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THERMAL STABILITY AND FLAMMABILITY OF BUTADIENE-ACRYLONITRILE RUBBER CROSS-LINKED WITH IODOFORM

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The paper discusses the results of thermal analysis and flammability of butadiene-acrylonitrile rubber, Perbunan NT 1845 of Bayer, cross-linked with iodoform. The properties of the iodoform vulcanizate have been compared with those of peroxide vulcanizate. The thermal analysis has been performed in air with use of a Derivatograph under air and nitrogen atmosphere as well as dynamic scanning calorimetry (DSC). The flammability of vulcanizates has been determined by the method of oxygen index and in air. The toxicity of the thermal decomposition and combustion products of the vulcanizates under investigation has been also determined. Based on complementary examinations, DTA and DSC curves have been interpreted from the point of view of thermal transitions of the conventionally and non-conventionally cross-linked nitrile rubbers. The glass transition temperature of the cross-linked polymer both in cooling and heating has been determined.

Keywords: *combustion products of elastomer, elastomer, flammability, thermal properties, toxicity of thermal decomposition*

Introduction

The cross-linking of elastomers consisting in spatial combining macromolecules with cross linkages, resulting in the formation of a three-dimensional network, is one of the conditions for a high elasticity to occur. A spatial network is mostly formed by conventional procedures such as the use of cross-linking compounds, high-energy radiation or aggregation of rigid blocks or ionic groups [1–4]. Interesting properties of polymeric materials such as limited flammability, increased stability and mechanical strength, antiseptic behaviour, improved electric conductivity, can be obtained by non-conventional cross-linking [5, 6]. The present paper shows unreported in the literature results of studies on the thermal stability and flammability of butadiene-acrylonitrile rubber that has been non-conventionally cross-linked with iodoform.

Experimental

The rubber under investigation, Perbunan NT1845 (NBR18) of Bayer, containing 18% by wt. of acrylonitrile, was cross-linked with iodoform, Aldrich Kat. No. 10.945-2. The elastomer mixture consisted of 100 parts by wt. NBR18 and 5 phr (parts by wt. per hundred parts by wt. of rubber) iodoform. The properties of the iodoform vulcanizate, WI, were compared with those of a rubber cross-linked in a conventional process with dicumyl peroxide, W. The composition of the conventional elastomer mixture was as follows: 100 parts NBR18, 0.4 phr dicumyl peroxide (purity 95%) of Merck-Schuchard, 5 phr ZnO and 1 phr stearic acid.

Rubber compounds prepared with the use of a laboratory rolling mill at room temperature were vulcanized in an electrical press at 160°C for a time, τ_{09}, determined by means of a WG2 vulcameter of Zach Metal Chem (Poland).

The cross-linking degree of rubbers, $1/Q_w$, and the content of sol fraction in vulcanizates were determined on the basis of equilibrium swelling measurements, Q_w, in toluene at 25°C for 48 h. During the swelling measurements, the solvent was replaced four times.

Limiting viscosity number of liquid products of thermal decomposition was determined using an Ubbelohde viscometer, with toluene as solvent. The temperature of measurements was 25°C.

The thermal analysis of vulcanizates was carried out by means of Derivatograph, Paulik–Paulik–Erdey system (MOM, Hungary) and differential scanning calorimetry, DSC-204 of Netzsch. The analysis was carried out in air using weighed portions of 90 mg at heating rate of 7.9°C min^{-1} within the temperature range from 20 to 800°C. In the case of DSC, the measurements were performed in inert gas, using portions of about 5 mg at heating rate of 10°C min^{-1} within the temperature range 20–100 and –100–500°C.

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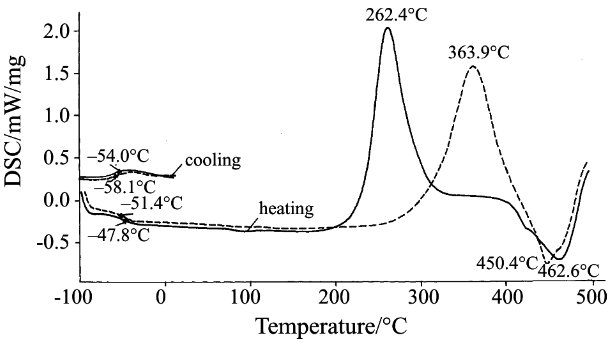

Fig. 1 DSC curves of iodoform vulcanizate (WI)

The flammability of vulcanizates was determined by the method of oxygen index, using an apparatus of our own design, according to the standard PN-ISO 4589-2. The flammability in air was also tested, using the same specimens as in the case of oxygen index. The specimen placed vertically were ignited for 15 s by means of burner supplied with a propane-butane mixture, and then the combustion time was measured [7].

The toxicity of the thermal decomposition and combustion products was tested by a chemical quantitative analysis of emitted CO, CO_2, NO_2, HCl and SO_2. In the case of the iodoform vulcanizate, the emission of HI was determined instead of HCl. The thermal decomposition and combustion of vulcanizate samples were carried out at 450, 550 and 750°C in accordance with PN-B-02855:1988. The determined average toximetric index, W_{LC50SM}, included all the mentioned components emitted at particular decomposition temperatures.

Results and discussion

The first exothermic transition of the iodoform vulcatizate recorded in the DSC curve at around 250°C is connected with the thermal cross-linking of elastomer (Fig. 1). This is confirmed by the considerable increase in the rubber cross-linking during heating up to 250°C (Table 1). The thermal cross-linking processes are accompanied by degradation, whose contribution is however low taking into account the sol content in vulcanizate WI before and after its heating. The sample mass decrement taking place during cross-linking is largely due to the decomposition of the cross-linker, which decomposes considerably slower in the polymeric matrix and within a higher temperature range. Under the influence of heat iodoform is intensively decomposed at 160°C (Fig. 2). A violent decomposition of the nitrile rubber cross-linked with iodoform starts at 370°C and initially it is of an exothermic character – a peak at T=390°C, however once the temperature exceeds 400°C, the rate of volatile destruction product formation is considerably higher than the rate of oxygen diffusion to the reaction zone and the decomposition becomes endothermic. The solid residue after sample decomposition, amounting to 24.4%, is almost completely burned as shown by the great exothermic peak in the DTA curve at 590°C (Fig. 3).

The peroxide vulcanizate of nitrile rubber undergoes two exothermic processes at 200 and 340°C (Fig. 2). At the beginning of the former there is a slight mass increment recorded in both TG and DTG curves, brought about by the increase in hydroperoxide groups due to thermooxidative processes. The decomposition of these groups, which are also included in the unheated rubber [8, 9], initiates cross-linking and degradation processes. The considerable increase in the sol content in vulcanizate W under the influence of its heating up to T=200°C indicates that the conventionally cross-linked rubber NBR18 undergoes thermal degradation processes (Table 1). The unchanged value of the cross-linking degree of vulcanizate W heated to the temperature of the first exothermic transition shows that the nodes of spatial network are not thermally decomposable.

Table 1 The results of vulcanizates thermal analysis in air

Parameter	WI	W	
Transition temperature	250	195	335
The sample mass loss/%	3.90	5	2.2
Crosslinking degree/1/Q_w [1]	0.62	0.20	1.19
Sol fraction content/%[2]	5.60	10.42	2.56
Thermal stability indexes/°C [3]	T_5=290 T_{50}=430	T_5=380 T_{50}=415	
Temperature of decomposition maximal rate/°C	430	410	
Decomposition maximal rate/dm/dt[4]	42	101	
Residue after thermal decomposition/%	24.4	22.2	

[1] Cross-linking degree before heating: 1/Q_w (WI)=0.24; 1/Q_w (W)=0.20;
[2] Sol fraction content before heating of vulcanizates: S(WI)=4.30%, S(W)=6.50%;
[3] T_5 and T_{50}: temperature of 5 and 50% of sample mass loss;
[4] Reading from DTG curves;
[5] Minimum increase of sample mass

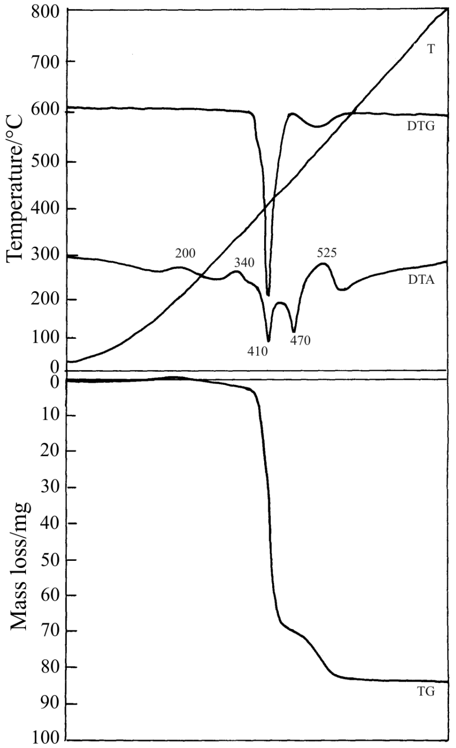

Fig. 2 DTA, TG and DTG curves of iodoform

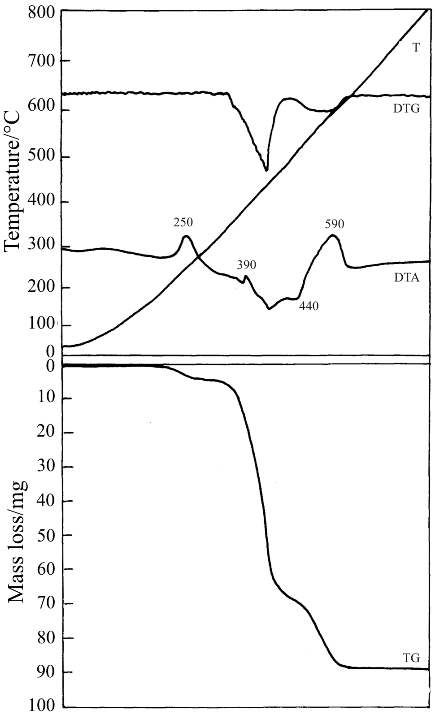

Fig. 3 DTA, TG and DTG curves of peroxide vulcanizate, W

Cross-linking processes take place within the second exothermic transition. The decomposition of the peroxide vulcanizate NBR18 begins at 380°C and proceeds violently with oxygen deficiency – superimposing endothermic transitions in the DTA curve at T=410°C and T=470°C. The residue after the decomposition of W, amounting to 22.2% of the sample mass, is burned at 525°C, thus at a considerably lower temperature than that in the case of WI (Table 1, Figs 1 and 3).

The results of thermal analysis under a neutral gas atmosphere indicate that the type of cross-linker used considerably affects the glass transition temperature, T_g, of the nitrile rubber (Fig. 4, Table 2). The results of our studies show that irrespective of the method of NBR18 cross-linking, the termination of the segmental mobility of macromolecules due to sample cooling takes place at a lower temperature and within a wider temperature range than its start-up in the heating process. The iodoform-cross-linked NBR18 shows considerably higher glass transition temperature than that of the rubber cross-linked with dicumyl peroxide. From the literature review it follows that the cross-linking of nitrile rubber with iodoform during the vulcanization of the rubber compound is accompanied by the polymer modification with iodine [10]. Thus, taking into consideration comparable cross-linking degrees of WI and W, we believe that the higher glass transition temperature of the non-conventionally cross-linked nitrile rubber results just from greater interactions of the iodine-modified macromolecules of polymer.

There is also observed a clear effect of the cross-linker used on the chemical changes in the butadiene-acrylonitrile rubber heated under a neutral gas atmosphere. In the case of WI, they proceed in two stages (Fig. 4). The first one, whose maximum appears at 262°C, results from the use of iodoform, while the other one taking place within the temperature range from 327 to 423°C, without a distinct maximum, is a symptom of the thermal polymerisation of diene mers.

Table 2 The results of vulcanizates thermal analysis in nitrogen

Sample	Cooling process		Heating process			
	T_g/°C	Temperature range of glass transition/°C	T_g/°C	Temperature range of glass transition/°C	Temperature range of crosslinking/°C	T_{dc}/°C
WI	–54.0	–68.3÷–39.8	–47	–58.8÷–36.9	200.0÷422.0	462.6
W	–58.1	–67.5÷–48.7	–51.4	–57.6÷–45.1	260.0÷430.0	450.4

T_{dc} – destruction temperature
The placed in the table temperatures have been determined from DSC curves using Taa computer program of Netzsch.

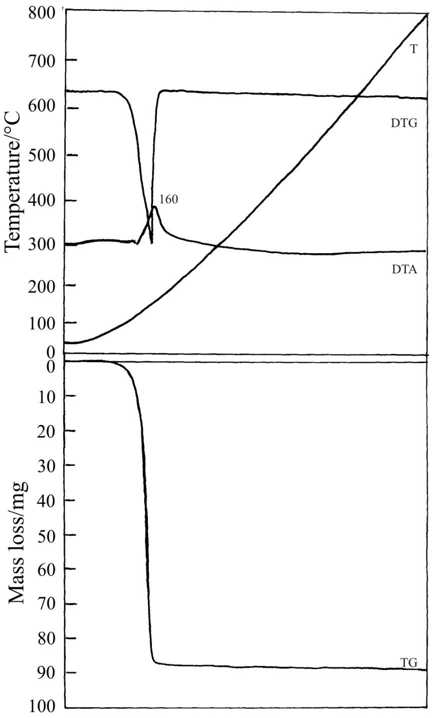

Fig. 4 TG, DTG and DTA curves of iodoform (WI and peroxide), (W vulcanizates)

The thermal polymerisation processes of diene mers of conventionally cross-linked NBR18 rubber take place at 260–430°C and their maximum rate appears at T=364°C (Fig. 4, Table 2). The thermal decomposition of the iodoform and peroxide vulcanizates is recorded in the DSC curves at 463 and 450°C, respectively.

From the TG and DTG curves obtained in air it follows that the rate of WI thermal decomposition is considerably lower than that of W (Fig. 1 and 3, Table 1), which, in our opinion, is due to the partly ionic destruction mechanism of the elastomer cross-linked with iodoform. This is significant information from the point of view of polymer flammability assessment, since the lower destruction rate, the lower amount of volatile and flammable decomposition products pass to the flame, which limits the processes of combustion. Thus, we expected the iodoform vulcanizate to show a reduced flammability, taking also into account a possible fact that during its destruction there will be formed iodine compounds inhibiting the free-radical reactions in the flame [11]. However, from the flammability tests it follows that the oxygen index value of vulcanizate WI is lower than that of W, while both vulcanizates are extinguished in air during comparable periods of time (Table 3). This is considered to be due to the formation of large quantities of liquid products of thermal decomposition during WI combustion; they flow down along the sample as an additional heat source and increase the contact with oxygen, which extends the zone of thermal changes in the solid phase of combustion. These products mainly include a strongly degraded nitrile rubber as from viscometric measurements it follows that the value of their limiting viscosity number [η]=0.0656 dL g^{-1}, while [η] of NBR18 amounts to 1.5413. The effect of liquid flowing-down products considerably exceeds the inhibiting action of iodine compounds in the flame, especially hydrogen iodide, whose presence was found during testing the toxicity of thermal decomposition and combustion products. From unpublished test results obtained at our Institute it follows that the processes of thermal degradation accompanying the combustion of iodoform-cross-linked elastomer can be completely eliminated, e.g. by an addition of antimony trioxide to the rubber compound, which results in a considerably increased OI due to the synergetic effects of iodine and antimony compounds.

Table 3 The results of vulcanizates flammability measurements

Sample	OI	Time of extinguishing/s	Toxicity index/ $W_{LC\ 50}$, g cm^{-3}
WI	0.270	49	12.60[1]
W	0.288	59	9.13

One of the fundamental properties that characterize the polymer behaviour under fire conditions is the toxicity of its gaseous products of thermal decomposition and combustion. The values of toximetric indices show that very toxic products are formed during thermal decomposition and combustion of both vulcanizates, but the toxicity of the conventionally cross-linked nitrile rubber is clearly higher than that of the non-conventionally cross-linked rubber.

Conclusions

The thermal changes in WI, recorded on DTA curves in air and in DSC curve under nitrogen at a temperature preceding its decomposition are associated with the thermal cross-linking of NBR18.

The iodoform-cross-linked nitrile rubber is characterised by a higher glass transition temperature than that of the corresponding rubber cross-linked with dicumyl peroxide. It is caused by increasing of macromolecular interactions of the elastomer modified with iodine during the rubber mix vulcanization.

The nitrile rubber cross-linked either with iodoform or dicumyl peroxide belongs to materials, which when ignited stop burning in air. The flammability of the iodoform vulcanizate determined by the OI test is higher than that of the peroxide vulcanizate despite its lower destruction rate under thermooxidative conditions. This is due to the formation of large quantities of liquid destruction products during WI combustion, which flowing down along the sample tested, are an additional factor of heat transfer, make the contact with oxygen easier and extend the zone of thermal reactions in the solid phase of combustion.

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