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The effect of metal oxide on the cure, morphology, thermal and mechanical characteristics of chloroprene and butadiene rubber blends

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Abstract

This paper discusses the role of metal oxides (MeO) in the cross-linking process and useful properties of chloroprene and butadiene rubber (CR/BR) blends. Iron(III) oxide (Fe_2O_3), iron(II,III) oxide (Fe_3O_4), silver(I) oxide (Ag_2O) or zinc oxide were used. It has found that every proposed metal oxide can be used as a cross-linking agent of the CR/BR blends. The degree of cross-linking was evaluated by means of vulcametric parameters, equilibrium swelling in selected solvents and Mooney–Rivlin elasticity constants. The properties of the cured CR/BR products, such as tensile strength, stress at elongation, tension set under constant elongation and compression set, were also investigated. The results revealed that all CR/BR/MeO vulcanizates were characterized by a high cross-linking degree and satisfying mechanical properties. The most important advantage of obtained rubber goods is very high resistance to flame. The increase in the oxygen index value for the $CR/BR/Fe_2O_3$, $CR/BR/Fe_3O_4$ and $CR/BR/Ag_2O$ vulcanizates compared to the standard cross-linked chloroprene rubber showed that presented metal oxides provided a positive effect on the resistance to flame of the new CR/BR/MeO composites. Satisfactory properties of the studied blends are related to the presence of the interelastomer bonding of both rubbers in the compositions.

Keywords Chloroprene rubber · Butadiene rubber · Metal oxide · Cross-linking · Elastomeric blends · Flammability

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Introduction

Chloroprene rubber (CR) is a high-performance material with a wide diversity of applications. It is a homopolymer of chloroprene [1, 2]. Polymer chains have almost entirely *trans*–1.4 configuration, but the main chain has also a very small amount of *cis*–1.4, 1.2 and 3.4 structures [3, 4]. Unlike other diene elastomers, chloroprene rubber cannot be cross-linked with sulfur due to the presence of substantially inactive $>C=C<$ bonds. Therefore, CR is conventionally cured with 5 phr of zinc oxide (ZnO) in the presence of 4 phr of magnesium oxide (MgO). The mechanism of CR curing is unclear [5]. Chloroprene rubber can be cross-linked with other metal oxides, such as iron(III) oxide, iron(II,III) oxide [6], tin(II) oxide [7], copper(I) oxide or copper(II) oxide [8]. Such obtained CR vulcanizates are often characterized by better mechanical properties than the conventionally cross-linked CR.

Chloroprene rubber is difficult to process; hence, it is often mixed with other elastomers. Blending of different rubbers to combine desirable properties of each component is a very common practice in the rubber industry. Rubber blending allows the production of new materials, obtaining the best processability and cost reduction in rubber product manufacturing process [9]. Chloroprene rubber has recently been combined with other elastomers to achieve special properties of either the CR-based compounds or compounds based on second ingredients. A few reports describe blends of CR with other rubber, such as natural rubber (NR) [10, 11], hydrogenated acrylonitrile–butadiene rubber (HNBR) [12, 13], styrene–butadiene rubber [14], butadiene rubber (BR) [15, 16] or chlorosulfonated polyethylene (CSM) [17] have been published thus far. The Salleh et al. [11] investigated two types of blends containing the natural rubber and chloroprene rubber or epoxidized natural rubber and chloroprene rubber. These blends were cross-linked with sulfur (S) in the presence of tetramethylthiuram monosulfide (TMTM), *N*-cyclohexyl2-benzothiazylsulfonamide (CBS), zinc oxide (ZnO) and magnesium oxide (MgO). It was found that natural rubber/recycled chloroprene rubber blend cross-linked rapidly than epoxidized natural rubber/recycled chloroprene rubber blend. In case of the CR/HNBR blends cured with dicumyl peroxide in the presence of zinc oxide, the tensile strength and thermal resistance depend on the amount of CR in these compounds and decrease with the content of CR [13]. Mingyi et al. [15] studied the structure and properties of chloroprene, butadiene rubber and styrene–butadiene–styrene copolymer (CR/BR/SBS) blends. The addition of styrene–butadiene–styrene copolymer to thermodynamically immiscible CR/BR blends improved the homogeneity and increased the tensile strength and cross-link density of vulcanizates. The CR/BR/SBS blends include sulfur, TMTD, zinc oxide, magnesium oxide and stearic acid. The low-temperature resistance, electrical insulation properties and mechanical properties of CR/BR blends were studied by Zheng et al. [16]. The BR incorporation to CR improved its low-temperature resistance and electrical insulation properties, while the tensile strength and elongation at break decreased to some extent. These blends were also cross-linked with sulfur in the presence of TMTD,

ZnO and MgO. The rheological and mechanical properties and thermal stability of polychloroprene/chlorosulfonated polyethylene (CR/CSM) rubber blends filled with nano- and micro-silica particles were studied by Marković [17]. The density of the nano-silica-filled CR/CSM rubber blends was lower than the micro-silica-filled samples, but the tensile strength and elongation at break were much higher. The nano-silica-filled CR/CSM blends were transparent at all filler concentration and have higher glass transition values than micro-silica-filled compounds. The higher values of the glass transition temperatures for the nano- than the micro-filled vulcanizates are indicated by DMA analysis. The nano-filled cross-linked systems have a larger number of SiO–C links than micro-filled cross-linked systems and hence increased stability.

The majority of tested blends containing chloroprene rubber with other elastomers were cross-linked with sulfur in the presence of activator and accelerator. And as we know, the sulfur reacts with unsaturated rubbers occurs through complicated radical substitution in the form of mono-($-S-$), di-($-S_2-$) or polysulfide bridges ($-S_x-$) [18–20]. Unfortunately, the sulfur cross-linking is relatively slow; therefore, it is necessary to use accelerators (e.g., thiazole, sulfonamide) and activators (e.g., ZnO, MgO). These substances reduce the time required for vulcanization, but most of them are harmful to environment and human health. The commonly used accelerators (2-mercaptobenzothiazole, TMTD, CBS) are classified as toxic materials and suspected to be carcinogenic. Additionally, the local vulcanization, reversion, tendency to caking (agglomerates have a negative effect on the vulcanization) and migration on the surface of blends and vulcanizates can occur using sulfur in the process of cross-linking [18, 20].

The aim of our research was to analyze the role of selected metal oxide (MeO) on the cross-linking process of CR/BR blends and the properties of the resulting products. The iron(III) oxide [21], the iron(II,III) oxide, the silver(I) oxide or the zinc oxide [22] were proposed. The use of such compounds resulted from the necessity to eliminate the conventional method of cross-linking and its disadvantages. We assumed that the CR/BR blends prepared and cross-linked with selected metal oxide would be characterized by increased resistance to flame and satisfactory thermal and mechanical properties. The blends containing chloroprene and butadiene rubbers have not been cross-linked so far by the method proposed in this work.

Experimental

Materials

Chloroprene rubber (CR) (Baypren®216 MV from Lanxess GmbH, Dormagen, Germany) and butadiene rubber (BR) (SYNTECA®44 from Synthos S.A., Poland) were used. Commercial additives, such as iron(III) oxide and iron(II,III) oxide, silver(I) oxide and zinc oxide (Sigma-Aldrich Chemical Co. Germany), were used as a cross-linking agent. Stearic acid (Chemical Worldwide Business Sp. z o. o.) was used as a dispersant.

Preparation and vulcanization of the rubber blends

The rubber blends were prepared in a conventional way using a laboratory two-roll mill with rolls of following dimensions: diameter = 150 mm and length = 300 mm. The rotational speed of the front roll was 20 rpm friction 1:1.25. The rubber blends were then pressed in an electrically heated hydraulic press. Teflon films were used as spacers preventing the adherence of blend to the press plates. Samples were vulcanized at a temperature of 160 °C, under pressure of 15 bars for 15 min.

Cure characteristic

Cross-linking density was determined on the basis of vulcametric measurement, equilibrium swelling, extraction in boiling acetone and Mooney–Rivlin elasticity constants. Vulcametric measurements were taken on a MonTech D-MRD 3000 rheometer for 60 min at 160 °C according to ASTM D5289-17 standard. For swelling experiments pieces, weighing 30–50 mg, were cut and immersed in toluene or heptane for 72 h at room temperature. The swollen samples were weighed on an analytical balance and then dried in a dryer at a temperature of 50 °C to a constant weight, and after 24 h they were reweighed. The real extract was calculated on the basis of the equation (Eq. 1):

$$E_r = \frac{m_1 - m_2}{m_1} \tag{1}$$

where m_1 is the sample weight before extraction (mg) and m_2 is the sample weight after extraction (mg).

On the basic of the Mooney–Rivlin equation (Eq. 2), the first $(2C_1)$ and second $(2C_2)$ elasticity constants were given:

$$C_1 + \lambda^{-1} \cdot C_2 = \frac{P}{2A_0 * \left(\lambda - \lambda^{-2} \right)} \tag{2}$$

where P is the deformation force at λ (kG), λ is the deformation ($\lambda = l/l_0$), l is the measuring section of the sample loaded with P (cm), l_0 is the measuring section of the unloaded sample (cm), A_0 is the cross-sectional area of the unloaded sample (cm^2), $2C_1$ is the first elasticity constant (kg/cm^2) and $2C_2$ is the second elasticity constant (kg/cm^2).

Thermal analysis

Thermal changes of CR/BR/MeO blends were carried out by differential scanning calorimetry (DSC) using a model DSC1 Mettler Toledo with heating run of − 100 to 250 °C and temperature increase rate 10 °C/min.

Morphology studies

The morphology of the CR/BR was evaluated using a scanning electron microscopy (SEM) by Hitachi S-4700 (Japan) with the ThermoNORAN energy-dispersive spectrometer (EDS) microanalysis adapter. The samples were sputter coated with carbon under high vacuum before an examination. The magnification of image was 5000.

Thermo-oxidative aging

The thermal aging of the CR/BR/MeO vulcanizates was performed in a forced circulating aging oven at 70 °C for 7 days. The aged specimens were then kept for a period of 24 h at room temperature for attaining the thermal equilibrium before measurements of their mechanical properties (stress at elongation of 100, 200, 300%, tensile strength, elongation at break). The changes of mechanical properties caused by thermo-oxidative aging were evaluated based on aging index (K) (Eq. 3):

$$K = \frac{TS_b' \cdot E_b'}{TS_b \cdot E_b} \tag{3}$$

where TS_b' is the tensile strength after thermo-oxidative aging (MPa), TS_b is the tensile strength before thermo-oxidative aging (MPa), E_b' is the elongation at break after thermo-oxidative aging (%) and E_b is the elongation at break before thermo-oxidative aging (%).

Mechanical test

Mechanical properties such as stress at the elongation of 100%, 200% or 300% (S_{e100}, S_{e200}, S_{e300}) tensile strength (TS_b) and elongation at break (E_b) of the vulcanizates were tested according to standard PN-ISO 37:2007 by means of a ZWICK tensile tester, model 1435.

Tension set under constant elongation

Determination of tension set under constant elongation was tested according to standard ISO 2285 by straining device, consisting of a metal rod with pairs of holders, one fixed and one moveable, for the ends of the test piece. Test pieces shall be in shape of stripe between 2 mm and 10 mm wide. The length of any given strip depends on the selected reference length and type of straining device. The measurement is taken using the Method C. After measuring the original length, the specimen is slowly elongated to its test length (25%). After 10–20 min, the elongated distance between markers is determined. Specimens are kept under constant temperature (70 °C) for 22 h. Thereafter, specimens are relaxed slowly and stored for 30 min on a nonsticking wooden surface. Finally, the relaxation length is determined and tension set (E) is calculated using the equation (Eq. 4):

$$E = \frac{(L_2 - L_1)}{L_1} \cdot 100 \tag{4}$$

where L_1 is the original, unstrained, reference length (mm) and L_2 is the strained reference length (mm).

Compression set

Samples for testing (diameter: 30 mm, thickness: 12.5 mm) were subjected to compression at 70 °C for 22 h, in accordance with ISO 815, B method. Spacer plates were used to achieve a deformation of 25%. After 22 h, the samples were cooled in a deformed condition at room temperature for 30 min. After the removal of compressive forces, the samples were conditioned for 30 min, and then, their thickness was measured. On the basis of the results obtained, the compression set (C), expressed as a percentage of the initial compression, is given by the formula (Eq. 5). The testing of each sample was repeated three times.

$$C = \frac{h_0 - h_i}{h_0 - h_s} \cdot 100 \tag{5}$$

where h_0 is the initial thickness of the test piece (mm), h_i is the thickness of the test piece after recovery and h_s is the height of the spacer.

Flammability

Flammability of the blends was determined by the oxygen index method using a Fire Testing Technology apparatus. The prepared samples with dimensions $50 \times 10 \times 4$ mm were ignited for 5 s by means of a gas burner supplied with a propane–butane mixture. The constant nitrogen flow rate was 400 l/h, while the concentration of oxygen was chosen so that the sample can be completely burned within 180 ± 10 s. The oxygen index (OI) was calculated as the percentage of oxygen and nitrogen volume in the mixture (Eq. (6)):

$$OI = \frac{O_2}{O_2 + N_2} \tag{6}$$

where O_2 is the oxygen flow rate (l/h) and N_2 is the nitrogen flow rate (l/h).

Results and discussion

Cross-linking of CR/BR blends with metal oxide

In this study, the role of metal oxides type on the cross-linking kinetics and the selected properties of blends containing chloroprene and butadiene rubbers (CR/

BR = 75/25) were assessed. For this purpose, iron(III) oxide (Fe_2O_3), iron(II,III) oxide (Fe_3O_4), silver(I) oxide (Ag_2O) or zinc oxide (ZnO) [23] were used as cross-linking agents. We have expected that such cured CR/BR blends will be characterized by a high cross-linking degree, but this parameter will depend on the type of used metal oxide.

Table 1 represents the cure characteristics of CR/BR blends cross-linked with different metal oxides. It follows that every proposed metal oxide can be used as a cross-linking agent of CR/BR blends. The MeO type affects the scorch time (t_{02}). The greatest scorch time (t_{02} = 7.77 min) was observed for blend cross-linked with iron(III) oxide, whereas, in the case of CR/BR/Fe_3O_4 and CR/BR/ZnO blends, shorter scorch time (4.14 min and 3.04 min, respectively) was observed. The incorporation of Ag_2O into the CR/BR blend clearly reduces the scorch time (t_{02} = 0.41 min). Based on vulcametric measurements, it was also found that cure time depends on the type of metal oxide. The cure time was almost three times longer when using silver(I) oxide or zinc oxide than when the using iron(III) oxide or iron(II,III) oxide. The viscosity of the blends depends on an elastomers ratio in blends. When the elastomers proportion in the blends is the same, the value of the minimal torque of blends should be similar. The M_{min} for CR/BR/Fe_2O_3, CR/B/Fe_3O_4 and CR/BR/ZnO blends was in a range of 0.52–0.62 dNm, whereas in case of CR/BR/Ag_2O higher value of this parameter (M_{min} = 1.1 dNm) was observed. The blend cross-linked with iron(III) oxide exhibits the highest cross-linking degree. For this blend, the torque increment after 30 min of heating was 6.36 dNm, whereas in the case of blends cross-linked with zinc oxide the value of ΔM_{30} was only 2.95 dNm. This significant difference in torque increment after 30 min of heating between used metal oxides (Fe_2O_3, Fe_3O_4, Ag_2O or ZnO) (step A) can be caused by a different activity of metal oxide in the reaction with hydrogen chloride and thus different rates of the formation of Lewis acid. During the heating of CR/BR blend with metal oxide, the Lewis acid ($[AgCl_2]^-$, $[ZnCl_4]^{2-}$ or $[FeCl_6]^{3-}$ from Fe_2O_3 or Fe_3O_4) (step B) is generated in situ and acts as a catalyst necessary for the interelastomer bonding within the rubbers (step C) [24]. The proposed cross-linking mechanism of CR/BR composites in the presence of metal oxide is shown in Scheme 1.

The effect of the curing agent type on the cross-linking degree was also determined by equilibrium swelling in toluene or heptane (Table 2). The results show that

Table 1 Cure characteristic of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO), T = 160 °C, t = 60 min

Metal oxide (2.5 phr)	t_{02} (min)	t_{90} (min)	M_{min} (dNm)	ΔM_{15} (dNm)	ΔM_{30} (dNm)
Fe_2O_3	7.77	14.50	0.62	5.81	6.36
Fe_3O_4	4.14	9.34	0.52	4.89	4.90
Ag_2O	0.41	26.51	1.10	5.03	5.47
ZnO	3.04	33.25	0.57	2.38	2.95

phr part per hundred parts of rubbers, t_{02} scorch time, t_{90} cure time, M_{min} minimal vulcametric torque, ΔM_{15}, ΔM_{30} torque increment after 15 or 30 min of heating
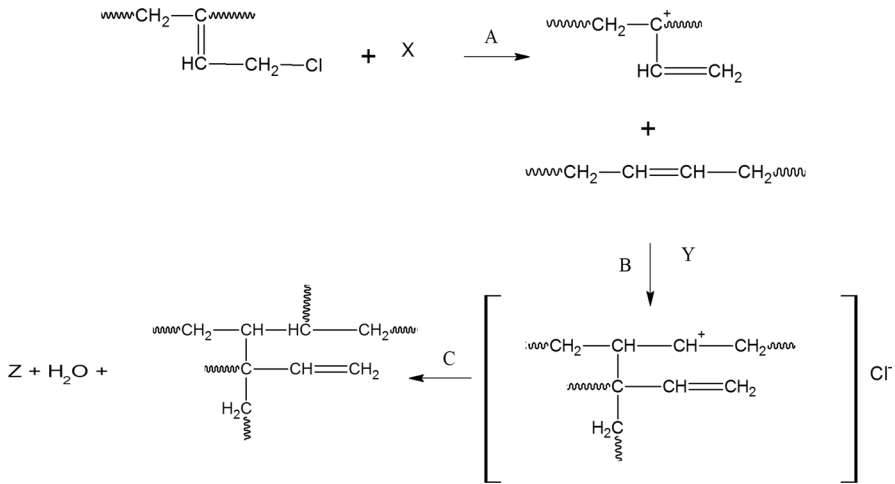
Scheme 1 Cross-linking mechanism of CR/BR blends in the presence of metal oxide (where X: Fe_2O_3, Fe_3O_4, Ag_2O or ZnO; Y: $[FeCl_6]^{3-}$, $[AgCl_2]^-$, $[ZnCl_4]^{2-}$; Z: $FeCl_3$, AgCl, $ZnCl_2$)

Table 2 Selected properties of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO)

Metal oxide (2.5 phr)	Q_v^T (ml/ml)	Q_v^H (ml/ml)	E_r (mg/mg)	$2C_1$ (kG/cm^2)
Fe_2O_3	6.20	1.04	0.069	2.44
Fe_3O_4	6.80	1.13	0.057	1.85
Ag_2O	6.65	1.08	0.044	1.67
ZnO	10.90	1.30	0.050	1.26

Q_v^T, Q_v^H equilibrium swelling degree in toluene or heptane, E_r real extract, $2C_1$ first elasticity constant

the highest cross-linking degree was obtained for the CR/BR/Fe_2O_3 vulcanizate. The values of Q_v^T for this sample were 6.20 ml/ml. It was also observed that the uptake of the aromatic solvent (toluene) was the highest for the vulcanizate cross-linked with zinc oxide ($Q_v^T = 10.90$ ml/ml). We have studied Mooney–Rivlin elasticity constants to evaluate the cross-linking density. The results confirmed our previous observations. The highest curing degree was achieved for CR/BR blend cross-linked with iron(III) oxide, because in this case the first elasticity constant was 2.44 kg/cm^2. For the blends cured with zinc oxide, the $2C_1$ value was the lowest (1.26 kg/cm^2), which indicates the lowest cross-linking degree. Dependently of the metal oxide used, the different real extract of studied blends was noticed. The sample containing Fe_2O_3 was characterized by the largest acetone extract (0.069 mg/mg), while the smallest E_r value (0.044 mg/mg) was obtained for the blend cross-linked with Ag_2O.
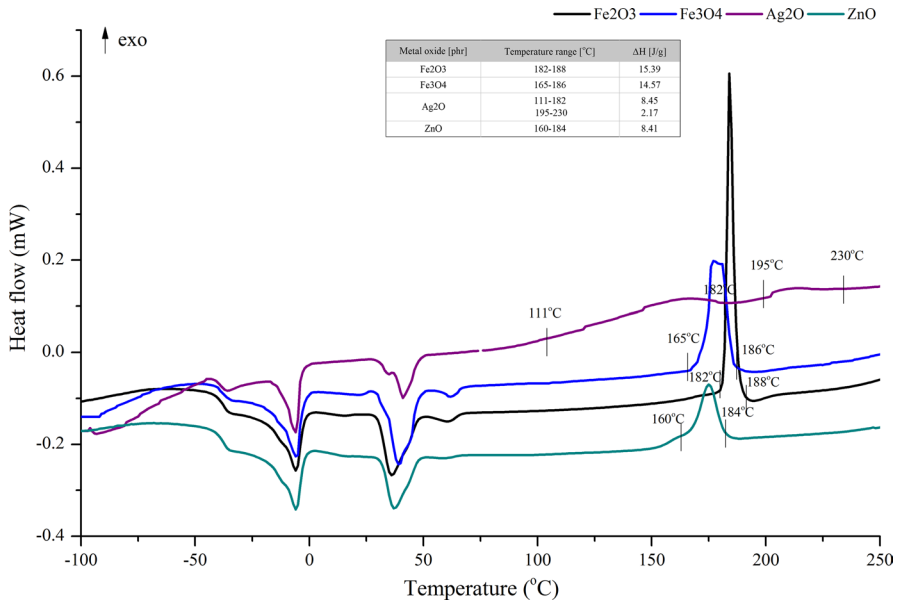
Fig. 1 DSC spectrum of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO), ΔH—enthalpy

Thermal analysis

The DCS curves of the CR/BR blends cross-linked with metal oxide are given in Fig. 1. The DSC thermogram is the result of all reactions occurring within the temperature range of interest. During the heating of the rubber compound, many reactions occur competitively; therefore, it is very difficult to measure the enthalpy for a specific reaction. The cross-linking depending on the type of CR/BR/MeO blends takes place in the temperature range from 111 to 230 °C. The enthalpy determined during the cross-linking can be correlated with the cross-linking density. The higher the enthalpy value, the more effective cross-linking process, and thus, the greater degree of cross-linking of the tested vulcanizates. In case of the CR/BR blends cross-linked with iron(III) oxide, the exothermic peak (temperature range from 182 to 188 °C) was very intense and narrow, while the enthalpy was the highest ($\Delta H = 15.39$ J/g). The cross-linking temperature range for the CR/BR/Fe_3O_4 blend increased, but the cross-linking enthalpy was also characterized by high value ($\Delta H = 14.57$ J/g). The lowest cross-linking enthalpy ($\Delta H = 8.41$ J/g) for the CR/BR/ZnO blend was observed. In case of the CR/BR/Ag_2O blend, two exothermic peaks have occurred. The first peak with the cross-linking enthalpy equal to 8.45 J/g occurred in the temperature range from 111 to 182 °C, while the second peak with the lower cross-linking enthalpy ($\Delta H = 2.17$ J/g) appeared in the temperature range from 195 to 230 °C. On the basis of determined cross-linking enthalpy, the highest cross-linking degree was

characterized by the CR/BR blend cured with iron(II) oxide or iron(III,IV) oxide, whereas the lowest degree of cross-linking was characterized by CR/BR/Ag$_2$O. The results obtained from DSC thermogram correlate with the results obtained from equilibrium swelling. As previously mentioned (Table 2), the CR/BR/Fe$_2$O$_3$ blend was characterized by the highest degree of cross-linking.

Morphology of CR/BR/MeO vulcanizates

The morphology of the surface of produced CR/BR/MeO vulcanizates is shown in Fig. 2. Our results show clear differences in the morphology of CR/BR composites cross-linked with various metal oxides. The rough surface with numerous furrows of the CR/BR composites cross-linked with Fe$_2$O$_3$ or Fe$_3$O$_4$ was observed. The surface of the CR/BR/Ag$_2$O vulcanizates consisted of various sizes oval particles that formed larger or smaller aggregates, whereas small and regular distributed particles in an elastomer matrix were presented in the CR/BR/ZnO vulcanizate. On the basis of the EDS analysis, various dispersions of metal oxide in the CR/BR matrix were found. Iron(II,IV) oxide and silver(I) oxide formed smaller or larger aggregates in the elastomer matrix, while iron(III) oxide and zinc oxide have been well dispersed.
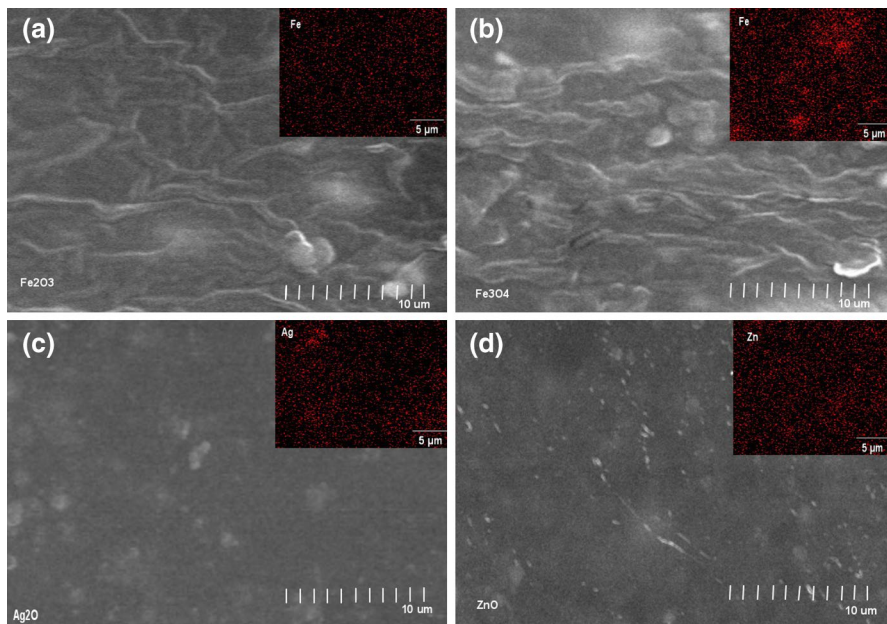

Fig. 2 SEM-EDS photographs of the surface of vulcanizates: **a** CR/BR/Fe$_2$O$_3$, **b** CR/BR/Fe$_3$O$_4$, **c** CR/BR/Ag$_2$O and **d** CR/BR/ZnO

Table 3 Mechanical properties of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO)

Metal oxide (phr)	S_{e100} (MPa)	S_{e200} (MPa)	S_{e300} (MPa)	TS_b (MPa)	E_b (%)	S'_{e100} (MPa)	S'_{e200} (MPa)	S'_{e300} (MPa)	TS'_b (MPa)	E'_b (%)	K
Fe_2O_3	0.76	1.20	1.58	10.05	735	0.91	1.23	–	1.28	210	0.04
Fe_3O_4	0.79	1.31	1.90	6.67	600	0.86	–	–	1.02	135	0.03
Ag_2O	1.30	2.57	3.24	5.96	420	–	–	–	0.73	95	0.03
ZnO	0.80	1.15	1.70	8.35	1100	0.61	0.99	1.50	7.48	935	0.76

S_{e100}, S_{e200}, S_{e300} stress at elongation of 100, 200, 300%, TS_b tensile strength, E_b elongation at break, S'_{e100}, S'_{e200}, S'_{e300} stress at elongation of 100, 200, 300% after thermo-oxidative aging, TS'_b tensile strength after thermo-oxidative aging, E'_b elongation at break after thermo-oxidative aging, K aging index

Mechanical properties of CR/BR/MeO vulcanizates

The mechanical properties (stress at elongation of 100, 200, 300%, tensile strength and elongation at break) of the CR/BR rubber blends were studied (Table 3). In case of CR/BR/Fe_2O_3 vulcanizates, the highest value of tensile strength ($TS_b = 10.05$ MPa) was obtained, whereas the sample cross-linked with ZnO, which was characterized by the lowest cross-linking degree, achieved tensile strength above 8 MPa, while vulcanizates with the addition of iron(II,III) oxide or silver(I) oxide showed the tensile strength equals to 6.67 MPa or 5.96 MPa, respectively. It was found that the resulting cured products were characterized by a low resistance to aging factors (Table 3). The mechanical properties for blends cross-linked with Fe_2O_3, Fe_3O_4 or Ag_2O after thermo-oxidative aging were significantly deteriorated. Regardless of the type of cross-linking agent (Fe_2O_3, Fe_3O_4, Ag_2O), the TS'_b value was approximately 1.00 MPa and the aging index was ~0.03. The tensile strength after thermo-oxidative aging for CR/BR/ZnO vulcanizate decreased from 8.35 MPa only to 7.48 MPa (in this case the aging index was 0.76). Such high resistance of this vulcanizate to aging factors is caused by the fact that zinc and its ions have a completely filled subcoat "*d*" and show an increased stability of the bivalent ions. Due to the fact that the Fe atoms occur on several degrees of oxidation, the CR/BR blends cross-linked with Fe_2O_3 or Fe_3O_4 reveal worse resistance to aging compared to samples containing ZnO. Silver in compounds also occurs on various degrees of oxidation; therefore, during the aging, the resistance of the CR/BR cured with silver oxide is very poor. Change in the oxidative state of metal in transition groups is one of the factors accelerating the degradation. Deterioration of mechanical properties after aging may be caused by the generation in situ of metal chloride (iron(III) chloride ($FeCl_3$) or silver(I) chloride (AgCl)) upon the heating of CR/BR blends in the presence of metal oxide (Fe_2O_3, Fe_3O_4 or Ag_2O). The metal chloride acts as a catalyst necessary for the interelastomer bonding within the rubbers, as well as this metal chloride also may cause degradation of butadiene rubber or chloroprene rubber, which has been proven by Dragunski [25] and Freitas [26]. Dragunski et al. [25] reported that the degradation of polybutadiene in the presence of iron(III) chloride occurs by the scission of double bonds initiated by cationic species while Freitas et al. [26] showed that polychloroprene in the solution degrades in the presence of $FeCl_3 \cdot 6H_2O$ combined with an exposure to polychromatic light. This process of such degradation was characterized as a photo-Fenton type.

In addition to the strength properties, the basic method used to determine the mechanical properties of materials is static compression test and static tensile test. Compression set test measures the ability of rubber to return to its original thickness after prolonged compressive stresses at a given temperature and deflection. As a rubber material is compressed over time, it loses its ability to return to its original thickness. Tension set is defined as an extent to which vulcanizates are permanently deformed after stretching for a time. It is expressed as a percentage of the original length, and it is important to many commercial rubber products which expand and contract in normal exploitation. For example, seals and gaskets are usually stretched and they must return to their original size in order to work properly in the specific application. This ability is expressed in the tensile set. Figure 3 shows the tension
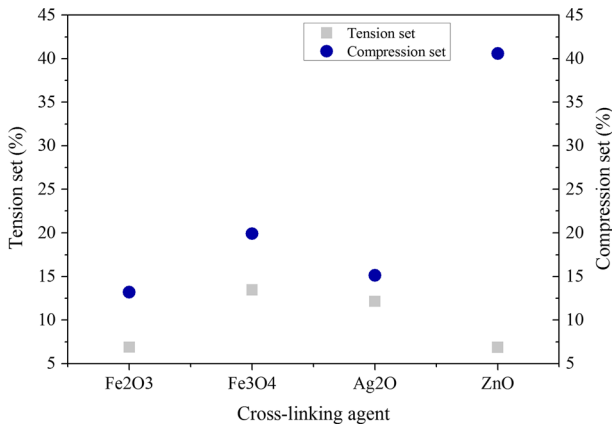
Fig. 3 Tension set and compression set of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO)

set and compression set of the CR/BR blends cross-linked with various types of cross-linking agent. The studied vulcanizates are characterized by low tension set ($E < 15\%$), what is desirable for rubber goods. The CR/BR blend cured with Fe_3O_4 or ZnO had the lowest tension set ($E = 6.87\%$). The highest E value (14.26%) was achieved for CR/BR/Fe_3O_4 sample. The compression set ($C = 13$–20%) for the materials cured with Fe_2O_3, Fe_3O_4 or Ag_2O was small, which indicates a high compression resistance. The unsatisfactory result ($C \sim 40\%$) has been achieved only for CR/BR/ZnO vulcanizates. Such a large compression set value can be associated with the lowest cross-linking degree of this vulcanizate. The results clearly indicate that all cured blends—except for the CR/BR/ZnO vulcanizate—are characterized by an excellent compression set.
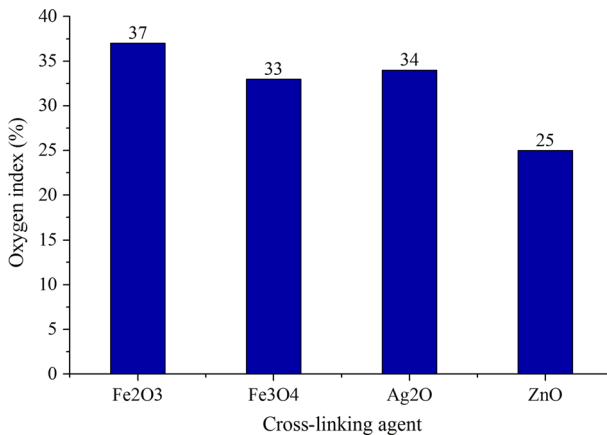

Fig. 4 Oxygen index of CR/BR blends cross-linked with metal oxide (2.5 phr of Fe_2O_3, Fe_3O_4, Ag_2O or ZnO)

Flammability

The oxygen index (OI) value of CR/BR/metal oxide vulcanizates are presented in Fig. 4. When the OI values of these composites were compared, it was found that the order in which the metal oxides increased the OI values was as follows: $ZnO < Ag_2O < Fe_3O_4 < Fe_2O_3$. The increase in the OI value for $CR/BR/Fe_2O_3$, $CR/BR/Fe_3O_4$ and $CR/BR/Ag_2O$ compared to the standard cross-linked CR (OI = 26%) [27] showed that these metal oxides provide a positive influence on the flammability of the CR/BR composites. However, the oxygen index of CR/BR/ZnO composites showed a slight decrease (OI = 25%). These produced vulcanizates belong to a flame retardant material [28]. The use of Fe_2O_3, Fe_3O_4 or Ag_2O as a cross-linking agent of CR/BR blends leads to the production of nonflammable materials (OI > 28.0%) [28]. Such differences in the obtained values of the oxygen index are probably due to the different ability of metals (in the used metal oxides) to form chloride complex compounds. The metals of groups 3–10 of the periodic table of elements, which are not fully filled subcoats d, are characterized by a particularly large tendency to form chloride complex compounds [29]. The higher ability to form complexes, the higher thermal stability, and thus, the increased resistance to fire [30]. The highest OI value obtained for $CR/BR/Fe_2O_3$ vulcanizate is probably due to Fe's ability to form an octahedral complex. In the case of silver atoms, the ability to form complex compounds is much smaller than for iron atoms, while the zinc does not form coordination compounds. Compounds during the combustion of the CR/BR/metal oxide may form between the metal ion and the chlorine-evolving atoms detaching themselves from the main chain of the chloroprene rubber. The resulting compounds inhibit the radical reaction of the combustion of the polymeric material.

Conclusion

The presented metal oxide—iron(III) oxide, iron(II,III) oxide, silver(I) oxide, zinc oxide—can be used as the cross-linking agents of new chloroprene and butadiene rubber (CR/BR) blends. The type of metal oxide affects on the curing degree and thermal and mechanical properties of the resulting rubber materials. Based on performed tests, it has found that cured CR/BR blends, regardless of the type of metal oxide, were characterized by a high cross-linking degree and good mechanical and thermal properties. The satisfactory mechanical properties of CR/BR/MeO vulcanizates probably result from the formation of interelastomer bonds between chloroprene and butadiene rubbers. The DSC curves show the significant changes in the intensities and widths of the exothermic peak in the temperature range from 111 to 230 caused by the difference rate of in situ formation of Lewis acid. Additionally, the advantages of proposed $CR/BR/Fe_2O_3$, $CR/BR/Fe_3O_4$, $CR/BR/Ag_2O$ and CR/BR/ZnO products are simple technology and low cost of the production of flame retardant or nonflammable materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human participants or animals rights This article does not contain any studies with human participants or animals performed by any of the authors.

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