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Mesophase development during thermal treatment of pitches

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The different carbon mesophase precursors as coal tar and petroleum pitches were analyzed for studying the mesophase formation. The influence of precursors characteristics, processing parameters (temperature, heating rate) on the development of mesophase stage was analysed. Raw materials were characterized from physico-chemical point of view (softening point, benzene insoluble fraction etc). The mesophase samples were characterized by optical, electronic microscopy (SEM), AFM and XRD and the coke yield were calculated.

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1. Introduction

In 1961 Brooks and Taylor [1] shown the existence of the carbon mesophase (MP) establishing its essential role to the graphite genesis by thermal treatment of the different carbon raw materials. Since that time, a large research activity has been developed on this subject.

The mesophase pitch is defined as a purified pitch with the mesophase content over 90 %. The mesophase has to fulfill some conditions: (1) must be totally insoluble in pyridine and practically insoluble in quinoline; (2) it has to have a volatiles content of about 10 %, determined at 1000°C; (3) by heating in an oxidizing medium (air) to develop liquid crystals.

Structurally, carbonaceous mesophase is a discotic and nematic liquid crystal phase [2] formed as an intermediate during the carbonization of certain polycyclic aromatic hydrocarbons, either as single moieties or as a part of complex mixtures such as petroleum and coal tar pitches [3]. The formations of mesophase pitch involves polymerization and condensation reactions, which lead to large planar and polyaromatic molecules (mesogens) [4].

MP is the essential source in designing and architecturing of many types of carbon materials in single component (carbon fibers [5], polygranular graphites [6], foam materials [7]) or as composites from micro to nanometric scale. The condition is the control of the nucleation and the growth of mesophase to preserve the MP spheres and to manipulate them in subsequent processes.

Depending on the nature of aromatic hydrocarbons from it, the mesophase is formed at temperatures in the range of 300 - 500°C. The formation temperature and the mesophase efficiency, do not depend only on the nature of the origin aromatic hydrocarbons, but also on the mean pressure and its nature (oxidizing, reducing, containing H_2 or inert gases), and, of course, on the heating treatment time.

The aim of the presented works was to study the mesophase development during the thermal treatment of pitches.

2. Experimental

Three different coal tar pitches (obtained by atmospheric distillation of coal tar at 340°C were used. A petroleum pitch was also studied. Characteristics of the initial pitches are presented in Table 1.

Table 1. The characteristics of the initial pitches.

Raw material	Characteristic					
	W^a, wt%	A^a, wt%	V^a, wt%	BI, wt%	QI, wt%	Softening point (R&B),°C
CTP1	0.1	0.7	59.5	29.6	11.7	70.0
CTP2	0.6	0.7	58.0	30.1	11.6	79.5
CTP3	0.8	0.4	49.8	35.3	8.7	85.0
PP	0.3	0.2	45.0	17.5	0.4	65.0

where: W^a - humidity content at the analysis state; A^a - ash content at the analysis state; V^a - volatiles content at the analysis state; BI – insolubles in benzene; QI – insolubles in quinoline (R&B) - refers to the "Ring and Ball" method; CTP- coal tar pitch.; PP – petroleum pitch

The coal tar pitches were solubilized in quinoline (QI), after that they were back-flow boiled of about 30 minutes and then were filtrated. The QI were removed, and the quinoline from the filtrate was recovered by distillation. The characteristics of quinoline free pitches are presented in Table 2.

Table 2.The characteristics of the pitches after the QI removal

Material	Characteristic			
	V[a], wt %	BI, wt%	QI, wt%	Softening point (R&B) °C
PCTP1	59.8	33.5	0.1	66.0
PCTP2	61.6	34.1	0.2	61.0
PCTP3	55.5	38.7	0.1	74.0
PP	45.0	17.5	0.4	65.0

Notations have the same significations as in Table 1.

The pitches obtained in this way were melted slowly in a porcelain crucible, and then pyrogenated with a heating rate of 3°C/min up to final temperatures between 350°C and 550°C, with the step of 20°C. The samples were maintained 30 min at final temperatures.

The optimum state for mesophase formation was considered the state in which the highest part of the pitch became anisotropic without the reaching at the complete coalescence of the optically active spherules [8 -12].

The mesophase pitch so obtained were summary characterized (the volatiles content determined at the temperature of 1000°C, the solubility in quinoline, the plasticity by the Gieseler method, with the determination of the specific temperatures.

3. Results

In Table 3 the values of the pyrogenation efficiencies in residue for the pitches after the QI removal, are shown. Pyrogenation efficiency is referring to the solid product resulted after the heating of pitches at a temperature in the maximum plasticity interval.

The four pitches have similar degassing shapes. It is interesting to notice the existence of heating interval specific to each pitch in which the efficiency in solid residue decrease [1].

Thus there are three steps during the degassing: (1) an interval of slow distillation - with a small rate of the decreasing of the efficiency in a solid product (350 – 450°C); (2) a region of intense decomposition - with a high rate, of the decreasing of the efficiency in a solid product (450-470°C); (3) a region of slow final degassing - with a very small rate of the decrease of the efficiency in a solid product (470-550°C).

It can be seen that the increasing of heating temperature lead to the decreasing of pyrogenation efficiency due to the direct dependency between temperature and volatile elimination.

It is expected that in the heating interval corresponding to the intense decomposition, the optimum temperature of the mesophase formation or at least the key moments of the coke optic structure formation can be found [13].

Table 3. Variation of the pyrogenation efficiencies (%) of the pitches depending on the temperature (°C).

Temp., °C	Pyrogenation efficiency, %			
	PCTP1	PCTP2	PCTP3	PP
350	93.1	87.8	88.9	94.6
370	89	84	85.3	86
390	86.7	80.8	81.2	77.1
410	83.9	79.1	79.5	70.9
430	81.8	78.7	77.4	64.7
450	76.8	74.1	73.3	63.9
470	58.6	63.1	57.2	60.1
490	58.1	62.9	53.3	51.8
510	56.4	58.6	54.5	52.4
530	53.5	59	53.4	52.2
550	51	58.8	53.2	52

The polarized light microphotographs visualizes the anisotropic properties of the mesophase obtained by heating PP pitch – Fig. 1 a-d. It can be seen that after heating up to 410°C the pitch is still isotropic. (Fig. 1 a). Small dimensions mesophase spheres, dispersed in a large amount of isotropic pitch matrix occure at 430°C (fig. 1 b). At 450°C the mesophase development is accelerated, increasing the dimensions and amount of spheres (fig. 1 c). At 470°C, coalescence of spheres appears in a large mosaic texture (fig. 1 d).

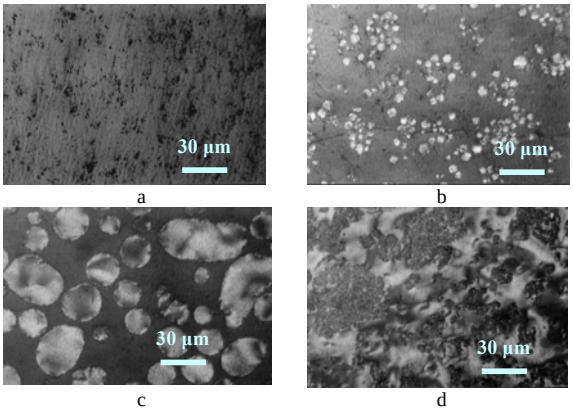


Fig. 1. Microscopical aspects at different " key temperatures" for PP a) 410°C; b)430°C; c)450°C;d)470°C

The obtained mesophases were structural investigated by XRD, SEM and AFM.

The XRD studies on mesophase growth are focused on the evolution of some specific structural parameters: the stack height (L_c), the average diameter of the graphene sheets (L_a) and the interlayer spacing (d_{002}). The structure of non-graphitized carbons can be described on the base of the Warren model [14], which is known as the "turbostratic carbon" model. According to this model, the basic structural unit is the graphene sheet, the sheets being

organized almost parallel and equidistant in stacks; the graphene sheets belonging to the same stack can be translated or rotated randomly in their plane, so that the tri-dimensional ordering of the carbon atoms is reduced to one bi-dimensional.

The XRD patterns of turbostratic carbon have several features: **1.** The presence of only a few broad peaks: (002) -2θ = 23 - 26°, (010) – at 2θ ≅ 43°, and (004) - often very weak, shadowed by (010); **2**. The (00*l*) type lines result from the stacking of the graphenes; **3**. The (h k 0) type lines, particularly (010), relates to the graphene sheet structure. The parameters were calculated as follows: L_c and L_a from the (002) and (010) line breadth respectively, applying the Scherrer formula $L = k \lambda / B \cdot \cos \theta$ with k=1 for tri-dimensional and k=1.84 for bi-dimensional ordering respectively; B=the corrected integral breadth: $B = B_{measured} - B_{reference}$.

The parameters depicting the stack height (L_c), the average diameter of the graphene sheets (L_a) and the interlayer spacing (d_{002}) are presented in Table 4.

Table 4. XRD parameters for PP heat treated at 450°C

sample/ parameter	L_c	L_a	$d_{(002)}$	L_c/L_a	L_c/d
PP at 450°C	23.9	49.2	3.42	0.48	6.99

In the Fig. 2 is presented the XRD pattern for PP at 450 °C.

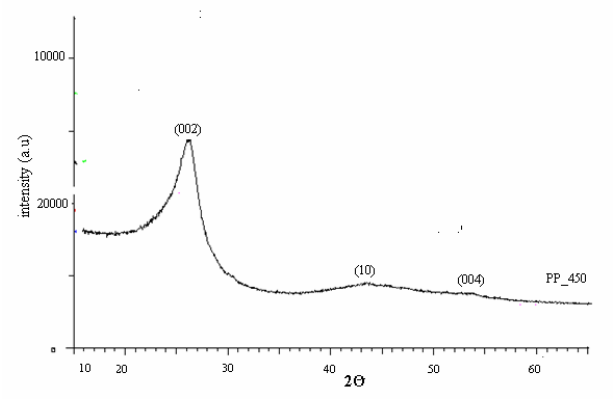
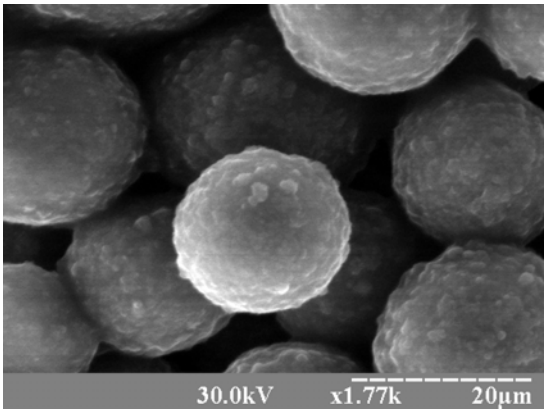


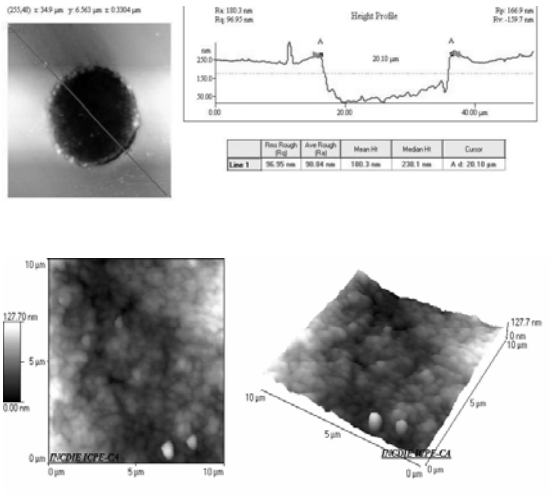
Fig. 2. XRD patterns for PP 450 °C.

It can be see that the PP at 450 °C presents characteristic lines over the turbostratic graphite lines from pitch and coke.

In Fig. 3. shown representative SEM and AFM micrographies for this pitch.



a



b

Fig. 3. SEM and AFM micrographs for PP 450°C

SEM and AFM investigations confirm also the XRD pattern, showing that mesophase spheres, with average dimension of about 20 µm, are crystalline.

4. Discussion

The analysis of the above results show that up to 410°C, all the pitches are totally isotropic without any changes. The QI free pitch (PCTPand PP) passes through a stage where smaller mesophase spherules are dispersed in isotropic pitch matrix (430°C), then, these spheres are increasing in dimensions and number, at 450°C as compared to 430°C. The QI free pitches gave mesophase pitches at the temperature of 450°C with great individual spherules (20 - 70 µm), having very little isotropic phase (1 - 2%) without coalescence. The total coalescence and the coke structure are observed at temperature of 510°C. The SEM and AFM investigations confirm also the XRD pattern, showing that mesophase pitches are crystalline.

In Table 5 are presented the characteristics of the mesophase pitches (MP1, MP2), obtained by PCTP1 and PCTP2 thermal treatment.

Table 5. The characteristics of mesophase pitches.

Sample	Characteristics						
	Form. temp. ^oC	Volatile content, wt % (1000^oC)	QI, wt %	Gieseler plasticity			
				T_i, ^0C	T_{max}, ^0C	T_f, ^0C	Plast., ^0C/min
MP 1	470	10.3	94.2	290	340	345	70.7
MP 2	470	11.7	92.7	280	338	350	53.3

It must be notice that between MP1 and MP2 samples there are some differences. Thus, the spherules are higher to the MP1 (110μm) as compared with MP2 (80 μm). The volatile content and the solubility in quinoline are little smaller in MP. The Gieseler plasticity is bigger in MP1. The plastic phase interval is higher for MP1 (55^{o}C) as compared to the MP2 sample (70 ^{o}C).

5. Conclusions

Taking into account the above analysis, it can be concluded that softening point of the pitches must to be relatively low (60 – 65^{o}C), correlated to a volatile content of about 60%. A smaller volatile content and a higher softening point indicate the preponderance of heavy aromatic compounds. A greater volatile content correlated to a higher softening point show the presence in a high quantity of aliphatic compounds with very long chains (over 20 – 25 carbon atoms).

The mesophase development is blocked by a high content of heavy aromatic compounds because of the impossibility of the plane structure orientation. Also, the aliphatic compounds do not allow the mesophase development because of their heating instability and higher reactivity, which leads to their breaking at relatively low temperatures and the elimination from the reaction mass followed by the remaining of some small reactive molecules, which will lead to a quickly "freezing" of the coke structure of mosaic type.

The fraction insoluble in benzene has to be of about 33 - 34 %. Higher content indicate the presence of heavy aromatic compounds, and smaller contents show even the presence of some aromatics with small molecular mass or the presence of some aliphatic compounds. These situations are unfavorable for mesophase development.

The obtained mesophase pitches are fulfilling the basic conditions: (1) are practically insoluble in quinoline (MP1 has a content of 94.2 wt% QI fraction and MP2, 92.7 wt% respectively); (2) the volatile content, determined at 1000°C, is of about 10 % in both cases; (3) the plastic phase interval is higher: for MP1 (55^{o}C) as compared to the MP2 sample (70^{o}C).

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