

Thermal properties and combustibility of cross-linked XNBR/CSM blends

Part II. Influence of the CSM kind

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Abstract The article describes the measurements results of the thermal properties of cross-linked blends of butadiene–acrylonitrile rubber (XNBR, Krynac X.7.50) and chlorosulfonated polyethylene containing different quantity of combined chlorine (CSM24—Hypalon 48, CSM29—Hypalon 20, CSM35—Hypalon 40, and CSM43—Hypalon 30) under inert gas (DSC) and in air (derivatography). The blends were non-conventionally cross linked at a temperature of 150 °C by means of MgO in the presence of stearic acid. The thermal curves obtained were interpreted from the point of view of phase transitions and chemical reactions of the macromolecular components used. It has been found that the elastomers investigated show a good compatibility brought about by the formation of both interpolymeric covalent bonds and interpolymeric and intrapolymeric ionic bridges, which play the role of a chemical compatibilizer. The results of the examinations performed show that the non-conventional cross-linked XNBR/CSM blends prove very good mechanical properties and are self-extinguished in air. Their flammability defined with the value of OI and combustion time in air clearly depends on the type of CSM.

Keywords Carboxylated butadiene–acrylonitrile rubber (XNBR) · Chlorosulfonated polyethylene (CSM) · Thermal analysis · Combustibility · Mechanical properties

Introduction

Imperfections in the processes of elastomers synthesis and cross linking cause that it is still the point at issue to seek alternative methods of producing new elastic materials showing sometimes specific properties, which would meet consumers' expectations. One of such methods of modifying high-molecular compounds consists in preparing polymer blends [1–11]. The properties of elastomeric materials obtained by non-conventional cross-linking elastomer blends have been examined for a long time at the Technical University of Łódź [1].

In earlier published papers [1, 12–14], we have found that the heating of the blends composed of carboxylated acrylonitrile-butadiene rubber (XNBR) and chlorosulfonated polyethylene (CSM) containing incorporated selected metal oxides or hydroxides [MeO, Me(OH)₂] leads to formation of both interelastomer covalent and ionic cross links and thus to the unconventional interelastomer curing in the blends studied. The cross-linking rate, the cross-linking degree, and the properties of the cured blends prepared in this way depend on XNBR/CSM ratio, the kind and amount of CSM used, and the kind and amount of metal compound incorporated into the blend as well. Further it has been found [15, 16] that the incorporation of different amount of magnesium oxides (8–32 wt%) into the XNBR/CSM blend (70/30 by weight, CSM containing 43 wt% of bound Cl) reduced combustibility of the prepared materials comparing to XNBR cured with MgO. These phenomena are connected both with the total Cl-content in the system and the specific action of MgO incorporated into the blends studied. The obtained results are the different thermal properties and the combustibility of CSM of different bound Cl-content [17, 18] and its different thermodynamic affinity to XNBR (XNBR

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solubility parameter $\delta = 20.5 \text{ MPa}^{1/2}$ [19], CSM solubility parameter $\delta = 18.3\text{--}19.9 \text{ MPa}^{1/2}$ depending on the total bound Cl-content in CSM [10]) which indicate that the XNBR/CSM blends containing different kinds of CSM (total bound Cl-content in the range: 24–43 wt%, potential flame-retardant agent) and cured with selected amount of MgO should exhibit the differentiated thermal properties and combustibility as well. Hence, the aim of this study is to investigate the effect of different kinds of CSM on the thermal properties and combustibility of the XNBR/CSM blends cured and filled with selected amount of MgO. MgO has been chosen and used due to its high crosslinking ability [13, 15, 16] and observed flame-retarding activity in the blends investigated [16].

Experimental

Materials

The subject of the present investigations concerned blends containing 70 parts by weight of carboxylated butadiene–acrylonitrile rubber (XNBR, Krynac X.7.50, a product from Bayer Lanxess, containing 7% by weight of combined acid and 27.5% by weight of combined acrylonitrile) and 30 parts by weight of chlorosulfonated polyethylene [CSM24 (Hypalon 48), CSM29 (Hypalon 20), CSM35 (Hypalon 40), and CSM43 (Hypalon 30), products from Du Pont Dow Elastomers, containing 24, 29, 35, and 43% by weight of chlorine totally combined and $\sim 1.1\%$ by weight of chlorine combined in $-\text{SO}_2\text{Cl}$ groups and $\sim 1\%$ by weight of combined sulfur].

Methods and analysis

The XNBR/CSM blends prepared at room temperature by means of a laboratory rolling mill were cross linked at a temperature of $150 \text{ }^\circ\text{C}$ using a cross-linking agent including 24 parts by weight of magnesium oxide (MgO from Ancor-P) in the presence of two parts by weight of fatty acid (stearin from POCh) per 100 parts by weight of the elastomer blend. The excessive content of MgO in investigation blends in relation to the twice as high stoichiometric quantity, in terms of the content of carboxyl groups, fulfills the function of filler in them. The blends were, respectively, designated with the following symbols: XNBR/CSM24, XNBR/CSM29, XNBR/CSM35, and XNBR/CSM43.

The cross-linking durations of particular XNBR/CSM blends were consistent in an electrically heated hydraulic press with the values of τ_{90} determined from the results of the cross-linking kinetic measurements obtained by means

of a WG-02 vulcameter with an oscillating rotor according to standard PN-ISO 3417:1994 [16].

The cross-linking degree of XNBR/CSM blends ($\alpha = 1/Q_w$), taking into account both crosswise ionic bonds and crosswise covalent bonds, was determined on the basis of the results of equilibrium swelling (Q_w) in toluene. The cross-linking degree ($\alpha' = 1/Q_{w,a}$), taking into account crosswise covalent bonds was determined from the results of equilibrium swelling ($Q_{w,a}$) in toluene after the action of ammonia vapors [16].

The measurements of equilibrium swelling were performed also in the case of samples heated in the derivatograph furnace up to appropriate temperatures determined from DTA curves [16].

The determinations of elasticity constants were carried out with dumbbell samples with a measurement section length of 20 mm and a width of 4 mm. The length of measurement sections before and after loading was determined by means of a cathetometer. The measurement was performed 30 min after each sample loading, and the weights were selected so that the sample elongation increment was each time up to 20% of the measurement section length. The measurement was carried out until 120% of the initial measurement section value was obtained. Elasticity constants were determined from Mooney–Rivlin's equation [20, 21].

The mechanical properties of cross-linked XNBR/CSM blends were tested according to standard PN-ISO 37:1998 by means of a Zwick tensile testing machine, model 1435, cooperating with a properly programmed computer. Dumbbells with a measurement section width of 4 mm were used to determine tensile strength (TS_b) and elongation at break (E_b) [16].

The thermal analysis of cross-linked blends was performed under both air and nitrogen atmospheres. 90 mg of samples were heated under air in a Paulik, Paulik Erdevy derivatograph furnace at a rate of $7.9 \text{ }^\circ\text{C}/\text{min}$ within the temperature range $25\text{--}800 \text{ }^\circ\text{C}$ using Al_2O_3 as a reference substance. Thermal curve sensitivities were as follows: $TG = 100$, $DTA = 1/5$, and $DTG = 1/20$.

Under nitrogen atmosphere, 5–7 mg of samples were heated in a DSC-204 furnace from Netzsch at a rate of $10 \text{ }^\circ\text{C}/\text{min}$ within the temperature range from -100 to $500 \text{ }^\circ\text{C}$.

The flammability of the cross-linked XNBR/CSM blends was determined by the method of oxygen index using an apparatus of our own construction [22]. The flammability of XNBR/CSM was also assessed on the basis of sample combustion time under air or time, after which the sample was extinguished. The sample shape and dimensions, its arrangement, and flame treatment time were the same as in the case of the oxygen index method [16].

Results and discussion

The thermal properties of high-molecular components of XNBR/CSM blends were the object of our earlier studies [16]. From them it follows that in the atmosphere of a neutral gas, the thermal stability of XNBR, determined by the range of temperature, at which the polymer maintains its elastic properties, is $\Delta T = -31 \div 263 \text{ }^\circ\text{C}$, where $T = -31 \text{ }^\circ\text{C}$ is its glass transition temperature (T_g) and $T = 263 \text{ }^\circ\text{C}$ is the temperature of the beginning of its cross-linking (T_c) (Table 1; Fig. 2). The range of temperature, at which XNBR maintains its elastic properties in the atmosphere of air is $\Delta T = -31 \div 180 \text{ }^\circ\text{C}$, since its thermooxidative cross-linking processes begin at $T = 180 \text{ }^\circ\text{C}$ [16]. The range of thermal stability of the chlorosulfonated polyethylene (CSM) under investigation can assume different values depending on the type of CSM. The upper limit of their thermal stability is determined by the temperature, at which the dehydrochlorination processes begin and bring about the thermal modification of polymer chains. This temperature, $190 \text{ }^\circ\text{C}$, is independent of the type of CSM and the atmosphere of the examinations performed. The lower limit of the thermal stability of

CSMs is determined by their glass transition temperature and in the case of CSM24, their crystallization temperature [18]. In this connection, the lowest ΔT is shown by CSM43 which has the highest temperature of the transition from glassy to elastic state (Table 1).

The comparative analysis of vulcаметric results leads to a conclusion that the increase in the content of chemically combined chlorine in the macromolecules of CSM does not exert any systematic influence on the optimal vulcanization time (τ_{90}) of the XNBR/CSM blends at $T = 150 \text{ }^\circ\text{C}$ (Table 2). On the other hand, it brings about an increase in the cross-linking degree of the blends investigated resulting from the presence of the interpolymeric covalent crosswise bonds of XNBR–CSM ($\sim\text{SO}_2\text{--O--CO}\sim$) as well as the interpolymeric crosswise ionic bonds ($2C_1, \alpha$; Table 2). It is the difference in the cross-linking degrees ($\alpha\text{--}\alpha'$) (Table 2) that testifies to the presence of the intrapolymeric ionic bonds of XNBR–XNBR ($\text{--CO--O}^{(-)(+)}\text{Mg}^{(+)(-)}\text{O--OC--}$) and the interpolymeric ionic bonds of XNBR–CSM ($\text{--CO--O}^{(-)(+)}\text{Mg}^{(+)(-)}\text{O--SO}_2\text{--}$) containing magnesium ions [16]. The crosswise bonds formed during vulcanization fulfill the role of a chemical compatibilizer of the blends investigated [16]. Owing to the presence of crosswise ionic bonds, the XNBR/CSM blends are characterized by very good mechanical properties within a wide range of cross linking as shown by the values of TS_b and E_b parameters (Table 2). Our findings show that in the case of the XNBR/CSM24, XNBR/CSM29, and XNBR/CSM35 blends cross-linked by means of 24 parts by weight of MgO, the contents of their crosswise bonds are comparable (Table 2). The findings published earlier show that MgO used in the cross linking of the XNBR/CSM blends fulfills the function of both cross linker and filler. It has been also found that the vulcanization of the XNBR/CSM blends results in decreased dimensions of MgO particles dispersed in the elastomeric matrix due to their participation in the formation of crosswise ionic bonds [16].

The similar solubility values of the macromolecular components of the blends investigated, amounting to: $\delta_{\text{XNBR}} = 20.5^{1/2}$; $\delta_{\text{CSM24}} = 18.3^{1/2}$; $\delta_{\text{CSM29}} = 19.2^{1/2}$; $\delta_{\text{CSM35}} = 19.5^{1/2}$; $\delta_{\text{CSM43}} = 19.6^{1/2}$ [19] indicate potential miscibility of the elastomers, which is confirmed by the

Table 1 Thermal properties of elastomers and their cross-linked blends in nitrogen atmosphere

Sample	Thermal parameters			
	$T_g/^\circ\text{C}$	$\Delta T_c/^\circ\text{C}$	$\Delta H_c/\text{J/g}$	$T_D/^\circ\text{C}$
XNBR [16]	-31	263–424	712	459
CSM24	-24 [18]	357–447	245	477
CSM29	-27 [18]	345–445	260	469
CSM35	-23 [18]	348–452	314	474
CSM43 [16]	10	328–346	398	335a
XNBR/CSM24	-26	245–416	376	463
XNBR/CSM29	-29	243–411	413	462
XNBR/CSM35	-28	243–414	478	466
XNBR/CSM43 [16]	-21	234–419	569	482

T_g glass transition temperature, ΔT_c temperature range of thermal cross linking, ΔH_c change of thermal cross-linking enthalpy, T_D temperature of destruction maximum rate, a gentle destruction process

Table 2 Influence of kind of CSM on the cross-linking degree of XNBR/CSM blends and their mechanical properties

Sample	τ_{90}/min	$2C_1/\text{MPa}$	α	α'	$\alpha\text{--}\alpha'$	TS_b/MPa	$E_b/\%$
XNBR/CSM24	48	3.25	0.248	0.196	0.052	21.2	586
XNBR/CSM29	42	4.50	0.292	0.247	0.045	24.1	592
XNBR/CSM35	49	6.53	0.258	0.209	0.049	26.9	629
XNBR/CSM43 [16]	53	11.91	0.337	0.321	0.016	27.5	525

τ_{90} optimal vulcanization time, $2C_1$ elasticity constant determined from Mooney–Rivlin, α crosslinking degree, taking into account both ionic and covalent crosswise bonds, α' crosslinking degree, taking into account covalent crosswise bonds, $\alpha\text{--}\alpha'$ indicator of the content of ionic cross linkages, TS_b tensile strength, E_b elongation at break

results obtained by the DSC method (Table 1; Figs. 1, 2, 3). Regardless of the CSM type used, the cross-linked XNBR/CSM blends are characterized by one glass transition temperature being intermediate between the T_g values of the elastomer components (Table 3; Figs. 1, 2, 3). From

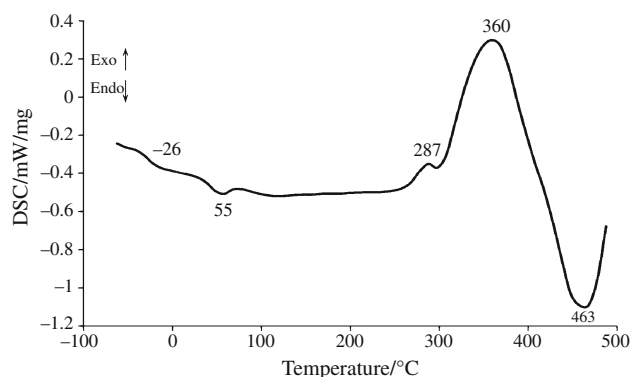


Fig. 1 DSC curve of cross-linked XNBR/CSM24 blend in nitrogen atmosphere

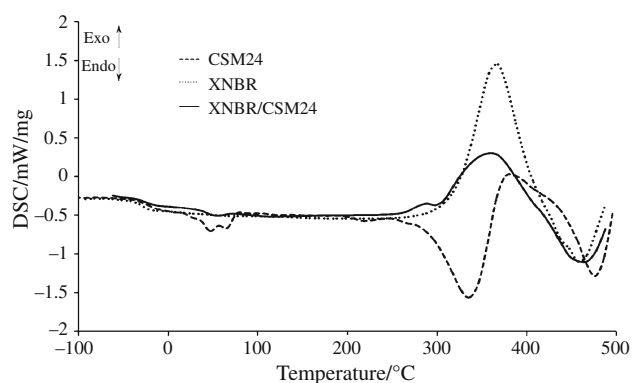


Fig. 2 DSC curves of XNBR, CSM24, and cross-linked XNBR/CSM24 blend in nitrogen atmosphere

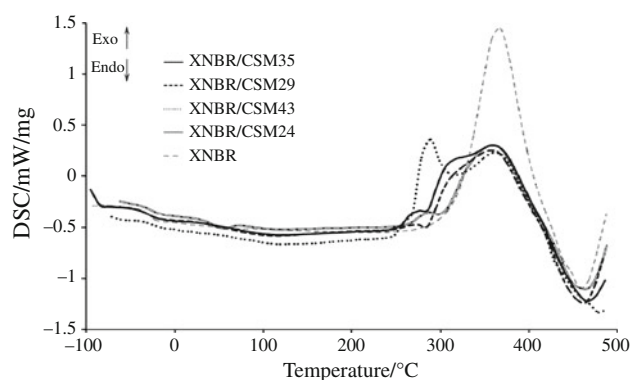


Fig. 3 DSC curves of XNBR and cross-linked XNBR/CSM blends in nitrogen atmosphere

the DSC curve of the cross-linked XNBR/CSM24 blends, it follows that the transition from glassy to elastic state takes place at $T = -26$ °C. The small endothermic transformation recorded on the thermal curve at $T = 55$ °C is connected with the melting of crystalline phase in CSM24, whose macromolecules can crystallize due to the lowest content of chemically combined chlorine among all the CSM investigated [18]. The great exothermic transformation of the vulcanized blends recorded on DSC curves, comprising two pronounced peaks in the case of XNBR/CSM24 and XNBR/CSM29 at $T = 287$ °C and $T = 360$ °C and three pronounced peaks in the case of XNBR/CSM35 and XNBR/CSM49 at $T = 261$, 285, and 360 °C, is connected with the processes of their thermal cross linking (Figs. 1, 2, 3). The beginning of the thermal cross linking of XNBR/CSM, which determines the end of their elastic state starts at $T = 245$ °C in the case of XNBR/CSM24 and shifts towards lower temperatures under the influence of the increase in chemically combined chlorine in the macromolecules of CSM (Table 1; Figs. 1, 2, 3). The comparative analysis of the values of the thermal cross-linking enthalpy (ΔH_c) of XNBR/CSM blends leads to a conclusion that the increase in chlorine content in the CSM macromolecules increases the yield of these processes (Table 1). The thermal cross-linking processes are accompanied by the destruction of elastomer macromolecules [16]. The temperature of the maximal destruction rate of XNBR and CSM macromolecules clearly increases with the increase in the content of chlorine in CSM (Table 1).

From the derivatographic analysis of the cross-linked blends, it follows that they are decomposed in three stages under the influence of heating (TG, DTG; Fig. 4). Based on the measurement results of the Q_w of vulcanized XNBR/CSMs before and after their heating in the derivatograph oven up to $T = 245$ and 305 °C, it was found that the first two transformations recorded on DTA curves at these temperatures were a symptom of their thermal cross linking in the atmosphere of air. The transformation at $T = 305$ °C is accompanied by a considerable sample weight loss amounting to 11% (Fig. 4) brought about by the commencing destruction processes of the vulcanized blend components and the evolution of HCl (T_{DI} ; Table 3). The violent destruction processes of the cross-linked blends begin at $T_{DI} \geq 355$ °C as shown by the two exothermic transformations recorded on DTA curve at $T = 405$ and 450 °C, respectively (Fig. 4). The thermal decomposition rate of the cross-linked XNBR/CSM (dm/dt_{II}) is considerably lower than the destruction rate of XNBR constituting the polymeric matrix (Table 3), which results from the presence of HCl evolving from the thermal decomposition reactions of the cross-linked blends, owing to which these reactions proceed according to both free-radical and ionic mechanism. This situation facilitates carbonization

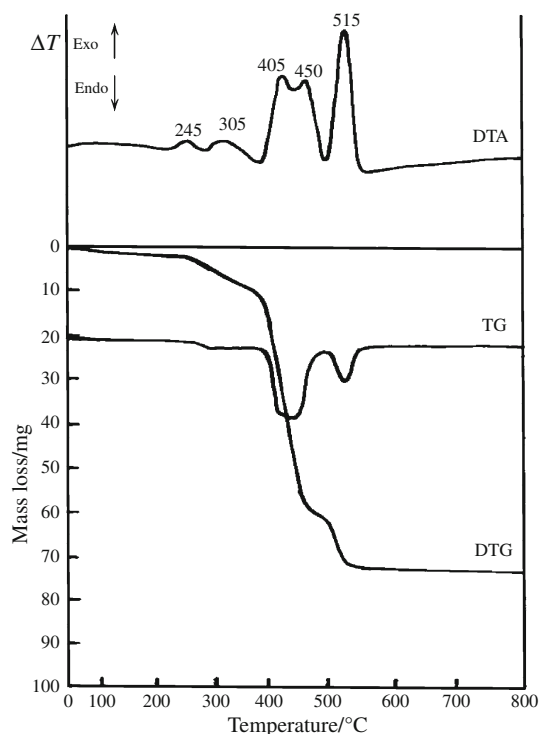


Fig. 4 Thermal curves (DTA, TG, and DTG) of cross-linked XNBR/CSM24 in air atmosphere

processes as shown by the considerable increase in the residue after the thermal destruction of the cross-linked XNBR/CSM blends (P_w) and the cross-linked elastomer (P_e) (Table 3). In the atmosphere of air, the residue after thermal decomposition is burned as indicated by the exothermic peak recorded at $T = 515$ °C (Fig. 4; Table 3). The high residue after the combustion of the solid residue resulting from the destruction of the cross-linked XNBR/CSM blends (P_{800}) is significantly influenced by MgO contained in them as cross linker (Table 3).

The results of previously performed tests show that XNBR belongs to polymers extinguishing in air (Table 4). The flammability of the CSMs used depends on the content of chemically combined chlorine [17]. CSM24 and CSM29 belong to the group of self-extinguishing polymers, while CSM35 and CSM43 belong to the group of non-flammable polymers. The XNBR/CSM blends under investigation are self-extinguished in air and their flammability defined by both the value of oxygen index (OI) and the combustion time in air (t) depends of the type of CSM (Table 4). The time, after which the XNBR/CSM blend extinguishes in air, is shortened with the increase in the content of chlorine in CSM (Table 4). The high OI values and the short times, after which the cross-linked XNBR/CSM blends extinguish in air, are due to HCl evolving under the influence of elevated temperature. HCl manifests its active action first of all in the flame to inhibit the chain reactions proceeding in it. At the same time, HCl as non-flammable gas decreases the concentration of gaseous flammable products within the combustion zone and retards the diffusion of oxygen to this zone. From the derivatographic analysis, it follows that HCl shows its active action also in the solid combustion zone where it decreases the thermal destruction rate of the cross-linked elastomers and facilitates their carbonization (Table 3). As a result, a lower quantity of volatile and flammable products of the destruction of the cross-linked polymer blends passes to flame. The structure of the boundary layer between the sample (solid phase) and flame (gaseous phase) is also of great importance in the combustion process. In this case, it is formed of carbonized elastomers. In this connection, this layer shows a high thermal stability and considerably retards the flow of mass and energy between the solid and gaseous phases during combustion. The lowest flammability defined with both the value of OI and the time of combustion in air (t) is shown by the cross-linked XNBR/CSM43 blend (Table 4), which results from its lowest thermal

Table 3 Thermal properties of XNBR and its cross-linked blends in air atmosphere

Sample	Thermal parameters											
	$T_5/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{DI}/^\circ\text{C}$	$T_{DI\text{max}}/^\circ\text{C}$	$dm/dt_I/\text{mm}$	$T_{DI\text{I}}/^\circ\text{C}$	$T_{DI\text{I}\text{max}}/^\circ\text{C}$	$dm/dt_{II}/\text{mm}$	$P_w/\%$	$P_e/\%$	$T_s/^\circ\text{C}$	$P_{800}/\%$
XNBR [16]	340	415	–	–	–	355 <i>a</i>	380	68	–	19.4	530	1.1
XNBR/CSM24	280	430	245	285	6	365	420	36	32.8	27.7	515	18.9
XNBR/CSM29	270	430	230	260	5	365	420	47	35.0	29.6	520	21.0
XNBR/CSM35	270	430	225	265	5	360	420	45	33.8	28.7	520	20.0
XNBR/CSM43 [16]	250	430	220	240	5	355	400	32	38.9	32.9	525	17.8

T_5 temperature of elastomer/blend 5% mass loss, T_{50} temperature of elastomer/blend 50% mass loss, T_{DI} temperature of the first stage of elastomer/blend thermal decomposition, $T_{DI\text{max}}$ maximum temperature of the first stage of elastomer/blend thermal decomposition, dm/dt_I maximum rate of the first stage of elastomer/blend thermal decomposition, $T_{DI\text{I}}$ temperature of the second stage of elastomer/blend thermal decomposition, $T_{DI\text{I}\text{max}}$ maximum temperature of the second stage of elastomer/blend thermal decomposition, dm/dt_{II} maximum rate of the second stage of elastomer/blend thermal decomposition, P_e residue after elastomer thermal decomposition, P_w residue after blend thermal decomposition, T_s combustion temperature of residue after elastomer/blend thermal decomposition, P_{800} residue after heating of elastomer/blend up to 800 °C, *a* temperature of XNBR thermal decomposition

Table 4 Combustibility of elastomers and their blends

Sample	<i>t</i> /s	OI
XNBR [16]	129	0.256
XNBR/CSM24	39	0.327
XNBR/CSM29	25	0.301
XNBR/CSM35	21	0.293
XNBR/CSM43 [16]	19	0.331

t Time after which the tested sample is extinguished in air, *OI* oxygen index

decomposition rate (dm/dt_{II} ; Table 3) and the highest yield of carbonization during this process (P_w , P_e ; Table 3). A significant influence on the reduction in the flammability of XNBR/CSM43 is also exerted by the great yield of the thermal cross-linking processes (ΔH_c ; Table 1). The thermal cross linking of elastomers is one of many chemical reactions proceeding in the solid phase of burning polymer that affect the boundary layer structure and consequently also the course of combustion.

Conclusions

Regardless of the type of CSM, its cross-linked blends with carboxylated butadiene–acrylonitrile rubber (XNBR) show one glass transition temperature (T_g), which indicates a good miscibility of both polymers. This compatibility results from the presence of interpolymeric crosswise covalent bonds as well as intrapolymeric and interpolymeric ionic bonds containing magnesium ions. The crosswise bonds formed during vulcanization of XNBR/CSM play the role of a chemical compatibilizer.

The thermal decomposition rate of the cross-linked XNBR/CM blends (dm/dt_{II}) is considerably lower than that of XNBR being the elastomeric matrix, which results from the considerable contribution of ionic reactions to the destruction of cross-linked blends.

The non-conventional cross-linked XNBR/CSM blends prove very good mechanical properties and belong to self-extinguishing materials in air. The time, after which the cross-linked blend extinguishes in air, is shortened with the increase in the content of chlorine combined in CSM.

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