EFFECT OF COMPOSITION ON THE GLASS TRANSITION AND RHEOLOGICAL PROPERTIES OF PITCH

B. Rand, S.C. West*, Bryan Ellis* and M. Turpin
School of Materials, University of Leeds, Leeds LS2 9JT,
and Dept. of Engineering Materials, University of Sheffield, Sheffield S1 4DU, UK.

Introduction

The rheological behaviour of pitch precursors is of major significance in the processing of advanced carbon materials, but is not yet fully understood. In this paper we examine the variation in rheological parameters of soluble fractions of the petroleum pitch Ashland A240. The soluble fractions were also recombined to elucidate the effects of composition on glass transition temperature, T_g, and carbon yield.

Experimental

Ashland A240 pitch was fractionated in heptane and the heptane insoluble fraction, HI, was further fractionated in toluene, yielding five samples, A240, heptane soluble fraction (HS), HI, HI/TS and HI/TI. These materials were characterised by thermogravimetry, size exclusion chromatography and vapour phase osmometry, dynamic thermal analysis (DMTA) and oscillatory stress rheometry. They were recombined in various proportions to compile binary and ternary systems whose carbon yields and T_g values were measured.

Results and Discussion

The C/H ratio, molecular weight, T_g, carbon yield and temperature of onset of weight loss during pyrolysis increased in the order TI>HI>A240>TS>HS as might be expected.

Recombining the fractions in binary systems showed that the variation of T_g (in K) and carbon yield (Y/%) with composition could be described by simple mixture rule expressions,eg

$$Y = M_1Y_1 + M_2Y_2 \quad ....(1)$$

$$1/T_g = M_1/T_{g,1} + M_2/T_{g,2} \quad ....(2)$$

where M and M are the mass fractions of the different soluble fractions. The applicability of equation (2) to pitch systems has already been discussed by Rand [1] and Barr and Lewis [2]. Figure 1 shows a typical example.

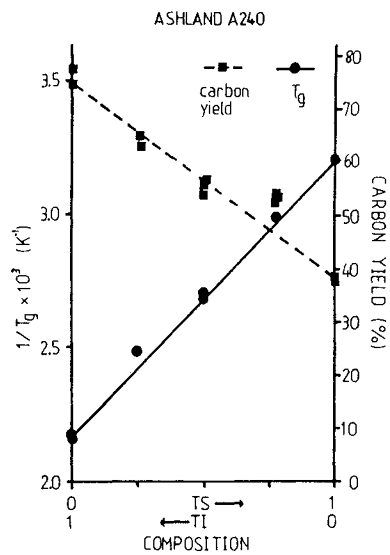

Figure 1. Mixture rule correlations for the recombined TS and TI fractions.

The three essential constituents of this pitch are the HS, HI-TI and HI-TS fractions. It was found that a three component mixture rule could adequately describe the compositional dependence of these two important characteristic parameters over the whole ternary diagram, as illustrated in Figure 2. This behaviour is highly significant, because if it applies generally to pitch fractions it can be used to guide blending procedures for better control over carbon precursor properties. This, however, remains to be established. There is likely to be a limit to the extent that such mixture rules can be applied to pitch systems. They seem to work well here because the pyrolysis behaviour is dominated by evaporative processes. However, for pitches that have been extensively heat-treated, cracking reactions become more significant and the mixture rule may no longer apply. It is interesting to note that it was possible to adapt the mixture rules here to describe the complete temperature dependence of the weight loss during pyrolysis of binary mixtures from the knowledge of the behaviour of the end members.

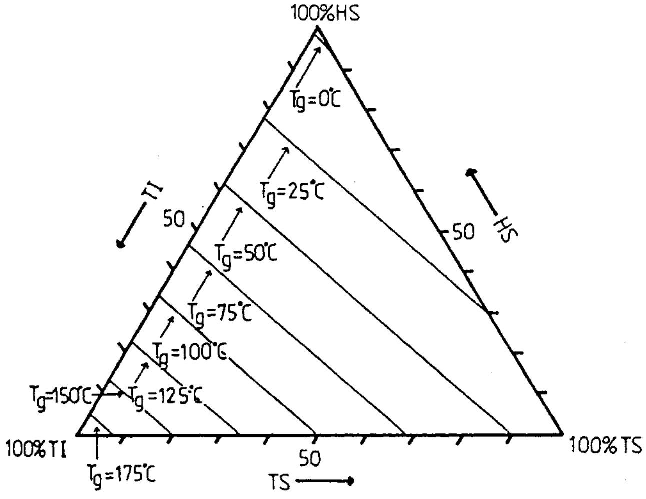

Figure 2. Ternary diagram for A240 constituents, showing iso-T_g lines.

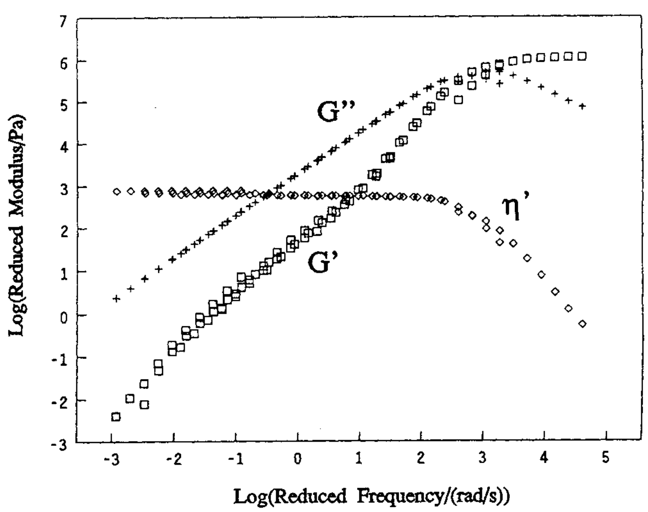

Figure 3. Master curves for viscoelastic parameters for A240 pitch at a reference temperature of 120°C.

It would be useful also if rheological behaviour could be predicted in a similar manner. This requires knowledge of the relationship between relevant parameters and the T_g. Turpin et al [3] have shown how oscillatory stress measurements can be used to characterise pitch systems. This technique has been used here to characterise the viscoelastic behaviour of the various fractions. Storage and loss moduli were determined as a function of frequency and temperature and combined to produce master curves. An example is shown in Figure 3 for A240.

From these data various viscosity coefficients can be derived. All the materials showed viscoelastic character at low temperatures and high frequencies. The behaviour was approximated to a simple Maxwell model and the relevant parameters, elastic modulus, viscosity and relaxation time established.

The temperature dependence of the frequency shift factors, a_T, required to construct the master curves, was found to follow the Williams-Landel-Ferry (WLF) model as demonstrated for other pitch and mesophase pitch systems[1,3,4]. The characteristic constants, c_1 and c_2, were determined for different reference temperatures and in particular for the glass transition temperature as reference. Using the latter values the temperature dependence of viscosity was predicted and shown to accord with experimental values obtained both within this study and, in the case of A240 pitch, with the manufacturers values. The WLF equation, or the related Fulcher equation, should be routinely adopted to characterise viscosity-temperature data for pitches. The c constants obtained from the analysis, however, were different for the various fractions and did not seem to vary in a systematic manner. Thus, whilst T_g can be predicted from mixture rules, in this system, it is not yet possible to predict the complete viscosity-temperature relationship. Future work will be directed towards establishing the factors that control the c constants.

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