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Note

Pyrolysis gas chromatography of capron (nylon-6) fibre stabilized with ethers of 4-oxydiphenylamine

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Of the amine stabilizers of capron (nylon-6) fibre, the ethers of 4-oxydiphenylamine (H-1, H-2, etc.) are advantageous as they cause relatively little dyeing of polyamides[1]. The thermal stabilizer H-1 is widely used in the chemical fibre industry[2].

In this work, pyrolysis gas chromatography (GC) was used to study the gaseous products of the thermal analysis of capron fibre and to compare the effect of ethers of 4-oxydiphenylamine of different structure[3]. The method has been used earlier by Alishoyev *et al.*[4] to compare stabilizers of polypyromellitimide.

EXPERIMENTAL

The method of pyrolysis GC, the apparatus, the construction of the reactor–pyrolyzer and the scheme for the analysis of the pyrolysis products have been used earlier[5] for the identification of different natural and chemical fibres.

The pyrolysis of a 2-mg sample is carried out in an atmosphere of inert gas in the reactor at 200–800° for 10–12 sec, then the pyrolysis products enter the separating column of the chromatograph in the stream of inert gas (carrier gas) and from there pass into the detector (YX-1 with a katharometric detector). The pyrolysis products were analysed in column I, containing medicinal charcoal, in column II, containing Chromosorb P (60–80 mesh) and 2,4-dimethylsulpholane (80:20), and in column III, containing Chromosorb P (60–80 mesh) and poly(ethylene glycol) PEG-1500 (80:20).

RESULTS AND DISCUSSION

Thermostabilized capron is used in the production of tyres that are subjected to variable mechanical and thermal overloads during use, and pyrolysis GC can give useful information about the processes that occur when these fibres are used. As the decomposition of different additives would also influence the decomposition of

TABLE I

PYROLYSIS PRODUCTS OF CAPRON (NYLON-6) AND THERMOSTABILIZERS AT 400°

Nos. 1–4 were determined in column I, 5–6 in column II and 17–21 in column III.

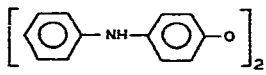
No.	*Pyrolysis product*	*Capron*	*Stabilizers*									
			H-1	*H-3*	*HC-1*	*HC-2*	*H-2*	*H-60*	*H-4*	*H-61*	*H-62*	*H-63*
1	H_2	tr.*	tr.	tr.	–	–	–	–	–	–	–	–
2	CO	+++**	+++	++	++	++	++	++	++	++	++	++
3	CH_4	+	+	+	+	–	–	tr.	tr.	tr.	tr.	+
4	CO_2	++	–	–	–	–	–	–	–	–	–	–
5	1-4 + C_2H_6	+++	+++	++	++	+	+	++	++	++	+	++
6	C_2H_4	+++	+++	+	+++	+++	+++	++	+++	+++	++	+++
7	C_3H_8	+++	++	++	+	+	+	+	+	++	++	++
8	C_3H_6	+++	+	+	+	tr.	–	+	+	++	++	++
9	2,2-Dimethylpropane	tr.	–	–	+	tr.	–	–	+	++	+	+
10	C_2H_2	+	tr.	–	–	–	–	–	tr.	tr.	–	tr.
11	Butene-1	+	tr.	tr.	–	–	–	–	+	+	+	+
12	Isobutene	tr.	–	–	–	–	–	–	tr.	tr.	–	tr.
13	*trans*-2-Butene	tr.	–	–	–	–	–	–	–	+	+	tr.
14	*cis*-2-Butene	tr.	–	–	–	–	–	–	–	+	+	tr.
15	2,2-Dimethylbutane	++	–	–	–	–	–	–	+	+	+	+
16	Pentene-1	tr.	–	–	–	–	–	–	tr.	+	+	+
17	Acetaldehyde	+	++	+	+	tr.	–	tr.	tr.	–	–	+
18	Benzene	+	+	tr.	tr.	tr.	tr.	+	tr.	tr.	–	tr.
19	Acetonitrile	+	–	–	–	–	–	–	–	–	–	–
20	Toluene	tr.	–	–	–	–	–	–	–	–	–	–
21	Acetone	–	–	–	–	–	+	–	–	–	–	–

* tr. = trace.

** +, ++, +++ = increasing amounts of pyrolysis products.

polyamides, the dependence of the pyrolysis products of stabilizers on their structure has also been investigated.

Samples of capron fibre containing amine stabilizers of the general formula



where R = $(CH_2)_x$ and x = 2 (H-2), 3 (H-60), 4 (H-4), 5 (H-61), 6 (H-62) or 10 (H-63);
R = $-(CH_2-CH_2)_2O$ (H-1); R = $-[CH_2-CH(OH)]_2O$ (H-3);
R = $-(CH_2CH_2)_2S$ (HC-2); or R = $-(CH_2-CH_2-O-CH_2-CH_2)_2S$ (HC-1) were investigated by pyrolysis GC.

In Table I the qualitative compositions of the pyrolysis products of capron fibre and the stabilizers are presented. The range of pyrolysis products of capron fibre does not depend on the type of stabilizer used, but in the presence of a stabilizer the yields of the individual pyrolysis products decrease.

The composition of the pyrolysis products of stabilizers depends on their structure. As a rule, stabilizers with short aliphatic chains decompose to a lesser extent and the pyrolysis products consist of only low-molecular-weight compounds. The yield of carbon monoxide in the pyrolysis products increases with increase in the length of the aliphatic chains of the stabilizers (Tables II and III).

TABLE II

DEPENDENCE OF THE YIELD OF CARBON MONOXIDE ON THE STRUCTURE OF ETHERS OF 4-OXYDIPHENYLAMINE

Stabilizer	*Temperature (°C)*	*CO (mmole per mmole of stabilizer)*	*Stabilizer*	*Temperature (°C)*	*CO (mmole per mmole of stabilizer)*
H-2	400	0.1	H-63	400	0.276
	500	0.18		500	0.363
H-60	400	0.176	H-1	400	0.25
	500	0.358		500	0.60
H-4	400	0.227	H-3	400	0.272
	500	0.368		500	0.62
H-61	400	0.235	HC-1	400	0.51
	500	0.282		500	1.05
H-62	400	0.237	HC-2	400	Trace
	500	0.40		500	0.244

Fig. 1 and Table III show the quantitative dependence of the yield of carbon monoxide and dioxide on temperature and the composition and structure of the stabilizer. At all temperatures the presence of the stabilizer inhibits the formation of carbon monoxide, but the inhibition mechanisms are different at different temperatures. As a rule, in the pyrolysis of the stabilized polyamide at 350° and below the effect of inhibition increases with increase in the distance between the amine inhibition centres in the molecule of the stabilizer, which agrees with results obtained by infrared spectroscopy[6]. In pyrolysis at 400° the inhibition mechanism changes (Fig. 1) and obviously decomposition of the stabilizers occurs (see Table I). The

TABLE III

DEPENDENCE OF YIELDS OF CARBON MONOXIDE AND DIOXIDE IN THE PYROLYSIS PRODUCTS OF POLYCAPROAMIDES ON THE STABILIZER AND TEMPERATURE

Stabilizer	*Concentration (%)*	*CO (mmole per mole of capron)*			*CO_2 (mmole per mole of capron)*		
		350°	*400°*	*500°*	*350°*	*400°*	*500°*
H-2	0.1	0.0427	0.0485	0.202	0.059	0.069	0.0775
	0.5	0.044	0.0565	0.173	0.069	0.0795	0.11
H-60	0.1	0.0427	0.0607	0.193	0.054	0.0668	0.066
	0.5	0.0427	0.0565	0.246	0.064	0.0619	0.067
H-4	0.1	0.0427	0.0565	0.21	0.054	0.09	0.095
	0.5	0.0427	0.0607	0.302	0.059	0.09	0.085
H-61	0.1	0.0416	0.0607	0.278	0.0495	0.069	0.082
	0.5	0.044	0.0685	0.194	0.0615	0.0744	0.129
H-62	0.1	0.039	0.0585	0.202	0.064	0.0744	0.0665
	0.5	0.0455	0.0645	0.226	0.069	0.069	0.085
H-63	0.1	0.0378	0.0645	0.262	0.051	0.069	0.0925
	0.5	0.039	0.0685	0.198	0.046	0.069	0.072
HC-1	0.1	—	0.0363	0.218	—	0.049	0.095
	0.5	—	0.040	0.25	—	0.051	0.095
HC-2	0.1	Trace	0.040	0.234	Trace	0.075	0.077
	0.5	Trace	0.040	0.186	Trace	0.077	0.080
Unstabilized capron	—	0.044	0.0645	0.17	0.046	0.0668	0.064

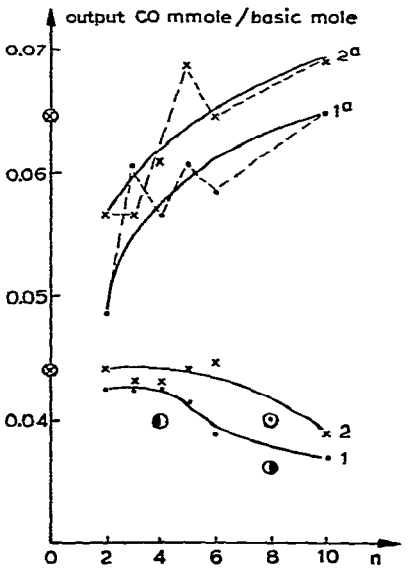


Fig. 1. Dependence of the yield of carbon monoxide on temperature, chemical structure and amount of stabilizer in the pyrolysis of polycaproamide fibre. 1, 350°, 0.1% of stabilizer; 1a, 400°, 0.1% of stabilizer; 2, 350°, 0.5% of stabilizer; 2a, 400°, 0.5% of stabilizer. ⊗, unstabilized capron, 350° and 400°; ◑, stabilized with 0.1% of HC-1, 400°; ⊙, stabilized with 0.5% of HC-1, 400°; ◐, stabilized with 0.5% of HC-2, 400°. n = Number of atoms in the aliphatic part of the amine.

yield of carbon monoxide in the pyrolysis products increases slightly with an increase in the amount of the stabilizer from 0.1 to 0.5% (w/w).

Sulphur-containing inhibitors (HC-1 and HC-2) inhibit the formation of carbon monoxide in the pyrolysis of capron much more than other inhibitors of the H-type. The formation of carbon monoxide in the pyrolysis of fibres that contain the inhibitors HC-1 and HC-2 begins at 350°.

CONCLUSIONS

The overall composition of the pyrolysis products of polycaproamide fibres has been studied by pyrolysis GC. It was found that all stabilizers consisting of ethers of 4-oxydiphenylamine inhibit formation of carbon monoxide. The quantitative dependence of the yield of carbon monoxide on the structure of the stabilizer in the pyrolysis of the capron fibre has been established.

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