

Flammability of vulcanizates of diene rubbers

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Abstract This article discusses the effect of the cross-linking of diene elastomers (BR, SBR, NBR), with the use of an organic peroxide or sulfur, on their flammability and fire hazard. Flammability tests were carried out by the method of oxygen index, combustion time (in air) and ignition temperature measurements. Fire hazard was determined on the basis of test results obtained by means of a cone calorimeter. Toxicometric coefficients ($RTFH_{CO/CO_2}$ and W_{LC50SM}) and the emission of polycyclic aromatic hydrocarbons (PAH) were determined. Test results were interpreted from the point of view of the chemical constitution of elastomer macromolecules as well as the structure of its network structure.

Keywords Spatial network · Diene rubbers · Flammability · Fire hazard · Toxicometric indices · Polycyclic aromatic hydrocarbons

Introduction

Elastomers constitute a large group of macromolecular compounds including among others diene homo- and copolymers, vinyl polymers, polyurethanes, polysiloxanes, polyethers as well as inorganic polymers. The majority of elastomers are flammable and only few of them can be recognized as flame-retardant or non-flammable. Generally, the flammability of elastomers depends on carbon and hydrogen contents in a macromolecule, varying within wide limits from 85% C and 15% H to 0% H, e.g. in non-flammable nitrosofluoric rubbers [1, 2].

The cross-linking of elastomers as well as the method of cross-linking considerably influences the course of their combustion. The combustion of non-cross-linked elastomers is accompanied by the formation of considerable amounts of liquid products of their thermal decomposition and combustion that constitute an additional source of heat and facilitate contact with oxygen. The formation of a spatial network, i.e., the combination of polymer macromolecules with crosswise bonds, prevents this phenomenon to an extent dependent on the chemical constitution and physical structure of elastomer, and the structure of spatial network and cross-link density [2–5]. The formation of liquid products of thermal decomposition and combustion can be considerably limited or eliminated by fillers added to a polymeric blend, whose cross-linking leads to filled elastomeric materials [5, 6]. A particular role in this respect is played by fillers of nano-dimensions, whose use allows one to obtain nanocomposites of unique properties [5–7].

This article presents our findings concerning the flammability and fire hazard of butadiene, butadiene–styrene and butadiene–acrylonitrile rubbers, conventionally cross-linked by means of sulfur or dicumyl peroxide (DCP), commonly used in rubber industry, taking into account the

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toxicity of gaseous products of thermal decomposition and combustion.

Experimental

Materials

We examined the following diene rubbers: cis-1,4-polybutadiene, homopolymer of butadiene, SKD II (BR), containing 87–93% of cis-1,4 mers from Voronezhsyntheskauchuk Russia, butadiene–styrene rubber, KER 1500 (SBR), containing 23.5% of combined styrene, from Synthos S.A, and butadiene–acrylonitrile rubber, NBR 2255V (NBR), containing 22% of combined acrylonitrile from Bayer.

The rubbers were cross-linked by means of DCP in the presence of zinc oxide (ZnO) or with the use of sulfur in the presence of ZnO and *N*-cyclohexyl-2-benzoyl sulfenamide (Tioheksam CBS). The peroxide vulcanizates of butadiene, butadiene–styrene and butadiene–acrylonitrile rubbers were denoted with BN, SN, and NN symbols, respectively. The sulfur vulcanizates of butadiene, butadiene–styrene and butadiene–acrylonitrile rubbers were denoted with BS, SS, and NS symbols, respectively.

Methods

Elastomeric blends were prepared at room temperature by means of a laboratory roll mill followed by vulcanization in steel molds placed between electrically heated press plates. The optimal time of vulcanization (τ 0.9) at a temperature of 160 °C was determined by means of a WG-2 vulcameter according to Standard PN-ISO 3417:1994.

The flammability of vulcanizates was determined by the method of oxygen index (OI) with the use of an apparatus from Fire Testing Technology Limited. For flammability tests, 50 × 10 × 4 mm samples were prepared. Using a constant nitrogen linear flow rate amounting to 40 ± 2 mm × s⁻¹ (volume flow rate 10.5 dm³/min), through a test column with a diameters of 75 mm, the oxygen concentration was selected so that the sample under testing was burned within time $t = 180$ s. The sample top was ignited for 5 s by means of a propane-butane gas burner. The numerical value of OI was calculated from the following formula:

$$OI = (C_F + k \times d) \div 100$$

where C_F is the final oxygen concentration, at which a sample is burned within 180 s, d is the step size between oxygen concentration changes during the test procedure, and k is the coefficient of proportionality.

In flammability measurements by the method of oxygen index, we did not take into account the sample burning

down processes in apparatus holder as it would require a higher oxygen concentration in the oxygen–nitrogen mixture flowing through the measurement column resulting in an increased value of OI confirmed in our previous paper [2].

We also tested flammability in air using identical samples as in the case of OI method. A sample in a vertical position was ignited with a gaseous burner as before for 5 s and its combustion time (t_s) was measured [2].

The temperature of ignition (T_Z), determined as the lowest temperature, at which a polymer sample heated in a strictly specified way releases a sufficient quantity of gases to produce a mixture with air that ignites from the flame of a gas burner, was determined by means of an apparatus from ANKO. Disintegrated rubber samples, 0.5 g in weight, were placed in acid-resistant steel test-tubes equipped with metallic lids with holes for gas to escape from the heated material. The test-tubes were electrically heated in an aluminum block within the temperature range $\Delta T = 150$ –400 °C.

The fire hazard of the elastomeric materials under investigation was determined by the method of cone calorimeter using an apparatus from Atlas Electric Devices Company [2, 8]. The results obtained by this method were used to determine the toxicity of the products of thermal decomposition and combustion of elastomers, taking into account the emission of carbon oxide and dioxide (RTFH_{CO/CO₂}) as well as compounds such as HCN, NO, NO₂, SO₂, CO, and CO₂ at temperatures of 450, 550, and 750 °C, according to Standard PN-B-02855:1988 (W_{LC50SM}) [2].

The contents of 13 polycyclic aromatic hydrocarbons (PAH) in the gaseous products of the thermal decomposition of cross-linked elastomers were determined by the method of liquid chromatography in a reversed phase system. HPLC LC 1150 set from GBC consisted of ERC-3415 gradient pump, UV LC 1200K detector and Hypersil Green PAH 5 μm column from Thermo Scientific. The analysis was carried out by the standard addition method (PAH Calibration Mix—Supelco) under the following conditions: 20 μl of sample, acrylonitrile–water mobile in accordance with the program (Time 0–2 min—65% water, time 2–16 min—65–0% water, 16–40 min—0% water) flow rate 2 ml/min, detection at 2504 nm. Reagents of HPLC purity were delivered by Merck.

Results and discussion

The combustion of the majority of elastomers is accompanied by the formation of liquid products of their thermal decomposition that are an additional factor of heat transfer, increasing contact with oxygen [2]. The quantity of the liquid products formed depends on the thermal properties

of rubbers. In general, these products are formed in large amounts in the case of polymers that are degraded under the influence of elevated temperature. A characteristic feature of the polydienes under investigation is their susceptibility to thermal cross-linking, which causes a considerable reduction in the quantity of liquid products resulted from their combustion. Nevertheless, liquid decomposition products occur also during the combustion of elastomers cross-linked by means of peroxide or sulfur.

The comparative analysis of the results listed in Table 1 leads to a conclusion that as in the case of non-cross-linked polydienes [2], the highest flammability, determined by both OI and combustion time (t_s), is shown by the vulcanizates of butadiene rubber (BN and BS). This is due to several causes. Among the polymeric materials investigated, the vulcanizates of that rubber (BN and BS), during their combustion, emit the highest quantity of liquid thermal decomposition products. The cohesion forces of cis-1,4-polybutadiene macromolecules, whose measure is the density of cohesion energy, are the lowest among those of the polymers tested [2].

This does not facilitate the susceptibility to form solid thermal decomposition products during the combustion of cis-1,4-polybutadiene and its vulcanizates, and consequently their carbonization processes are retarded. The formation of solid carbonized products of the thermal decomposition of polymeric materials considerably facilitates the creation of a boundary layer between the solid and gaseous combustion zones. During the combustion of NBR and SBR and their vulcanizates, thermally stable and porous boundary layers are formed by strongly cross-linked and partly carbonized elastomers, retarding the transport of mass and energy between flame and sample and consequently reduces their flammability (Table 1). Both the OI and ignition temperature (T_Z) values of vulcanizates are

Table 1 The results of flammability investigations of cross-linked diene elastomers

Sample	OI	t_s/s	$T_Z/^\circ\text{C}$	
NBR	0.265 ^a	0.180	300 [2]	335 [2]
NN		0.205	276	357
NS		0.215	289	366
SBR	0.260 ^a	0.195	206	348 [2]
SN		0.210	194	350
SS		0.220	283	355
BR	0.259 ^a	0.180	180	336 [2]
BN		0.195	170	357
BS		0.207	250	362

^a Measurement taking into account after-burning sample in apparatus holder

NBR Butadiene–acrylonitrile rubber, SBR butadiene–styrene rubber, BR butadiene rubber

higher than those of non-cross-linked polymers. Thus, the vulcanization of the rubber tested reduces their flammability. However the vulcanization of elastomers does not affect their combustion time in air (t_s), which seems to be due to the fact that the complex mechanism of polymer combustion in air is different than that under the OI test conditions. In the latter case, the emitting heat is systematically carried away from the zone of chemical processes through the nitrogen–oxygen mixture flowing at a constant rate. In this connection, not always a longer combustion time in air of a polymeric material corresponds to a higher value of its OI. However it should be underlined that the structure of spatial network in the elastomers investigated exerts a clear influence on their flammability. Sulfur vulcanizates (NS, SS, BS) are characterized by a considerably lower flammability determined by the values of OI, t_s and T_Z than that of peroxide vulcanizates (NN, SN, BN) (Table 1). This may be due to the oxidation of sulfide bonds to sulfene and thiosulfoxyl acids and then to SO_2 and, to a small extent, to SO_3 in the boundary layer of the burning elastomer cross-linked with sulfur. These acids can fulfill a function of catalysts of the ionic decomposition of peroxides, while the sulfur oxides passing to flame can inhibit chain oxidation processes [3, 9].

The comparative analysis of test results listed in Table 2 leads to a conclusion that the structure of spatial network of the elastomers investigated also exerts a clear effect on fire hazard parameters. Although the ignition temperature (T_Z) of sulfur vulcanizates (NS, SS, BS) is clearly higher than that of peroxide vulcanizates (NN, SN, BN) (Table 1), polydienes cross-linked with peroxide are characterized by a longer time to ignition (TTI) from several to a dozen or so seconds (Table 2), which, in case of fire hazard, is of essential importance.

On the other hand, the considerably lower mass loss rate (MLR) of SS and BS vulcanizates in comparison to SN and BN seems to be the cause of a clearly lower heat release rate (HRR_{MAX}) during the combustion of cis-1,4-polybutadiene and butadiene–styrene copolymer cross-linked with sulfur (Table 2). In this connection, the sulfur vulcanizates of these elastomers show also the smallest fire hazard associated with fire propagation rate ($1/t_{\text{flashover}}$). From the point of view of smoke emission (SEA), the greatest fire hazard is posed by SBR rubber regardless of the method of its cross-linking (Table 2). This is brought about by the presence of aromatic rings in the macromolecules of this elastomer that during combustion initiate the formation of large amounts of carbonized products of thermal decomposition and carbon black [10]. The highest emission of CO_2 during the combustion of peroxide cis-1,4-polybutadiene vulcanizate in comparison with other materials tested contributes to the high value of fire hazard determined with toxicometric coefficient ($\text{RTFH}_{\text{CO}/\text{CO}_2}$).

Table 2 The means values of parameters of vulcanizates of diene rubbers determined by cone calorimeter

Sample	NN	NS	SN	SS	BN	BS
Time to sustained ignition, TTI/s)	38	32.7	70.96	55.01	67.18	53.64
Total heat release, THR/MJ \times m ⁻²	70.1	69.8	87.89	73.37	84.51	69.74
Peak heat release rate, HRR _{MAX} /kW \times m ⁻²	2270.1	2378.5	2248.28	1391.71	3787.89	1385.39
Average heat release rate, HOC/MJ \times m ⁻²	35.3	36.4	34.81	35.33	42.12	31.77
Average mass loss rate, MLR/g \times s \times m ⁻²	18.1	22.1	50.4	20.8	58.25	19.89
Average specific extinction area, SEA/m ² \times kg ⁻¹	869.2	992.35	1098.54	1122.26	772.83	1090.89
Average CO yield/kg \times kg ⁻¹	0.0674	0.0755	0.0821	0.0713	0.1193	0.0762
Average CO ₂ yield/kg \times kg ⁻¹	2.42	2.42	2.4333	2.2456	3.0199	2.3557
Fire hazard, 1/ <i>t</i> _{flashover} /kW \times m ⁻² \times s ⁻¹	59.74	72.74	31.68	25.29	56.38	25.82
Relative toxic fire hazard, RTFH _{CO/CO₂} /-	0.0144	0.0218	0.0243	0.0115	0.0409	0.0119

Table 3 The results of toxicity investigations of the products of thermal decomposition and flammability of diene rubbers vulcanizates

Sample	Temperature/°C	Emission (mg/g)						Ratio CO ₂ /CO	Toxico metric index W _{LC50SM}
		HCN	NO	NO ₂	CO	SO ₂	CO ₂		
NN	450	17.06	4.08	0.00	95.06	6.42	345.07	3.63	11.28
	550	9.67	3.39	1.42	251.2	4.02	1321.0	5.25	
	750	2.03	4.36	0.82	52.92	0.63	3575.0	67.55	
NS	450	30.84	4.08	0.00	50.02	43.63	225.89	4.51	6.66
	550	10.02	3.39	0.47	241.0	13.76	863.23	3.58	
	750	1.86	5.89	0.53	59.28	38.65	3421.0	57.70	
SN	450	–	–	–	83.0	13.8	3.2	0.03	33.47
	550				76.7	10.4	12.9	0.17	
	750				32.1	0.0	67.9	2.11	
SS	450	10.1	0.4	–	62.7	26.0	0.8	0.01	24.15
	550	4.3	0.2		75.5	16.2	3.9	0.05	
	750	3.5	0.7		16.9	42.0	37.0	2.18	
BN	450	–	–	–	67.5	29.7	2.8	0.04	15.67
	550				60.1	28.5	11.4	0.19	
	750				43.9	16.8	39.3	0.89	
BS	450	5.7	0.4		64.0	27.0	2.9	0.04	14.47
	550	3.4	0.1		17.9	76.6	2.0	0.11	
	750	4.6	0.3	–	29.4	36.7	29.0	0.98	

On the other hand, from the point of view of the toxicometric coefficient (W_{LC50SM}), taking into account a considerably higher number of emitted toxic substances during the combustion of polymeric materials (HCN, NO, NO₂, SO₂, CO, and CO₂), the greatest fire hazard is posed by the vulcanizates of butadiene–acrylonitrile copolymer (NN, NS), especially sulfur vulcanizate (NS) (Table 3). The products of the thermal decomposition and combustion of these vulcanizates belong to the group of very toxic substances. This is due to the emission of considerable amounts of toxic nitrogen compounds, especially HCN. From Table 3 it follows that the toxicity of the products of thermal decomposition and combustion of polymeric

materials depends to a large extent on the structure of elastomer spatial network. Large amounts of SO₂ emitted during the combustion of sulfur vulcanizates bring about a considerably greater fire hazard in terms of combustion gas toxicity compared with that of peroxide vulcanizates.

In recent years, a growing importance has been attached to the problem of the emission of PAH resulting from the thermal decomposition and combustion of polymers and polymeric materials. Based on the results obtained by the method of liquid chromatography, it was found that the cross-linking of the polymers investigated clearly reduced the emission of PAH in the gaseous products of their thermal decomposition and combustion (Table 4) [2].

Table 4 Polycyclic aromatic hydrocarbons in μg in the gaseous products from the thermal decomposition and combustion of diene rubbers vulcanizates

Sample	NN/ $\mu\text{g/g}$ sample	BN/ $\mu\text{g/g}$ sample	SN/ $\mu\text{g/g}$ sample	NS/ $\mu\text{g/g}$ sample	SS/ $\mu\text{g/g}$ sample	BS/ $\mu\text{g/g}$ sample
Naphthalene, Np	1.1003	16.8546	2.8217	0.2570	1.1052	7.1940
Acenaphthylene, Acy	1.3031	0	0.5435	1.7590	1.2038	19.0709
Acenaphthene, Acc	22.7064	581.3723	43.577	7.1485	5.1323	216.9552
Fluorene, F	0.3063	10.5468	0	0.6746	0.8035	1.4701
Phenanthrene, Ph	0.1424	3.0468	0	0.0642	0	1.4179
Anthracene, An	0.0560	1.0767	0.6155	0.0321	0.4033	0.5597
Fluoranthene, Fl	0.6127	0	0	0.1405	0	0
Pyrene, Py	0.1812	6.1888	1.6346	0.1485	0.5172	2.1641
Benzo[a]anthracene, B[a]An	0.0647	0.0815	0.4236	0	0.2032	0.1567
Chrysene, Chry	0.0604	0.6012	0.1598	0.0080	0.3479	0
Benzo[b]fluoranthene, B[b]Fl	0	0.5774	0	0.1646	0.2586	0
Benzo[a]pyrene, B[a]Py	–	–	–	–	–	–
Dibenzo[a,h]anthracene, dB[a, h]An	–	–	–	–	–	–

Polycyclic aromatic hydrocarbons are a group of organic compounds which have received considerable attention because of the documented carcinogenicity in experimental animals of several of its members. PAHs are fused compounds built on benzene rings. When a pair of carbon atoms is shared, then the two sharing aromatic rings are considered fused. The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane. From the point of view of human health the most importance have PAHs from the range between naphthalene (C_{10}H_8) and coronene ($\text{C}_{24}\text{H}_{12}$) [11]. In this range, there are a large number of PAHs differing in the number and position of aromatic rings, with varying number, position and eventual chemistry of substituents on the basic ring system. Physical and chemical properties of PAHs vary with molecular weight.

Among the most studied PAHs is the five-ring benzo[a]pyrene (BaP, $\text{C}_{20}\text{H}_{12}$) that has been demonstrated to mutate cells in culture and cause cancer in whole-animal assay.

In recent years, a growing importance has been attached to the problem of the emission of PAHs resulting from the thermal decomposition and combustion of polymers and polymers materials, e.g., tyres.

Formation of mono-, and polyaromatic species, via pyrolysis of alkanes to produce olefins which are subsequently aromatized by a Diels-Alder type reaction to form PAHs, is well known. For example Fairburn et al. examined the flash pyrolysis of n-hexadecane in a microreactor at temperatures between 576 and 842 °C. They showed that hexadecane initially pyrolyses to form light alkanes in the range of C_1 to C_3 and olefins in the range of C_2 to C_{15} .

Further decomposition at higher temperatures or increased reaction time, produces a decomposition of the heavier olefins to light olefins (C_4 to C_6) and, subsequently, formation of diolefins such as butadiene via dehydrogenation of the lighter olefins [12, 13]. The butadiene then immediately combines with available light olefins such as ethane and propene to form simple aromatic compounds, such as benzene, toluene, ethylbenzene and styrene, via the Diels-Alder reaction. Higher molecular weight PAHs are then formed by further reaction between aromatic compounds and olefins [14, 15].

The smaller emission of PAH during the thermal decomposition of cross-linked elastomers in relation to non-cross-linked polymers is due to the decrease in the concentration of diene mers in macromolecular chains during vulcanization. [2, 12, 13].

Conclusions

The flammability and fire hazard of the vulcanizate tested by us depend on both the chemical constitution of elastomer and the method of its cross-linking thus on the structure of its spatial network.

The smaller flammability of SBR and NBR vulcanizates than that of BR vulcanizates results from the formation of a carbonized isolating boundary layer in butadiene–styrene copolymer and a cyclized isolating layer in butadiene–acrylonitrile copolymer.

The smaller flammability of sulfur vulcanizates compared to that of peroxide vulcanizates is brought about by the oxidation of sulfide groups to sulfene and thiosulfoxyl

acids and then to SO_2 or SO_3 in the boundary layer of the burning elastomer. The resultant acids fulfill the function of the catalysts of ionic peroxide decomposition, while the sulfur oxides passing to flame constrain the chain oxidation processes.

Large SO_2 amounts emitted during the combustion of sulfur vulcanizates, compared to those of peroxide vulcanizates, contribute to their considerably greater fire hazard from the point of view of combustion gas toxicity.

The cross-linking of the elastomers investigated radically limits the emission of PAH in the gaseous products of their thermal decomposition.

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