Thermochimica Acta, 52 (1982) 297–304
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHARACTERIZATION OF PITCHES BY DIFFERENTIAL SCANNING CALORIMETRY AND THERMOMECHANICAL ANALYSIS

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(Received 21 July 1981)

ABSTRACT

Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA) have been used to measure the glass transitions of pitch materials Glass transition temperatures (T_g) were determined with the DSC technique for pitches derived from coal tar, petroleum, and model compounds The T_g values bear a fixed relation to the Mettler softening point (T_s) with $T_g/T_s = 0.80$ The TMA procedure was preferred for mesophase-containing pitches Analogous to mixed polymer systems, the glass transition temperatures for the mesophase pitches could be related to the contents and the T_g values of the low molecular weight (pyridine soluble) and the high molecular weight (pyridine insoluble) fractions

1 INTRODUCTION

Thermal analysis techniques are now routinely used to characterize polymers and to provide information on such diverse properties as miscibility of blends, crystallinity, phase transitions, reactivity, and stability. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) have been the most extensively used thermal analysis methods for studying carbonaceous materials such as pitches [1], tars [2] and polynuclear aromatic mixtures [3]. However, the techniques of differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), which have proved to be valuable for studying glass transitions and phase changes in polymers, have only recently been tried with carbonaceous materials.

The glass-like nature of coal tar pitch was demonstrated by the detection of a glass transition which appeared as a discontinuity in the volume expansion–temperature curve [4]. Stadelhofer [5] determined directly the glass transition temperature (T_g) of a coal tar pitch by using DSC. A DSC method was also used by Huynh et al. [6] for determining the effects of molecular composition on the T_g for asphalts. Rand et al. [7] explored several techniques for determining T_g in pitches. The penetrometry method of TMA was found more suitable than DSC for detecting T_g in coal extract pitch and in pitches containing high amounts of quinoline insolubles. Broadline proton nuclear magnetic resonance was more reliable than DSC for measuring T_g for a petroleum pitch heat-treated to the mesophase stage [8].

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Differential scanning calorimetry measurements have not yet been reported for mesophase pitches, although DSC has been widely used to characterize individual liquid crystalline compounds [9].

In the present paper, we have determined T_g values for isotropic and mesophase pitches derived from petroleum, coal tar, and model compounds by using both DSC and TMA. Penetration TMA results are related to the pyridine insoluble contents for a series of mesophase pitches. For comparison with mesophase pitches, DSC was used to investigate thermal transitions of the aromatic liquid crystalline compound, *p*-quinquephenyl.

2 EXPERIMENTAL

The isotropic petroleum and coal tar pitches were obtained from commerical sources. Higher melting point pitches were prepared by vacuum distillation. Pitches from the model compounds acenaphthylene, anthracene, and naphthalene were prepared by published procedures [10,11]. Mesophase-containing pitches were made by heat treating the appropriate precursors at temperatures above 380°C in a nitrogen atmosphere. The insolubles content of heat-treated pitches was determined by Soxhlet extraction with pyridine. The aromatic hydrocarbon *p*-quinquephenyl was obtained from K and K Chemical Co and was purified by vacuum sublimation. Softening points of the pitches were measured by using a standard ASTM procedure and a Mettler FP-5 unit.

The DSC measurements were obtained with a DuPont 990 Thermal Analyzer in combination with a 910 DSC unit. Samples weighing 5–30 mg in sealed aluminum pans were heated in flowing nitrogen at a rate of 10°C $\min^{-1}$. An empty aluminum pan was used as a reference. Pitches were heated to temperatures slightly above T_g to fuse the samples and then cooled rapidly with liquid nitrogen prior to scanning for thermal transitions.

Temperatures and heats of transition for *p*-quinquephenyl were determined from duplicate DSC curves. The samples (3–5 mg) were contained in hermetic sealed aluminum pans and heated at 5°C $\min^{-1}$ in argon. Enthalpy values were calculated by measuring the areas of transition peaks and by using indium as a calibration standard.

Thermomechanical analysis studies were carried out with either a Perkin-Elmer model TMS-1 with a DSC-1B control unit or a DuPont TMA model 942 and a 990 Thermal Analyzer. Powered pitch samples were pressed into pellets that were 6 mm in diameter and 3–6 mm thick. The Perkin-Elmer unit was operated in a penetration mode with a 12 g weight on the probe, a helium flow of 60 $\mathrm{cm}^3\ \min^{-1}$ and heating rates of 5°C or 10°C $\min^{-1}$. The DuPont TMA was also operated in a penetration mode in flowing nitrogen and a heating rate of 5°C $\min^{-1}$. Some of the TMA and DSC data were processed with the help of a PDP 11/40 computer.

3 DISCUSSION OF RESULTS

3.1. *DSC of isotropic pitches*

Distinct glass transitions were observed in DSC scans of coal tar, petroleum, and acenaphthylene pitches. Figure 1 shows repetitive DSC scans for a typical petroleum pitch which has a Mettler softening point of 152°C. The initial scan exhibited an endotherm in the vicinity expected for T_g with a maximum at 103°C. The second scan, which was made immediately after cooling the sample rapidly from 240°C to −10°C, shows a well-defined T_g with an onset temperature of 83°C. The endothermic peak is no longer visible in the thermogram of the quenched pitch sample. Figure 2 presents a DSC curve from the first heating of an acenaphthylene pitch with a Mettler softening point of 234°C. The T_g measured at the onset temperature is 134°C and the transition is clearly visible. The anomalous endotherm was not observed for this material. Rand and Shepherd [7] attributed endothermic peaks in the initial DSC scans of petroleum pitches to a partial ordering in structure similar to crystallization in polymers. Although anomalous endotherms similar to those observed for pitches have been reported for polymers, the origin of the peaks is controversial. Wrasidlo and Stille [12] considered endothermic peaks for polyquinoline glasses to be first-order transitions involving paracrystalline structures formed in the glassy material. In contrast, Petrie [13] attributed endothermic peak behavior in organic glasses to a relaxation of enthalpy during annealing at temperatures below T_g. According to the view of Petrie and others [14], the endotherms do not represent first-order transitions. Since no evidence for crystalline or pseudo-crystalline structures is present in isotropic pitches, we prefer the approach of Petrie for explaining the origin of endothermic peaks.

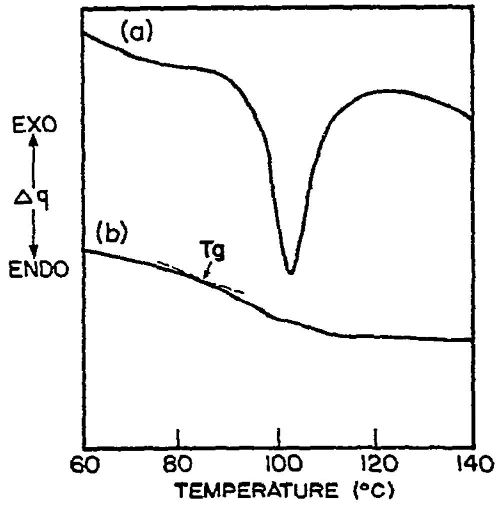


Fig 1 DSC curve for isotropic petroleum pitch; (a) first heat, (b) second heat on quenched sample Sample size, 27 7 mg, atmosphere, N_2, heating rate, 10°C min^{-1}

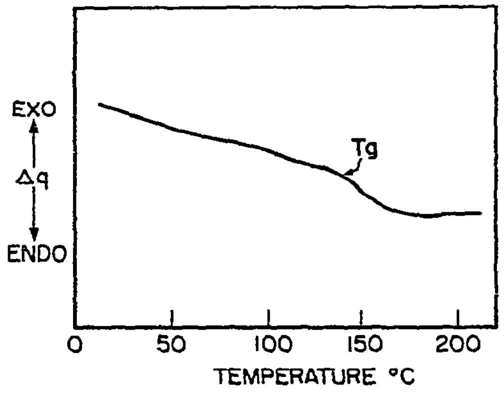


Fig 2 DSC trace for isotropic acenaphthylene pitch.

TABLE 1

Softening points and glass transitions (DSC) for isotropic pitches

Pitch	Mettler softening point (T_s) (°C)	Glass transition (T_g) by DSC (°C)	
		Onset	Span
Coal tar	110	34	38
	126	38	28
	151	60	43
	173	83	30
Petroleum	122	50	18
	130	55	20
	152	83	20
	178	102	21
	188	108	21
	202	103	29
Acenaphthylene	234	134	29

Glass transition temperatures and softening points are listed in Table 1 for several isotropic coal tar and petroleum pitches, as well as for a pitch made from acenaphthylene. For each of these pitches, changes in softening point are paralleled by changes in glass transition temperature. The span of the glass transition region (Table 1) ranged from 18° to 43°C for the pitches examined.

3.2 *DSC of mesophase pitches*

Unlike the isotropic pitches, well-defined T_g values were not obtained for mesophase-containing pitches. However, measurable T_g values could be detected for

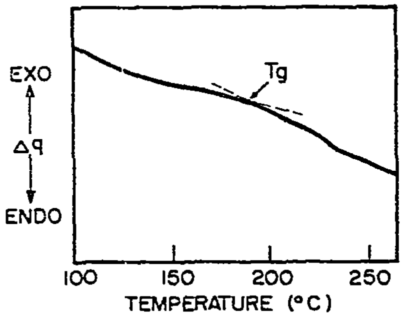


Fig 3 DSC trace for naphthalene mesophase pitch

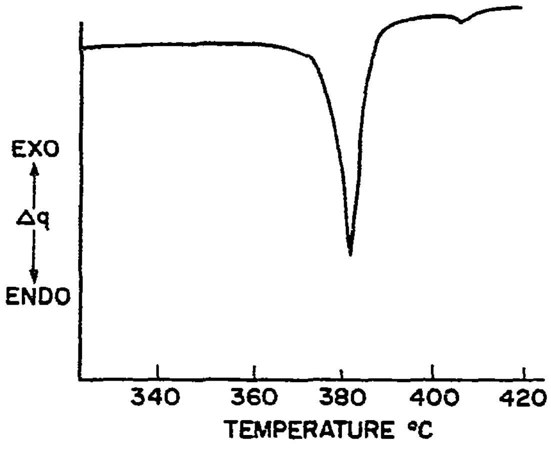


Fig 4 DSC trace for the liquid crystal forming compound p-quinquephenyl

completely anisotropic pitches prepared from the model compounds acenaphthylene, anthracene, naphthalene, and from a petroleum-derived pitch. The DSC curve determined for a completely anisotropic pitch from naphthalene is shown in Fig 3. Glass transitions could not be observed for mesophase pitches which contained appreciable amounts of isotropic phase.

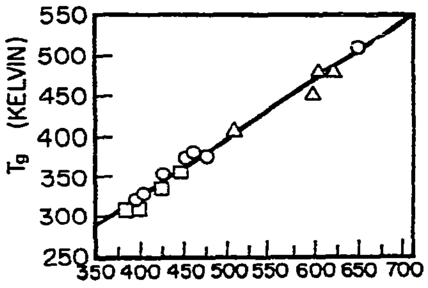


Fig 5 Relation between T_g values in Kelvin and Mettler softening points in Kelvin for isotropic and mesophase pitches. □, coal tar-derived pitches, O, petroleum-derived pitches, △, model compound-derived pitches

The DSC technique gives well-defined transitions for single liquid crystalline compounds. For example, Fig. 4 presents a DSC curve for the aromatic hydrocarbon *p*-quinquephenyl. This compound is known to form a liquid crystal [15]. Peaks corresponding to the solid-to-nematic and the nematic-isotropic transformations with transition temperatures of 381 and 406°C, respectively, are readily apparent. The corresponding ΔH values are 11.0 and 0.4 kcal mole^{-1}. Difficulties in obtaining reasonably intense DSC transitions for the mesophase pitches must, therefore, be related to their highly complex constitution and not to their liquid crystalline character.

The T_g values determined in this study for both the isotropic and mesophase pitches show a fixed relation to the Mettler softening point. In Fig. 5, the T_g values in Kelvin are plotted against the Mettler softening point (T_s) in Kelvin for both types of materials. The two sets of data show a linear correlation of the form

$$T_g\ (\text{Kelvin}) = 0.80 T_s\ (\text{Kelvin})$$

The coefficient of variation for the factor was 3%. An analogous correlation exists in the Beaman–Boyer empirical rule, where T_g is approximately two-thirds the crystalline melting point for many polymers [16,17].

3.3 *TMA of pitches*

Thermomechanical analysis was used in a penetration mode to measure T_g for mesophase and isotropic pitches. The TMA method is attractive for mesophase pitches because of the difficulties encountered in detecting the T_g of these materials by DSC. Figure 6 shows a TMA penetration curve for a petroleum-derived mesophase

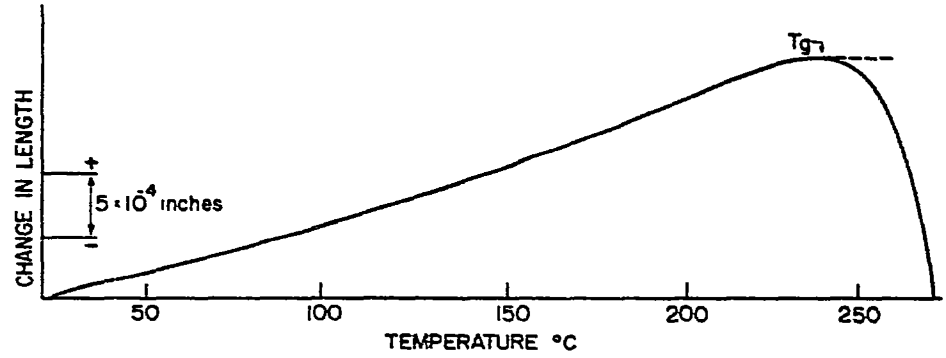


Fig 6 Penetration TMA curve for petroleum-derived mesophase pitch

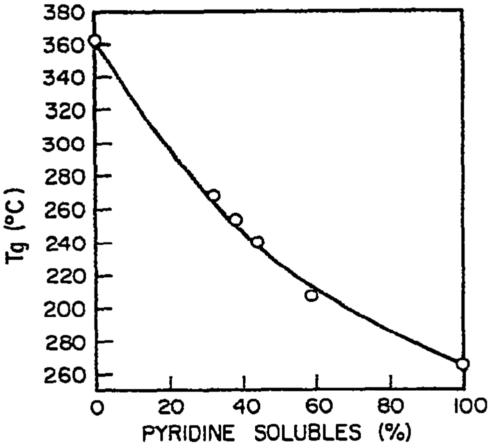
pitch. Similar curves were obtained for other mesophase and isotropic pitches with the Perkin-Elmer TMS-1 instrument. The point of penetration which was used to determine T_g is indicated in Fig. 6. The T_g values obtained by both the TMA and DSC methods are listed in Table 2 for mesophase pitches. The two sets of data are in good agreement, with the T_g values from TMA only 3°C to 5°C lower than those from DSC. The T_g values from the TMA measurements fit the same relationship with the Mettler softening temperatures as that derived for T_g values from DSC. In contrast to the mesophase pitches, TMA measurements on isotropic pitches yielded penetration points significantly different from DSC glass transitions. Penetration points were an average of 24°C higher than glass transitions determined on the same isotropic pitches by using DSC. Clearly, DSC is the preferred technique for determining T_g values for isotropic pitches, whereas, for most mesophase pitches, penetration TMA is the better choice

Experimental TMA data were also obtained for a series of petroleum pitches which had been heat-treated through the mesophase stage. Heat treatment of pitch is known to effect thermal polymerization, and the magnitude of the polymerization change has often been equated to a decrease in solubility in selected solvents [18]. In Fig. 7, the penetration TMA values are plotted as a function of the pyridine solubles (PS) content of the heat-treated pitches. The data for 0% and 100% PS were obtained on the fractions extracted from a pitch containing approximately 50% PS. The TMA data for pitches with PS contents higher than 60% did not fit the correlation because of a heterogeneous phase composition.

TABLE 2

Glass transition temperatures for mesophase pitches by TMA and DSC methods

Mesophase pitch precursor	Glass transition (T_g) (°C)		Softening point (T_s) (°C)
	TMA	DSC	
Anthracene	183	178	325
Acenaphthylene	208	205	348
Naphthalene	210	207	338



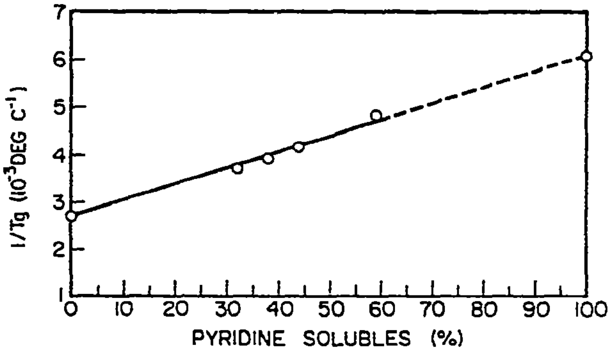


Fig 7 Glass transition as a function of pyridine solubles content in heat-treated petroleum pitches

Fig 8 Plot showing linear relationship between $1/T_g$ and pyridine solubles content of heat-treated pitches

The correlation of T_g data with molecular composition is well known for miscible polymer blends. The data can be interpreted by using an expression proposed by Fox for random copolymers or for polymer–diluent blends [19]. The Fox equation was applied to the heat-treated pitches in the following form

$$\frac{1}{T_g} = \frac{W_{PS}}{T_{gPS}} + \frac{W_{PI}}{T_{gPI}}$$

where T_g, T_{gps}, and T_{gpI} are glass transitions for the blend, pyridine solubles, and pyridine insolubles, respectively; W_{ps} and W_{pI} are weight fractions of the pitch blends. The Fox equation has been discussed by Wood [20] as a special case of a more general relationship for copolymers. As may be seen from Fig. 8, a plot of $1/T_g$ versus percent PS for the components and blends is linear. This result implies that, at least within the composition range of the experimental blends, the components are primarily compatible.

The Fox equation was used to calculate the solid curve in Fig. 7 The calculated curve is a good fit to the experimental data, again demonstrating the feasibility of the copolymer approach to analyzing penetration TMA data for heat-treated pitches

ACKNOWLEDGEMENT

We wish to thank S.L. Hager for performing some of the thermal analysis measurements.

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