

INFLUENCE OF SULFUR ON CARBONIZATION OF PITCH BINDERS FOR STRUCTURAL CARBON COMPOSITES

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Introduction

The use of sulfur additives for the modification of pitch binders has a long history in the manufacturing of carbon composite materials. The principle reason for the addition of sulfur is to increase the carbon yield [1-4]. However sulfur is also soluble in melted pitch [5], and facilitates mixing of the raw components prior to molding by reducing the overall viscosity. Several other well-known facts regarding sulfur additions to carbon precursors are briefly summarized below:

- Sulfur reacts with hydrocarbons at temperatures in excess of 150°C. Initially sulfur reacts with unsaturated bonds forming "sulfur bridges" between molecules. This process is similar to the process of vulcanization for the strengthening of natural rubber. Concurrently, sulfur also reacts with hydrogen to form hydrogen sulfide, H₂S. The latter reaction is quite intensive at 180°C, such that it is used for the preparation of H₂S on a laboratory scale [6].
- The microstructure of cokes obtained from pitches modified with sulfur has a tendency to exhibit less crystalline order than for unmodified pitches. When sulfur additions exceed 10 wt. %, three-dimensional cross-linking occurs, stopping the development of the mesophase. The resulting coke in such case has a glassy-like isotropic structure [4,5]. Our work supports these findings. We obtain completely isotropic microstructures upon addition of 15 wt.% of sulfur .
- At ~400°C, sulfur reacts with carbon to yield non-stoichiometric surface [7] and bulk [8-10] compounds. In these compounds, sulfur exists in the form of thioethers, disulfide bonds, heterocyclic structures, and sulfur bridges. The sulfur content in carbon-sulfur non-stoichiometric compounds can be as high as 50 wt. %. Further heat treatment prompts the removal of sulfur. Depending on the amount of sulfur combined at 400°C, the sulfur content can decrease to as low as 1.4 -5 wt. % by 1000°C.
- At temperatures in the range, 1500-1700°C, investigators note a further reduction in sulfur [11]. Sulfur eliminates in the forms of CS₂ and CS. This has been argued to be the principle cause of "puffing," which is a rapid and irreversible expansion of the coke structure occurring in the temperature region between 1300-1700°C. In the same temperature regime, sulfur also promotes low temperature graphitization. The catalysis of graphitization by sul-

fur is believed to be due to the selective elimination of carbon atoms hindering lattice growth in the form of carbon-sulfur gaseous species.

We are interested in the effects sulfur additions in the range of 5 to 15 wt. % with respect to microstructural development in the interest of improving composite strength, σ_{max} , and toughness, K_{Ic} .

Experimental

Raw materials. Two pitches are studied. The first is a petroleum derived pitch, A-240, from Ashland Inc. A-240 has a softening point of 110°C and density of 1.24 g/cc at 25°C. The second pitch is a coal tar pitch (CTP) from Koppers Industries Inc. The CTP pitch has a softening point of 110°C and density of 1.33 g/cc at 25°C. A-240 converts into a needle coke, and CTP produces a coke with a mosaic microstructure.

Prior to carbonization, the pitch samples are ground (-100 mesh), and mixed with sulfur (Aldrich Chem Co #21,519-8).

Anode coke from Conoco Inc. (#6901983) and natural crystalline graphite flake from Cometals Inc. are used as fillers in the carbon composites. A Phenol-formaldehyde resin, VARCUM 29389, from OxyChem Co. is used for the final impregnation of the composites.

Carbonization. Carbonization of all pitch samples, mixtures thereof with sulfur additions (0, 5, 10, and 15 wt. %), and pressed composites is carried out in an Ar atmosphere. Samples are initially heated slowly at 1°C/min up to 900°C and then 5°C/min thereafter to a final temperature of 1200°C. All samples are soaked at 1200°C for 4 hours and then cooled at 20°C/min. All composites are carbonized in a loosely packed powder-bed made of coke to retain sample shape during heating.

Composites. The composition of the composites is: 40 wt.% binder, 59 wt.% anode coke (as graphitized flakes), and 1 wt. % graphite flake. For modification of the binder, sulfur is added at concentrations of 0, 5, 10 and 15 wt. % in the same manner as with the pitch carbonizations.

Optical microstructure. Specimens for optical microscopy are prepared by encapsulating the carbonized pitches or C-C composites into epoxy resin mounts. The encapsulated samples are subsequently polished first with silicon carbide sand papers (Cat # MI21-400, MI21-600 and MI21-1200), and finally with a diaD1ond compound (Cat # M203). All materials are from Metlab corporation.

Microscopic observations in polarized light are carried out on a BH-2 Olympus microscope, linked to a computer-controlled digital camera. DMCI. For most observations, a magnification of 200X is sufficient. The microscope polarizer and analyzer are oriented perpendicular to each other for analysis under polarized light Polaroid DMC Direct V2.0 software is used to acquire all images, and final image editing is performed using Adobe Photoshop 5.0. SEM images are obtained using an Amray Electron Microscope.

Thermogravimetric analysis (TGA). TGA experiments are performed with a TAG 24 Setaram thermoanalyzer. Samples of roughly 40 mg are tested in a platinum crucible at heating rates of 5°C/min to a final temperature of 1000°C. All tests are performed at 95 kPa pressure with a flowrate of 20 sec/min. Carbonization analysis is carried out in flowing ultra-high purity argon and reactivity analysis is done in flowing air.

X-ray diffraction (XRD). The crystalline structure of the carbonized materials is characterized using x-ray diffraction. The XRD patterns were generated from coke powder powder specimens (-200 mesh) with and additional 5 wt. % silicon powder (Union Carbide Corporation, Carbon product Division, Parma, Ohio) for an internal standard. The samples are scanned using a Philips PW 1050 X-ray diffractometer operating at 40 kV and 20 mA, using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.1540591$ nm). All samples were scanned using a step size of $0.02^\circ 2\theta$ with a dwell time of 2 sec. The (111) silicon reference peak at $2\theta = 28.443^\circ$ is used to calibrate the 2θ scale, and correct for any instrumental error .

Results

Thermogravimetric analysis. The differential thermal decomposition profiles of the pitch-sulfur mixtures in flowing ultrahigh purity Ar are given in Figures 1 and 2. In the presence of sulfur, the carbon yield is remarkably higher, approximately 20 wt. % or greater .The intensive weight loss in the pitch-sulfur mixtures occurring just after 150°C continues up to approximately about 550°C. In the range, 150-300°C the rates of the weight-loss for both pitch and pitch-sulfur mixtures are similar .However , after 300°C the weight-loss is visibly slower for the pitch-sulfur mixtures. After 550°C, the weight loss is slow, not exceeding 2-3 wt. %. While the CTP has a higher carbon yield than the A-240,

there is practically no difference in the carbon yield for both binders after an addition of 15 wt. % of sulfur .

Optical microscopy. Optical microstructures of the carbonized binders are presented in Figures 3 and 4.

The CTP during carbonization converts into a coke possessing a mosaic microstructure (Fig.3a). Areas with fine mosaics are separated by moderately anisotropic regions. The mosaic areas range between 40 and 200 microns. Addition of 5 wt. % sulfur does not change the structure significantly, except for minor reductions in the size of the anisotropic regions (Fig.3b). For the samples with a level of 10 wt.% sulfur, the microstructure of the carbonized material changes considerably (Fig.3c). More than 75% of the examined area is comprised of a very fine mosaic structure. At the same time, anisotropic areas are more pronounced. The binder containing 15 wt. % sulfur results in an isotropic microstructure after carbonization (Fig.3d). An important feature of materials obtained from the CTP binders is absence of any cracks. Even the glassy-like material obtained from binder with 15 wt.% sulfur does not show signs of any stress accumulation during heat-treatment.

The A-240 carbonizes into a coke with an extremely pronounced anisotropic microstructure (Fig.4a). Addition of 5 wt.% of sulfur does not result in any observable changes. Figure 4b presents another type of structure, which can also be found in materials obtained from pure A-240. Addition of 10 wt.% sulfur results in a significantly finer microstructure (Fig.4c). Isotropic, glassy-like carbon is obtained after carbonization with 15 wt.% sulfur (Fig.4d). Contrary to the coke microstructures obtained from CTP pitch, the microstructures of the A-240 samples exhibit intense cracking. The isotropic material displays intensive inner stresses.

The microstructures of the composite materials prepared from the CTP binders are presented on Figure 5. The composite obtained from a modified binder has lower porosity, but also displays poor contact between the surface of the matrix walls and impregnating resin.

XRD. The diffraction patterns are quite typical for cokes, featuring a wide reflection corresponding to the (002) planes of the graphite-like structures. This reflection is used to evaluate the interlayer distance, d_{002} , and crystallite size, L_c . The results are tabulated in Table I. The sulfur additions have a slight influence on the interlayer distance and crystallite size. Only the formation of glassy-like carbon is accompanied by a decrease in the crystallite size, L_c and increase in the interlayer distance, (002). This result is especially pronounced for the A-240 derived materials.

SEM. The SEM images of the carbonized binders are shown

in Figure 6. Additions of sulfur increase porosity and decrease wall thickness. Foaming during carbonization increases with the concentration of sulfur added to the binder. The surface of the walls also becomes smoother as a result of the sulfur additions

Testing of the composites. Thermal decomposition behavior of the composite samples, obtained from different binders are tested using TGA in flowing air. These results are given in Figures 7 and 8. For all samples, two unique temperature regions are distinguishable. The first region, in the temperature range, 250°C - 400°C, is accompanied by a mass loss of 20 - 40 %. The second region, between 450°C and 700°C, continues until the samples are fully burnt out. This region starts at higher temperature for the binders modified with sulfur. The temperature shift is nearly 100°C, and appears only for the samples impregnated with the resin. On the other hand, samples that weren't impregnated only show one weight loss trend, independent of any binder modifications.

Discussion

In organic chemistry, sulfur is known as a “soft” oxidizing agent as it is more selective than oxygen or oxidizers such as chlorine. When sulfur interacts with hydrocarbons, there are only a few possible reactions that can occur: combination with hydrogen or carbon as in H_2S and CS_2 , or formation of sulfur bridges between hydrocarbon molecules, forming mercaptanes or thioethers. Simple thermodynamic calculations show that the formation of H_2S is theoretically possible at temperatures higher than 50°C. Reactions resulting in the formation of CS_2 , however, are only possible at temperatures in excess of 400°C.

On this basis, it can be concluded that sulfur removes hydrogen at relatively low temperatures by either directly combining with, or cross-linking hydrocarbon molecules. The latter would be accompanied by a decrease in volatility. At temperatures greater than 400°C, any sulfur added to the binder is already complexed with hydrocarbon molecules and thus unreactive. Accompanied by this event is an increase in the carbon yield.

The greater the quantity of sulfur added, the more sulfur bridges are formed leading to more rapid increase in molecular weight. Higher viscosity and intense foaming also result (Fig. 1, 2, 6).

The combination of binder molecules and increasing viscosity prevent orientation of the aromatic molecules with each other. In the extreme case of sulfur addition, we observe the formation of a glassy-like, isotropic carbon (Fig. 3d and 4d) with increased inter layer distances and decreased

crystallite sizes (Table 1).

The modification of binder with sulfur additions has a strong effect on the surface properties of the carbonized matrix. The roughness of the surface disappears as the microstructure becomes completely isotropic and “glass-like”(Fig.6b). It is not surprising, therefore, that such a surface exhibits poor contact with the impregnating resin and leads to the formation of pores at the wall-resin interface (Fig.5).

In this particular instance, the differences in material structures do not have strong effect on their subsequent reactivities. However, the carbonized bodies do show differences in reactivity as a function of different resin impregnations as shown by differences in decomposition behavior in flowing air (Fig. 7,8). This result is unexpected. It is well accepted that the reactivity of carbons scale inversely with increasing crystallinity [12]. The possible reason for this is that glassy carbon is different from polycrystalline forms, and naturally much more stable.

Conclusions

Sulfur added to pitch binders in quantities less than 10 increase carbon yield and slightly change structure and properties of the carbon materials. Additions of sulfur in quantities 10 wt.% or more remarkably change structure of carbon matrix at all levels: crystallite organization, microscopic morphology, surface features, and macro-pore structure.

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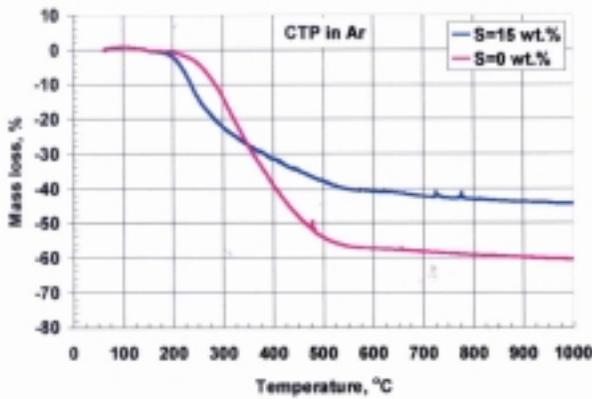


Figure 1. Thermogravimetric analysis of CTP a.r. and with 15wt.% of S, in 95kPa Ar flowing at 20scc/min

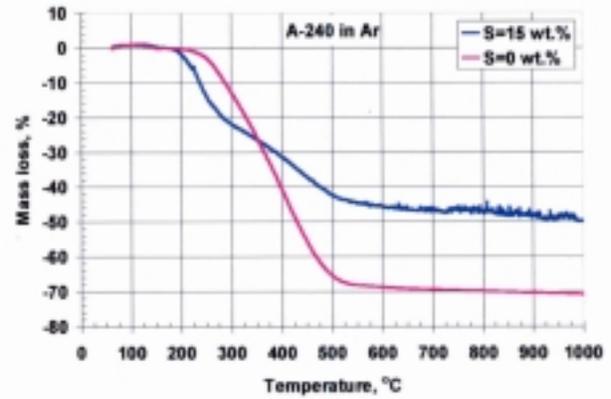


Figure 2. Thermogravimetric analysis of A-240 a.r. and with 15 wt.% of S, in 95kPa Ar flowing at 20scc/min.

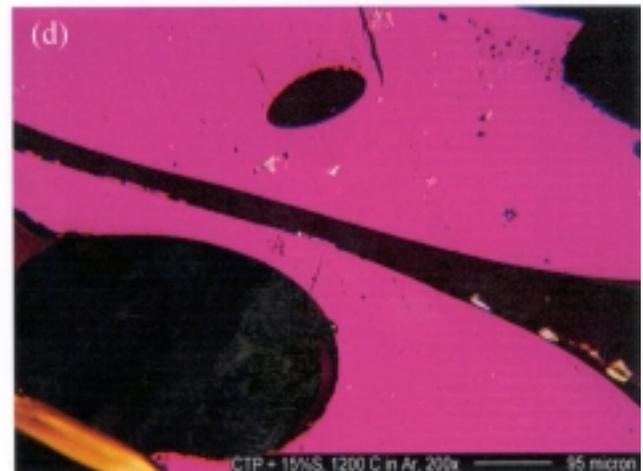
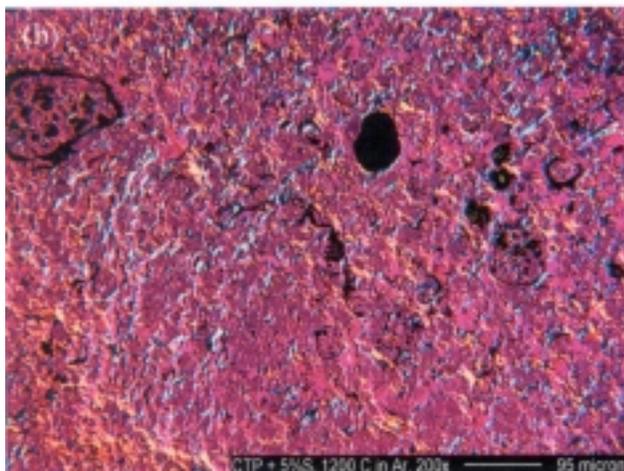
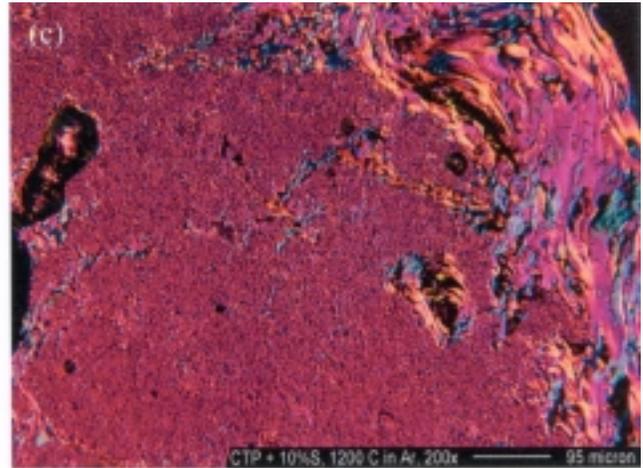
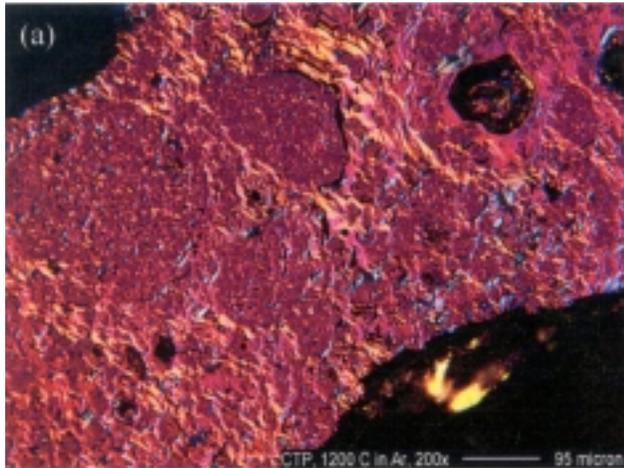


Figure 3. Polarized light optical microstructure of the carbonized CTP and CTP with sulfur additions: (a) —0 wt.% of S, (b) —5 wt.% of S, (c) —10 wt.% of S, (d) —15 wt.% of S; magnification 200x.

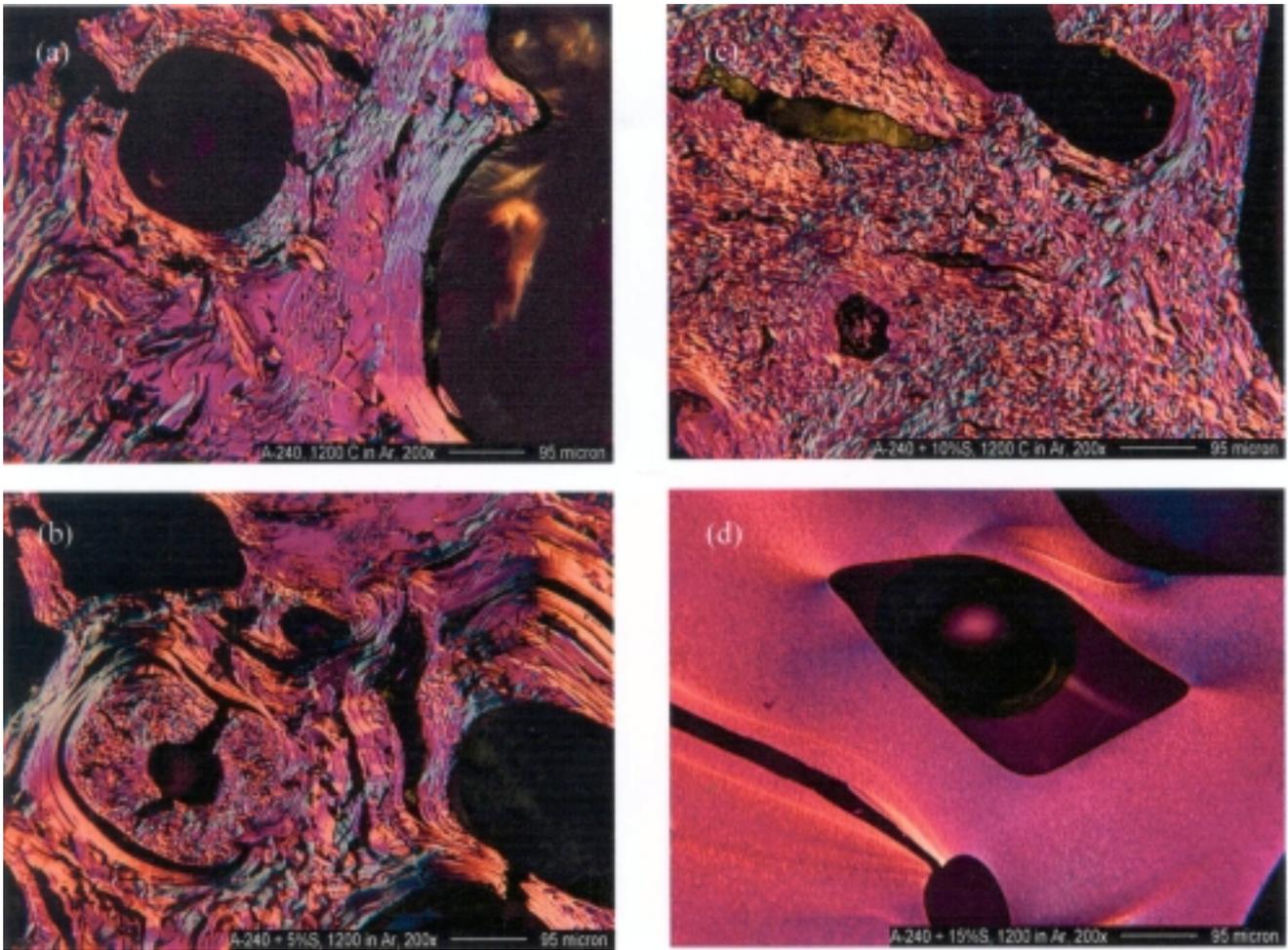


Figure 4. Polarized light optical microstructure of the carbonized A-240 and A-240 with sulfur additions: (a) —0 wt.% of S, (b) —5 wt.% of S, (c) —10 wt.% of S, (d) —15 WT.% of S; magnification 200x.

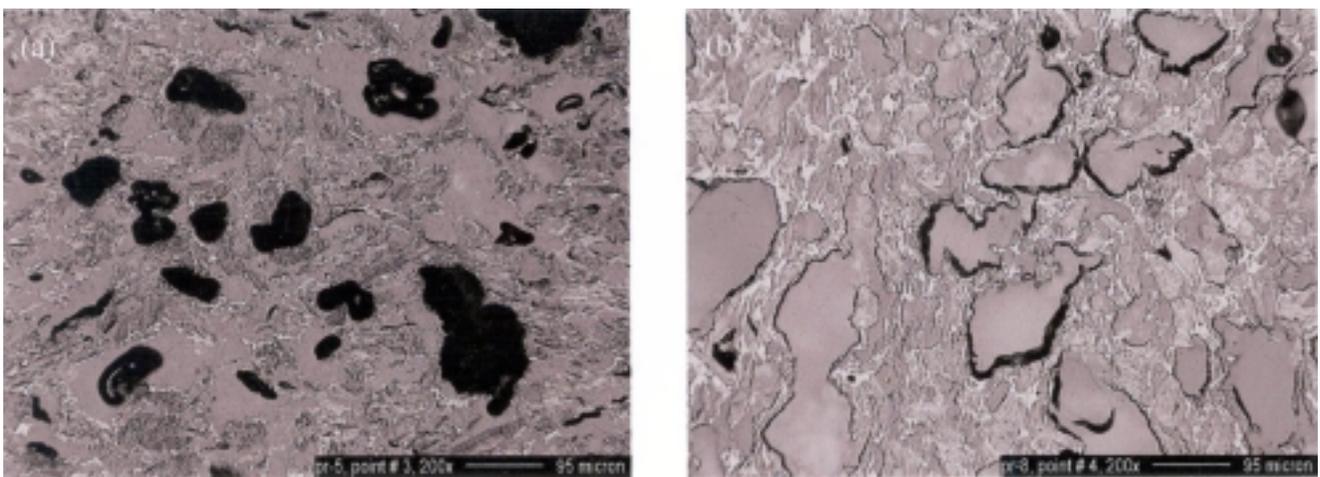


Figure 5. Optical microstructure of the C-C composites obtained with using CTP binder. (a) no sulfur- was added; (b) 15 wt. % of sulfur- was added into CTP.

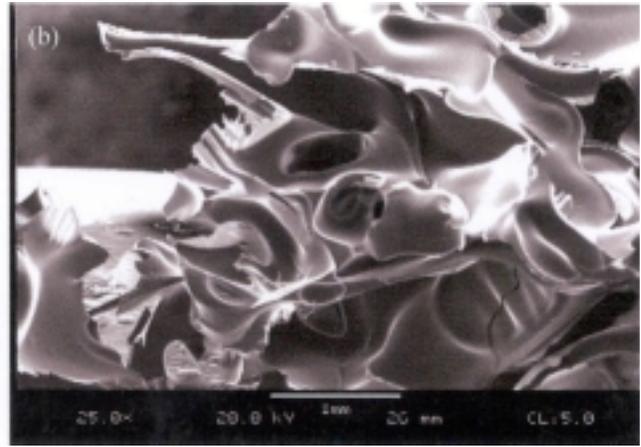
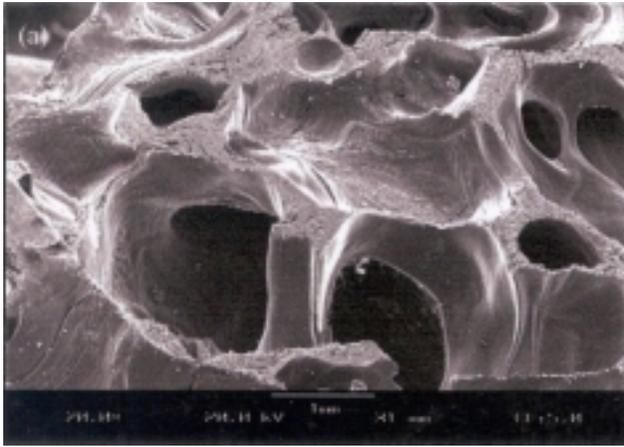


Figure 6. Backscattered SEM images of the carbonized binder. (a) —A-240; (b) —A-240 and 15 wt.% of sulfur.

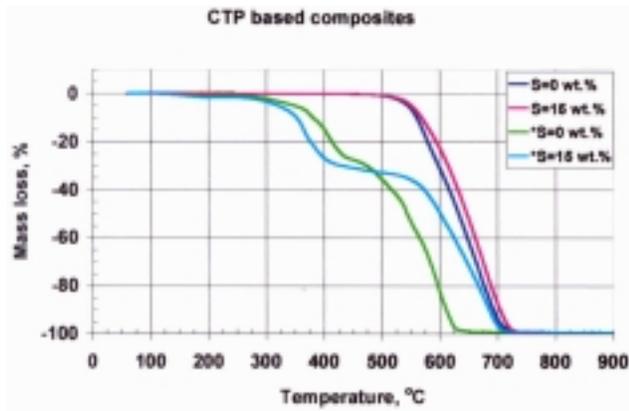


Figure 7. Thermogravimetric analysis of composites containing CTP based binder with sulfur additions in 95kPa air flowing at 20scc/min. *) After impregnation with the resin.

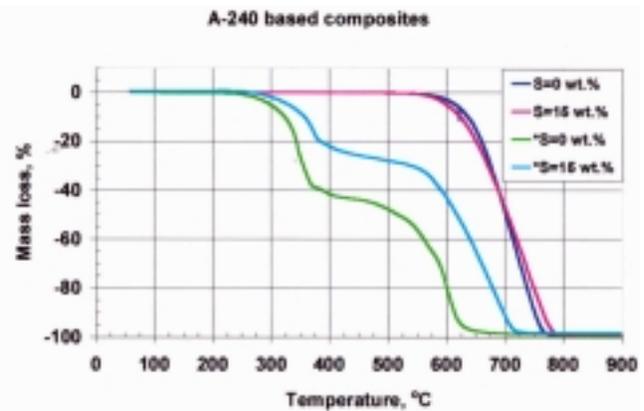


Figure 8. Thermogravimetric analysis of composites containing A-240 based binder with sulfur additions in 95kPa air flowing at 20scc/min. *) After impregnation with resin.

Table 1. Results of the XRD analysis of carbonized binders.

[S], wt. %	CTP		A-240	
	d_{002} , nm	L_{c2} , nm	d_{002} , nm	L_{c2} , nm
0	0.3476	<10	0.3476	<10
5	0.3471	<10	0.3477	<10
10	0.3480	<10	0.3488	<10
15	0.3494	<10	0.3545	<10