

DEVELOPMENT OF SELF-ASSOCIATIONS DURING PRIMARY CARBONIZATION

Sylvie Bonnamy and Sandrine Delpoux

CRMD, CNRS - Université d'Orléans, 1B rue de la Férellerie, 45071 Orléans Cedex 2, France
bonnamy@cnsr-orleans.fr

Introduction

Primary carbonization begins with softening. It ends was defined by van Krevelen [1] as the end of condensable hydrocarbon release (volatiles) preceding non condensable gas release (secondary carbonization). The product obtained at the end of primary carbonization was assimilated to a brittle solid (semi-coke) by Brooks and Taylor [2]. The semi-coke was characterized after quenching at room temperature. The end of primary carbonization (solidification) is thus marked by Vickers microhardness measurements [1, 3].

Before softening the precursor is a macromolecule containing polyaromatic entities covalently bound by side-chains and eventually linked by heteroatoms (O, S,...) [1,4]. During heat treatment the macromolecule is broken provoking softening. Then successive self-associations of polyaromatic entities happen characterized by TEM, optical microscopy (OM), thermal and elemental analyses, Infrared spectroscopy [4]. The first studies [5, 6] were applied to materials containing oxygen ($0.024 < (O/C)_{at} < 0.4$). They have shown a common general trend :

- after softening volatiles begin to release concomitant with an increasing formation of aromatic CH. Polyaromatic molecules saturated by side-chains associate face to face by 2 or 3 forming basic structural units (BSU) dispersed in lightest molecules (suspensive medium),
- at the maximum rate of volatile release (maximum in the derivative of the weight loss curve, or inflection point in the curve $(H/C)_{at} = f(HTT^{\circ}C)$ [3], aliphatic CH decrease markedly whereas aromatic CH increase almost at the maximum. Anisotropic bodies suddenly demix (local molecular orientations or LMO) and solidification succeed in a very narrow range of HTT. As a result LMO occurrence and solidification could not be separated.
- beyond the maximum of aromatic CH, as aliphatic CH becomes negligible or nil, spins develop up to a maximum corresponding to the total departure of hydrogenated functions (secondary carbonization).

Experimental

The difficulties in the correct determination of the events between LMO occurrence and solidification were attributed to the excess of oxygen acting as a cross-linker, so that new samples were chosen, the oxygen content of which being lower and nil so as to correlate definitely infrared data to other physico-chemical (thermal analyses, Vickers microhardness) and textural data (at micro (OM) and nano (TEM) scales). An asphaltene (14618) with $(O/C)_{at}$ 0.014, an atmospheric residue

Arabian Light (AL) with $(O/C)_{at}$ 0.008 and a pitch free of oxygen (Ashland 240) were chosen [3,7] (Table).

FTIR data were recorded on a Nicolet 710 spectrometer, on KBr pellets of finely ground and dispersed powdered samples (0.5 wt%), heat-treated at various temperatures. The band areas were measured after separation from the baseline in the range 3000 - 2700 cm^{-1} to evaluate the aliphatic CH (CHali) and in the range 920 - 630 cm^{-1} to evaluate the aromatic CH (CHaro).

Results

The low content and the absence of oxygen allow to differentiate the following steps during primary carbonization (Table and Fig.): anisotropic bodies demixtion (or LMO occurrence), then coalescence up to LMO final size (100% anisotropy) and solidification (asymptot in the Vickers microhardness curve) [3,7].

Materials containing oxygen:

Whatever the amount of oxygen any sample, as Arabian Light and 14618, follow the same trend:

- at the maximum rate of volatile release CHali decreases, CHaro increases, LMO occurs (LMO occ. in the figure) and increases in size.
- near the maximum of CHaro, as CHali is negligible or nil, LMO get their maximum size (100% anisotropy) concomitant with solidification (Figure and Table).
- at LMO occurrence the anisotropic bodies are liquid crystals of various types and sizes depending on the balance between oxygen and hydrogen expressed by a factor F, atomic ratio of oxygen over hydrogen [4,7]. As F decreases, liquid crystals appear at higher temperatures and their sizes increase (Table). In the same manner at 100% anisotropy (solidification), LMO final size also increases as F decreases, following the linear relationships $\log LMO \text{ size} = -170 F + 22$ [4,7].
- after solidification, the decrease of CHaro down to zero follows a unique curve common to 14618 and AL (Figure).

Materials devoid of oxygen (Ashland 240):

Surprisingly, the pitch A240 free of oxygen is very poor in hydrogen relative to the others and its behavior is entirely different. At first a tremendous deficit of CHali is associated to a very high amount of CHaro (Table and Figure). Therefore LMO occurrence is produced at a large value of CHaro, whereas 100% anisotropy occurs in the same CHaro range where other products are simultaneously 100% anisotropic and brittle solids. However, if Ashland 240 is 100% anisotropic it is still plastic [3] and its solidification point is considerably displaced to a low value of CHaro and a negligible value of CHali.

In addition LMO final size does not fit with the linear relation with F since either the anisotropic bodies (35 μm in size) or the

final LMO size are larger than the ordinate at the origin of F (22 μm).

Nevertheless, it is worthwhile to note that the CH_{aro} decrease of Ashland 240 also superimpose with the curve common to other products.

Conclusion

The concept of colloidal system applied to primary carbonization [4,8,9] helps to understand its mechanism.

After dispersion of BSU carrying side chains inside light suspensive medium, a viscous liquid similar to a sol is formed. As volatiles escape, BSU concentrate and the second major event is the LMO occurrence, i.e. the formation of a strong molecular association by self-association of oriented BSU (anisotropic bodies demixtion). The elemental composition of the product at this point is the key factor of the subsequent events. Here two cases must be considered:

- BSU edges are saturated jointly by hydrogenated functional groups and cross-linkers as oxygen,
- BSU edges are only saturated by hydrogenated functions (Ashland 240).

Therefore in the second case an excess of CH_{aro} replaces cross-linkers and maintains plasticity at 100% anisotropy. In the first case 100% anisotropy and solidification coincide.

Solidification is the last event of primary carbonization which corresponds to the disappearance of suspensive medium. However since BSU are entirely saturated by side groups including hydrogenated groups they remain independent entities. It is only for this reason that BSU are more or less free to rearrange and coalesce further during secondary carbonization. The more cross-linking between adjacent BSU the less freedom. It is thus clear that the end of primary carbonization does not correspond to a polymerization, i. e. it does not correspond to a growth of aromatic layer diameter.

References

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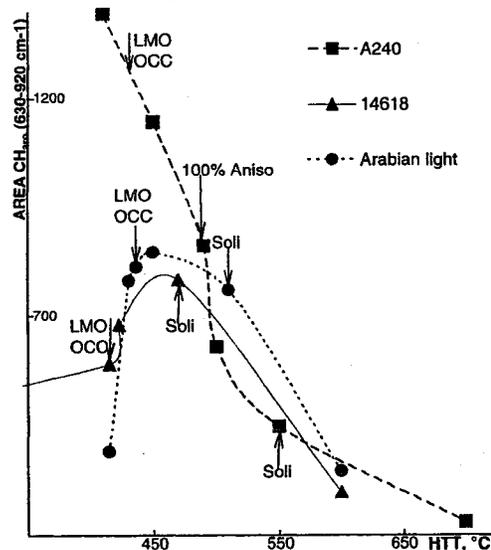


Figure 1. Plot of the absorption band areas of aromatic CH as a function of heat treatment temperature.

Table. Physicochemical, textural, microtextural and infrared data corresponding to the main steps of carbonization (heating rate : 0.5°C/min).

sample	(H/C) _{at initial}	(O/C) _{at initial}	F = (O/H) _{at LMO occurrence}	LMO occurrence 0.5°C/min				100% anisotropy no solidification			100% anisotropy and Solidification			Final LMO size at 1000°C 0.5°C/min
				HTT°C	Anisotropic bodies	FTIR CHali	FTIR CHaro	HTT°C	FTIR CHali	FTIR CHaro	HTT°C	FTIR CHali	FTIR CHaro	
14618	1.20	0.014	0.023	415-420	C	1250	400				470	250	780	mosaics 1 μm
Arabian Light	1.60	0.008	0.011	435	A+B+C	3550	800				510	94	760	mosaics 6-10 μm
Ashland 240	0.69	nil	0.004	420-430	A	160	1350	490	40	800	550	22	450	bands >> 22 μm

Anisotropic bodies : A = Brooks and Taylor mesophase spheres [2]

B and C : other types of mesophase [3,7]

For Ashland 240 : A = 35 μm and 3 to 6 μm size [3,7]

For Arabian Light : A (= 3 to 6 μm size) + B (= 350 - 1000 nm size) + C (= 150 nm size) [3,7]. For 14618 : C (= 150 nm size) [7].

FTIR CH ali : 3000 - 2700 cm^{-1} bands

FTIR CH aro : 920 - 630 cm^{-1} bands