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STUDIES ON THERMAL DECOMPOSITION OF PITCH-POLYMER COMPOSITIONS

J. Zieliński[1], B. Pacewska[1], T. Brzozowska[1] and J. Machnikowski[2]

[1]Warsaw University of Technology, Institute of Chemistry, Płock
[2]Wrocław University of Technology, Wrocław, Poland

Abstract

The temperature range of phase transitions has been established for coal–tar pitches modified with various types of polymers. Mass loss rate was determined in relation to modifying polymer type. Simultaneous thermoanalytical method (DTA, DTG, TG), appeared to be very useful in studies on pitch-polymer compositions.

Keywords: coal–tar pitch-polymer compositions, thermal stability

Introduction

Coal–tar pitches constitute a coal by-product that has not yet been fully utilized. Owing to its interesting physicochemical properties, coal–tar pitch can find numerous applications. Nevertheless, the ever-exacting requirements set on the quality of applied bitumens, among other things, in the refractory materials, electrode and construction industries, they have to be modified with polymers used as additives. Studies on the development of the mesophase in the pitch and the yield of semi-coke in the carbonization process have confirmed the usefulness of some selected polymer compounds used as bitumen modifiers [1].

Experimental

Temperature plays a particular role in the carbonization of coal–tar pitch and of pitch-polymer compositions. Therefore, it is essential to determine the stages of thermal decomposition and the temperature intervals of phase transitions in coal–tar pitch containing a polymer as additive and to evaluate the usefulness of the derivatographic (TG) methods for examining pitch-polymer compositions.

For these investigations, pitch-polymer blends were used, containing a constant proportion (10 wt%) of a polymer; they were differing in chemical structure, property data and origin. Pitch was modified with poly(vinyl chloride) (PVC), polystyrene (PS), atactic polypropylene (APP), poly(ethylene terephthalate) (PET), polysaccharide (Cellulose), and a coumarone-indene resin (CIR), butadiene-styrene copolymer (Coriflex), unsaturated polyester resin (polyester), poly(ethylene gycol) (PEG).

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Table 1 General conditions of preparation of pitch-polymer compositions

No.	Components	Temp./°C	Total mixing time/h	Remarks
*1	Pitch+PVC	130–150	1	*T*=150°C, ca. 10 min
2	Pitch+PS	350	6	N_2 atm., no fractions collected, PS first dosed in *T*=220°C
3	Pitch+APP	180	2	
4	Pitch+Cariflex	350	6	N_2 atm., no fractions collected, Cariflex first dosed in *T*=250°C
5	Pitch+PET	310–320	6	N_2 atm., no fractions collected, PET first dosed in *T*=150°C
6	Pitch+polyester	100–105	0.5	After 0.5 h of mixing MEK peroxide and Co naphthenate were added as activator and hardening accelerator, 10 and 0.5 phr, resp.
7	Pitch+PEG	120–160	0.5	
8	Pitch+Cellulose	250	6	N_2 atm., Cellulose first dosed in *T*=150°C
9	Pitch+CIR	150	0.5	

*mixing in air

Compositions were prepared under the conditions enabling homogeneous and stable systems to be obtained. The general conditions of preparation of the pitch-polymer compositions are summarized in Table 1.

Thermogravimetry was used in combination with DTG and DTA to study the transitions occurring in the compositions prepared.

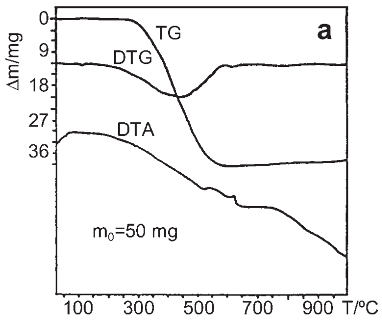

Fig. 1 Representative TG, DTG and DTA curves of a – coal–tar pitch, b – pitch-PET (10 wt%) composition

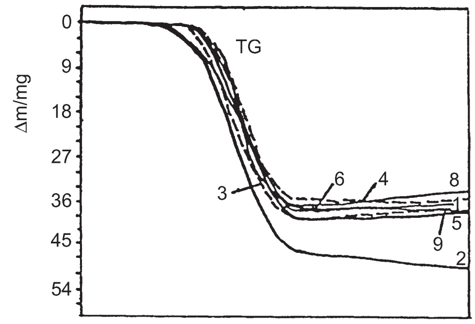

Fig. 2 TG curves of coal–tar pitch and pitch-polymer compositions: 1 – coal–tar pitch, 2 – pitch+CIR, 3 – pitch+polyester, 4 – pitch+Cariflex, 5 – pitch+APP, 6 – pitch+PEG, 7 – pitch+Cellulose, 8 – pitch+PS, 9 – pitch+PVC

A Hungarian-made Derivatograph C was used to record TG, DTG and DTA curves for individual samples, 50 or 100 mg in mass, at a heating rate of 10°C min^{-1} over a temperature range of 20–1000°C in a nitrogen atmosphere. Representative thermoanalytical curves are shown in Fig. 1.

Analysis of the TG curves, both for the starting pitch and for its compositions with various polymers added in an amount of 10 wt%, shows that the curves follow similar courses (Fig. 2 and data in Table 2).

Over the temperature range 200–580°C, the samples are seen to lose 50–62% of their original mass (TG curves). And there are no conspicuous thermal effects evident in the DTA curves. In the very complicated pattern of thermal decomposition of coal–tar pitches, several component processes follow in parallel. Pyrolysis and the

Table 2 Thermal stability of coal–tar pitch and of pitch-polymer compositions as established by derivatographic analysis

No.	Composition	Mass loss/mg	Mass loss *vs.* Original sample mass/%	Initial decomposition temperature/°C	Final decomposition temperature/°C
1	Pitch	27.00	54.00	250	580
2	Pitch+PVC	27.00	54.00	180	570
3	Pitch+PS	25.50	51.00	200	580
4	Pitch+APP	27.50	55.00	250	570
5	Pitch+Cariflex	25.00	50.00	200	570
6	Pitch+PET	52.00*	52.00	200	580
7	Pitch+polyester	27.00	54.00	200	570
8	Pitch+PEG	25.00	50.00	250	550
9	Pitch+Cellulose	50.00*	50.00	200	570
10	Pitch+CIR	31.00	62.00	200	580

*with respect to 100 mg sample

accompanying evolution of volatile fractions can be associated with cleavage of hydrocarbon skeletons, partial abstraction of functional groups, formation of simple and benign compounds like CO_2 and CH_4, condensation and polymerization of the resulting species, transfer and evolution of hydrogen, *etc.* [2]. Some of these processes are endothermic and require thermal energy to be supplied (e.g, distillation of volatiles), whereas others generate thermal energy. The latter include the reactions of condensation, polymerization or isomerization. The parallel-consecutive course of the endothermic and exothermic processes results in a practically complete compensation of thermal effects in the DTA curves over the temperature range 200–600°C.

The analysis of the DTG curves (Fig. 3) shows that, in the temperature range considered, the samples are losing mass at varying rates that are related to the type of additive used. Pure coal–tar pitch is decomposed at once. Compositions containing additives like Cariflex, polyester, coumarone-indene resin, atactic polypropylene and PEG produced DTA curves that followed similar courses.

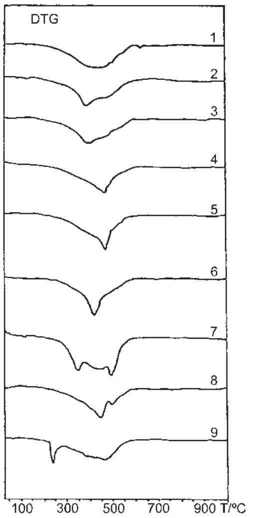

Fig. 3 DTG curves: 1 – coal-tar pitch, 2 – pitch+CIR, 3 – pitch+polyester, 4 – pitch+Cariflex, 5 – pitch+APP, 6 – pitch+PEG, 7 – pitch+Cellulose, 8 – pitch+PS, 9 – pitch+PVC

The addition of polystyrene, polysaccharide, poly(ethylene terephthalate), or poly(vinyl chloride) in an amount of 10 wt%, gives rise to differentiated rates of mass loss as a function of temperature and time, and to two or even three maxima in the DTG curves (Fig. 3) that reveal some independent process stages to follow.

Over the range 650–900°C, the DTA curves of the pitch-polymer compositions (Fig. 4) reveal the occurrence of an exothermic effect that is associated with no mass loss (TG and DTG curves in Fig. 1).

Both the intensity and the temperature range of this effect are related to the type of polymer used in a given pitch-polymer composition (Fig. 4). The effect is likely to

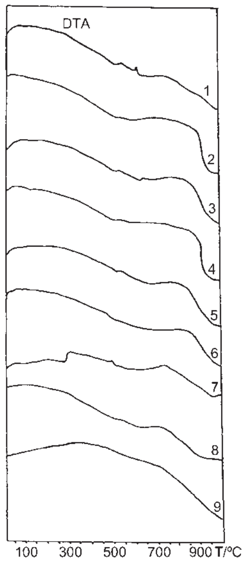

Fig. 4 DTA curves: 1 – coal–tar pitch, 2 – pitch+CIR, 3 – pitch+polyester, 4 – pitch+Cariflex, 5 – pitch+APP, 6 – pitch+PEG, 7 – pitch+Cellulose, 8 – pitch+PS, 9 – pitch+PVC

be associated with the thermodynamically spontaneous process of ordering of the structure of the carbon residue.

Conclusions

A deeper analysis of the present results on the effect of the polymer addition on thermal transitions occurring in coal–tar pitch is in progress. It is intended to recognize the effect of the polymer on the development of the mesophase and on the yield of semi-coke in the processes of carbonization and of synergistic phenomena. This analysis will be based on a comparison with the mechanism of thermal decomposition of pure components that are now investigated.

References

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