Journal of Thermal Analysis, Vol. 50 (1997) 889-896

THERMAL STABILITY AND COMBUSTIBILITY OF BUTYL AND HALOGENATED BUTYL RUBBERS

G. Janowska, L. Slusarski, M. Koch[1] *and U. Wincel*[1]

Institute of Polymers, Technical University, Łódź
[1]Military Institute of Chemistry and Radlometry, Warsaw, Poland

(Received April 2, 1996; in revised form November 5, 1996)

Abstract

The effects of flame retardants such as hydrated aluminium oxide, antimony trioxide and chloroparaffin on the thermal properties and flammability of sulphur vulcanizates of butyl and halogenated butyl elastomers were studied. The thermoanalytical curves of the elastomers were interpreted. Greater tendencies to thermal degradation were observed for halogenated butyl elastomers than for the original butyl rubber elastomer. This was confirmed by elastomer combustibility studies. The use of these flame retardants allowed the formation of self-extinguishing vulcanizates of the investigated elastomers.

Keywords: combustibility, decomposition, degradation, destruction, flame retardant, flammability, scission, thermal analysis

Introduction

Because of their special features, e.g. high thermal and chemical resistance, low permeability of gases and good mechanical properties under static and dynamic conditions, butyl rubbers, i.e. isobutylene and isoprene or butadilene copolymers and halogenated butyl rubbers, are widely used in military technology. For this reason they have been extensively studied in our laboratories [1–7]. In this work, the effects of flame retardants on the thermal properties and flammability of butyl, chlorobutyl and bromobutyl rubbers and their sulphur vulcanizates are demonstrated. The compositions of rubber mixtures were chosen by taking into consideration their rheological and mechanical properties.

Experimental

Materials

The materials investigated were elastomers: butyl-BK-1675T, chlorobutyl-HT-1066 (1.12% Cl), bromobutyl Polysar X2 (1.97% Br), and their sulphur vul-

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

canizates without or with the following mixture of flame retardants: hydrated aluminium oxide 70.6%, chloroparaffin (70.4% Cl) 17.7%, antimony trioxide 11.7%. The elastomer compositions contained 38% of the flame retardant mixture.

Methods

Rubber compounds with the compositions given in Table 1 were vulcanized in an electrical press at 150°C. The optimum vulcanization time, τ_{09}, was determined with a Monsanto rheometer.

Table 1 Results of thermal analysis and complementary studies of butyl, chlorobutyl and bromobutyl rubbers

Symbol of rubber	$\overline{M}_n$	$\overline{M}_{n'}$	$K_d=\frac{\overline{M}_n}{\overline{M}_{n'}}$	E_a/kJ mol^{-1}
BK1676T	194 400	37 200	5.23	127.6
HT1066	131 000	11 200	11.70	121.7
Polysar X2	103 900	9 400	11.05	123.7

$\overline{M}_n$ – Molecular weight or rubber
$M_{n'}$ – Molecular weight of rubber heated to 290°C
K_d – degradation degree
E_a – destruction activation energy

Thermal analysis was carried out with the Paulik-Paulik-Erdey derivatograph under the following conditions: atmosphere: air, standard substance: Al_2O_3, temperature range: 25–800°C, sample mass: 90 mg, heating rate: 7.9°C min^{-1}. Samples for analysis were prepared by disintegration of the elastomer or vulcanizate into small cubes about 1 mm in size. Destruction activation energies were calculated from the thermal curves by the Freeman-Carrol method [8]. Thermal stability indexes T_5 and T_{50}, corresponding to a 5 and 50% loss in mass, respectively, were determined from the TG curves. The molecular weights of polymers before and after heating to 290°C were determined with a Knauer osmometer, with toluene as solvent.

The flammabilities of the polymers and their sulphur vulcanizates were determined by the oxygen index (OI) method according to ASTM D2863-74, and also in air. In the second case, a sample clamped in the vertical position was ignited within 15 s and the burning time was measured.

Results and discussion

Figures 1–3 show TG, DTG and DTA curves of the investigated polymers. The thermal transitions in the temperature range 220–330°C indicate thermooxi-

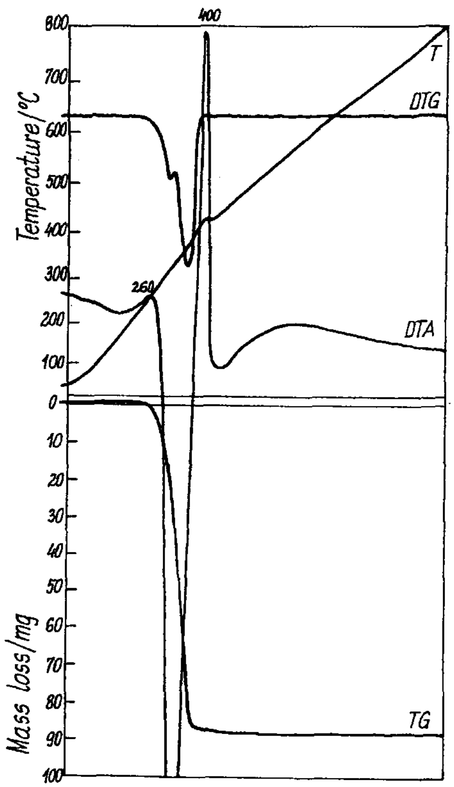
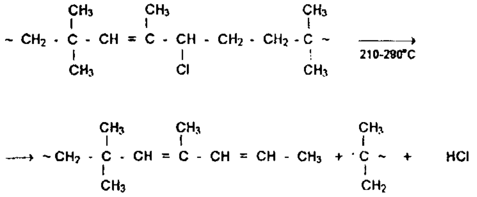


Fig. 1 Thermoanalytical curves of butyl BK-1675T

dative reactions and degradation accompanied by destruction of the elastomers (Tables 1 and 2). The endothermic peaks at 390°C in the DTA curves are connected with polymer destruction. A very small residue burns out at *T*>400°C.

Greater degrees of thermal degradation were observed for the helogenated butyl rubbers than for the butyl rubber. This is surely due to dehydrohalogenation in the temperature range 210–290°C. The elementary analysis results revealed that the halogenated butyl rubbers heated to 290°C were free from halogen. We anticipated dehydrochlorination and degradation to occur as follows:



$$\sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-\underset{Cl}{CH}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}\sim \xrightarrow[210\text{-}290°C]{}$$

$$\longrightarrow \sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH=CH-CH_3+\cdot\underset{CH_2}{\overset{CH_3}{C}}\sim + HCl \qquad (1)$$

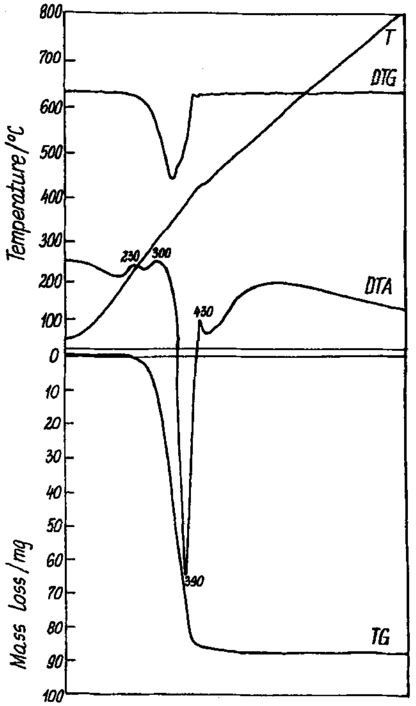


Fig. 2 Thermoanalytical curves of chlorobutyl HT-1066

Simultaneously, thermooxidative reactions occurred because the samples were heated in air.

Sulphur vulcanization did not essentially change the thermal curve profiles. The presence of silica (Ultrasil VN3 in the vulcanizate caused an increase in the mass remaining after heating of a sample at 800 °C [9].

The flame retardants used reduced to some extent the thermal stabilities of the vulcanizates. This holds for both the T_5 and the T_{50} values (Table 2 and Fig. 5). The considerable volatility and thermal degradability of the chloroparaffin is the most probable reason for this effect. A further increase in the sample residue after heating to T=800°C was observed, corresponding approximately to the content of Sb_2O_3. The results of elastomer flammability investigations are listed in Table 3. In contrast with our expectation, uncrosslinked halogenated butyl rubbers were a little more flammable than butyl rubber. This tendency was also observed for the flammability of crosslinked elastomers tested in air. In our opinion, the observed effect is caused by dehydrohalogenation of the isoprene units at elevated temperature, which favours degradation of an elastomer.

It could not be excluded that HCl or HBr split off in the first stage caused ionic decomposition of the peroxy group formed. We earlier recognized the ability of

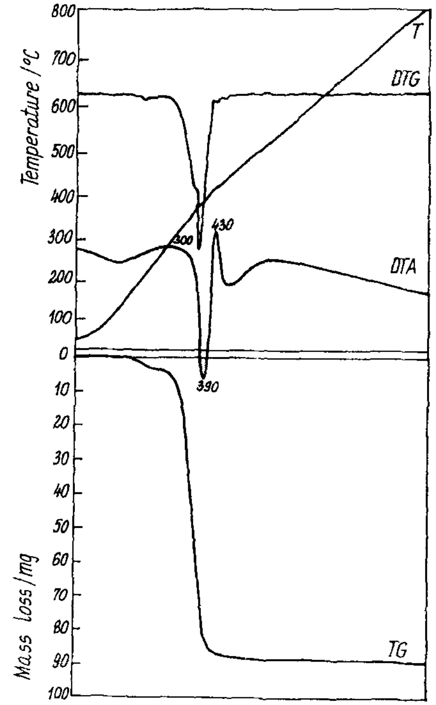


Fig. 3 Thermoanalytical curves of bromobutyl Polysar X2

diene monomer units and other unsaturated groups, contained in butyl rubbers to undergo free radical crosslinking [1].

Besides the mechanisms of the reactions, the behaviour of samples during burning in air atmosphere is also symptomatic. In the case of the halogenated butyl rubbers, a large amount of liquid products is formed, which flow along the sample, acting as heat transfer agent. This process also occurs during burning of the butyl rubber, but to a considerably lesser degree. Thus, the boundary layer between the uncrosslinked polymer sample and the flame is composed of strongly degraded macromolecules and liquid products of their decomposition [1, 9]. Crosslinking of the rubber of the addition of colloidal silica, Ultrasil VN3, reduces their flammability. A more thermally stable boundary layer is formed in this case [9]. Ultrasil VN3 can also absorb volatile flammable products of elastomer destruction. The addition of a chloroparaffin at Sb_2O_3 mixture affords a possibility to obtain self-extinguishing vulcanizates. Sb_2O_3 alone exerts no perceptible flame-retardant action [10–12]. Together with halogen-containing compounds, however, it produces a marked synergistic effect. No entirely satisfactory interpretation has yet been offered for this. It is believed, however, that the most important reactions take place in the gas phase. A change in radical chain

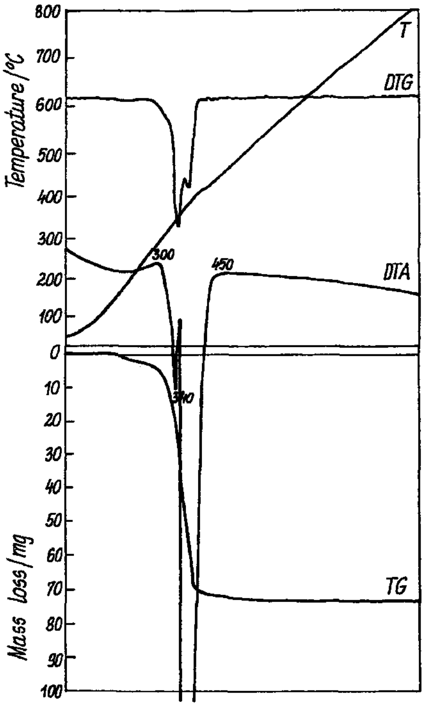


Fig. 4 Thermoanalytical curves of butyl BK-1675T sulphur vulcanizate

mechanism is considered. In the theory proposed by Pitts, $SbCl_3$ is formed via the intermediate SbOCl, which is actually the effective agent. Sb_2O_3 and HCl first yield SbOCl, which breaks down to $SbCl_3$ over a relatively wide temperature range [13]:

$$Sb_2O_3 + 2HCl \xrightarrow{\sim 250^\circ C} 2SbOCl + H_2O \tag{2}$$

$$5SbOCl \xrightarrow{245-280^\circ C} Sb_4O_5Cl_2 + SbCl_3 \tag{3}$$

$$4Sb_4O_5Cl_2 \xrightarrow{410-475^\circ C} 5Sb_3O_4Cl + SbCl_3 \tag{4}$$

$$3Sb_3O_4Cl \xrightarrow{475-565^\circ C} 4Sb_2O_3 + SbCl_3 \tag{5}$$

$SbCl_3$, as the actual flame retardant, acts as a radical interceptor like HCl or HBr. The trivalent antimony facilitates the formation of halogen radicals, which affect the radical chain reaction of flame spread. It is also probable that $SbCl_3$

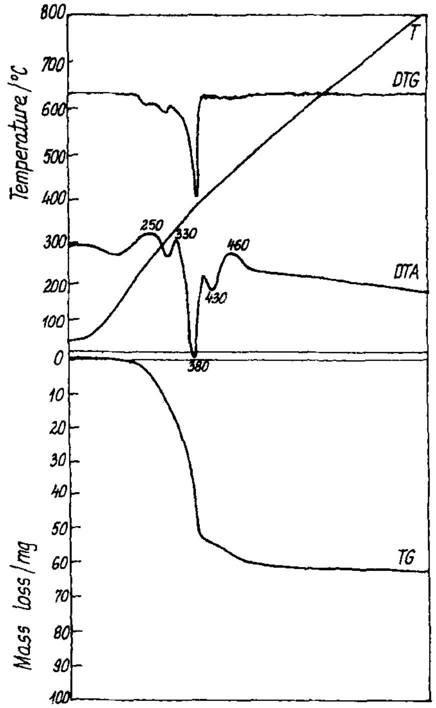


Fig. 5 Thermoanalytical curves of butyl BK-1675T sulphur vulcanizate containing flame retardants

Table 2 Results of thermal analysis of rubbers and their vulcanizates

Symbol of rubber	T_5/°C	T_{50}/°C	$T_{\text{range of decomposition}}$/°C	Sample residue at 800°C/%
BK-1675[1]	295	360	295–450	1.1
HT-1066[1]	285	350	285–450	2.2
Polysar X2[2]	295	370	295–470	1.1
BK-1675[2]	285	370	285–460	18.9
HT-1066[2]	285	370	285–480	21.1
Polysar X2[2]	285	380	285–500	21.1
BK-1675[3]	250	380	250–500	31.1
HT-1066[3]	240	380	240–500	31.1
Polysar X2[3]	240	390	240–500	32.2

[1] rubbers

[2] vulcanizates

[3] vulcanizates containing flame retardants

Table 3 Flammabilitz determination results

Symbol of polymer	Oxygen index value (OI)	Flammability in air, combustion time/s
BK 1675T[1]	0.238	350
HT-1066[1]	0.227	230
Polysar X2[1]	0.216	220
BK 1675T[2]	0.296	390
HT-1066[2]	0.296	360
Polysar X2[2]	0.304	370
BK 1675T[3]	0.320	1
HT-1066[3]	0.324	self-extinguishing, 3
Polysar X2[3]	0.326	5

[1] rubbers
[2] vulcanizates
[3] vulcanizates containing flame retardants

evolves as a heavy vapour which forms a layer over the condensed phase, stops oxygen attack and thus chokes the flame [10].

The halogenated butyl rubbers adhesion to textiles and other materials is better than does butyl rubber. Our investigations proved that these rubbers protected with appropriate flame retardants could be used as fabric coatings intended for special clothing.

References

1 L. Ślusarski, G. Janowska, J. Thermal Anal., 19 (1980) 435.
2 L. Ślusarski, J. Thermal Anal., 29 (1984) 905.
3 L. Ślusarski and G. Janowska, Polymery, 27 (1982) 13.
4 G. Janowska, Materials of Conference 'Polymer Modification', Duszniki-Zdrój-Poland 1993, p. 316.
5 G. Janowska, Proc 6th Conference on Calorymetry and Thermal Analysis, Zakopane-Poland, 1994, P4/1.
6 L. Ślusarski, G. Janowska, M. Koch, U. Wincel, Bulletin of Military Institute of Chemistry and Radiometry, 2 (1994) 153.
7 G. Janowska, L. Ślusarski, M. Koch, U. Wincel, Polymery, 40 (1995) 690.
8 E. S. Freeman and B. Carrol, J. Phys. Chem., 62 (1958) 394.
9 G. Janowska and L. Ślusarski, J. Thermal Anal., 45 (1995) 1579.
10 J. Troitzsch 'International Plastics Flammability Handbook', Hanser Publishers, Munich, Viena, New York 1990, p. 46.
11 G. Janowska, L. Ślusarski, B. Wojciechowska, Proc. of Conference 'Progress in the Rubber Industry, Elastomers '95, Warsaw-Poland 1995, p. 69.
12 G. Janowska, Proc. of International symposium Flame '95, Poznan-Poland 1995, p. 13.
13 J. J. Pitts, P. H. Scott and D. G. Powell, J. Cell. Plast., 6 (1970) 1, 35.