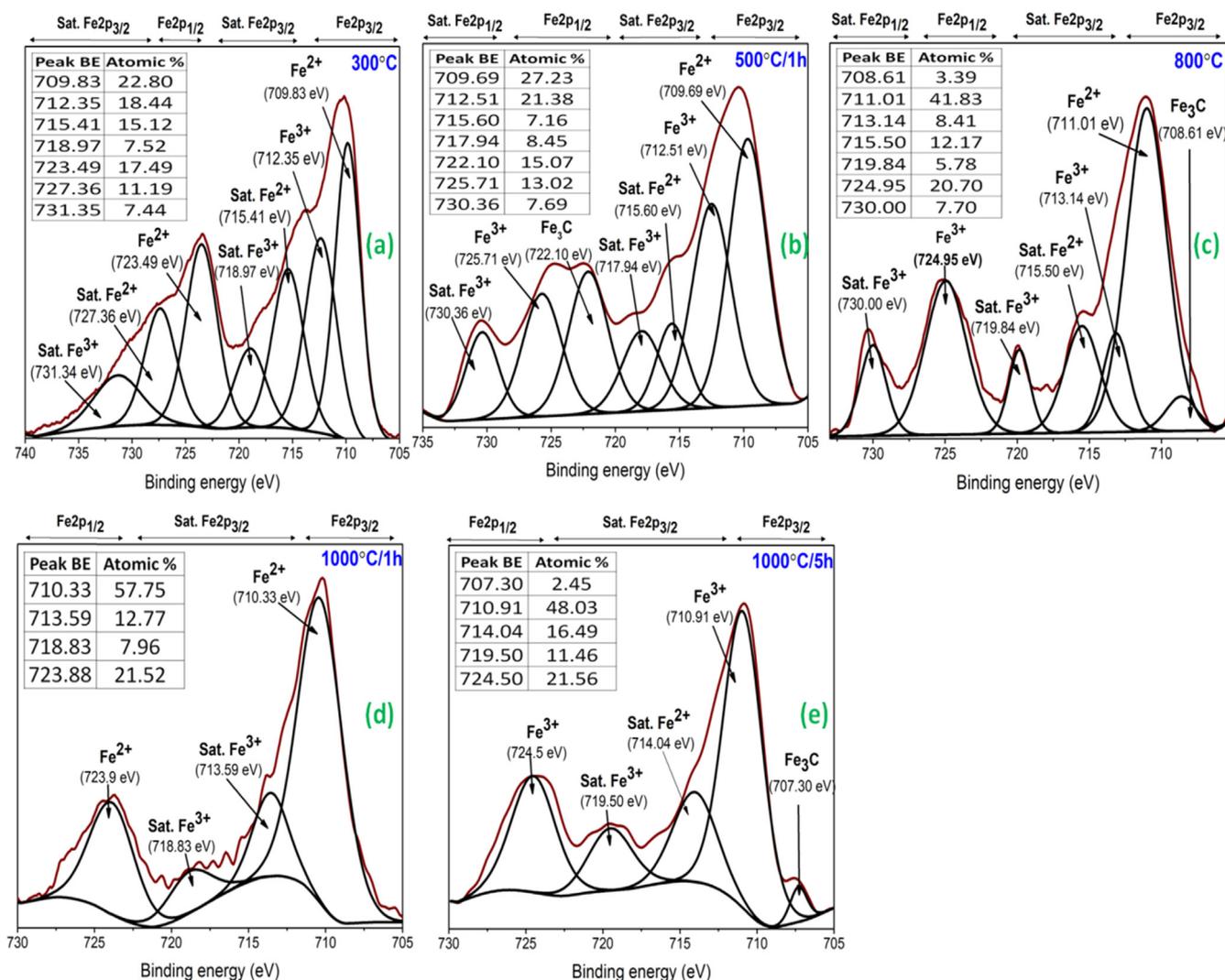


Fig. 8. The XPS Fe2p spectra of 1.5Rs-5Fc formulation as a function of heat treatment temperatures. BE = Binding Energy.

process. Although it is not yet conclusive, the reactivity of the glassy carbon can be affected by atoms bond strength. As mentioned, the T_i values of 1.5Rs-A3 and 2Rs-A3 were significantly higher than Rs-A3 (from the commercial resin). Their oxidation initiation temperatures were 562 °C and 585 °C, respectively, compared to 438 °C that was obtained for Rs-A3. The T_i values may be related to a combination of factors especially bond strength, which should significantly influence it, as oxidation comprises a bond breaking and forming reactions. Edwards et al. [42] reported that the macromolecular structure of non-graphitizing polymeric materials is not only preserved but they developed even greater bonding during pyrolysis. Consequently, the oxidation of 2Rs carbon, which has stronger cross-linking due to the formation of more methylene bridges during the curing stage started at a higher temperature compared to 1.5Rs-A3.

- iii. This section discusses the oxidation resistance of carbon derived from resole formulations containing ferrocene (Fig. 9c) with a high amount of graphitic structure in their composition. The attained structural rearrangement during pyrolysis should lead to a reduction in the number of edge atoms and improved oxidation resistance. As seen from Table 4, the T_i values of these carbon samples were lower than those derived from the unmodified resins, which implied that oxidation began at a lower temperature or earlier. As observed, the crystallization of resole resin carbon requires minimum cross-linking during the curing stage and the

graphitization of the formulations containing ferrocene produce carbons (i.e. sp^2 carbon) with a slightly lower binding energy. Hence, their oxidation onset temperature was lower (as expected) than those of the plain resin carbon. Nevertheless, because of the ordered structure associated with graphite generation, the overall carbon loss was still relative to the pristine ones. At this instance, crystallinity seems to be the responsible controlling factor for their overall stability in the high-temperature oxidizing environment. This type of trend is similar to the earlier observation by Talabi et al. [43]. Consequently, the advantages associated with the binder graphitization in carbon-containing refractories may be better related to improved thermomechanical properties such as hot modulus of elasticity as reported by Jansen [2].

Furthermore, to determine the role of graphitization, the carbon loss percentage from T_i to 800 °C and from 800 °C to 1000 °C was compared, as shown in Table 5. The analysis assumed two parameters, namely, atoms bond strength and organization as the oxidation rate-controlling factors. The carbon loss per minute at the lower temperature region (T_i -800 °C) of the graphitized samples (i.e., 1.5Rs-A3 and 2Rs-A3) were lesser compared to the non-graphitic ones. At higher temperature region, the glassy carbon derived from the unmodified resin exhibited lower carbon loss rate. This pattern suggests that atoms arrangement presents a significant role at the beginning of oxidation when lower energy was available for bond breaking. However, bond strength may

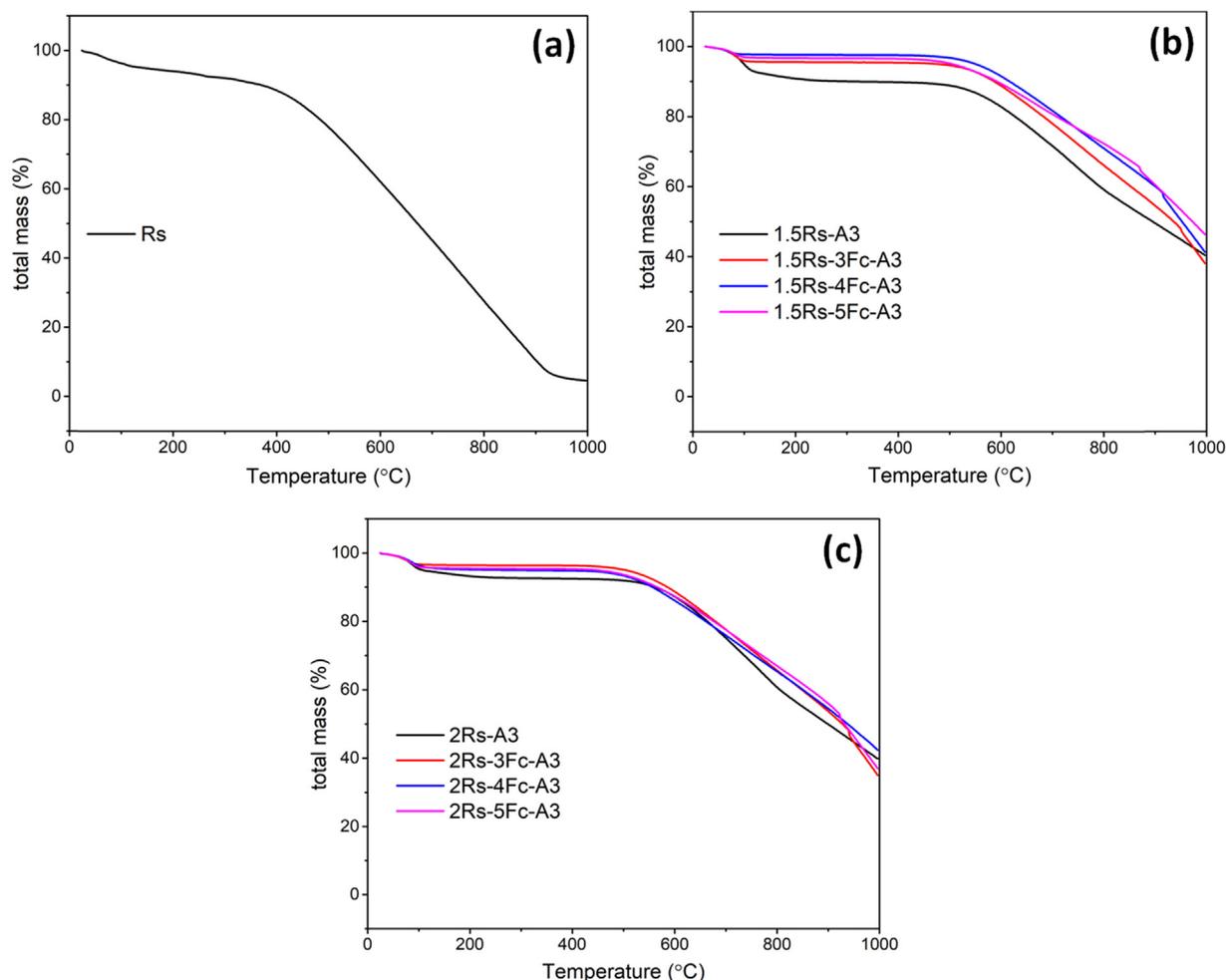


Fig. 9. TG curves of carbon samples derived from: (a) plain commercial resin and plain and modified (b) 1.5Rs resin and (c) 2Rs resins during oxidation resistance measurements. A3 = heating procedure at 3 °C/min.

Table 4

Effect of graphitization and composition on oxidation stability of resole resin carbon.

Samples	Carbon loss (%)	T _i (°C)	GL (%)
Rs-A3	80.8	438	0
1.5Rs-A3	55.9	562	0
2Rs-A3	53.4	585	0
1.5Rs-3Fc-A3	55.6	552	64
1.5Rs-4Fc-A3	54.1	541	66
1.5Rs-5Fc-A3	48.2	522	71
2Rs-3Fc-A3	58.9	537	63
2Rs-4Fc-A3	50.5	531	63
2Rs-5Fc-A3	55.8	518	65

be the controlling factor at more elevated temperatures and the onset of oxidation.

Another important aspect is the oxidation reaction direction, either in the a-axis or basal plane one. As expected, if reactivity is more pronounced in the a-direction, crystallization will be the controlling factor and the carbon loss rate in the basal plane-direction should depend more on bond strength (due to strong covalent bond). Considering that edge site atoms are more reactive than those of basal plane, graphitization, which favors their reduction should lead to improved oxidation resistance in the a-direction [44–46]. On the other hand, lower carbon loss will occur if oxidation proceeds in the c-direction due to the strong covalent bond within their atoms. The oxidation of plain graphite crystals followed a well-defined crystallographic plane along the

Table 5

Carbon loss at different temperature range starting from the oxidation onset temperature.

Samples	T _i -800 °C			800–1000 °C		
	Carbon loss (%)	Time (minutes)	Loss per minute	Carbon loss (%)	Time (minutes)	Loss per minute
1.5Rs-A3	58.8	23.81	2.47	41.2	20	2.06
2Rs-A3	57.0	21.52	2.65	43.0	20	2.15
1.5Rs-3Fc-A3	48.9	24.81	1.97	51.1	20	2.56
1.5Rs-4Fc-A3	44.4	25.87	1.72	55.6	20	2.78
1.5Rs-5Fc-A3	45.8	27.77	1.65	54.2	20	2.71
2Rs-3Fc-A3	49.8	26.26	1.89	50.2	20	2.51
2Rs-4Fc-A3	53.9	26.94	2.00	46.1	20	2.31
2Rs-5Fc-A3	46.4	28.17	1.65	53.6	20	2.68

polar edges of graphene layers due to oxygen chemisorption. However, pyrolytic carbon from phenolic resin oxidized more in the c-direction [23,47]. These observations further explained why the overall performance of the graphitized and non-graphitic carbons in a high-temperature oxidizing environment might appear similar.

Generally, the results show that several factors including atoms bond strength and atomic arrangement control the oxidation resistance of pyrolytic carbons derived from either the plain or modified resins. These observations agree with Chang et al. and Ruff et al. assumption [47,48] that carbon oxidation is influenced by several factors, which

include the extent and accessibility of its surface, bond strength of its atoms and the composition.

4. Conclusions

Ferrocene has been found to be an excellent graphitizing agent for resole in the chemistry and structure of the investigated resin. The highest graphitization level of 71% is attained with the addition of 5 wt % Fc to the laboratory synthesized product (i.e., 1.5Rs with formaldehyde to phenol ratio = 1.5) after stepwise heating at a heating rate of 3 °C/min. Compared to 2Rs (formaldehyde to phenol ratio = 2.0) and the commercial product (Rs), 1.5Rs resole formulations containing ferrocene are more susceptible to graphitization. The lower amount of methyl functional group and methylene bridges, which resulted in lesser cross-linking degree during the curing stage favor their crystallization. This observation shows that a high degree of bonding at the initial stage of pyrolysis will limit the amount of generated graphite. The interlayer spacing of carbon derived from the resole formulations is close to those of graphite (0.3352 nm). The addition of ferrocene to resole can lead to the formation of Fe and Fe₃C, which act as active sites for the atoms reorganization that promoted graphite generation.

Atoms arrangement and bond strength have been found to influence the oxidation resistance of carbon derived from resoles. Due to the combination of rate controlling-parameters, the overall thermal stability of the graphitized samples in the oxidizing environment is similar to the non-graphitic ones. Nevertheless, the benefits derived from graphitization of resole carbon in CCR products are not limited to only oxidation resistance.

Based on this study, 1.5Rs resole synthesized with a formaldehyde to phenol molar ratio equal to 1.5 containing ferrocene addition of not less than 3 wt% is recommended as a binder for the production of carbon-containing refractories. Moreover, the addition of ferrocene (up to 5 wt%) will not affect the resin flow behavior nor limit its processability during the refractory production.

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