9,10-BIS(CHLORMETHYL)ANTHRACENE - CURING AGENT OF COAL TAR PITCH

Jaroslava SVÍTILOVÁ, Vladimír MACHOVIČ and František KOLÁŘ*

Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, V Holesovičkách 41, 182 09 Prague 8
*Corresponding author's e-mail: kolar.irsm.cas.cz

ABSTRACT
Modified coal tar pitch was prepared by Friedel-Crafts reaction with 9,10-bis(chloromethyl)anthracene (BCMA). With the aid of IR and Raman's spectroscopy it was found that BCMA reacted completely with aromatic components of pitch. This modification leads to a significant increase of the carbonisation residue of coal tar pitch without the structure of carbonisate being greatly affected.

KEYWORDS: coal tar pitch, modification, curing, carbonization

INTRODUCTION

Coal tar pitch has a highly condensed structure. It contains low/molecular substances of the naphthalene, phenanthrene or anthracene type, as well as multi-nuclear complexes with rel. mol. weights of several hundreds. In order to understand this colourful mix at least a little better, it is convenient to divide the pitch into several fractions with regard to solubility in solvents differing in the solubility parameter. Usual is division into the following fractions: HS (substance soluble in hexane), TS (substances soluble in toluene), QS (substances soluble in quinoline) and QI (substances not soluble even in quinoline).

One must realise that the fractionation of pitch components by solubility is purely formal. A number of structural changes occur in pitch due to increased temperature. Products are thus created, which differ in solubility from the original pitch. The literature describes experiments providing evidence that, e.g., substances insoluble in toluene, already belonging to the QS group in terms of the above classification (Košťál, and Janík, 1989) are generated by heating the TS fraction to relatively low temperatures (350 to 450 ^{o}C). This has to be taken into account in treatments of pitch under increased temperature such as filtration.

In pitch pyrolysis, low-boiling components, such as anthracene, phenanthracene, etc., are distilled first. Under heating and normal pressure this process is concluded at about 500 ^{o}C. Evidently the components, which do not evaporate, have no part in the resultant carbonisation residue. It is, therefore, convenient to work at higher pressures. Dehydrogenation occurs at temperatures of about 500 ^{o}C, when the pitch begins to solidify. Dehydrogenation reactions, during which C-H bonds split, and large, planar molecules of condensed aromatic hydrocarbons are created (Brooks et al., 1965; Fitzer, 1973).

As already mentioned, the escape of low-molecular components in the first stage of the process significantly decreases the carbonisation residue. Apart from the pressure carbonisation already mentioned, the reaction abilities of pitch can be exploited, and the low-molecular components can be transformed to higher-molecular components by suitable choice of chemical adjustment of the precursor. A whole series of chemical reaction of pitch components, which lead to condensation, polymerisation or screening of the system, is available. For example, dehydrogenation cycling taking place in the presence of Lewis acids. However, the increase of the carbonisation residue is not very significant (Mochida, 1975).

In dehydrogenating aliphatic and cyclic aliphatic components with the aid of elementary sulphur or selenium, hydrogen does not split in elementary form, as in the case of classical solidification of pitch, but as hydrogen sulphide. In terms of energy this is more convenient, so that the reaction occurs already at temperatures of about 180 ^{o}C (Fitzer, 1973). The dehydrogenation reactions are concluded at 200 to 270 ^{o}C, the carbonisation yield increases appreciably without restricting the ability of the subsequent graphitisation (Kolář et al., 1995).

In the case of sulphur, however, a stoichiometric amount has to be applied, because its surplus leads to competitive reactions and screening of aromatic molecules by sulphide bridges. The latter are thermally very stable, dissolving at temperatures of around 1000 ^{o}C, and may cause puffing during graphitisation. Amorphous selenium has an effect

similar to sulphur, however, dehydrogenation takes place at higher temperatures (250 to 350 °C). As opposed to sulphur, there is no danger of puffing if an over-stoichiometric amount is applied, because selenium bridges do not form.

The methyl groups can be converted into carbonyls by oxidation with atmospheric oxygen. In the pitch thus treated, Elbs cyclisation reaction takes places after several hours of heating at a temperature of about 370 °C; the aromaticity increases significantly, which is reflected in a high carbonisation residue (Blanco, 2000).

The Friedel-Crafts method can be introduced into the aromatic nucleus of several aryls, because the reaction does not end with the introduction of the first. A further alkyl enters mainly the m-position. A mix of oligomers, resembling coal tar pitch, is created by co-polymerisation of anthracene with benzyl alcohol in the presence of Lewis acids at temperatures of around 200 °C (Otani, 1986)

This paper descried the possibility of increasing the carbonisation residue of the reaction of coal tar pitch with 9.10-bis(chloromethyl)anthracene, which was prepared by chloromethylation of anthracene.

EXPERIMENTS

INITIAL TAR PITCH

Coal tar pitch 70LQI (by DEZA, a.s.) was used for the modification. The characteristics of the pitch, provided by the manufacturer, are shown in Tab. 1.

Table 1 Properties of coal tar pitch 70LQ

Softening point	84.1 °C
Insoluble toluene	15.10 %
Insoluble quinoline	2.60 %
Ash	0.12 %

Preparation of 9.10-bis(chloromethyl)anthracene (BCMA)

The mix of 360 ml of dioxane and 60 ml of concentrated hydrochloric acid was saturated with gaseous hydrogen chloride. Then 45 g (0.2525 mol) anthracene and 38 g of 95% paraformaldehyde were added. The mix, slowly stirred was heated under moderate reflux and a flow of fine HCl bubbles was introduced for a period of about 2 hrs. After mixing the mix was left to reflux for another 3 hrs, and after 16 hrs of standing, fine, yellow powder was filtered off, of a product, which was washed by dioxane three times. The yield was 41.5 g (65%) 9,10-bis(chloromethyl)anthracene (melting point 253-255 °C).

Preparation of modified coal tar pitch

Reaction mixes of coal tar pitch 70LQI, containing 0, 21.4 and 39.1 wgt. % BCMA were prepared. The curing took place in quartz crucibles at temperatures of 150 °C (2 hrs) and subsequently 250 °C (2 hrs).

Co-polymerisation of anthracene and benzyl alcohol took place in the presence of p-toluene sulphonic acid (weight ratio 100:20:5) at a temperature of 200 °C for 5 hrs.

Subsequent carbonisation of all samples took place in nitrogen at a heating rate of 70 °C/hr up to a maximum temperature of 1000 °C. The cooling rate was 100 °C/min.

Infrared spectroscopy

Infrared spectra of pitch samples were recorded as KBr pellets in a ratio of 1:300 (pitch:KBr) with a Nicolet 740 infrared spectrophotometer using 128 accumulations of a spectrum at a resolution of 2 cm^{-1}. Parameter $A_{Char}/(A_{Char}+A_{Chal})$ was determined from the areas of the bands between 3100 – 3000 cm^{-1} (A_{Cha}) and 3000 – 2750 cm^{-1} (A_{Cha}). The orthosubstitution index (OSI) was determined as the ratio of intensities of the following bands $I_{750}/(I_{750}+I_{840}+I_{880})$, the basic line passing through points 920 and 660 cm^{-1}.

Raman spectroscopy

Raman spectra were collected using a LabRam HR System (Jobin Yvon). The 532 and line of laser were used for excitation. An objective (x100) was used to focus the laser beam on the sample. The scattered light was analysed by spectrograph with a holographic grating (600 gr/mm), slit width 100 μm and open confocal hole (1000 μm). The adjustment of the system was regularly checked using a silicon sample and by measurement in the zero-order position of the grating. The time of acquisition of a particular spectral window was optimised for individual sample measurements (approx. 10 s). Three accumulations were co-added to obtain a spectrum.

The bands in the spectrum were separated with the aid of the Galactic PeakSolve 1.05 Program. The spectrum was separated into four bands, the G and D bands being fitted with the aid of the Lorentz function and the bands at 1200 and 1550 cm^{-1} with the aid of the Gauss function.

RESULTS AND DISCUSSION

The copolymerisation of anthracene with benzyl alcohol in the presence of p-toluene sulfonic acid produced at a temperature of 200 °C a dark product resembling coal tar pitch. After carbonation in nitrogen the carbonation residue amounted to 26 wgt. %, whereas the initial anthracene evaporated completely under the same conditions.

The reaction of coal tar pitch with BCMA at a temperature of 150 °C releases hydrogen chloride and increases the viscosity of reaction mixtures. The reaction is sufficiently fast and it did not have to be catalysed. The modified pitch thus prepared was still fusible; complete curing occurred at a temperature of 250 °C during 2 hours.

Table 2 Effect of adding BCMA on the residue after curing and carbonation

Sample	BCMA added	Residue after curing Weight %	Residue after carbonation
0	0	95.1	35.0
2	21.35	93.1	43.0
3	39.10	88.5	60.8
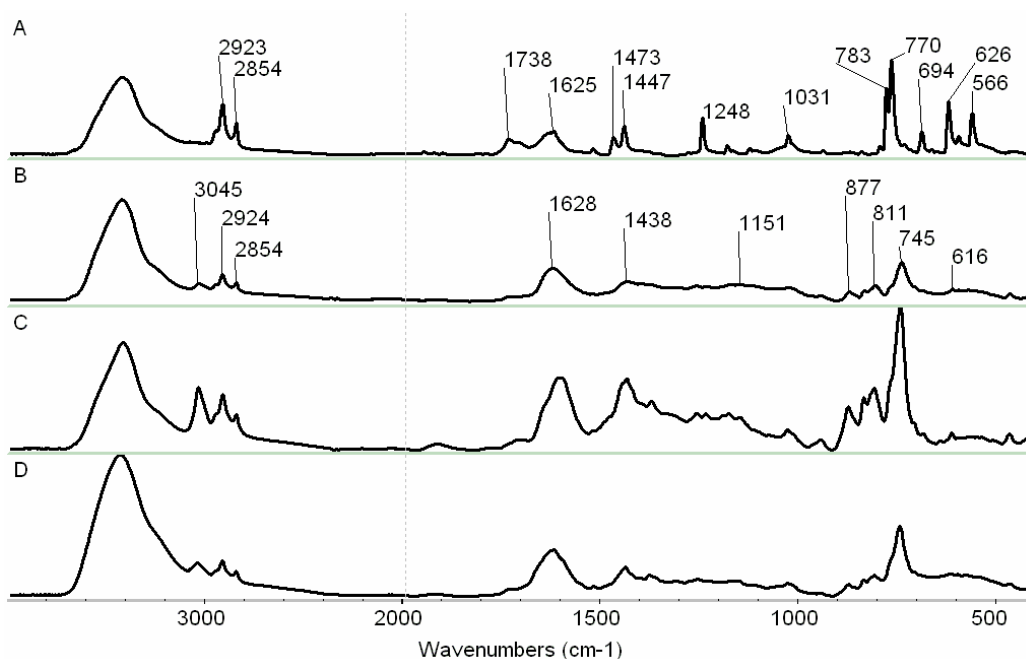
Fig. 1 Infrared spectra of BCMA (A), the original pitch (B), the pitch heat in air at 250 ^{o}C (C) and of pitch 39.10% BCMA heated in air at 250 ^{o}C (D)

If carbonation takes place in the inert atmosphere of nitrogen, the carbonation residue of modified pitch is higher, because the low-boiling components such as anthracene, phenanthracene, etc., have already transformed in the reaction with BCMA to poly-aromatic structures. The weight residues after curing W_{cur} and carbonation W_{carb} are given in Tab. 2. The table indicates that the carbonation residue of the studied pitch increases with addition of BCMA. Figure 1 shows the infrared spectra of BCMA, of the original pitch, of the pitch heated in air at 250 ^{o}C, and of pitch with an addition of 39.10% BCMA heated in air at 250 ^{o}C. The figure indicates that BCMA bands are absent from thermally treated pitch, and that BCMA has become fully incorporated in the studied aromatic system during thermal treatment.

The spectra of thermally treated pitch and pitch after BCMA has been added do not differ in quality from the spectrum of the original pitch. They only differ in the relative intensities of bands. The aromaticity index, defined by the ratio $A_{Char}/(A_{Char}+A_{Chal})$, was calculated from the spectra of all samples; A_{Char} is the area of the bands of valency vibrations of aromatic C-H bonds, and A_{Chal} is the area of the bands of valency vibrations of aliphatic C-H bonds. The results have shown (refer to Table XX) that the original pitch displays the lowest aromaticity, which increases significantly when the pitch is heated. After heating at 250 ^{o}C the sample with BCMA added displays higher aromaticity than the original sample of pitch, but does not reach a value as high as that of the heat original sample of pitch. This decrease in aromaticity is apparently caused by the smaller discharge of low-boiling fractions due to the addition of BCMA and also to the presence of methyl groups in BCMA.

Table 3 Parameters obtained with infrared spectroscopy

Sample		$[A_{Char}/(A_{Char}+ A_{Chal})]\times100$	$[I_{748}(I_{748}+I_{814}+I_{880}] \times100$
7/05	Original pitch	21.58	66.97
6/05	Pitch (HTT 250 °C/air)	48.06	60.79
5/05	Pitch+BCMA (HTT 250 °C/air)	34.22	75.33
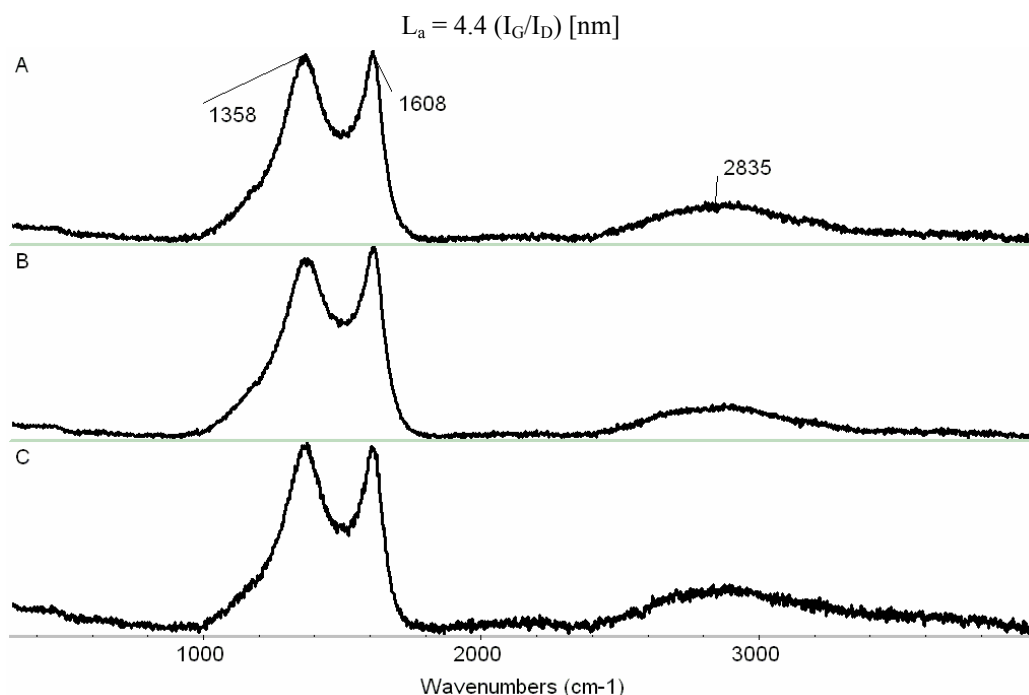
Fig. 2 Raman spectra of the original pitch pyrolysed in nitrogen at 1000 °C (A) and of pitch with additions of 21.35 and 39.10 % BCMA, pyrolysed in nitrogen at 1000 °C (spectra B and C, respectively)

Apart from the aromaticity index, also the ortho-substitution index (hereinafter referred to only as OSI) is used in the FTIR analysis of pitch; the latter index is defined as the ratio $I_{750}/(I_{750}+I_{840}+ I_{880})$, where I_{750} is the intensity of the band of ortho-substituted aromatic rings, I_{840} is the intensity of the band of out-of-plane C-H vibrations in the aromatic rings, containing two and/or three adjacent aromatic hydrogen atoms and, finally, I_{880} is the intensity of the band of penta-substituted aromatic rings. An increase in OSI indicates splitting of molecules into smaller fragments and, on the contrary, a decrease is indicative of the predominance of condensation reactions, i.e. of the polymerisation of the aromatic system. In this case a moderate decrease of the index was observed during the heating of the original pitch at 250 °C in air. After adding BCMA and subsequent heating the polymerisation of the condensed system increased as can be seen from the increase of the OSI.

The Raman spectroscopy is used to determine the order of the carbon system and for determining the size of graphitic crystallinites in coal tar pitch (Cottinet, 1988; Akezuma, 1987; Urban et al., 2003). Two pronounced bands can be found in the Raman spectra of less ordered carbon materials at 1350 cm^{-1} (band "D" – disorder) and at 1600 cm^{-1} (band "G" – graphitic). The growth of crystallinites of carbon material caused by temperature can be observed on the changes in the position, width and relative intensity of both the "D" and "G" bands.

It was found that during heating the intensity of the G band increases and of the D band decreases. The ratio of intensities I_D/I_G diminishes, band D becomes narrower and displaced towards low values wave numbers. A broad band at 1550 cm^{-1}, which was assigned to the amorphous graphitic phase, appears in the spectra of carbon samples. Further bands, appropriate to sp^3 bonds, were observed at 1230 and 870 cm^{-1}.
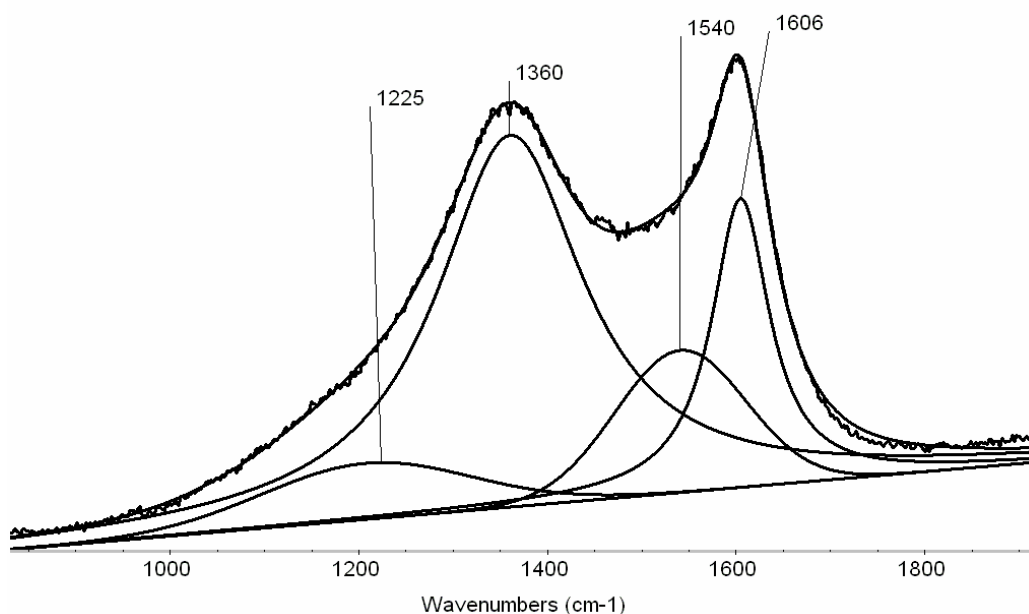
Fig. 3 Separation of bands in the Raman spectra of pitch (Sample 9/05)

Table 3 Parameters obtained with Raman spectrometry

Sample (HTT 1000 °C/N$_2$)	Peak	FWHM	Peak	FWHM	Peak	FWHM	Peak	FWMH	L$_a$ (nm)
Pitch	1168	192	1352	193	1545	153	1603	70	1.22
Pitch+BCMA (21.35%)	1207	261	1361	189	1541	163	1605	74	1.32
Pitch+BCMA (39.10%)	1162	184	1354	191	1547	148	1604	69	1.32

The ratio of integrated intensities (areas) of the D and G bands and the magnitude of the graphitic structure parameter L$_a$ (size of grafen layers) determined by XRD, were found to be linearly correlated (Tuinstra, 1970). The authors suggested the following empirical relation for the 514.5 nm laser: The studies of amorphous hydrogenated carbon materials have disclosed that the D and G modes are sensitive to the type of bond, e.g., sp^2 and sp^3 bonds.

The Raman spectra of the original pitch, pyrolysed in nitrogen at 1000 °C and of pitch with additions of 21.35 and 39.10% BCMA, pyrolysed in nitrogen at 1000 °C are shown in Fig. 2. The spectra of all three kinds of pitch are nearly identical. For comparing all three materials analysed the L$_a$ index was determined with the aid of band separation, shown in Fig. 3. The spectrum in the range of 800 – 2000 cm^{-1} was separated into four bands. The graphitic (~1600 cm^{-1}) and disorder bands (~1350 cm^{-1}) were fitted with the aid of the Lorentz function, and the bands at 1200 cm^{-1} and 1550 cm^{-1} using the Gauss function. The results of the band separation are in Tab. 3.

The table shows that the effect of treating pitch with BCMA with pyrolysed pitch is not significant as regards the positions and half-widths of the D and G bands. They can, therefore, be considered very similar in terms of structure. The size of the graphen structures of the pyrolysate of the original pitch is very slightly smaller compared with the pyrolysates of pitch with additions of BCMA, as can be seen from the L$_a$ values.

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