

# The effect of chlorosulphonated polyethylene on thermal properties and combustibility of butadiene–styrene rubber

G. Janowska · A. Kucharska-Jastrząbek

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**Abstract** This article describes the test results of thermal properties and flammability of the unconventionally cross-linked blends of chlorosulfonated polyethylene (CSM) and butadiene–styrene rubber (SBR) by means of zinc oxide or nano-zinc oxide. The thermal curves have been interpreted from the point of view of the chemical transitions of elastomers and their blends. It has been found that the content of combined chlorine in CSM exerts a significant influence on the cross-linking kinetics of CSM/SBR blends, their thermal properties and flammability.

**Keywords** Elastomeric blends · Cross-linking · Interpolimeric cross links · Thermal analysis · Thermal properties · Combustibility

## Introduction

Elastomers constitute a group of polymers that are characterized by elasticity within a wide range of temperature. It results from the low rotation barrier of atom groups around single bonds in the main chain of macromolecule. The characteristic properties of elastomer structural materials manifest themselves after the cross-linking of rubber by both conventional and unconventional methods. The preparation of new polymeric materials with interesting,

sometimes specific properties is possible by blending polymers. One of the problems that make the preparation of elastomer blends difficult is their thermodynamic immiscibility, which brings about a diversified morphology of mixtures and their unsatisfactory properties. Thus, it is of paramount importance to know the methods of increasing the component compatibility as well as the dependence of the cross-linking process on the type of functional groups in elastomers. Hence, growing attention has been paid to research aiming at searching for new methods of controlling interelastomer reactions by an appropriate selection of low molecular substances that specifically react with the functional groups of macromolecular components of the blend. This makes it possible to interbond elastomer chains due to the formation of interpolymeric cross links that determine the final properties of the product of cross-linking.

Elastomer blends are often prepared with the use of butadiene–styrene rubber, commonly used in the rubber industry [1–7]. This article describes unpublished results of testing the thermal properties and flammability of the blends of the mentioned rubber with chlorosulphonated polyethylene cross-linked by means of zinc oxide or nano-zinc oxide.

## Experimental

Studies were focused on two chlorosulphonated polyethylene with different content of chlorine: CSM24 (24% of combined Cl) and CSM43 (43% of combined Cl)—commercial products of Du Pont Dow Elastomers. Under investigation there was also styrene-butadiene rubber, SBR, containing 23.5% of styrene mers, product of Synthos S.A. Elastomer blends containing 85 phr of SBR

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G. Janowska (✉) · A. Kucharska-Jastrząbek  
Faculty of Chemistry, Institute of Polymers and Dye  
Technology, Technical University of Łódź, Łódź, Poland  
e-mail: janowska@p.lodz.pl



**Table 2** Thermal properties of elastomers and their cross-linked blends

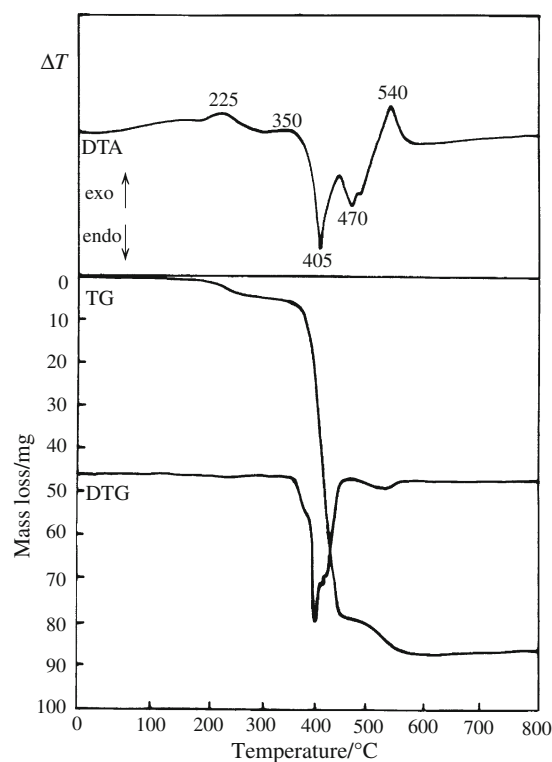
| Sample                    | Thermal parameters       |                      |                         |                      |                   |      |                      |              |
|---------------------------|--------------------------|----------------------|-------------------------|----------------------|-------------------|------|----------------------|--------------|
|                           | $T_g/^\circ\text{C}$ [7] | $T_5/^\circ\text{C}$ | $T_{50}/^\circ\text{C}$ | $T_d/^\circ\text{C}$ | $dm/dt/\text{mm}$ | Pe/% | $T_s/^\circ\text{C}$ | $P_{800}/\%$ |
| SBR                       | -53                      | 285                  | 415                     | 360                  | 65                | 13   | 505                  | 2.2          |
| CSM24                     | -24                      | 250                  | 420                     | 375                  | 60                | 15   | 485                  | 5.5          |
| CSM43                     | 10                       | 230                  | 375                     | 380                  | 30                | 21   | 505                  | 2.2          |
| CSM24/SBR <sub>Zno</sub>  | -50                      | 240                  | 420                     | 370                  | 57                | 26   | 560                  | 7.8          |
| CSM24/SBR <sub>nZno</sub> | -48                      | 240                  | 415                     | 370                  | 50                | 24   | 505                  | 5.5          |
| CSM43/SBR <sub>Zno</sub>  | -39                      | 200                  | 415                     | 360                  | 47                | 36   | 535                  | 12.8         |
| CSM43/SBR <sub>nZno</sub> | -44                      | 200                  | 415                     | 360                  | 48                | 29   | 520                  | 7.8          |

$T_g$  glass transition temperature,  $T_5$  temperature of elastomer/blend 5% mass loss,  $T_{50}$  temperature of elastomer/blend 50% mass loss,  $T_d$  temperature of elastomer/blend thermal decomposition,  $dm/dt$  maximum rate of elastomer/blend thermal decomposition, Pe residue after elastomer/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, SBR styrene-butadiene rubber, CSM24 chlorosulphonated polyethylene containing 24% of combined Cl, CSM43 chlorosulphonated polyethylene containing 43% of combined Cl

parameters accounting to  $\Delta\delta = 2.1$  and  $\Delta\delta = 0.7$ , respectively, one should expect a better compatibility in the case of CSM43/SBR. Our results obtained by the method of differential dynamic calorimetry (DSC) have shown that under the influence of blends cross-linking in the presence of ZnO as well as  $n\text{ZnO}$  there is a good compatibility of the polymers under investigation as shown by a single temperature of their transition from glassy to elastic state, being higher than  $T_g$  of SBR and lower than  $T_g$  of CSM (Table 2) [7].

Butadiene-styrene rubber, similarly as butadiene and butadiene-acrylonitrile rubbers, can be thermally cross-linked under the influence of heating in air. In the case of SBR, the cross-linking takes place within two ranges of temperature,  $\Delta T_1 = 180\text{--}300^\circ\text{C}$  and  $\Delta T_2 = 300\text{--}360^\circ\text{C}$ , as indicated by two exothermic transitions recorded in the DTA curves at  $T_1 = 225^\circ\text{C}$  and  $T_2 = 350^\circ\text{C}$  (Fig. 1). The cross-linking processes at  $\Delta T_1$  proceed due to the decomposition of hydroperoxide groups including in elastomer and formed in the rubber by heating [14–16], while those at  $\Delta T_2$  proceed by the thermal polymerization of butadiene mers. The thermal cross-linking of SBR is accompanied by a sample mass loss of 4.5%. The destruction of the thermally cross-linked SBR begins at  $T_d = 360^\circ\text{C}$ , as indicated by two endothermic transitions recorded in the DTA curve at  $T = 405^\circ\text{C}$  and at  $T = 470^\circ\text{C}$ . The high exothermic peak at  $T_s = 540^\circ\text{C}$  is connected with the combustion of the polymer destruction residue (Fig. 1).

The thermal properties of chlorosulfonated polyethylene were the subject of our previous studies [17, 18]. The content of combined chlorine or sulfur does not exert any significant influence on the character of thermal transitions of CSM in air atmosphere (Fig. 2) [18]. From the analysis of TG curves [18], it follows that the thermal decomposition of CSM proceeds in three stages (Fig. 2). At  $T = 180^\circ\text{C}$

**Fig. 1** DTA, TG, and DTG curves of SBR

starts the mass loss of sample due to the evolution of hydrogen chloride (first stage) as indicated by a small endothermic transition in the DTA curve at  $T = 210^\circ\text{C}$  (Fig. 2). The next, also small and endothermic peak at  $T = 300^\circ\text{C}$  is connected with intensive evolution of HCl, which results in the thermal modification of CSM macromolecules due to the formation of conjugated double bonds,  $\sim\text{CH}=\text{CH}-\text{CH}=\text{CH}\sim$ , similarly as in the case of PVC. The

increase in the chlorine content clearly increases the rate of this process and decreases the sample residue after its ending (Fig. 2). The presence of unsaturated bonds in the thermally modified CSM macromolecules facilitates their thermal cross-linking at  $\Delta T = 320\text{--}380\text{ }^\circ\text{C}$ . The thermally cross-linked CSM undergoes destruction at  $T_d \geq 390\text{ }^\circ\text{C}$ , as indicated by the exothermic transition at  $T = 410\text{ }^\circ\text{C}$  (Fig. 2). The high exothermic peaks on DTA curves at  $T_S = 485\text{ }^\circ\text{C}$  and at  $T_S = 505\text{ }^\circ\text{C}$  are connected with the combustion of residue after CSM24 and CSM43 destruction. The presence of combined chlorine in CSM cause the increase of the maximum combustion temperature,  $T_S$  (Fig. 2) [18].

Similarly as under the atmosphere of neutral gas [17], the addition of CSM exerts a significant influence on the thermal properties of SBR in air (Figs. 1, 3, 4). Regardless of the content of combined chlorine in CSM, the DTA curves of CSM/SBR<sub>ZnO</sub> blends show two exothermic transitions: the first clearly seen at  $T_1 = 210\text{ }^\circ\text{C}$  (Fig. 3) and  $T_1 = 200\text{ }^\circ\text{C}$  (Fig. 4), and the second one broadened at  $T_2 = 290\text{ }^\circ\text{C}$ . Based on the results of equilibrium swelling, the sample of the investigation blends before and after their heating at the temperature  $T_1$  and  $T_2$ , we have been stated that within the temperature range of these transitions, the vulcanized mixtures of polymers are thermally cross-linked. The first transition is a symptom of the continuation of chemical reactions (1–3) that are accompanied by other

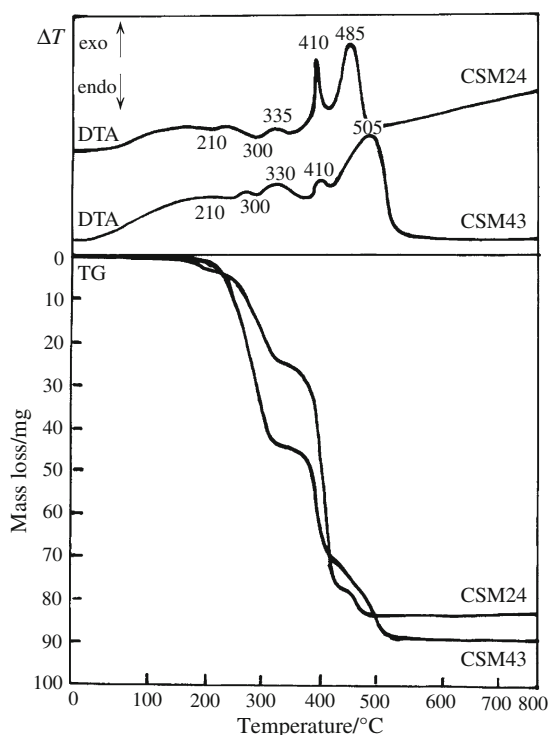


Fig. 2 DTA and TG curves of CSM24 and CSM43

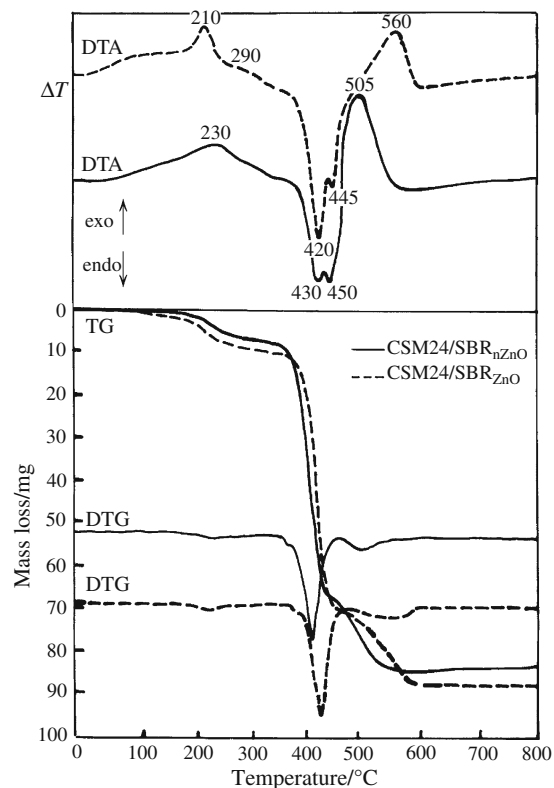
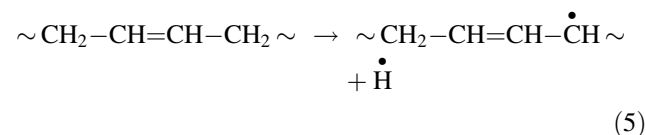
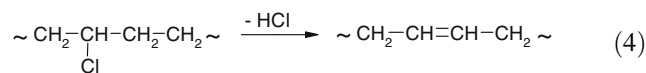
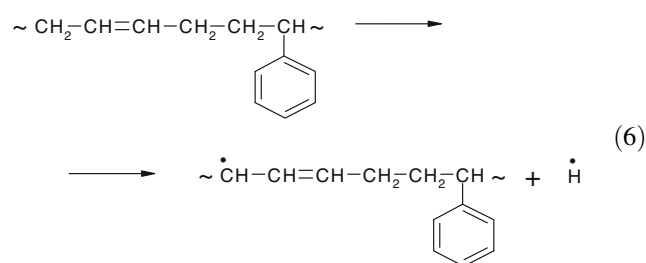


Fig. 3 DTA, TG, and DTG curves of CSM24/SBR

free-radical processes such as dehydrochlorination resulting in the mentioned thermal modification of CSM macromolecules (reaction 4) [7]. The double bonds in SBR macromolecules and those formed in CSM macromolecules facilitate the  $\text{H}^\bullet$  radical splitting off due to further heating, thus within the range of the second exothermic transition (reactions 5–7) [7].



or



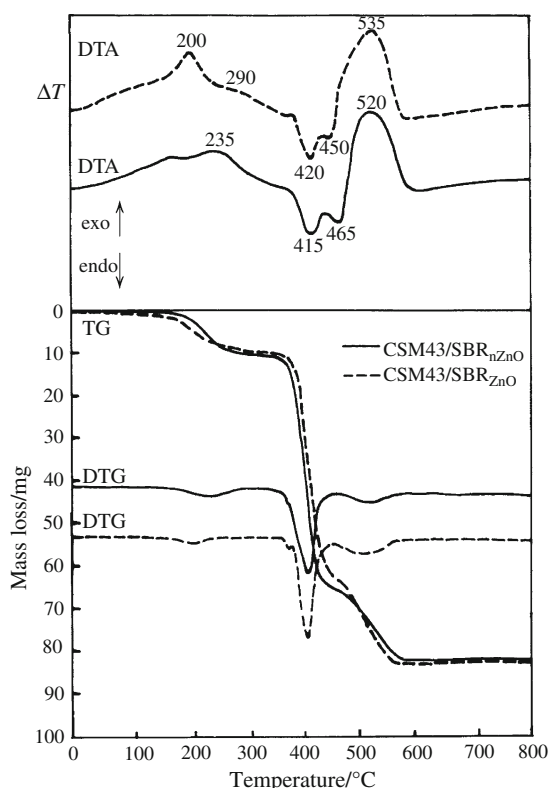
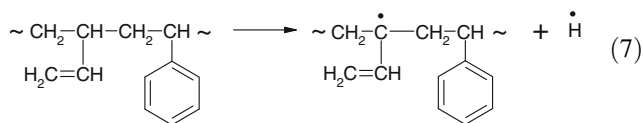
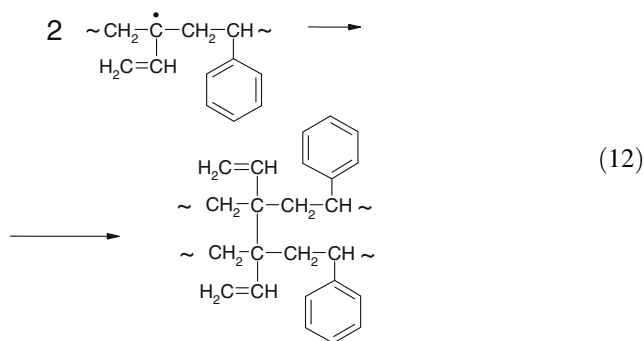
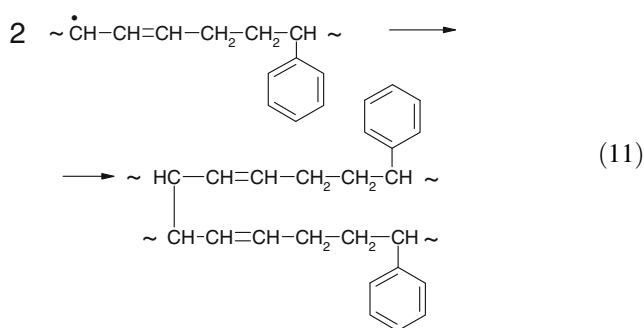
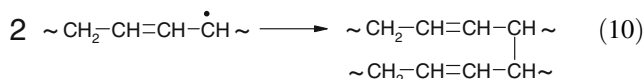
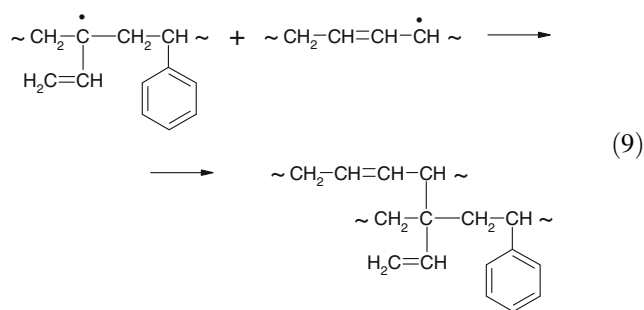
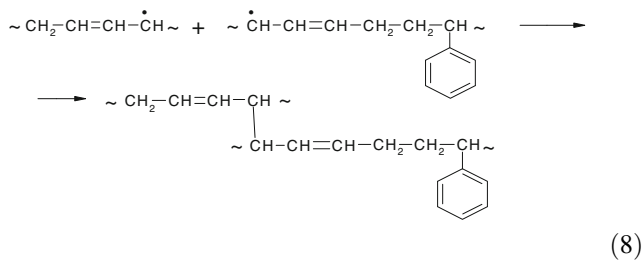


Fig. 4 DTA, TG, and DTG curves of CSM43/SBR

or



The recombination of macro-radicals results in further polymer co-cross-linking, i.e. the formation of interpolymeric network structure (reactions 8, 9) as well as in self-cross-linking (reactions 10–12) [7].



The thermal cross-linking of the vulcanized CSM/SBR blends in the presence of nano-zinc oxide (CSM/SBR<sub>nZnO</sub>) are confirmed by the broad exothermic peak in the DTA curve, whose maximal rate occurs at  $T = 230$  °C (Fig. 3) and  $T = 235$  °C (Fig. 4). Within the temperature range of the ascending exotherm of these transitions, there proceed reactions (1–4), while the others can take place at a higher temperature. The destruction processes of the blends under investigation begin at  $T \sim 370$  °C (Table 2, Figs. 3,4).

The destruction rate ( $dm/dt$ ) of CSM24/SBR<sub>nZnO</sub> blend is considerably lower than that of the component polymers, with the effect of nano-zinc oxide being clearly seen (Table 2). Under the influence of increased chlorine content in CSM the decomposition rate of CSM43/SBR,  $dm/dt$ , is decreased in comparison with CSM24/SBR. This results from the contribution of ionic processes to the destruction of blends due to the evolution of high quantities of HCl. Both the thermal decomposition rate ( $dm/dt$ ) and the residue of elastomers after their destruction (Pe) exert a significant influence on the flammability of polymeric materials. The decrease in the polymer destruction rate reduces its flammability by limiting the quantity of volatile and flammable products of the thermal decomposition. The same effect is exerted by the increase in the value of Pe that determines the polymer susceptibility to form solid products of thermal decomposition. Based on the analysis of the results listed in Table 2, one should state that the values of Pe are considerably higher than the values of Pe of the component polymers. Thus, the thermal destruction of the cross-linked blends is accompanied by its carbonization. The combustion of the residue after the blends destruction begins at  $T \geq 460$  °C, as indicated by a high exothermic transition in the DTA curves (Figs. 3, 4).

The SBR used in the blends under investigation belongs to the group of flammable elastomers (Table 3). Chlorosulfonated polyethylene CSM24 is a self-extinguishing polymer, while CSM43 is a non-flammable polymer (Table 3) [18]. The addition of CSM to SBR brings about a considerable reduction in its flammability determined by both the value of oxygen index (OI) and the combustion time in air (Table 3). This is due to the decreased destruction rate ( $dm/dt$ ) of the cross-linked CSM/SBR blends under thermooxidative conditions and increased residue (Pe) after this process in comparison with SBR (Table 2). In this connection, a lower quantity of flammable products of thermal decomposition of elastomers passes to flame. The test results show that the combustion time of the cross-linked blends in air is prolonged under the

influence of increased chlorine content in CSM, which is not accompanied by an increase in the value of OI (Table 3). This is due to the fact that the complex physico-chemical processes during polymer combustion under the conditions of oxygen index measurement, where a considerable portion of the emitted heat is carried away outside by the flowing oxygen/nitrogen mixture at a constant rate, proceed in a different way than that under the conditions of combustion in air. In this connection, a longer time of polymer combustion in air not always corresponds to an increased value of OI [19–21].

## Conclusions

The increase in the chlorine content in CSM exerts a significant influence on the cross-linking kinetics of CSM/SBR blends.

Under influence of CSM/SBR blend cross-linking in the presence of ZnO as well as nZnO, there is a good compatibility of polymers. This makes it possible to interbond elastomer chains due to the formation of interpolymeric cross links.

Under the influence of increased chlorine content in CSM both the thermo-oxidative decomposition rate of CSM/SBR blends and residue after their destruction are decreased.

The residue after thermo-oxidative destruction of CSM/SBR is considerably higher in comparison with component polymers.

The addition of CSM to SBR brings about a considerable reduction in its flammability determined by both the value of oxygen index and the combustion time in air.

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**Table 3** Combustibility of elastomers and their blends

| Sample                    | <i>t</i> /s     | OI     |
|---------------------------|-----------------|--------|
| SBR                       | 206             | 0.293  |
| CSM24                     | 18 <sup>a</sup> | >0.375 |
| CSM43                     | Incombustible   | >0.375 |
| CSM24/SBR <sub>Zno</sub>  | 252             | >0.375 |
| CSM24/SBR <sub>nZno</sub> | 246             | >0.375 |
| CSM43/SBR <sub>Zno</sub>  | 290             | 0.375  |
| CSM43/SBR <sub>nZno</sub> | 270             | 0.375  |

<sup>a</sup> self-extinguishing sample

*t* time of burning in air, OI oxygen index

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