

PROPERTIES AND MOLECULAR STRUCTURE OF PITCH PRODUCED IN AIR-BLOWING REACTION

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Introduction

The pitch precursors used for general-purpose carbon fiber are prepared by an air-blowing reaction on an industrial scale. The air-blowing reaction mechanism is complicated because of the contact with oxygen, the simultaneous effects of heat treatment, and distillation that is caused by a pressure drop in the system due to air-blowing. Therefore, in order to investigate the role of oxygen, heat and distillation in the air-blowing reaction, we studied the polymerization of coal tar pitch in an oxygen reaction, the heat-treated reaction, and distillation by observing the molecular structures of material pitch and product pitch with NMR and ESR measurements¹⁾.

Experimental

Coal tar was filtered, then distilled to obtain QI free coal tar pitch. Material pitch was heated at 330°C under a pressure of 2.1 MPa at a dried N₂ flow rate of 5Nl/min for the standard conditions (Run 2). For the effects of oxygen, distillation and heat-treating, the blowing gas was replaced with air only (Run 1), the reaction pressure only was changed to 0.1, 0.02 MPa (Runs 3,4), and the reaction temperature only was changed to 430°C (Run 5) from standard conditions, respectively. The product pitches were characterized by softening point (SP), polarized-light microscopic observation, solvent fractionation, and NMR and ESR analysis.

Results and Discussion

The changes in the general properties and the SP

of the pitch samples with reaction time are shown in Table 1 and Figure 1, respectively. The oxygen reaction is mostly effective in raising the SP of the pitch (around 280 °C) without mesophase sphere generation, to increase QI, and to reduce BS. By distillation, the SP of the pitch can be raised to 170~200 °C without mesophase sphere generation by effectively removing the volatile fractions, which is the main cause of low yield. However, the heat-treated reaction resulted in the formation of an anisotropic texture and hardly any rise in the SP.

Table 1 Yield and analytical data of pitches.

Run No.	Reaction time(min)	Yield(wt%)				Isotropic content(%)
		Total	QI	QS-BI	BS	
Original	0	100	0.0	18.3	81.7	100
	90	96.5	16.3	29.9	50.3	100
1	180	95.0	36.2	15.2	43.6	100
	280	93.4	44.2	12.7	36.5	100
2	180	-	-	-	-	100
	280	98.3	1.0	20.5	76.8	100
3	180	-	-	-	-	100
	280	56.3	0.1	12.9	43.4	100
4	180	-	-	-	-	100
	280	46.5	0.1	11.2	35.1	100
5	180	99.0	6.3	27.3	65.5	98
	280	98.3	9.9	25.7	62.7	80

QI: Quinoline Insoluble; QS-BI: Quinoline Soluble-Benzene Insoluble; BS-AcI: Benzene Soluble-Acetone Insoluble; AcS: Acetone Soluble.

Figure 2 shows the chemical structure change for pitches in the ¹³C-NMR resulting from each reaction. The oxygen reaction greatly decreases the side chain carbon, bridged carbon and naphthenic carbon according to the rise in the SP. The distillation decreases the side chain carbon a little and increases the bridged carbon (methylenic bonding between the two aromatics in the molecules), which are revealed by

eliminating low molecular weight materials. The reaction mechanisms of pitch accompanying the rise in the SP are very different between the oxygen reaction and distillation.

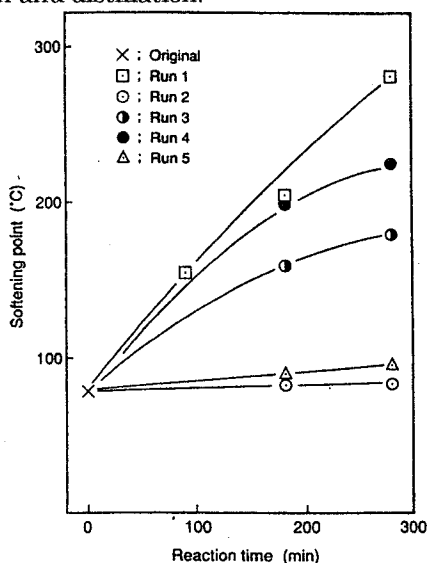


Fig.1 Change in the softening point of pitches with reaction time.

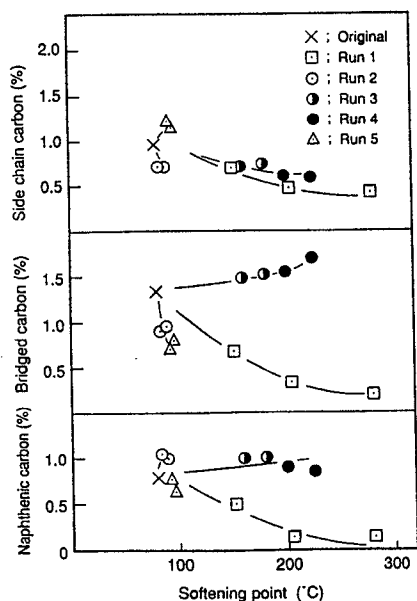


Fig.2 The variation of chemical structure of pitches with softening point.

Fig 3 shows the peak-to-peak line width (ΔH_{msl}) of the ESR analysis technique resulting from each reaction. The change in ΔH_{msl} is determined by the balance of dipolar and exchange interactions in the electron spins of the system. The decrease in ΔH_{msl}

of heat-treated pitch is related to an increase in the exchange interaction derived from the formation of large polyaromatic compounds which give rise to anisotropic and QI content. However, for the distillation pitch, the change in ΔH_{msl} remains constant until its SP becomes around 200°C and it is believed that little change occurred in the aromatic ring structure. The gradual decrease in the ΔH_{msl} of the oxygen reaction is mainly related to a decrease in the dipolar interaction derived from the dehydrogenation (elimination of the aliphatic structure). From the NMR and ESR results, the inconsistent change concerning the decreased aliphatic structure and undeveloped aromatic ring structure was observed in the oxygen reaction. Accordingly, it is assumed that the oxygen reaction is polymerized with crosslinked bonding, mainly biphenyl-type bonding between the two aromatics²⁾.

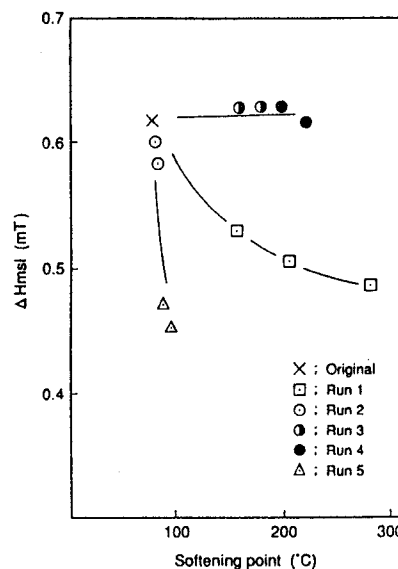


Fig.3 The variation of peak-to-peak line-width(ΔH_{msl}) of pitches with softening point.

References

1. C. Yamaguchi, H. Matsuyoshi, J. Mondori, S. Baba, H. Kumagai, and Y. Sanada, *Tanso (in Japanese)* [No.162], 78 (1994).
2. C. Yamaguchi, J. Mondori, A. Matsumoto, H. Honma, H. Kumagai, and Y. Sanada, *Carbon* 33, 193 (1995).