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THE USE OF THERMOANALYTICAL METHODS FOR EVALUATION OF CARBONACEOUS MATERIALS AFTER THERMAL DEGRADATION

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ABSTRACT

In this study the possibility of using of thermoanalytical methods for the identification of changes in carbon-containing natural and synthetic materials after their thermal degradation is examined. For this purpose the thermograms of various cokes and char residues of polyvinylchloride, polystyrene, polyamide prepared under different temperatures were compared. The results obtained can be utilized in cokes quality characterization and fire investigation in case of polymer char residues.

INTRODUCTION

In this study the possibility of using of thermoanalytical methods for the characterization of solid char residues from polymeric materials is examined. The char residues remain due to uncomplete combustion of plastics during the fire. Valuable information required for the purpose of fire investigation can be provided by relevant analyses of solid residues. These analyses can also help when estimating the intensity of heat, which influenced the materials in the fireground. Furthermore, our interest concerns the formation of solids during the carbonization. The characteristics of the carbonaceous materials were obtained by microscopy, elemental analyses, IR spectroscopy, NMR-spectroscopy of the extract and other analytical methods.

By comparison the thermoanalytical data of char residues of the same polymer prepared by the isothermal degradation at various temperatures specific relations were found. In this way, carbonaceous residues of polyvinylchloride (PVC), polystyrene (PS), polyamide (PA) and coal pitch coke (CPC) were analysed.

EXPERIMENTAL AND RESULTS

Specimens of PVC (softened), PS (Krasten 552), PA (Silamid 6) and their char residues produced by isothermal degradation at various temperatures in the range of 250 to 900 °C were submitted to the thermal analyses (Derivatograph MOM Budapest).

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PVC char residues

A complete dehydrochlorination up to 300°C is characteristic for the thermal degradation of PVC. After the hydrogen chloride liberation (i.e. above 300 °C) a gradual exothermal maximum shift takes place when the temperature increases. The same shift can be also observed in the temperature corresponding with the peak tops on the DTG curves. The value of the thermograms are resumed in Tab. 1.

PS char residues

Polystyrene belongs to the polymers after degradation of which only a small char residue (1 to 5 weight %) in the form of brittle high-porous char remains. The result is that the exothermal maximum of all char residues are in the temperature range of 400 to 470 °C.

PA-6 char residues

PA-6 carbonaceous residues show three characteristic exotherms on the DTA curve. The first two of them form characteristic double peak in the range of 350 to 430 °C where the shift of the second exotherm to the lower temperatures takes place with the increasing temperature under which the samples were prepared.

The third exotherm above 800 °C is not observed.

The characteristics obtained are resumed in Tab. 2.

Additional characteristics were obtained when analysing the DTG and TG curves. Two stages of weight loss can be observed on the TG curves. The h_1/h_2 relation (as indicated in the TG curve in fig. 1) varies significantly in dependence on the temperature under which the char residue has been prepared. The decrease of values of h_1/h_2 relation vs the degradation temperatures shows Tab. 3.

The characteristic course of the DTG curve corresponds with the stages of weight loss on the TG curves (fig. 1). This characteristic course of the DTG curves can be also considered as a feature for identification of the degraded PA. The peak position shifts to the lower temperature values in the dependence on the increasing temperature under which the char was prepared (Tab. 2).

Other carbonaceous materials

The thermal analysis was used to find structural changes of various carbonaceous materials in the course of the thermolysis.

Table 1

The peak shift on the DTA, DTG curves vs temperature of preparation of the char residues (PVC)

No	Temperature (°C)		
	preparation of char residues	DTA-exoth.	DTG-peak
1	-	380	265
2	400	463	491
3	500	480	532
4	550	513	533
5	870	724	778

Table 2

Characteristic exotherms of PA-6 carbonaceous materials. The shift of DTG-peaks

No	Temperat. of prepar. of char residue (°C)	Temperature of exothermal peaks (°C)			
		1.exoth.	2.exoth.	3.exoth.	DTG-peak
1	-	340	396	518	402
2	350	350	430	526	392
3	380	375	420	497	388
4	400-410	342	417	507	386
5	840-850	352	410	-	334

Table 3

The dependence of h_1/h_2 relation vs degradation temperature of PA

Temperature of prepar. of char residues (°C)	h_1/h_2 relation on the DTG curves
-	12,1
350	3,0
400-410	1,7
840-850	0,25

Table 4

Diferential thermal analyses of carbon samples

Sample	Temperature (°C)		
	T_1	T_v	ΔT
pitch	400	550	150
semicoke A	490	540	50
semicoke B	625	720	95
coke (950 °C)	610	730	120
coke (1300°C)	640	750	110

For the analysis a powder specimen in the mixture with Al_2O_3 was used. For the interpretation of the records the DTA curve was used. Exothermal peaks corresponding with the exothermal oxidation reaction were evaluated by the starting temperature of the oxidation reaction (in accordance with the reccomendation of ICTA). The results are summarized in Tab. 4. Both the temperature of the exothermal reaction peak T_v and the value of difference between T_v temperature and the beginning of the exothermal reaction T_1 simultaneously increase with the increasing temperature.

CONCLUSIONS

On the basis of these partial results attained for the carbonized products of several synthetic polymer materials and coke chemical semi-products, the methods of the thermal analysis (praticularly TG and DTA analysis) can be recommended to identify the polymer material, which was thermally degraded. By comparison of char residues obtained from the same polymer the intensity of their thermal degradation may be found. In the case of the coke chemical material the structural changes in the mass, and so the quality of the carbonized material can be determined.

REFERENCES

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Fig.1 The h_1/h_2 relation of PA-6 char residues