Effect of halogenless flame retardants on the thermal properties, flammability, and fire hazard of cross-linked EVM/NBR rubber blends

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Abstract This paper presents the results of investigating the thermal stability, flammability, and fire hazard of cross-linked EVM/NBR blends unfilled and filled with halogenless flame-retardant compounds such as melamine cyanurate or magnesium hydroxide. The thermal analysis of the blends was carried out in the atmosphere of air. The activation energy of the composite destruction was determined by two non-isothermal methods: Flynn–Wall–Ozawa's and Kissinger's methods. The flammability of the composites obtained was determined by the method of oxygen index and on the basis of their combustion in air. The fire hazard of the vulcanizates investigated was determined with the use of a cone calorimeter and on the basis of toxicometric parameters W_{LC50SM}. The test results have shown that the flame retardants used increase the thermal stability of the cross-linked blends and decrease their flammability, and thereby allow one to obtain self-extinguishing or non-flammable polymeric materials. The cross-linked EVM/NBR blends filled with these flame-retardant compounds are characterized by good mechanical properties and reduced fire hazard.

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Introduction

Elastomers and materials made of them are commonly used almost in all fields of live. Despite numerous ecological restrictions and considerable amounts of process and postconsumer wastes, often difficult to recycle, the production and consumption of elastomers and related materials have been systematically increased worldwide. Hence, the problem of the flammability reduction of rubber products or making them non-flammable is of special importance on account of a serious health and life hazard and environmental pollution due to considerable emission of smoke and products, especially toxic compounds, during their thermal decomposition and combustion.

From the review of literature data, it follows that 55–80 % of all the fatal accidents during fires are caused by poisoning with the products of thermal decomposition and combustion as well as smoke [1, 2]. These easily penetrate human organism as a result of inhalation and absorption by skin.

The thermal decomposition and combustion of elastomeric materials most often results in the formation of toxic compounds such as carbon oxide, hydrogen chloride, hydrogen cyanide, nitrogen and sulfur oxides, nitro-compounds, organic halogen derivatives including those of dibenzo-*p*-dioxins and dibenzofurans [3, 4]. A serious hazard is also the emission of polycyclic aromatic hydrocarbons (PAH) [5, 6]. The most harmful substances causing environment toxicity include the first six compounds mentioned, as they emit in the highest amounts and their effect on human

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organism is quick, while the values of threshold limit value-time weighed average (TLV-TWA) are very low [7].

The foundation of action aimed at the reduction in human losses is the laboratory test results including the measurements of the potential formation rate of thermal decomposition and combustion products, quantity and rate of smoke emission under set combustion conditions, heat quantity emitted, increase in oxygen deficit, and mutual relations between these parameters. Testing elastomeric materials under the same kinetic and thermal conditions, one can estimate their behavior during fire. Such tests allow one also to attempt to modify the composition of these materials in order to increase their resistance to ignition or to reduce the emission of toxic products during combustion.

This paper presents the test results concerning the thermal stability and fire hazard of the cross-linked ethylene-vinyl acetate (EVM)/NBR rubber blends. The effect of halogenless flame retardants on the thermal properties and fire hazard posed by the composites under investigation was elucidated.

Experimental

Materials

The test materials included EVM rubbers with different contents of vinyl monomeric units in the macromolecules of Levapren 450 (L450) and Levapren 800 (L800) from Lanxess Company, containing 45 ± 1.5 % and 80 ± 2 % vinyl acetate mers, respectively, and NBR 2255 V containing 22 % of combined acrylonitrile from Lanxess Company.

The mixtures of L450 or L800 with NBR (EVM/NBR: L450/NBR, L800/NBR) were prepared at ratios of 30:70 (EVM/NBR70: L450/NBR70, L800/NBR70); 50:50 (EVM/NBR50: L450/NBR50, L800/NBR50); and 70:30 (EVM/NBR30: L450/NBR30, L800/NBR30).

Mixtures EVM with NBR were cross-linked by means of dicumyl peroxide, DCP, (0.6 phr) in the presence of zinc oxide, ZnO, (5 phr).

Melamine cyanurate (CM) (POCh Gliwice), magnesium hydroxide (Martinswerk, GmbH), and Magnifin H5 (Mg), were used as flame retardant and were incorporated into L450/NBR30 or L800/NBR30 mixtures in the following quantities: melamine cyanurate 50 phr magnesium hydroxide 60 or 80 phr.

Methods

Preparing elastomer blends and their vulcanization

Mixtures EVM with NBR were prepared at room temperature with the use of a laboratory roll stand with roll

dimensions $D = 150$ mm, $L = 300$ mm. The rotational speed of the front roll was 20 rpm, friction 1.1.

Blends EVM with NBR were vulcanized in steel molds placed between electrically heated press shelves. The optimal vulcanization time $(\tau_{0.9})$ at a temperature of 160 °C was determined by means of a WG-2 vulcameter according to PN-ISO 3417:1994.

Thermal properties rubbers and their vulcanizates

The thermal properties of cross-linked mixtures were determined under air atmosphere within the temperature range of 25–700 °C, by means of the thermal analyzer Jupiter STA 449 F3 from Netzsch Company (weighed portions 5–10 mg, heating rate 10 °C min^{-1}).

Thermal analysis under nitrogen at −100 to 500 °C was carried out by the method of differential scanning calorimetry using a DSC-204 micro-calorimeter (Netzsch) and 5–7 mg weighed portions at a heating rate of 10 °C min^{-1}.

Determination of activation energy of decomposition investigation vulcanizates

The activation energy of decomposition of vulcanizates EVM/NBR and their composites containing appropriate flame retardants have been calculated by the use of Flynn–Wall–Ozawa and Kissinger's methods.

The analysis is based on the well-known Flynn–Wall–Ozawa isoconversional method. This isoconversional integral method, suggested independently by Flynn and Wall and Ozawa uses Doyle's approximation of the temperature integral. This method is based on the equations [8–12]:

$$\log \beta = \log \frac{AE}{Rg(\alpha)} - 2.315 - \frac{0.457E}{RT} \tag{1}$$

where β is the heating rate °C min^{-1}; A, the pre-exponential factor; E, activation energy of decomposition in kJ mole^{-1}; R, the universal gas constant; α, the degree of conversion; T, the absolute temperature to reach the conversion; and

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{2}$$

is the integral conversion function.

Thus, at a constant conversion (α = const.), the plot log β versus (1/T), obtained from a series of experiments performed at several heating rates, should be a straight line whose slope allows evaluation of the activation energy:

$$\text{slope} = \frac{d(\log \beta)}{d(1/T)} = 0.4567 \left(\frac{E}{R} \right) \tag{3}$$

To apply this isoconversional method, heating rates of 5, 10, and 15 °C min^{-1} were chosen. In this study, the

conversion values of 10, 20, 30, 40, 50, 60, 70, 80, and 90 % have been used, which would give α values 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9, respectively, for the Flynn–Wall–Ozawa method.

Kissinger's method Kissinger's method is one of the differential methods that have been used by researches to determine the activation energy of solid state reactions from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The advantage of this method is that even without a precise knowledge of the reaction mechanism and reaction order, the activation energy can be determined from the following equation [13, 14]:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}} \tag{4}$$

where β is the heating rate, T_{max} is the temperature corresponding to the inflection point of the thermal degradation curves which corresponds to the maximum rate, A is the pre-exponential factor, E is the activation energy, α_{max} is the maximum conversion, and n is the order of the reaction. From the slope of the plot of $\ln(\beta/T_{max}^2)$ versus $1000/T_{max}$, E can be calculated.

Flammability

The flammability of vulcanizates was determined by the oxygen index (OI) method, using an apparatus from Fire Testing Technology Ltd and $50 \times 10 \times 4$ mm specimens. With a constant nitrogen flow rate through a measurement column ($\varnothing = 75$ mm), amounting to 40 ± 2 mm s^{-1}, the oxygen concentration was selected so that the way that the sample was completely burned within time $t = 180$ s. The sample top was ignited for 5 s by the gas burner supplied with LPG [15, 16].

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 for 5 s and its combustion time (t_s) was measured.

The vulcanizates under investigation were examined by the use of a cone calorimeter from Fire Testing Technology Ltd. Elastomer samples with dimensions of ($100 \times 100 \pm 1$) mm and thickness of (2 ± 0.5) mm were tested at horizontal position with the heat radiant flux density 35 kW m^{-2}. During tests, the following parameters were recorded: initial sample mass, time to ignition (TTI), sample mass during testing, total heat released (THR), effective combustion heat (EHC), average mass loss rate (MLR), heat release rate (HRR), and sample final mass.

The structure of the rubber combustion residue analyzed by means of a cone calorimeter was assessed on the basis of photographs taken under a microscope equipped with the recording software Motic Images Plus.

Toxicity

The toxicity of the gas products of vulcanizates decomposition and combustion was assessed on the basis of the quantitative chemical determination of the specific emission of CO, CO_2, HCN, NO_2, HCl, and SO_2 at temperatures of 450, 550, and 750 °C, according to the standard PN-B-02855:1988.

The parameter that takes into account the concentration of all gases (CO, CO_2, HCN, NO_2, HCl, and SO_2) emitted at temperatures $T = 450$, 550, and 750 °C is known as a toxicometric index, W_{LC50SM}, described by Eq. 5 [17].
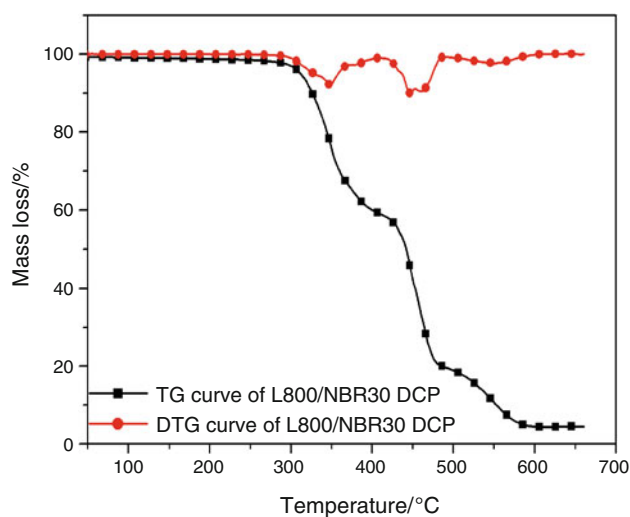

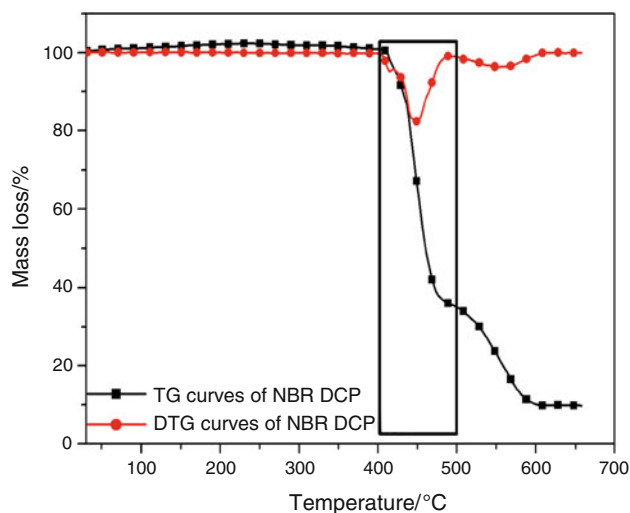**Fig. 1** Thermal curves cross-linked blend of L800/NBR 30

Fig. 2 Thermal curves of NBR rubber cross-linked by the dicumyl peroxide (DCP)

Table 1 Thermal properties of cross-linked blends of EVM and NBR rubbers

Sample	ΔT_1/°C	$T_{5\ I}$/ °C	$T_{50\ I}$/ °C	$T_{RMAX\ I}$/ °C	dm/dt_I/ % min^{-1}	ΔT_2/°C	$T_{5\ II}$/ °C	$T_{50\ II}$/ °C	$T_{RMAX\ II}$/ °C	dm/dt_{II}/ % min^{-1}	ΔT_S/°C	P_{700}/ %
L450/ NBR30	250–400	295	340	345	8.22	400–500	420	455	445	10.71	500–615	5.47
L450/ NBR50	290–390	305	345	340	3.59	390–500	420	455	445	14.35	500–610	6.98
L450/ NBR70	260–400	310	355	365	2.12	400–515	425	465	470	22.79	515–650	6.82
L800/ NBR30	250–400	265	345	350	7.94	400–490	420	450	445	9.98	490–620	5.21
L800/ NBR50	280–395	295	335	340	4.56	395–490	425	450	450	11.41	490–625	5.33
L800/ NBR70	265–410	305	345	345	2.32	410–510	425	455	450	13.74	510–675	5.87

L450/NBR30, blend of EVM 450 and NBR (70:30) rubbers cross-linked by DCP; L450/NBR50, blend of EVM 450 and NBR (50:50) rubbers cross-linked by DCP; L450/NBR70, blend of EVM 450 and NBR (30:70) rubbers cross-linked by DCP; L800/NBR30, blend of EVM 800 and NBR (70:30) rubbers cross-linked by DCP; L800/NBR50, blend of EVM 800 and NBR (50:50) rubbers cross-linked by DCP; L800/NBR70, blend of EVM 800 and NBR (30:70) rubbers cross-linked by DCP; ΔT_1, temperature range of first decomposition stage; ΔT_2, temperature range of second decomposition stage; $T_{RMAX\ I}$, temperature of maximum rate of first thermal decomposition stage; $T_{RMAX\ II}$, temperature of maximum rate of second thermal decomposition stage; $T_{5\ I}$, $T_{50\ I}$, temperature of sample 5 and 50 % mass loss during first thermal decomposition stage; $T_{5\ II}$, $T_{50\ II}$, temperature of sample 5 and 50 % mass loss during second thermal decomposition stage; dm/dt_I, maximum rate of first thermal decomposition stage; dm/dt_{II}, maximum rate of second thermal decomposition stage; ΔT_S, temperature range of residue burning after the thermal decomposition of sample; P_{700}, residue after heating up to $T = 700$ °C

Table 2 Activation energy destruction values of cross-linked blends

Activation energy of destruction/kJ mol^{-1}

	Flynn–Wall–Ozawa method		Kissinger method	
	Ea_I/ kJ mol^{-1}	Ea_{II}/ kJ mol^{-1}	Ea_I/ kJ mol^{-1}	Ea_{II}/ kJ mol^{-1}
L450/ NBR30	142.3	237.8	140.3	237.3
L450/ NBR50	206.6	271.4	205.9	272.9
L450/ NBR70	220.4	233.1	220.1	232.1
L800/ NBR30	161.7	227.6	160.9	228.1
L800/ NBR50	209.2	238.3	205.8	244.3
L800/ NBR70	218.5	205.3	218.9	204.1

Ea_I Activation energy of first stage of thermal decomposition, Ea_{II} activation energy of second stage of thermal decomposition

$$W_{LC50SM} = \frac{W_{LC50M450} + W_{LC50M550} + W_{LC50M750}}{3} \quad (5)$$

W_{LC50SM} index is the arithmetic average of $W_{LC50M(T)}$ indices

$$\frac{1}{W_{LC50M(T)}} = \sum_{i}^{n} \frac{1}{W_{LC50}} \quad (6)$$

where n is number of gaseous products, W_{LC50} is maximum toxic concentration of gaseous product formed during thermal decomposition and combustion of testing material in the "T" temperature

$$W_{LC50} = \frac{LC_{50}^{30}}{E} \quad (7)$$

where E is emission, g g^{-1}; LC_{50}^{30} is lethal concentration of gaseous product of thermal decomposition and combustion of test material which cause a 50 % lethality of test animals during 30-min exposure

Mechanical properties

The strength properties of composites were determined according to PN-ISO 37:1998, using an apparatus from ZWICK, model 1435, connected to a computer with an appropriated software and dumbbell samples with a measurement section width of 4 mm and a thickness of about mm.

Results and discussion

Thermal analysis

The L450/NBR and L800/NBR blends tested after cross-linking showed one value of glass transition temperature. In the case of L450/NBR30 and L800/NBR30 blends, it

Table 3 Thermal properties of blends of EVM and NBR rubbers containing flame retardant

Sample	ΔT_1/°C	$T_{5\ I}$/°C	$T_{50\ I}$/°C	$T_{RMAX\ I}$/°C	dm/dt_I/% min^{-1}	ΔT_2/°C	$T_{5\ II}$/°C	$T_{50\ II}$/°C	$T_{RMAX\ II}$/°C	dm/dt_{II}/% min^{-1}	Pw/%	P_{700}/%
L450/NBR30	250–400	295	340	345	8.22	400–495	420	455	445	10.71	21.0	5.47
L450/NBR30/ CM50	250–415	290	355	350	6.07	415–500	430	465	470	10.88	20.6	8.62
L450/NBR30/ Mg60	290–400	305	360	360	5.77	400–495	420	460	465	9.66	33.8	28.5
L450/NBR30/ Mg80	290–400	315	360	360	5.89	400–495	420	460	470	8.00	38.1	33.5
L800/NBR30	250–400	265	345	350	7.94	400–490	420	450	445	9.98	20.2	5.21
L800/NBR30/ CM50	250–405	290	350	350	9.30	405–495	415	455	465	7.63	21.8	8.61
L800/NBR30/ Mg60	290–405	315	355	350	7.39	405–495	420	460	470	5.03	35.3	28.7
L800/NBR30/ Mg80	290–410	320	360	350	6.92	410–495	425	460	470	4.64	39.1	33.56

L450/NBR30/CM50 blend of EVM 450 and NBR (70:30) rubbers containing 50 phr of melamine cyanurate, L450/NBR30/Mg60 blend of EVM 450 and NBR (70:30) rubbers containing 60 phr of magnesium hydroxide, L450/NBR30/Mg80 blend of EVM 450 and NBR (70:30) rubbers containing 80 phr of magnesium hydroxide, L800/NBR30/CM50 blend of EVM 800 and NBR (70:30) rubbers containing 50 phr of melamine cyanurate, L800/NBR30/Mg60 blend of EVM 800 and NBR (70:30) rubbers containing 60 phr of magnesium hydroxide, L800/NBR30/Mg80 blend of EVM 800 and NBR (70:30) rubbers containing 80 phr of magnesium hydroxide, Pw residue after the thermal decomposition of polymeric composites
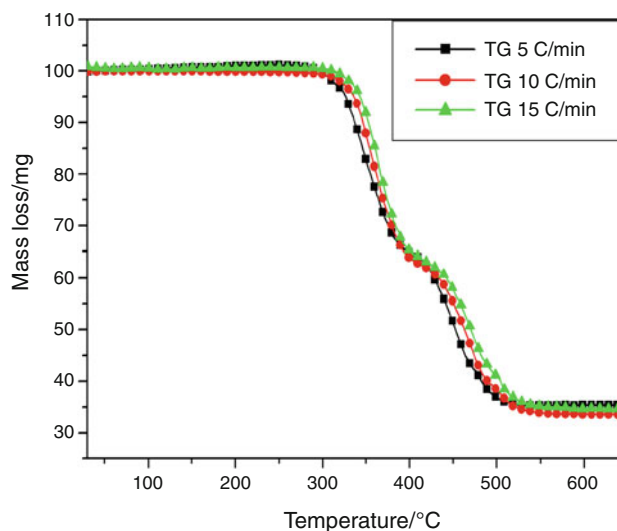
Table 4 Activation energy destruction values of L450/NBR30 and L800/NBR30 blends containing appropriate flame retardant

Activation energy of destruction/kJ mol^{-1}				
	Flynn–Wall–Ozawa method		Kissinger method	
	Ea_I/ kJ mol^{-1}	Ea_{II}/ kJ mol^{-1}	Ea_I/ kJ mol^{-1}	Ea_{II}/ kJ mol^{-1}
L450/NBR30	142.3	237.8	140.3	237.3
L450/NBR30/ CM50	150.1	239.2	152.2	240.1
L450/NBR30/ Mg80	152.2	275.4	153.0	276.3
L800/NBR30	161.7	227.6	160.9	228.1
L800/NBR30/ CM50	170.1	225.0	171.2	225.1
L800/NBR30/ Mg80	177.3	240.5	177.8	241.1

Fig. 3 TG curves of L800/NBR30/Mg80 blend

amounts to $Tg = -24$ and 5 °C, respectively. This indicates a good co-miscibility of the elastomers tested resulting from interelastomeric reactions.

The thermal decomposition of cross-linked blends of L450 and L800 rubbers with NBR proceeds in three stages (Fig. 1).

The first of them, at $\Delta T_1 = 250$–400 °C, is connected with the deacetylation processes of acetic acid and thereby with the formation of unsaturated polyenes. The second stage of thermal decomposition proceeding at $\Delta T_2 = 400$–500 °C is connected with both the thermo-oxidizing processes of

unsaturated compounds resulting in the formation of aliphatic and aromatic gaseous products, and with the thermal decomposition of NBR (Fig. 2). The final stage of decomposition occurring at $\Delta T_3 = 500$–675 °C is connected with the combustion of the cross-linked blend residue.

The content of nitrile rubber in cross-linked blends clearly influences their thermal stability. An increase in the content of a high-molecular composite component with a greater resistance to heat at elevated temperature, i.e., NBR rubber, increases the blend decomposition start temperature (parameter ΔT_I and $T_{5\ I}$) (Table 1) and considerably
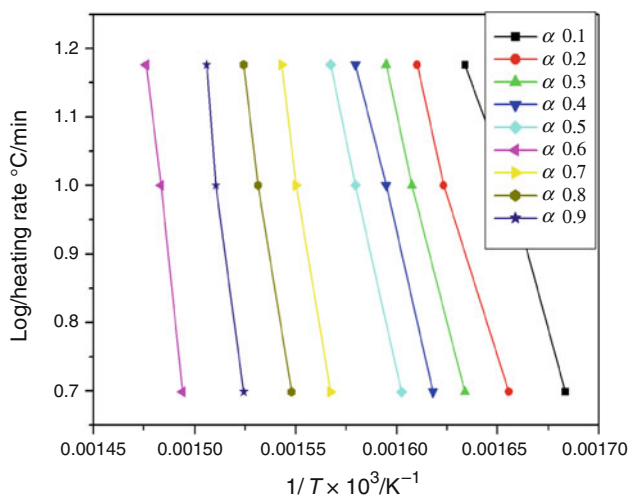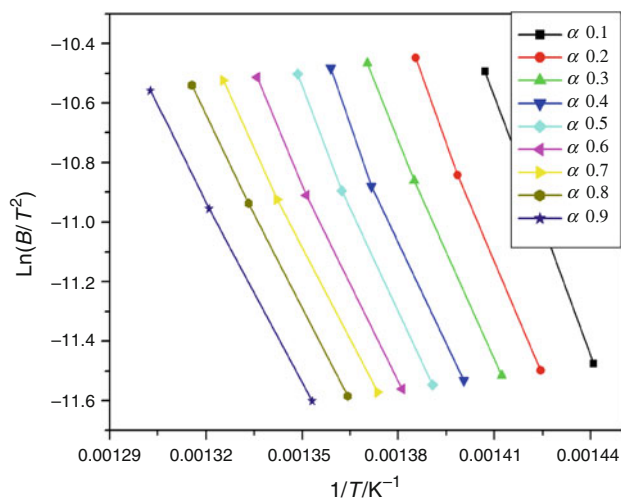
Fig. 4 The relation of first stage decomposition of L800/NBR30/Mg80 vulcanizate as a function of its conversion calculated using F–W–O method
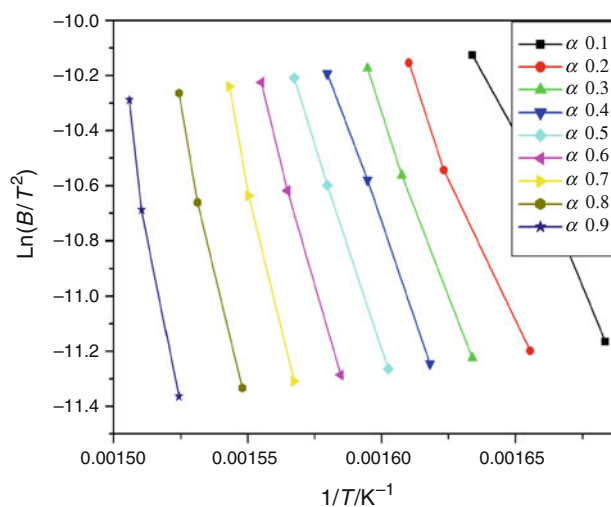
Fig. 6 The relation of first stage decomposition of L800/NBR30/Mg80 vulcanizate as a function of its conversion calculated using Kissinger method
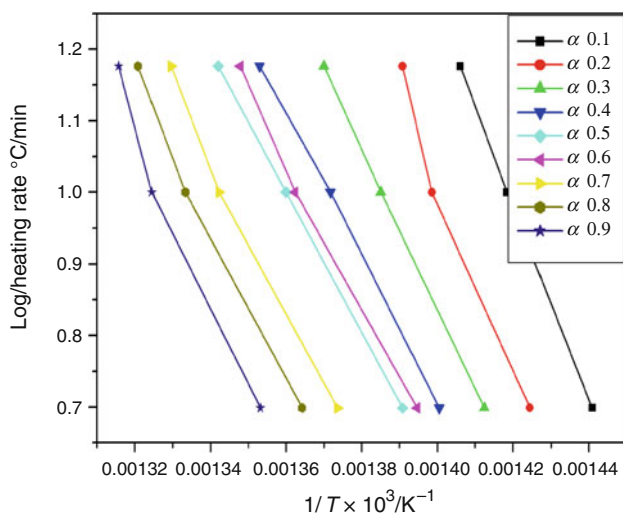
Fig. 5 The relation of second stage decomposition of L800/NBR30/Mg80 vulcanizate as a function of its conversion calculated using F–W–O method

Fig. 7 The relation of second stage decomposition of L800/NBR30/Mg80 vulcanizate as a function of its conversion calculated using Kissinger method

decreases the decomposition rate, dm/dt_I, of the polymeric material obtained.

The parameter of thermal stability, dm/dt_{II}, is connected with destruction processes, whose intensity also depends on the content of NBR. However, it should be emphasized that the destruction reactions are accompanied by the cyclization of adjacent nitrile groups proceeding within a wide temperature range, which influences not only the combustion temperature of the thermal decomposition residue, ΔT_s, and parameter P_{700} (Table 1), but also the energy of destruction activation, especially that of the first thermal decomposition stage of the cross-linked blends (Table 2).

The incorporation of conventional halogenless flame retardants, such as melamine cyanurate or Magnifin H5 into L450/NBR30 and L800/NBR30 blends decisively changes their thermal stability (Table 3). Under the influence of magnesium hydroxide, the temperature of the beginning of blend thermal decomposition increases by about 40 °C regardless of the type of Levapren (Table 3). The thermal stability factors, $T_{5\ I}$ and $T_{50\ I}$, are also considerably increased. It should be also mentioned that the maximal temperature of thermal decomposition, $T_{RMAX\ II}$, indicating the intensity of destruction processes, is shifted to the range of higher temperatures.

Table 5 Flammability test of investigated blends

Sample	Combustion time in air/s	Oxygen index (OI)
L450/NBR30 DCP	549	0.251
L450/NBR30/CM50	62[a,b]	0.285
L450/NBR30/Mg60	47[a,b]	0.353
L450/NBR30/Mg80	–[c]	0.392
L800/NBR30	232[a,b]	0.280
L800/NBR30/CM50	–[a,c]	0.351
L800/NBR30/Mg60	–[a,c]	0.380
L800/NBR30/Mg80	–[a,c]	0.434

[a] Time of ignition equal 30 s

[b] Self-extinguishing sample

[c] Non-flammable samples

An important parameter determining both the thermal stability of a polymeric composite and its flammability is the thermal decomposition rate, dm/dt. A decrease in the decomposition rate of polymeric materials exerts a positive influence on the reduction in their flammability. A decrease in the decomposition rate of polymeric materials exerts a positive influence on their flammability. This results from the formation of lower quantities of volatile, flammable products of pyrolysis passing into flame, which reduces the rate of free-radical reactions proceeding in it. The flame retardants used clearly influence the values of parameters dm/dt_I and dm/dt_{II}. The reduction in the first stage decomposition rate of the composites tested results first of all from the decrease in the concentration of their vinyl-acetate monomeric units under the influence of the flame retardant used. Lower values of parameter dm/dt_{II} also result from a lowered segmental mobility of polymeric chains due to mutual interactions of macromolecules with the flame-retardant fillers.

The presence of flame retardants in the composites tested also influences the value of the destruction activation energy, especially that of macromolecules containing unsaturated bonds (the second stage of thermal decomposition). Parameter Ea clearly increases in the presence of melamine cyanurate, and especially in the presence of magnesium hydroxide (Table 4, Figs. 3, 4, 5, 6, 7), which confirms that the flame-retardant compounds used fulfill the function of screens protecting the polymer against the action of elevated temperature.

Table 6 Flammability test of blends EVM and NBR rubbers obtained by the method of cone calorimeter (fire hazard)

| Sample	TTI/s	THR/MJ m^{-2}	HRR/kW m^{-2}	HRR$_{max}$/ kW m^{-2}	EHC/ MJ kg^{-1}	EHC$_{max}$/ MJ kg^{-1}	Percentage mass loss/%	MLR/g m^{-2} s^{-1}
NBR DCP	60	24.1	290	414.1	25.3	52.4	98.9	29.6
L450/NBR30	76	27.3	78.2	326.2	13.8	73.9	91.7	13.5
L450/NBR50	61	29.6	92.2	340.2	12.7	76.5	87.0	13.0
L450/NBR70	62	37.2	171.9	463.1	19.4	74.9	81.8	20.3
L800/NBR30	92	27.3	94.7	282.7	11.4	70.7	98.4	17.2
L800/NBR50	71	34.8	103.7	340.4	15.7	61.8	100	15.7
L800/NBR70	58	40.7	180.0	502.9	19.2	78.3	91.3	19.8

TTI Time to ignition, THR total heat release, HRR heat release rate, HRR$_{max}$ max heat release rate, EHC effective heat of combustion, MLR average specific mass lost rate

**Table 7** Flammability test of blends containing appropriate flame retardants

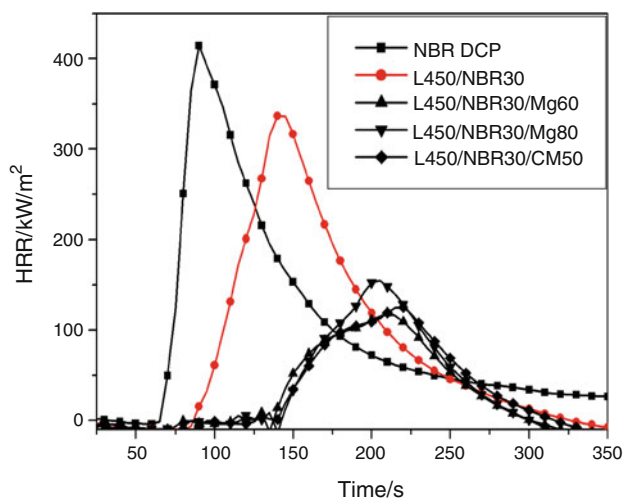| Sample	TTI/s	THR/MJ m^{-2}	HRR/kW m^{-2}	HRR$_{max}$/ kW m^{-2}	EHC/ MJ kg^{-1}	EHC$_{max}$/ MJ kg^{-1}	Percentage mass loss/%	MLR/ g m^{-2} s^{-1}
L450/NBR 30	76	27.3	78.2	326.2	13.8	73.9	91.7	13.5
L450/NBR30/CM50	123	10.8	15.2	118.9	3.35	25.7	92.7	9.81
L450/NBR/30/Mg60	126	12.0	14.9	155.1	3.81	64.8	70.9	11.3
L450/NBR30/Mg80	126	11.6	20.5	125.4	5.38	35.1	65.6	10.6
L800/NBR30	92	27.3	94.7	282.7	11.4	70.7	98.4	17.2
L800/NBR30/CM50	92	9.1	26.1	105.9	4.46	24.9	86.2	11.5
L800/NBR30/Mg60	98	10.2	28.1	93.2	5.43	48.5	69.0	10.5
L800/NBR30/Mg80	105	6.9	12.7	56.1	2.45	18.9	66.1	8.9
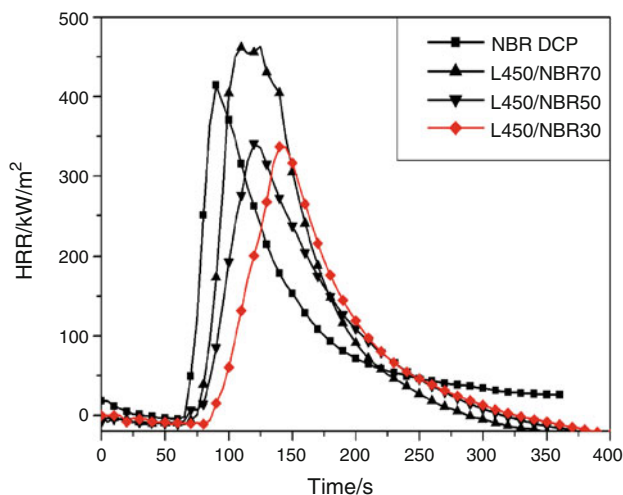
Fig. 8 HRR curves of blends of EVM 450 and NBR rubbers
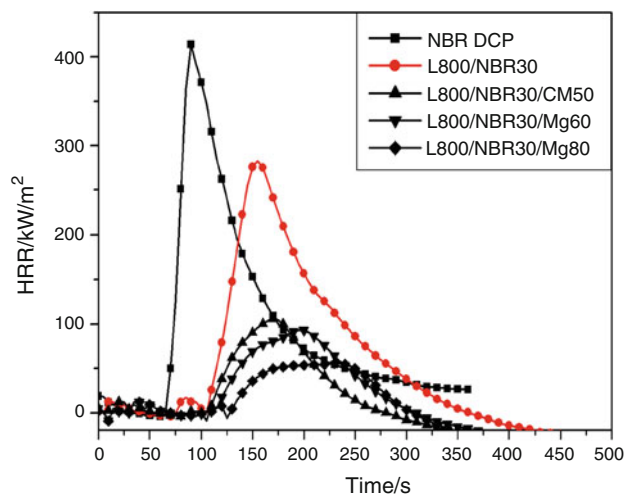
Fig. 11 HRR curves of blends of EVM 800 and NBR rubbers containing appropriate flame retardants
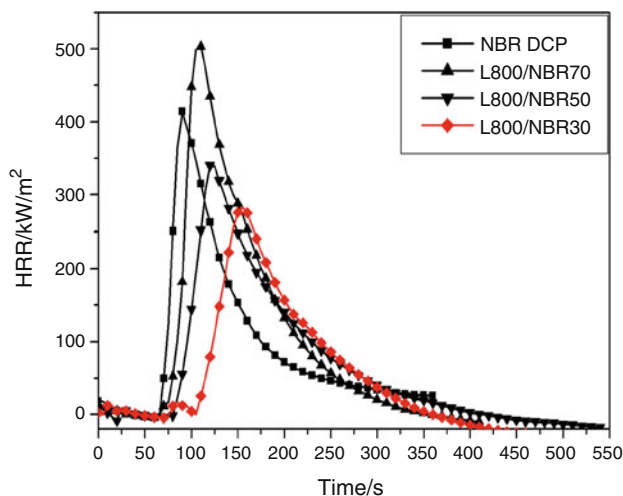
Fig. 9 HRR curves of blends of EVM 800 and NBR rubbers
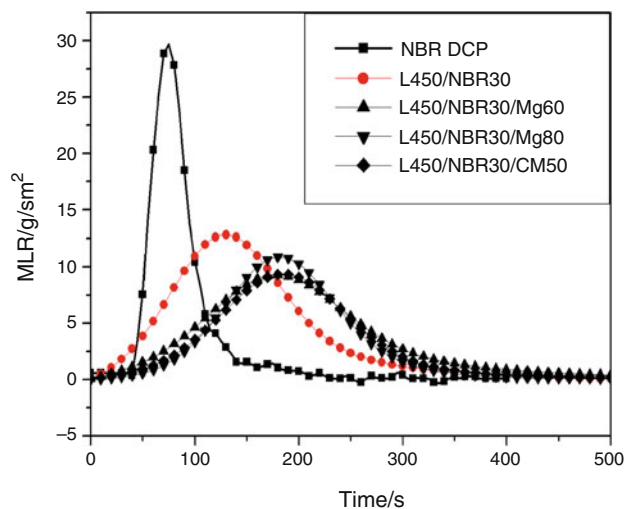
Fig. 12 MLR curves of blends of EVM 450 and NBR rubbers containing appropriate flame retardants

Flammability and fire hazard

From the point of view of a reduction in flammability, both the combustion (parameter P_{700}) and thermal decomposition (Pw) residues play a significant function (Table 3). The latter parameter is becoming more and more important. The most effective flame retardants are those which during the combustion of polymeric materials bring about the formation of a carbonized residue instead of pyrolysis products or with their minimal portion [18].

The comparative analysis of the test results obtained by the method of thermal analysis in air (Table 3) leads to a conclusion that melamine cyanurate does not exert any significant effect on the thermal decomposition residue of the composite investigated compared to magnesium

Fig. 10 HRR curves of blends of EVM 450 and NBR rubbers containing appropriate flame retardants

hydroxide. However, each of the flame retardants used considerably reduces the flammability of the polymeric materials obtained. Under the influence of melamine cyanurate, the L450/NBR30 composite is extinguished after 62 s (parameter t_s, Table 5), while in the presence of magnesium hydroxide after 47 s. The increased content of $Mg(OH)_2$ in the blend tested from 50 to 60 phr results in a nonflammable material (Table 5). Regardless of the type and content of the flame retardant, the cross-linked L800/NBR30 composite does not ignite (t_s, Table 5).

It should be also emphasized that the self-extinguishing polymeric materials obtained ignited in air under the influence of flame source within 30 s. The nonflammable

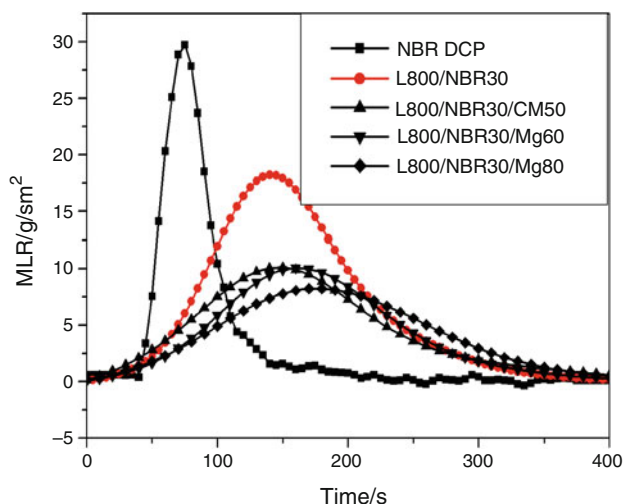Fig. 13 MLR curves of blends of EVM 800 and NBR rubbers containing appropriate flame retardants

polymeric materials obtained also neither burned nor glowed under the gas burner flame acting for 30 s.

An important parameter for comparing the flammability of polymeric materials is OI. Materials for which OI < 0.21 (oxygen content in the combustion atmosphere is below 21 %) belong to inflammable materials, while those, whose OI > 0.28 are considered to be nonflammable. From the data listed in Table 5, it follows that taking into account the values of OI, all the materials tested, containing the flame retardant, should be rated among flame retardant and nonflammable materials [19, 20].

Evaluating the fire-safety of polymeric materials only on the basis of OI, one should act with due caution. The assumption that a material showing OI > 0.28 should not burn in air, is not under laboratory conditions a sample burns with a flame similar to that of a candle, while in practice, combustion most often proceeds from below upward. During such combustion, if the direction of flame movement and that of oxygen/nitrogen mixture flux are the same, successive sample portions are intensively heated by the heat flux flowing upwards, which facilitates combustion and decreases the value of OI.

To determine the fire hazard of the materials investigated under real fire conditions, blend samples without and with added proper flame retardants were tested with the use of a cone calorimeter (Tables 6, 7).

From the data listed in Table 6, it follows that among the L450/NBR and L800/NBR composites tested, L450/NBR30 and L800/NBR30 blends are characterized by the lowest fire hazard expressed by TTI, total heat emitted, heat emission rate, and maximal heat emission rate as well as ECH and MLR (Table 6; Figs. 8, 9).

Fig. 14 Pictures of residue after combustion composites: **a** L450/NBR30/CM50, **b** L450/NBR30/Mg80, **c** L800/NBR30/CM50, **d** L800/NBR30/Mg80
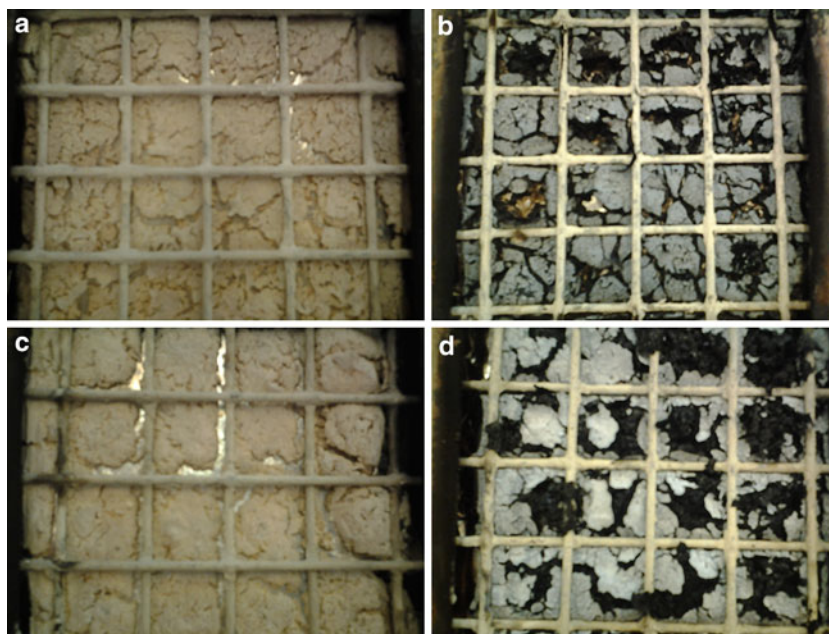
Table 8 Emision gaseous, toxic products forming during thermal decomposition of blends EVM 800 and NBR rubbers

Sample	$Tr/°C$	Emission/g g^{-1}					
		CO	CO_2	HCN	NO_2	HCl	SO_2
L800/NBR30	450	0.015	0.05	0.0024	0.00001	0.00005	0.0001
	550	0.108	1.519	0.0072	0.00002	0.0013	0.0001
	750	0.084	1.938	0.0031	0.00002	0.0018	0.0001
L800/NBR30/CM50	450	0.012	0.153	0.0004	0.00002	0.0019	0.0001
	550	0.063	0.1619	0.0006	0.00009	0.0024	0.0001
	750	0.023	1.943	0.001	0.00014	0.0018	0.0001
L800/NBR30/Mg80	450	0.0012	0.073	0.0026	0.00001	0.0007	0.0001
	550	0.092	0.6	0.0017	0.00004	0.0003	0.0000
	750	0.006	1.370	0.0003	0.00004	0.0000	0.0001

Tr Temperature of decomposition

Table 9 The values of toxicometric indices determined during thermal decomposition blends of EVM 800 and NBR rubbers

Sample	$Tr/°C$	$W_{LC50}/g\ m^{-3}$						W_{LC50M}	W_{LC50SM}
		CO	CO_2	HCN	NO_2	HCl	SO_2		
L800/NBR30	450	245	3,908	67	19,358	2,009	14,000	50.2	27.0
	550	35	129	22	10,968	777	14,000	12.0	
	750	45	101	52	10,094	556	14,000	18.7	
L800/NBR30/CM50	450	320	1,280	364	12,202	529	14,000	115.0	62.1
	550	59	121	255	2,393	421	14,000	31.4	
	750	165	101	155	1,485	547	14,000	40.1	
L800/NBR30/Mg80	450	304	2,682	62	18,645	1,340	14,000	48.2	56.2
	550	41	328	96	12,105	3,836	14,000	26.0	
	750	620	143	568	5,786	1,97,037	14,000	94.4	

Table 10 Mechanical properties of investigated composites

Sample	Stress/MPa			TS$_b$/MPa	E_b/ %
	100 %	200 %	300 %		
L450/NBR30	1.87	4.24	–	6.03	224.0
L450/NBR30/CM50	2.39	3.71	–	4.47	232.0
L450/NBR30/Mg60	2.81	5.17	8.19	9.33	303.8
L450/NBR30/Mg80	3.40	5.04	7.75	8.52	294.8
L800/NBR30	1.54	3.80	–	6.75	259.1
L800/NBR30/CM50	2.62	3.97	–	6.42	289.2
L800/NBR30/Mg60	4.16	7.16	–	9.75	292.2
L800/NBR30/Mg80	4.80	6.62	9.15	9.08	278.9

TS$_b$ Tension strength, E_b elongation at break

The considerably reduced fire hazard of L450/NBR30 and L800/NBR30 composites in relation to the remaining blends results from the higher concentration of vinyl-acetate monomeric units in the volume unit. These units are deacetylated releasing acetic acid and diluting the flammable, often toxic products of the blend thermal decomposition.

The fire hazard of the cross-linked L450/NBR30 and L800/NBR30 blends decreases under the influence of halogenless flame retardants (Table 7).

Taking into account the quantity of flame-retardant incorporated into the blend and the fire hazard parameters, such as total emitted heat, heat emission rate, and mass loss rate, it should be concluded that melamine cyanurate shows a similar effectiveness of reducing fire hazard to that of magnesium hydroxide. The reduction in the fire hazard of the blends tested by the halogenless flame retardants (Figs. 10, 11, 12, 13) may be caused by their action in both gaseous and solid phases [21–24].

The flame-retarding effect of melamine cyanurate is connected with its endothermic decomposition (cooling effect), release of nonflammable ammonia, and formation of condensation products, such as melam, melem, and melon, whose presence in the boundary layer formed during the combustion of elastomeric blend impedes the transport of mass and energy between the solid and gaseous phases of the material under combustion, dilutes volatile destruction products (Fig. 14a, c) [25, 26].

Water vapor released during the decomposition of magnesium hydroxide decreases the energetic balance of the material under combustion and dilutes the volatile products of composite destruction decreasing the concentration of flammable gases [27]. Magnesium oxide resulted from the decomposition of $Mg(OH)_2$ facilitates carbonization processes on the surface of the material under combustion (Fig. 14b, d).

It should be clearly emphasized that the flame-retardant compounds used also decrease the toxicity of gaseous products formed during the thermal decomposition and combustion of the elastomeric materials investigated.

Table 8 shows the emission of six most harmful gases for living organisms occurring during the decomposition of L800/NBR30 blend as well as L800/NBR30/CM50 and L800/NBR30/Mg80 composites. It should be stated that in the presence of halogenless flame-retardant compounds, the emission of toxic CO and HCN was considerably decreased in relations to L800/NBR30 sample.

Undoubtedly, the reduced emission of these gases results first of all from the emission of biologically neutral gases, e.g., water vapor.

It should be also noticed that as a result of the combustion of the composite filled with melamine cyanurate (this compound contains 60–70 % by wt. of nitrogen), the specific emission of NO_2 increased to a very small extent.

Table 9 shows the values of toxicometric parameters. The value of W_{LC50SM} according to standard PN-88/B-02855 is the classification basis of the products of thermal decomposition and combustion into the following groups:

$W_{LC50SM} \leq 15$ very toxic products

$W_{LC50SM} > 40$ moderately toxic products.

Based on the above classification, the products formed during the decomposition of L800/NBR30 composites should be rated among toxic products, while those resulted from the decomposition of composites filled with the flame retardants used belong to moderately toxic products.

It should be underlined that the laboratory test results fail to completely reflect the real hazard occurring under natural conditions during fire. However, they allow one to perform a comparative analysis of the combustion results of various materials under the same conditions, which gives the basis for the assessment which of the material tested, constitutes greater hazard for man and the environment during fire.

Mechanical properties

Practically, selecting flame-retardant compounds, one should take into account a distinct reduction in the flammability of polymeric materials, maintaining or improving their physical and mechanical parameters at the same time.

From the data listed in Table 10, it follows that melamine cyanurate slightly deteriorates the mechanical properties of the composites obtained. On the other hand, the functional properties of the materials obtained are improved under the influence of magnesium hydroxide. It is not without significance that the processing of elastomeric blends containing the flame retardants on a roll stand is also considerably easier.

Conclusions

The thermal properties of cross-linked EVM/NBR blends depend on the content of NBR rubber. An increase in the NBR content in the composites investigated increases their temperature of the beginning of thermal decomposition and considerably decreases the rate of the first thermal decomposition stage, dm/dt_I.

The incorporation of conventional halogenless flame retardants into L450/NBR30 and L800/NBR30 blends significantly improves the thermal stability of the polymeric materials obtained. This contributes to a considerable reduction in their flammability and makes it possible to obtain self-extinguishing or nonflammable composites.

Taking into account the quantity of flame retardant incorporated into the blends and fire hazard parameters, such as the THR, HRR, and mass loss rate, it should be stated that melamine cyanurate shows a similar effectiveness to that of magnesium hydroxide.

The gaseous products of the thermal decomposition and combustion of L800/NBR30 containing no flame retardant are rated among toxic compounds, while those resulted from the thermal decomposition of the composite filled with flame retardants are classified to the group of moderately toxic products.

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