

## DSC study of chlorosulphonated polyethylene

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**Abstract** The results of thermal analysis of speciality elastomers CSM with different chlorine and sulphur contents is presented in the article. The thermal curves obtained under the atmosphere of inert gas have been interpreted from the point of view of phase transitions and chemical reactions of the examined polymers during their heating. It has been stated that from among the investigated chlorosulphonated polyethylenes, only CSM24, which has the lowest chlorine content, contains a crystalline phase, clearly influences on its  $T_g$  temperature. Results of the thermal analysis obtained under inert gas atmosphere have been compared with results obtained under termooxidative atmosphere. Irrespective of the research atmosphere, the thermal decomposition of investigated CSM takes place in three stages. The maximum rate of thermal destruction of modified by heating elastomers,  $dm/dt$ , decreases with the increase in chlorine content in the sample having been heated.

**Keywords** Chlorosulphonated polyethylene · CSM · Crystallization · Glass transitions · Thermal analysis · Thermal curves · DTA · DSC · DTG · TG · Thermal properties · Thermal cross-linking

### Introduction

Thermal analysis methods play an important role for characterization of structure–properties relationships in

individual polymers and polymer blends. Several techniques are widely applied for the investigation of phase structure, thermal properties of polymer blends [1–3]. In the present work, two thermal analysis techniques, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) [4–16], were used for characterization of modified polyethylene [17–27].

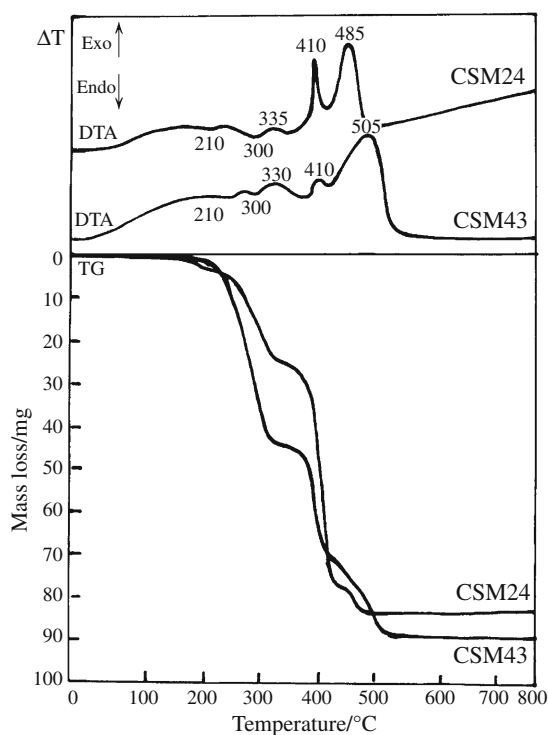
Chlorosulphonated polyethylene (CSM) is a specialty elastomer, produced by modification and functionalization of polyethylene (PE) performed during simultaneous actions of chlorine and sulphur dioxide on PE (usually PE-LD) dissolved in  $\text{CCl}_4$  in the presence of radical initiators. Commercial products contain 25–45 wt% of combined Cl and 1.0–2.2 wt% of combined sulphur. This means that on the average 1 Cl atom falls on 5–7 C atoms, while a single chlorosulphonic group ( $-\text{SO}_2\text{Cl}$ ) falls on 80–100 °C atoms in the main chain of CSM. Over 90% of Cl combined in CSM occurs in secondary groups ( $\text{R}^1\text{R}^2\text{CHCl}$ ) in the main chain, up to 3.5%—in tertiary groups ( $\text{RR}^1\text{R}^2\text{CCl}$ ), up to 3%—in  $\text{RCH}_2\text{Cl}$  groups, including terminal groups, and the remaining combined Cl—in chlorosulphonic groups. The technological, performance and cohesive properties as well as chemical reactivity of CSM depend on the quantity of combined Cl and S [28–32].

The replacement of some number of H atoms in the PE chain with  $-\text{Cl}$  and  $-\text{SO}_2\text{Cl}$  groups distorts the structure of regularity of its chain and consequently results in products with different susceptibility to crystallization, dependent on the quantity of Cl combined with the given CSM [33]. Based on fragmentary literature reports [34] and structural condition-dependent properties of elastomers [32, 35], one can also expect that the content of combined Cl and chlorosulphonic groups will exert a significant influence on their thermal properties, both in air and inert gas atmospheres.

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Our earlier investigations have revealed that the content of combined chlorine and sulphur exerts no significant influence on the character of thermal changes in CSMs under the air atmosphere (Fig. 1) [36]. From the analysis of thermogravimetric curves, TG, it follows that the thermal decomposition of the polymer under investigation proceeds in three stages. At a temperature of 180 °C, there begins the mass loss of the samples due to hydrogen chloride evolution, which is revealed by a slight endothermic transformation recorded in differential thermal analysis (DTA) curves at  $T = \sim 210$  °C. The initial temperature of elastomers thermal decomposition does not depend on the chlorine content in CSM. The next stage connected with intensive HCl emission starts at  $T = \sim 250$  °C. The increase in the chlorine content in the CSM is accompanied by a clear increase in the rate of this process and a decrease of the sample residue after its termination. After heating of CSM up to 320 °C, the contents of chlorine and sulphur in polymers are considerably decreased. Taking into consideration analysis of TG and derivative thermogravimetry (DTG), we have stated that HCl evolution can proceed according to chain mechanism what brings about formation of conjugated system of double bonds  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$  as in the case of polyvinyl chloride, PVC [36].

The DTA curves of the examined CSM within the temperature range:  $\Delta T = 320\text{--}380$  °C show an exothermic transformation connected with the thermal cross-linking of the polymer modified by heating (Fig. 1). We consider that



**Fig. 1** DTA, TG and DTG curves of CSM24 and CSM43 [36]

this process is caused by the presence of unsaturated bonds in macromolecule chains, which are established as a result of their thermal modification. The thermally cross-linked CSMs are decomposed at  $T \geq 390$  °C. The temperature of the second stage of elastomers thermal decomposition increases with the increase in chlorine content in CSM macromolecules, while the rate of CSM destruction decreases with the increases in chlorine content, which consequently results in an increased sample residue after termination of this process. In our opinion, the hydrogen chloride that continues to emit during the thermal decomposition plays the part of catalyst of ionic decomposition of cross-linked macromolecules. In the case of CSM24 and CSM29 that have lower chlorine contents as compared with those of the remaining polymers, a homolytic decomposition predominates whose rate is, therefore, considerably higher than that of the remaining CSM. The mentioned mechanism of auto-inhibition does not decide about the thermal stability of the examined CSM as particularly confirmed by the temperature of elastomers 50% mass loss,  $T_{50}$ , but it plays a significant part in reducing their flammability [36].

The DTA curves of the examined CSM at a temperature over 430 °C show a high exothermic peak connected with the combustion of residues after their thermal decomposition (Fig. 1). The temperature of the maximum combustion rate increases with the increase in chlorine content in CSM; the temperature range of this process is also broadened.

Taking into account thermal stability indices under the air atmosphere,  $T_5$  and  $T_{50}$ , CSM24 shows the highest thermal stability among the examined CSMs [36].

The present article shows unreported in the literature results of studies of thermal properties of CSM under the nitrogen atmosphere.

## Experimental

Our studies were focused on CSMs with different contents of combined Cl (24–43 wt%)—i.e. commercial products of Du Pont Dow Elastomers under the trade marks: Hypalon 48, Hypalon 20, and Hypalon 30, containing 24, 29, 35 or 43 wt% of combined Cl and 1.0, 1.4, 1.0 or 1.1 wt% of combined sulphur (manufacturer's data confirmed by elementary analysis), further denoted with symbols CSM24, CSM29, CSM35 and CSM 43, respectively (Table 1). The research included also CSM43HV (chlorosulphonated PE with higher viscosity compared with CSM43).

The thermal analysis of elastomers was carried out in inert gas atmosphere by means of DSC of Netzsch, DSC-204, and thermogravimetry (TG) of Netzsch, TG-209, using portions of about 5 mg at heating rate of 10 °C  $\text{min}^{-1}$  within temperature range of 20 to  $-100$  and  $-100$  to

**Table 1** The results of elemental analysis of CSM

Content of	Heating to $T = 330\text{ }^{\circ}\text{C}^{\text{a}}$	Chlorosulphonated polyethylene				
		CSM24	CSM29	CSM35	CSM43	CSM43HV
Chlorine/mass%	Before heating	22.20	29.23	35.00	43.00	43.00
	After heating	0.62	1.45	1.80	7.53	5.75
Sulphur <sup>b</sup> /mass%	Before heating	–	1.30	–	–	–
	After heating	–	0.45	–	–	–

<sup>a</sup> In air atmosphere

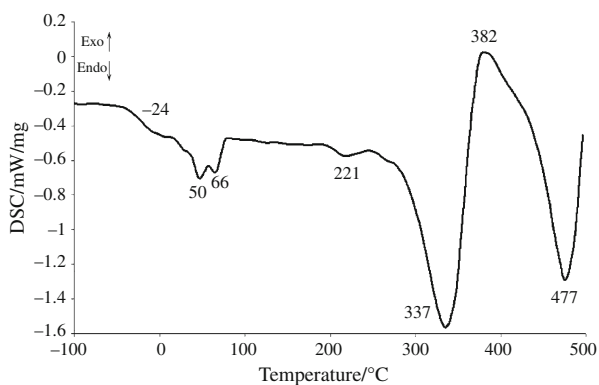
<sup>b</sup> Evaluated only for CSM29

500 °C in the case of DSC measurements and 20 to 500 °C in the case of TG measurements.

The content of chlorine and sulphur in investigated polymers before and after their heating was determined based on the results of elementary analysis made in Centre of Molecular and Macromolecular Investigations of Polish Academy of Science in Lodz.

## Results and discussion

The content of combined chlorine and sulphur exerts the influence both on phase transitions and chemical changes in CSM under the inert atmosphere. The transition from the glassy to the elastic state of CSM24 takes place at  $T_g = -24\text{ }^{\circ}\text{C}$  (Fig. 2, Table 2). At  $T = 13\text{ }^{\circ}\text{C}$ , two endothermic transitions begin; they are connected with the melting of the crystalline phase of chlorosulphonated PE. Two maxima in the melting endotherm and a wide temperature range of this phase transition indicate the presence of areas with different degrees of order and different contents of defects. The DSC curve of CSM24 show two further endothermic transitions at  $T = 221\text{ }^{\circ}\text{C}$  and  $T = 337\text{ }^{\circ}\text{C}$  brought about by the hydrogen chloride splitting off as confirmed by the slow mass loss of sample starting at  $T = 255\text{ }^{\circ}\text{C}$  (Fig. 3). The maximum rate of this process

**Fig. 2** DSC curve of CSM24

associated with a 15% mass loss takes place at  $T = 358\text{ }^{\circ}\text{C}$ , thus, at a temperature at which the next exothermic transition begins (Figs. 2, 3). In our opinion, it is a symptom of the cross-linking of thermally modified CSM24 macromolecules under oxygen-free atmosphere, which is accompanied by a systematic but low mass loss within the temperature range from 375 to 448 °C (Fig. 3). A violent polymer decomposition begins at  $T = 450\text{ }^{\circ}\text{C}$ , while the maximum rate of this process takes place at  $T_d = 477\text{ }^{\circ}\text{C}$  (Fig. 2).

The chlorine content in the polymers under investigation influences the character of their thermal transitions under nitrogen atmosphere. The transition of CSM29 from the glassy to the elastic state takes place at  $T_g = -27\text{ }^{\circ}\text{C}$ , thus at a lower temperature than that of CSM24 (Fig. 4, Table 2). The higher chlorine content in CSM29 than that in CSM 24 increases the polarity of macromolecules and their interactions, which should result in the rise in  $T_g$ . At the same time, the increase in the chlorine content through considerable distortion of the polymer chain structure makes its crystallization impossible. In that case, amorphous CSM29 shows lower  $T_g$  as compared with that of crystalline CSM24 (Table 2). Under the influence of increased chlorine contents in CSM29, CSM35 and CSM43, their temperatures of transition from the glassy to the elastic state rise. The content of chlorine in CSMS CSM43 and CSM43HV is the same (Table 1), however, their  $T_g$  temperatures are different (Table 2). From the manufacturer's data, it follows that the viscosity of CSM43HV according to Mooney ML 1 + 4 (100 °C) is 115, while the viscosity values of the remaining examined CSM are similar ranging from 30 to 55. The higher viscosity of CSM43HV results from higher molecular weight of this polymer, but unexpectedly its  $T_g$  is lower in comparison with CSM43. It may be caused by higher degree of branching chains of CSM43HV or conditions of chlorosulphonation process.

The course of the chemical changes recorded in the DSC thermal curves of chlorosulphonated PE: CSM24, CSM29, CSM35 and CSM43HV is similar. Both in air [36] and inert gas atmosphere, the TG curves show three stages of

**Table 2** The results of thermal analysis of CSM in nitrogen atmosphere

	Chlorosulphonated polyethylene				
	CSM24	CSM29	CSM35	CSM43	CSM43HV
$T_g/^\circ\text{C}$	-24	-27	-23	10	3
$\Delta T_g/^\circ\text{C}$	-27 to -21	-31 to -23	-25 to -21	3-13	1-5
$T_m/^\circ\text{C}$	50 and 66	-	-	-	-
$\Delta T_m/^\circ\text{C}$	13-80	-	-	-	-
$\Delta T_0/^\circ\text{C}$	193-358	191-344	174-349	240-328	174-349
$\Delta H_0/\text{J g}^{-1}$	-258	-258	-271	-148	-218
$T_{tc}/^\circ\text{C}$	382	370	369	335	362
$T_d/^\circ\text{C}$	477	469	474	335	470
$dm/dt/\%/min$	-24	-11	-11	-5	-9

$T_g$ —glass transition temperature

$\Delta T_g$ —temperature range of glass transition

$T_m$ —melting point

$\Delta T_m$ —temperature range of melting

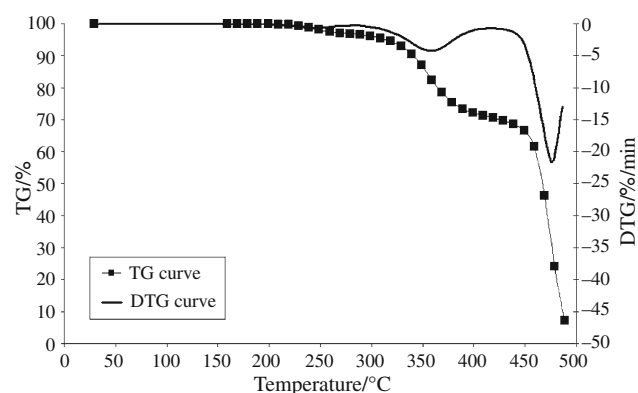
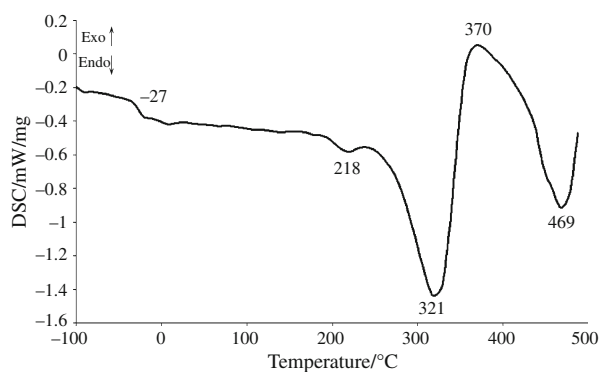
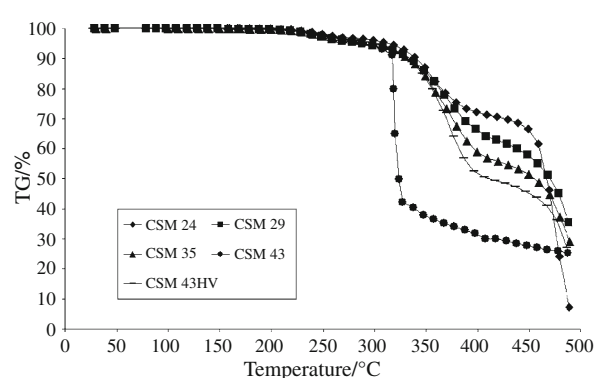
$\Delta T_0$ —temperature range of dehydrochlorination

$\Delta H_0$ —enthalpy of dehydrochlorination

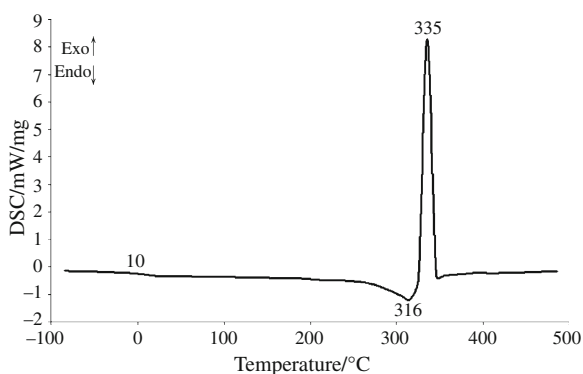
$T_{tc\ max}$ —maximum temperature of thermal cross-linking

$T_{d\ max}$ —maximum temperature of thermal destruction

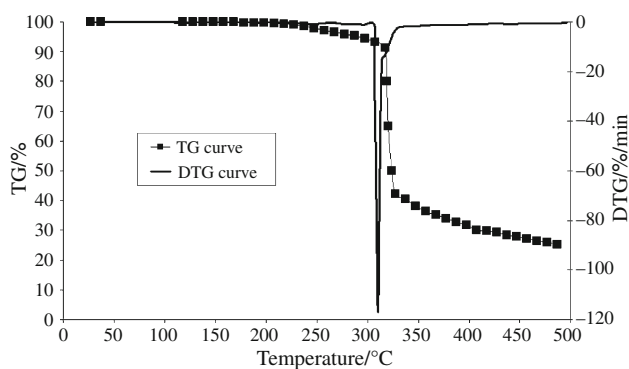
$dm/dt$ —maximum rate of elastomer thermal destruction

**Fig. 3** TG and DTG curves of CSM24**Fig. 4** DSC curve of CSM29**Fig. 5** TG curves of CSM

thermal decomposition (Fig. 5). The increased chlorine contents in these polymers clearly decrease the temperature of chlorine hydrogen splitting off, but they exert no significant influence on the temperature of their maximum decomposition rate,  $T_d$  (Table 2). Among the examined polymers, the highest mass loss due to the thermal decomposition of sample at  $T = 500^\circ\text{C}$  takes place in CSM43 (Fig. 5). We believe that the increase in the thermal modification of the polymers under investigation, dependent on the chlorine content, facilitates the increase in the residue after their thermal decomposition under the neutral gas atmosphere. From among the examined polymers with similar viscosities according to Mooney, CSM43 has the highest chlorine content. From the DSC curve of this polymer, it follows that the processes of HCl splitting



**Fig. 6** DSC curve of CSM43



**Fig. 7** TG and DTG curves of CSM43

off start at  $T = 200$  °C, and in comparison with the previously discussed CSM they proceed with the lowest yield assessed from the values of process enthalpy,  $\Delta H_0$ . In the case of CSM24, CSM29 and CSM35, it amounts to  $-258$ ,  $-258$  and  $-271$   $\text{J g}^{-1}$ , respectively. On the other hand,  $\Delta H_0$  of CSM43 is  $-148$   $\text{J g}^{-1}$ . From the analysis of DSC and TG curves of CSM43, it follows that the sharp, exothermic peak recorded at  $T_{tc} = 335$  °C is connected with processes of violent thermal cross-linking accompanied also by a violent destruction of the thermally modified polymer (Figs. 6, 7).

The DSC curves of the examined PE, except CSM43, at  $T_d \approx 470$  °C show an endothermic peak connected with the thermal destruction of the polymer modified by heating. The maximum rate of this process,  $dm/dt$ , decreases with the increase in chlorine content in the sample having been heated (Table 2). It results from autoinhibition mechanism. In case of CSM24, containing 22% mass of combined chlorine, the radical breakdown of macromolecules predominated. Together with increase of chlorine content in CSM, it superiority follows that destruction process proceeds according to ionic mechanism. We discovered that in the air atmosphere that influence has the same character. However, in termoxidative atmosphere, we observed linear relation  $dm/dt$  of chlorine content in the CSM macromolecules [36].

The presented results of measurements confirm the known, with regard to other polymers, significant effect of the chemical chain structure and the type and quantity of modifying substituents on the thermal properties of macromolecular compounds.

## Conclusions

The content of combined chlorine and sulphur exerts significant influence on phase transitions of CSM. From among the examined CSMs, only CSM24, which has the lowest chlorine content, contains a crystalline phase.

It has been stated clearly influence of molecular weight of CSM on their glass transitions temperature. CSMs denoted with symbols CSM43 and CSM43HV have the same chlorine content in macromolecules, but their  $T_g$  are different.

Irrespective of the research atmosphere, the thermal decomposition of investigated CSM takes place in three stages. The maximum rate of thermal destruction of modified by heating elastomers,  $dm/dt$ , decreases with the increase in chlorine content in the sample having been heated.

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