THE EFFECT OF THE INSERTION METHOD ON THE MODIFICATION OF MESOPHASE PITCH BY CARBON BLACK

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Introduction

Foreign solid particles of regular coal tar pitch (CTP), such as primary insoluble in quinoline (QI) or carbon black (CB), influence the formation of mesophase spheres and theirs mesostructure [1].
Primary QI change the structure of the spheres in their vicinity by "pined" effect.
In the first studies with CB particles, in regular CTP, were observed:

- The attachment to the surface region restricts the coalescence of the spheres, inhibiting effect [2].
- In the matrix, increases the viscosity, preventing the coalescence of spheres during the heat treatment [2].

This effects can be distinguish using solvent fraction extracts from CTP, either with low (LMW - soluble in toluene, TS) or high molecular weight (HMW - soluble in quinoline, QS). The rheological behavior of LMW extract pyrolisis show a useful instrument to appreciate changes that take place in pitch and mesophase pitch [3].
Based of this consideration were investigated viscoelastic behavior of HMW - extract pyrolisis mixed with CB particles in different amounts.
Other aim, of this work, is defining more precisely the CB role referring to adsorption phenomena at the spherules surface, coalescence, and heterogeneous nucleation.
These effects are useful in the design of new composite materials, based on mesophase pitch with extension to nanoparticles systems.

Experimental

HMW pitch with low QI content, was extracted from quinoline - CTP solution (Table 1). Then the extract was mixed with different amounts of CB (Table 2).
The purified coal tar pitch (PCTP) and the mixtures, were pyrolised at 430^{o}C with a soak time of 3h. Both products were characterized by optical microscopy. The glass transition temperature, T_g, and viscosity behavior, n', were measured by dynamical mechanical thermal analysis (DMTA), in shear mode.

Table 1 Selected properties of CTP (Romanian origin) used in the present study.

Character. Pitch	V* wt.%	B.I. %	Q.I. %	S.P.** (^{o}C)
CTP	52.2	31.5	9.1	78
PCTP	61.6	31.5	3	60

* Volatile content; ** Softening point

Table 2 Selected properties of CB (Fast Extrusion Furnace) used in the present study

Characteristics	Values
Iodine absorption, mg I/g	51
Fisher diameter, μm	0.25
Humidity, %	0.5
Volatile matter, %	2
Ash, %	0.5
pH	7.8
Apparent density, g/cm^3	0.2581

CB was selected with basic character (pH = 7.8) to have labile oxygenated functions (low -OH groups), in small amounts and to keep a good capacity of adsorption/desorption on surface.

Results and discussion

DMTA results present several distinctive aspects regarding to the first stage (to 150^{o}C) and final stage (up to 400^{o}C) of pyrolisis (Fig.1).
PCTP - CB being a mechanical mixture, T_g is expected to have a same values (60^{o}C).
In the first stage, the volatile losses have a different behavior with CB amount. CB adsorbs a part of volatiles and subsequently desorbed with a low rate, the residual desorption take place in T_b. After T_b, the mixture has a regular behavior. The CB increases the viscosity in pitch.
In the second stage, starting with 400^{o}C, two factors must be taken in account:

- The loss of labile oxygenated functions and violent dehydrogenation from aliphatic -CH groups;
- Local adsorption/desorption of hydrogen at the CB surface.

The residence time of hydrogen, at the CB surface, increases the transformation rate of pitch in mesophase. This effect can be associated with an entropy decreasing.

At this part, the viscosity has a suddenly decreasing (T_c). The mesophase growth take place simultaneous with gradual hydrogen desorption. With CB content, the mesophase amount increases. In spite of mesophase pitch high content, the spheres morphology is dramatically changed (Fig.2, 3, 4, and 5).
Probable the micro-regional flow, in pitch, has a major influence in the sphere morphology.

Conclusion

The insertion of CB in purified pitch has more complex role:

- The amount of mesophase pitch increases with CB content (an advantage for carbon yeild in next heat treatment);
- The coalescence isn't prevented by CB;
- CB particles have not an inhibitor effect.

References

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2. Wang Y.G. et all., *Carbon* 1999, 37;2; 307-314;
3. Rand B., *Physical properties and thermal processing of pitch and mesophase pitch*, invited lecture NATO ASI Carbon, Antalya 1998.

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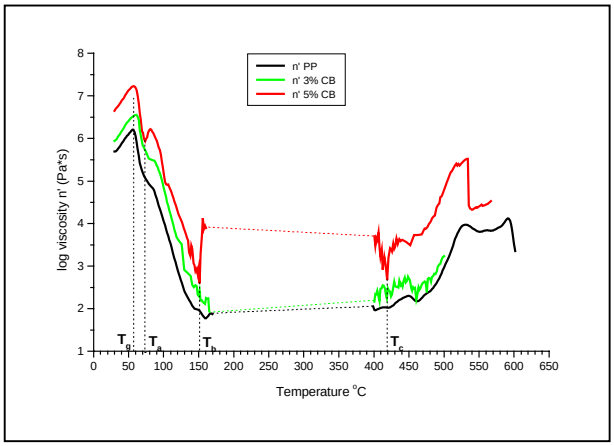

Fig.1 Dynamic viscosity, in shear mode

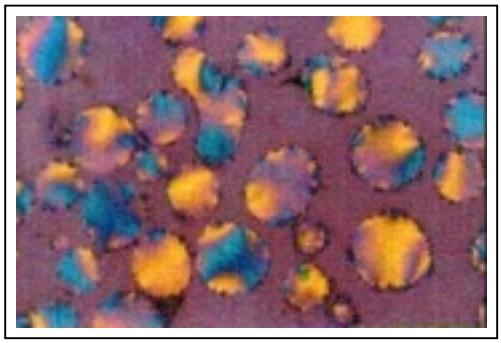

Fig.2 Mesophase pitch at 430°C polarized light (x40)

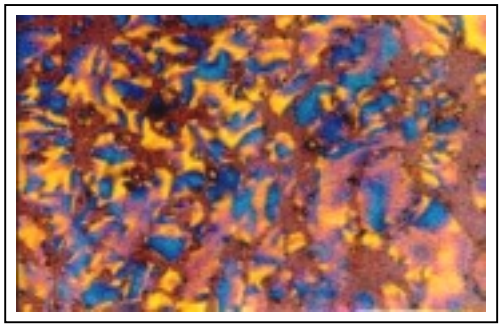

Fig.3 Mixture with 3% CB polarized light (x40)

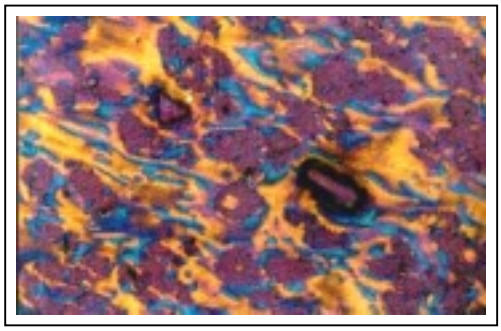

Fig.4 Mixture with 5% CB polarized light (x40)

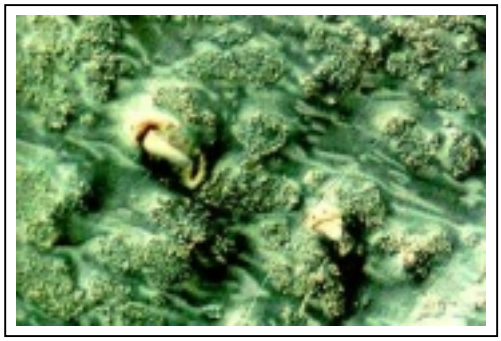

Fig.5 Mixture with 5% CB bright light (x40)