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LOW FIELD NUCLEAR MAGNETIC RESONANCE OF STRUCTURAL ALTERATIONS IN COAL TAR PITCH SUBJECTED TO HEAT TREATMENT

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Abstract. Development of anisotropy in tar pitches under heat treatment was measured by hot centrifugation and by low field NMR technique through the spin-lattice relaxation time of the hydrogen nucleus (T_1H). By using a double exponential model for T_1H calculations it was possible to quantify the size of the isotropic and anisotropic domains, suggesting that low field NMR is a suitable technique to address anisotropy in pitches.

Keywords: coal tar pitches, anisotropy, nuclear magnetic resonance.

1. Introduction

The characterization of raw materials is of fundamental importance for predicting the properties of carbonaceous industry products. Besides the parameters traditionally used for characterization, such as density and coking value, there are also methods that involve solvent extraction. Thus, in production of pitches, coke, graphite electrodes and even more advanced carbon materials, such as fibers and composites, it is essential to use appropriate methods that allow for the characterization of different fractions involved, among which the determination of toluene insolubles and quinoline insolubles can be cited.

The toluene insolubles (TI) have a molar mass between 650 and 2000 g/mol, being known as fraction C2 or free carbon. This fraction is considered to be responsible for the aggregating ability of pitches and acts as the accelerator in the condensation reactions, increasing the bulk viscosity [1]. The quinoline insolubles (QI) have the molar mass over 2000 g/mol being known as C1, primary or secondary fraction. The primary QI, also known as natural QI, are constituted by coals, cokes, pyrolytic carbon, refractory materials, condensed aromatic hydrocarbons *etc*. The secondary QI, also known as alpha resins, are obtained through heat treatment of pitches being the main constituents of mesophase spheres [2].

The mesophase consists of planar aromatic compounds of high molecular mass organized as spheres dispersed in an isotropic medium with a high degree of molecular order. The aromatic planes in the spheres are stacked in parallel arrays. As the heat treatment progresses the spheres coalesce forming extended regions of uniform orientation [3]. Mesophase is also known as the anisotropic fraction of the sample being the amount of mesophase expressed as a sample anisotropy percentage, A. The anisotropy percentage strongly influences the spinnability of anisotropic pitches [4].

There is not yet an analytical procedure that can accurately quantify the mesophase in a pitch, *i.e.* the anisotropic fraction, although there are promising results in NMR [5, 6]. The relative amount between the isotropic and anisotropic phases can be determined with some approximation by extraction with hot quinoline or *N*-methyl-pyrrolidinone (NMP). The isotropic fraction is soluble in these solvents, but not the mesophase due to its high molar mass [7]. There is a trend towards the use of *N*-methyl-pyrrolidinone instead of quinoline, due to its lower toxicity and increased sensitivity to lower amounts of mesophase [8-10]. The results obtained with NMP can be correlated to that obtained by ASTM D 2318, using quinoline, through the use of a correction factor [11].

The coal tar pitches have higher QI and TI amounts than petroleum pitches (petroleum pitch is obtained by heat treatment of a concentrate of asphaltic material). In carbon fiber production from pitches a high QI amount leads to the formation of a material with a high solid content. These solid carbon particles can accelerate the formation of coke during the heat treatment of the pitch, causing the fiber to break during its extrusion or thermal treatment. So, although the petroleum pitches are less aromatic than coal tar pitches, they can present advantages as precursors to

carbon fiber production [12]. The coal tar pitches are well suited to the production of graphite electrodes with increased mechanical resistance due to their higher QI content. According to Chung [12] coal tar pitches have a toluene insolubles percentage higher than that of petroleum pitches (32 % against 7 %) and a quinoline insolubles percentage of 12 %, against 0.2 % for petroleum pitches.

The coal tar pitches contain an excess of solid particulates, possibly originated from the refractory lining of furnaces where they are prepared or from coked material. These particles are accounted as insoluble by the solvent extraction techniques, introducing errors in the pitch anisotropy determination [13]. Due to its insensitivity to these particles, nuclear magnetic resonance (NMR) techniques seem to be a better option to obtain these values.

Low field nuclear magnetic resonance measures the time needed by a population of spins in a magnetic field to recover from a disturbance promoted by a resonant radiofrequency. The process by which the spin system attains equilibrium from a non-equilibrium state is called spin-lattice relaxation, characterized by the time T1, where lattice means the surrounding molecules providing exchange of energy through a molecular motion [14].

Low field NMR can measure, among others, the spin-lattice relaxation time for hydrogen nucleus, through the inversion-recovery technique. The time constant T1 of this relaxation is sensitive to the molecular dynamics of solids, informing about the size of the domains present in the material. Variations in this parameter are due to variations in molecular organization or interactions [15].

The goal of this work is to determine the relaxation time T1 for coal tar pitches before and after heat treatment, correlating these results with anisotropy percentages, as obtained by hot centrifugation, in order to observe structural changes due to the heat treatment that are capable of affecting the molecular dynamics of these materials.

2. Experimental

Coal tar pitches: provided by Asfaltos Vitória LTDA.

*Reactor for 1.2 l***:** built in stainless steel, provided with a mechanical stirring. It has an internal volume of 1200 ml; PID temperature controller; gas injector and discharge valve in the bottom, allowing for the removal of samples during the process.

*Heat treatment***:** the starting coal tar pitch, sample PA 00, was heated in the 1.2 liters reactor at 723 K for two hours, under nitrogen atmosphere and bubbling. After that three samples were obtained 20 min apart from each other, under the same conditions of temperature and nitrogen bubbling. These samples were labeled PA 01, PA 02 and PA 03, respectively.

Determination of specific gravity of coal tar pitches (ρ)*:* helium pycnometer, model UPY-001, Quantachrome Instruments.

Determination of the carbon yield content value (*CY*): Micro Carbon Conradson Residue NMC 440, Normalab, using ASTM D 2416. Repeatability: 1 %.

Determination of the softening point (*SP*): Thermal System Mettler FP-90 with FP-83 cell, using ASTM D 3104, reliable for softening points up to 453 K.

For pitches with the softening point above 453 K the procedure presented by Py X. *et al.* [16] was adopted, that assumes as the softening point, the temperature corresponding to a sample viscosity of 1000 Pa·s. These assays were realized in a rotational rheometer HAAKE RheoStress 1.

Determination of toluene insolubles (*TI*): these determinations were realized according to ASTM D4312. Repeatability: 1 %.

Determination of N-methyl-pyrrolidinone insolubles (*QI*): based on ASTM D 2318, but using *N*-methyl-pyrrolidinone (NMP) instead of quinoline. The results obtained with NMP can be correlated to the results obtained using quinoline, as described by Freitas and Castro [11]. Repeatability: 1 %.

Determination of Beta resins (βR): the amount of β-resins is the difference between the toluene insolubles and the quinoline insolubles, as obtained by correlation with *N*-methyl-pyrrolidinone insolubles [11].

Determination of anisotropy percentage (*A*): using the procedure described by Dutra *et al.* [17], the coal tar pitches were grinded, weighted and disposed in glass vials; the samples were centrifuged at 3600 rpm at 673 K for 30 min. The heavier anisotropic fraction in each vial was separated from the top fraction. The fractions were weighted and the anisotropy percentage was calculated.

Low Field Nuclear Magnetic Resonance characterization: all measurements of spin-lattice relaxation time, T_1H, were conducted using a low field NMR spectrometer, Resonance Maran Ultra 23 (23 MHz for the hydrogen nucleus). The pulse sequence used was an inversion – recovery (5T1 - 180° - *t* - 90° acquisition). The 90° pulse, 4.6 μs, was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty *t* data points, ranging from 0.1 to 5000 ms, with 8 scans each and 5 s of recycle delay. The temperature for all analysis was 300 K. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the commercial WINFIT program, which comes with the spectrometer.

3. Results and Discussion

Table 1 presents the physico-chemical results obtained for the original coal tar pitch (PA 00) and the results for the pitches after heat treatment (PA 01, PA 02 and PA 03).

The results presented in Table 1 indicate that the material underwent changes as an effect of the heat treatment, leading to an increase in specific gravity, coking

value and softening point. These properties are important for the production of carbon derivatives, being related to the thermal stability of the pitches and, after the production, to the mechanical properties of the products.

Table 1

Results obtained for coal tar pitches before and after heat treatment

Sample	ρ, g/cm^3	*CY*, %	*SP*, K	NMP I, %	QI (c), %	TI, %	βR, %	Aniso, %
PA 00	1.330	53.92	378.8	12.46	6.50	25.16	18.66	22.86
PA 01	1.350	64.47	413.0	19.10	11.81	32.28	20.47	28.11
PA 02	1.383	78.34	474.4	34.86	28.16	47.76	19.60	33.26
PA 03	1.414	88.58	579.7	52.58	49.33	65.45	16.12	82.09

Notes: ρ – specific gravity; *CY* – coking value; SP – softening point; NMP I – *N*-methyl-pyrrolidinone insolubles; QI – quinoline insolubles (calculated according to [11]); TI – toluene insolubles; βR – *beta*-resins; Aniso – sample anisotropy.

The increasing in the softening point value is related to the sample viscosity and could be due to a decreased molecular mobility following the removal of the volatiles from the sample as a result of the heating and nitrogen bubbling. Besides that, the condensation and polymerization reactions increase the molecular mass of the samples, affecting their specific gravity and viscosity.

The *beta*-resins content decreased with the progress of the heat treatment, as consequence of the production of bigger and more stable molecules. The condensation reactions can lead to the molecular reorganization, accounting for the increasing in the anisotropy of the samples.

Coal tar pitches are more aromatic than petroleum pitches of similar softening points, which can be verified through the carbon/hydrogen proportion. Since the bigger aromaticity decreases their reactivity the heat treatment imposed to coal tar pitches was longer and under higher temperatures than the treatment applied by Dutra *et al.* [18] for petroleum pitches.

Low field NMR analysis was used in order to increase the understanding of the molecular behavior of these materials and of the changes they undergo after the heat treatment. Table 2 shows the spin-lattice relaxation values for the samples before (PA 00) and after heat treatment, as calculated by a single exponential model.

Table 2

Single exponential T_1H values of coal tar pitches before and after heat treatment

Sample	T_1 H (ms)
PA 00	800
PA 01	523
PA 02	289
PA 03	135

Table 2 shows that the heat treatment promoted an intense decrease in the T_1H values. The pyrolysis of coal tar pitches (or petroleum pitches) leads to the formation of large aromatic and mostly planar molecules, called mesogens, constituents of the mesophase. The formation of the mesogens implies in dehydrogenation, dealquilation and condensation reactions, that leads to a major molecular reorganization [19].

The high T_1H value for the pitch before heat treatment suggests an isotropic behavior of the sample, as expected from the variety of the molecules present. The decrease in the T_1H values as the treatment time increases suggests a widening in the distance between hydrogen nuclei, due to the dehydrogenation and condensation reactions, that corresponds to the increase in the samples aromaticity.

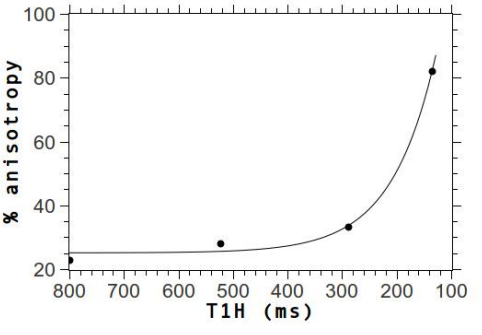

Fig. 1. Sample anisotropy against single exponential T_1H values of coal tar pitches before and after heat treatment (the line is just a guide for the eyes)

Fig. 1 shows the single exponential T_1H plotted against the sample anisotropy. The curve shows a strong exponential relation, suggesting that the mechanism of hydrogen removal is of a cooperative type. This could be explained by a random removal of hydrogen atoms from

different molecules as the heat treatment proceeds, leading to the existence of a few molecules able to promote the creation of an anisotropic region in the beginning of the process. As the heat treatment advances there is a geometric progression in the number of molecules aromatic enough to reorganize as a mesophase.

The spin-lattice relaxation times were also calculated by a double exponential model, in accordance to an interpretation that the samples are constituted of two different domains. Table 3 shows the T_1H values so calculated.

Table 3

Double exponential T_1H values of coal tar pitches before and after heat treatment

Sample	T_1 H, ms	Domain, %
PA 00	118	8
	974	92
PA 01	16	7
	591	93
PA 02	31	18
	420	82
PA 03	39	43
	381	57

In this double exponential analysis, the relaxation time of the bigger domain decreases strongly with the progression of the heat treatment, as observed for the single exponential analysis. The smaller domain increases its extension and seems to couple with the larger domain, thus affecting its relaxation time, that implies in a decrease in mobility or molecular diffusion in the smaller domain.

In the beginning most (92 %) of the coal tar pitch sample seems to be an isotropic domain, due to the random and disperse nature of its molecules. As the heat treatment progresses this multimolecular domain undergoes a gradual conversion to mesogens that pack in a spherical, low energy, arrangement. As the process goes on the spheres suffer a coalescence forming molecular aggregates, highly oriented and with low mobility. These aggregates are formed inside the isotropic domain thus originating the mesophase with the progression of the treatment.

In the double exponential model it is reasonable to suppose that the domains showing the smaller T_1H values correspond to the mesophase. Also, these are the smaller domains, at least in these first steps of the heat treatment. Fig. 2 shows the percentage of these domains against sample anisotropy. The curve shows almost linear relation between the values obtained by the two different techniques, NMR and centrifugation. The derivative of this curve is related to the growth in the density of the mesophase, since the sample anisotropy is calculated by the ratio of the isotropic regions mass to the mesophase mass, while domain percentage, as obtained by NMR, is related to the domains volume.

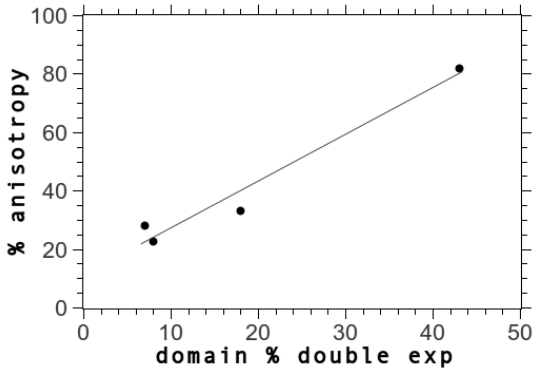

Fig. 2. Sample anisotropy against domain percentage for domains with smaller T1H of coal tar pitches before and after heat treatment for double exponential model (the line is just a guide for the eyes)

4. Conclusions

This study shows the potential of the spin-lattice relaxation times obtained through the low field NMR technique as a tool for morphological characterization of materials that behave as liquid crystals and show the structural reorganization, as coal tar pitches.

A strong exponential relation could be observed between T_1H values, as obtained by a single exponential model, and percentage of anisotropy, as obtained by hot centrifugation, which could be helpful in understanding the anisotropy formation mechanisms. This result suggests that the hydrogen removal mechanism is of a cooperative type.

Also, the double exponential model used for T_1H calculations allowed separating the contributions of isotropic and anisotropic domains. The results suggest a linear correlation between the domain percentage of the smaller anisotropic domain, as obtained by NMR, and the sample anisotropy, as obtained by centrifugation. The rate of this curve indicates a linear growth in the density of the mesophase.

The present work shows that low field nuclear magnetic resonance should be used as a complementary tool to address anisotropy in pitches, being able to provide the data necessary to a more comprehensive understanding of the molecular behavior of the samples under heat treatment.

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ДОСЛІДЖЕННЯ СТРУКТУРНИХ ЗМІН ВУГІЛЬНОГО ПЕКУ ПРИ ТЕРМІЧНОМУ ОБРОБЛЕННІ ЗА ДОПОМОГОЮ ЯДЕРНОГО МАГНІТНОГО РЕЗОНАНСУ СЛАБКОГО ПОЛЯ

Анотація. *З використанням гарячого центрифугування і ЯМР слабого поля проведено дослідження анізотропії вугільного пеку при його термообробленні. За допомогою подвійної експоненційної моделі кількісно визначено розміри ізотропних і анізотропних областей, припускаючи, що ЯМР слабого поля може бути використаний для визначення анізотропії пеків.*

Ключові слова: *вугільний пек, анізотропія, ядерний магнітний резонанс.*