DIFFERENCES IN THE MOLECULAR STRUCTURE OF AIR-BLOWN AND THERMALLY TREATED COAL-TAR PITCHES

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Introduction

Thermal treatment and air-blowing are treatments that are widely used to improve pitch properties. The mechanisms involved have been extensively studied. It is generally accepted that pitch air-blowing yields cross-linked structures with bridge-bonded macromolecules, through the formation of oxy-radicals [1]. On the other hand, pitch thermal treatment generates planar and condensed molecules, usually accompanied by mesophase generation [2]. The effects of both types of treatments on pitch composition and properties are difficult to compare, mainly because these treatments have been applied to pitches of different origin and characteristics, and also under very different conditions.

In this work, a commercial impregnating coal-tar pitch was thermally treated and air-blown, for different periods of time. Experimental conditions for both treatments were selected to obtain pitches with a similar degree of polymerization but a different chemical composition. In this way, a more direct comparison between the treated pitches is possible.

Experimental

A commercial impregnating coal-tar pitch supplied by Química del Nalón was selected as raw material. Pitch air-blowing was carried out at 275°C under air for times varying between 10 and 30 h [3]. The resultant pitches were labeled AB10, AB18, AB25 and AB30, respectively. Thermal treatment was performed at 430°C under nitrogen for periods of time between 2 and 6 h. The resultant pitches were labeled as C1, C2, C3, C4 and C5, respectively [4].

Pitches were characterized by their mesophase content, softening point, carbon yield, insoluble content in toluene and N-methyl-2-pyrrolidone (NMP), elemental composition, aromaticity index, iodine index and X-ray diffraction parameters. In addition, the behavior of the pitches during pyrolisis was monitored by thermogravimetric analysis. Experimental details of all the analyses have been described previously [3, 4].

Results and discussion

Pitch air-blowing and thermal treatment caused an increase in the degree of pitch polymerization, which is reflected by the increase in pitch softening point, carbon yield and insoluble content in toluene and NMP with increasing time of treatment (Table 1).

One of the first evidences of the formation of different molecular structures during each treatment is the fact that the air-blown pitches are completely isotropic, while the thermally treated pitches developed mesophase, its content increasing with increasing time of treatment. This suggests that molecules in the thermally treated pitches are more planar than in the air-blown pitches, where the cross-linked structures generated make the stacking of the molecules to form mesophase difficult. This was also confirmed by the X-ray diffraction results, which showed a higher degree of ordering for the thermally treated pitches. Moreover, for the air-blown pitches the iodine indices decreased with increasing time of treatment, as a result of the cross-linking.

The different structures generated are the result of the different polymerization mechanisms that occur during each type of treatment. In the case of the thermal treatment, aromatic condensation of the molecules takes place, which is reflected by a higher increase in the C/H ratio of the pitches. On the other hand, in the first stages of pitch air-blowing a substantial removal of aliphatic hydrogen (naftenic structures and methyl groups) occurs, resulting in a high aromaticity index for the air-blown pitches.

Differences between the pitches can also be observed in their thermogravimetric analyses. Figure 1 shows the DTG curves of pitches AB25 and C2, both with similar carbon yields. The polymerization that occurs during air-blowing generates molecules which undergo thermal reactions at temperatures around 400°C, as a result of their cross-linked structures, which are thermally unstable.

Conclusions

Thermal treatment and air-blowing promote pitch polymerization. Although the extent of polymerization seemed to be similar, the air-blown pitches were completely isotropic whereas the thermally treated pitches developed mesophase.

Thermally treated pitches have a higher content of light compounds than the corresponding air-blown pitches, as a result of the polymerization of the light components favored by the oxygen during air-blowing.

Air-blowing promotes an extensive removal of aliphatic hydrogen during the initial stages of the treatment, which is reflected by the considerable increase of the aromaticity indices and C/H ratio of the pitch. The aromatic condensation that takes place during the thermal treatment of pitches causes a greater removal of hydrogen than the formation of cross-linked structures.

Differences in the molecular structure of the two types of pitches are confirmed by the results from iodine up-take and X-ray diffraction. Thermally treated pitches have a higher degree of structural ordering than air-blown pitches, where cross-linked structures can be considered as dominant.

References

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Acknowledgements

Authors would like to thank CICYT (Project MAT95- 0206 and MAT97-0677) for financial support. C. Blanco is grateful to MEC for her research grant.

Table 1. Main properties of pitches.

Pitch	MC	SP	CY	TI	NMPI
Parent	0	97	34.6	20.0	4.7
AB10	0	139	48.0	36.6	13.6
AB18	0	168	57.6	44.6	18.9
AB25	0	197	61.8	51.8	24.9
AB30	0	210	62.7	52.0	27.1
C1	10	149	54.0	43.9	20.7
C2	25	174	61.4	53.9	29.8
C3	37	190	65.6	57.5	34.7
C4	46	-	74.6	67.5	45.6
C5	65	-	79.4	69.0	49.6

MC, mesophase content (vol. %)
SP, Mettler softening point (°C)
CY, carbon yield (wt. %)
TI, toluene insolubles (wt. %)
NMPI, N-methyl-2-pyrrolidone insolubles (wt. %)

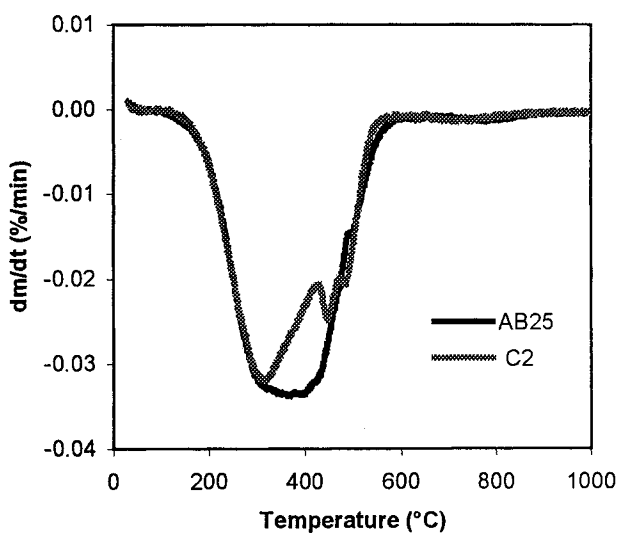

Figure 1. DTG curves of a thermally treated pitch and an air-blown pitch.