

# ROLE OF ACIDIC AND BASIC FRACTIONS IN COAL TAR

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## INTRODUCTION

Binder and impregnation pitches are obtained by distillation of coal tars. The main chemical structure encountered in coal tar pitch is of hydroaromatic type with molecular masses ranging from a few hundreds to over thousand Daltons. Polar molecules mainly phenols and pyridinic compounds are also present in small amount. It is known that polar molecules exert an influence on the thermal stability of coal tars but their precise role is still not clearly established. In particular, the amount and the shape of solid aggregates present in coal tar seems to be linked with the presence of polar molecules. The aim of the present study is to determine the influence of acidic and basic compounds on the thermal behaviour of coal tars. Like pitches, tars are glassy solids at low temperature and undergo a glass transition upon heating. In a previous study on binder pitches, it was shown that the apparent activation energy of the relaxation process associated with the glass transition depends on the mean size of the structural units present in the materials [1]. Hence, the glass transition characteristics of a series of coal tar samples containing various types of polar compounds have been determined in relationship with their content of solid particles or aggregates.

## EXPERIMENTAL

A coal tar sample, CT, with a QI content equal to 1.5% was separated into three fractions by distillation. The lighter one is composed of water, benzene, toluene and xylenes and represents about 1% by weight of the tar. The intermediate one (22.1%) is further split into three fractions by liquid-liquid extraction in order to separate the acidic (phenols) and the basic (pyridinic compounds) fractions from the hydrocarbons, HC. The acidic, A, and basic, B, fractions represent 1.9 and 0.6% b.w. of the tar respectively. The heaviest part of CT is the bottom of the distillation, *i.e.* the coal tar pitch, CTP. The various fractions were recombined by mixing at 410 K under mechanical stirring in air in order to obtain reconstituted coal tars, RCT, (sample weight equal to 500 g) of different polarity as shown in Table 1. In all cases, the reconstituted tar samples represent more than 96% b.w. of the starting coal tar sample. Glass transition temperature,  $T_g$ , and apparent activation energy of enthalpy relaxation,  $\Delta h^*$ , were determined

by differential scanning calorimetry (dsc) following a procedure described elsewhere [1]. Two types of pretreatment conditions of the tar samples have been considered: (i); heating at 373 K in the dsc cell and measurement followed by immediate cooling (quenching), and (ii); storage at 256 K for 20 days, *i.e.* at a temperature slightly above  $T_g$ . In both cases  $T_g$  and  $E_a$  were determined by cooling from the pretreatment temperature using different cooling rates varying from 50 to 0.2 K/min [1]. Solid particles or aggregates were detected by optical microscopy using transmitted light through thin layer of samples. The amount of solid matter was determined by image analysis and is comparable to the QI content (Table 1).

Table 1. Composition of reconstituted coal tars

Sample	Composition	Particle content (%)
CT	untreated	2
RCT1	CTP + HC	6
RCT2	RCT1 + A	5
RCT3	RCT1 + B	5
RCT4	RCT1 + A + B	5

## RESULTS AND DISCUSSION

CT preheated at 373 K exhibits a glass transition centered at 226 K. After storage at 256 K an endothermic peak (10 to 15 J/g) is found between 263 and 313 K in addition to the glass transition due to the melting of crystallized fractions formed upon storage. The removal of the crystallizable compounds from the glass-forming part of tar does not significantly affect the value of  $T_g$  as indicated in Table 2. In contrast, the value of  $\Delta h^*$  slightly decreases after storage indicating a change in the relaxing units responsible for the glass transition phenomenon. For the tar sample without polar compounds, RCT1,  $T_g$  is slightly smaller than for the untreated tar CT. After storage  $\Delta h^*$  significantly increases which indicates that the size and/or the extent of interaction between relaxing units has been increased in absence of phenols and pyridines.

Upon addition of polar compounds to RCT1,  $T_g$  is not significantly affected but  $\Delta h^*$  is modified since its value slightly increases upon addition of phenols

(RCT2) whereas it decreased after incorporation of the basic fraction (RCT3) as shown in Table 2. These results suggest that the presence of phenols promotes hydrogen bonding between the hydroaromatic molecules which tends to increase the mean size and/or the interaction energy of the relaxation units responsible for the glass-forming system. It is interesting to note that the addition of a small amount of molecules of opposite polarity produces a reverse effect on the association of the molecular structure of the glassy tar. Moreover the incorporation of both acids and bases leads to an intermediate value suggesting a kind of compensation effect between molecules of different polarity (RCT4). Since CT and RCT4 have nearly the same chemical composition, their glass transition characteristics should be identical. In fact CT has a slightly lower  $T_g$  which may be attributed to the lightest molecular fraction (water, benzene, toluene and xylenes) representing about 1 % b.w. Also a lower value of  $\Delta h^*$  for RCT4 is probably due to the absence of water traces present in CT which may act in a way similar to phenols (tendency to increase  $\Delta h^*$ ).

After storage at 256 K, the dsc curve for each reconstituted tar sample shows also an endothermal peak (6 - 7 J/g) and their  $T_g$  values are quite comparable. Nevertheless, the effect of polar compounds on  $\Delta h^*$  is noticeable (Table 2). After storage,  $\Delta h^*$  increases in presence of bases whereas it only slightly decreases when the phenolic fraction is incorporated. Moreover the presence of phenols or pyridinic compounds tends to diminish the variation in  $\Delta h^*$  as compared to the non-polar tar RCT1. Interestingly, the simultaneous presence of acidic and basic compounds leads again to a stabilization effect of the coal tar since  $\Delta h^*$  does not change after storage (RCT4).

Table 2. Glassy characteristics of coal tar samples

Sample	Quenching		Storage	
	$T_g$ (K)	$\Delta h^*$ (kJ/mol)	$T_g$ (K)	$\Delta h^*$ (kJ/mol)
CT	226	230	229	190
RCT1	233	205	234	300
RCT2	233	225	236	205
RCT3	233	160	233	210
RCT4	232	210	234	210

After combination of the two main tar fractions (CTP and HC), the amount of solid matter increases significantly and the incorporation of polar fractions does not affect its value (Table 1). Polar fractions have however an effect on the morphology of the

solid particles as shown by the cumulative distribution curves of particle sizes (Fig. 1). In the untreated tar, the mean particle size is smaller than in the reconstituted tars. Hence the recombination of the various fractions leads to larger particles or aggregates. Addition of phenols tends to decrease the particle size as compared to the non-polar tar (RCT1). Interestingly, bases have an opposite effect. Hence, small amounts of polar fractions appear to play also an important role on the dispersability of the insoluble matter.

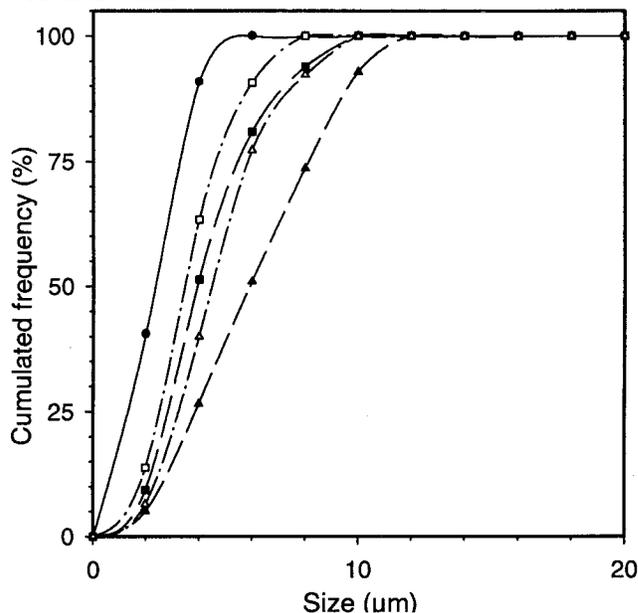


Fig. 1 : Cumulative size distribution of isotrope particles ( $\Delta$  RCT1,  $\square$  RCT2,  $\blacktriangle$  RCT3,  $\blacksquare$  RCT4,  $\bullet$  CT).

## CONCLUSION

This study evidences that the presence of small amounts of polar compounds like phenols or pyridines affects the glassy characteristics of a coal tar as well as its content in solid particles. The change in activation energy of the relaxation process associated with the glass transition indicates that polar compounds exert a strong influence on the size and/or the association of the structural units undergoing the glass transition phenomenon. The simultaneous presence of both acidic and basic compounds leads to a stabilization effect of the tar which becomes less sensitive to storage condition at low temperature and with a higher dispersability of solid particles.

## REFERENCES

1. P. Ehrburger, Ch. Martin and J.L. Saint Romain, Fuel, **70**, 783 (1991).