

INVESTIGATION OF THERMAL DEGRADATION OF POLYMERS CONTAINING CHLORINE BY THERMOGRAVIMETRY

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The thermal degradation of chlorine-containing polymers used in a rubber technology has been investigated in a nitrogen atmosphere. The characteristics of degradation have been compared on the basis of thermogravimetry, carbon residues and chlorine elimination. The observed structure-dependent differences in degradation of the investigated polymers are discussed.

When heated in an atmosphere of inert gas or in air, polymers with hydrocarbon chain structures containing chlorine undergo thermal or oxidative degradation processes, sometimes connected with crosslinking [1–4]. High temperature causes accelerated dehydrochlorination, with simultaneous formation of unsaturated bonds in the hydrocarbon chains, followed by chain scission. As a result of the destruction process, volatile products and a non-volatile residue are formed, which burn in an oxygen atmosphere or in air. Hydrogen chloride evolution proceeding at lower temperature, is usually distinctly separated from polymer chain degradation. Sircar and Lamond [5] showed that dehydrochlorination can be exothermic or endothermic, depending on the polymer structure, the medium and the reaction mechanism.

In the literature there are many publications concerning the study of polymer degradation. As regards chlorine-containing polymers, most attention has been devoted to the investigation of polyvinyl chloride [6–11] and polychloroprene [12–14].

Chloropene rubber shows a higher thermal stability in comparison with PVC, and the HCl evolved does not catalyze the degradation reaction, in contrast with the case of PVC. The main stage of dehydrochlorination proceeds at higher temperature for polychloroprene than for polyvinyl chloride, and is not separated so distinctly from the subsequent stages of chain destruction. It has been shown that 90% of the chlorine content is evolved in the first, main destruction stage.

Dodson and McNeill [15] were concerned with the study of chlorinated rubbers and especially chlorinated polyisoprene. Similarly as for other chlorine-containing polymers, the degradation of chlorinated rubbers proceeds in two stages. However, 95% of the chlorine, in the form of HCl, is evolved in the first stage.

Dodson and McNeill also studied the thermal degradation of polyvinylidene chloride (73% chlorine), which was found to lose only half of the chlorine content in the first degradation stage. Elimination of the remaining chlorine is very difficult

and needs a high temperature, as the dehydrochlorination is inhibited by steric effects, proceeding with more and more difficulty as the distance between the H and Cl atoms in the chain increases.

Dudley and Smith [16–17] proved that chlorosulphonated polyethylene is characterized by a three-stage thermal degradation, and that the degradation process is initiated by the elimination of weakly-bonded chlorosulphonic groups, probably with the evolution of labile chlorine.

Despite many investigations date, a series of problems connected with the kinetic as well as the mechanism and thermal stability of these polymers have not been explained. The relation between the character of the degradation and the structure

Table 1
Characteristics of polymers

Type of polymer	Chemical formula	Trade name	Chlorine content in polymer, %	
			theoretical	experimental
Polychloroprene	$\left(-\text{CH}_2-\underset{\text{Cl}}{\text{C}}-\text{CH}-\text{CH}_2- \right)_n$	Skypren B - 30	37	33.7
		Butaclor MC-10	37	34.2
Homopolymer of epichlorhydrin	$\left(-\text{CH}_2-\underset{\text{CH}_2\text{Cl}}{\text{CH}}-\text{O}- \right)_n$	Hydrin 100	38	35.6
Copolymer of epichlorhydrin	$\left(-\text{CH}_2-\underset{\text{CH}_2\text{Cl}}{\text{CH}}-\text{O}-\text{CH}_2-\text{O}- \right)_n$	Hydrin 200	24–26	24
Terpolymer of epichlorhydrin		Hydrin 400	24–26	23.7
Polyethylene	$\left(-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2- \right)_n$		0	0
Chlorinated polyethylene	$\left(-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_2- \right)_n$		42	42.0
Chlorosulphonated polyethylene	$\left[\left(-\text{CH}_2-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_2- \right)_n - \right.$ $\left. -\underset{\text{SO}_2\text{I}_m}{\text{CH}}- \right]$	Hypalon 20	29	28.5
		Hypalon 40	35	33
Polyvinyl chloride	$\left(-\underset{\text{Cl}}{\text{CH}_2}-\text{CH}_2- \right)_n$	PVC	56	52.0

of various chlorine-containing polymers has not been investigated under comparable conditions either. In the available literature there are no data concerning the thermal degradation of epichlorhydrin elastomers.

The purpose of the present paper is the comparison of the thermal degradation of some polymers containing chlorine by using thermogravimetry. The TG method yields information concerning the degradation temperature and the rate of weight changes.

Such information can be utilized as the basis for evaluation of the possibility of using thermogravimetry for quantitative analysis of rubber vulcanizates. So far [18–19], this method has been employed with success for analysis of the composition of hydrocarbon rubber vulcanizates.

Experimental

Materials and investigation methods

The subjects of investigation were chlorine-containing polymers with various structures of the main chain, commonly used in rubber technology. They are listed in Table 1. For comparison, polyethylene was also taken into account in these investigations.

Thermal degradation was carried out in a nitrogen atmosphere in a Perkin–Elmer TGS-1 Thermobalance at a heating rate of 20°/min, using 5 mg samples. Thermogravimetric weight loss TG and DTG curves were recorded. From the curves the weight losses and temperature ranges for various degradation stages were determined, as well as the non-volatile residue obtained after heating at 550° in a nitrogen atmosphere.

Determination of chlorine content was performed on samples heated to a given temperature. The Schöniger method used consists in burning samples in oxygen in the presence of a platinum catalyst, and determining the chloride percentage by titration.

Results and discussion

Characteristics of thermal degradation

The characteristics of thermal degradation of the investigated polymers are presented in Figs. 1–2 and Table 2. These data show that the character of the thermal degradation, the value of the carbon residue and the thermal stability are different, depending on the structure and the chlorine content.

As expected, the thermal degradation of polyethylene proceeds in one stage, with maximum rate at 495°.

Chlorinated polyethylene is characterized by a two-stage degradation. The first stage is connected mainly with hydrogenchloride evolution; it occurs in the tem-

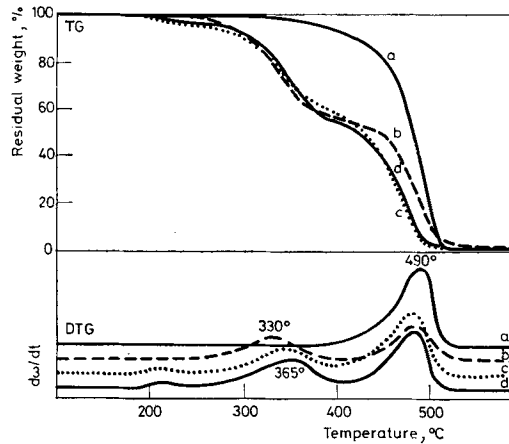


Fig. 1. TG and DTG curves of the polymers: *a*) polyethylene, *b*) chlorinated polyethylene, *c*) Hypalon 20 *d*) Hypalon 40. Heating rate: $20^{\circ} \text{ min}^{-1}$

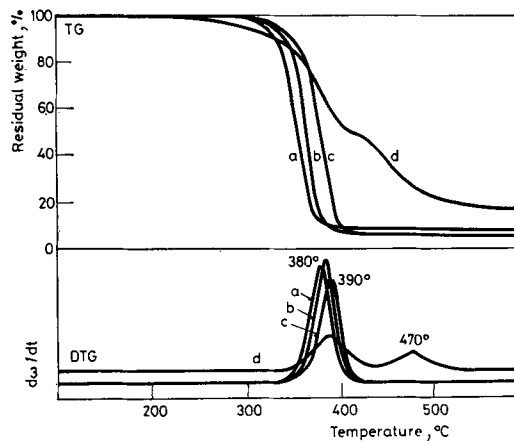


Fig. 2. TG and DTG curves of the polymers: *a*) Hydrin 100, *b*) Hydrin 200, *c*) Hydrin 400, *d*) Skypren B-30. Heating rate: $20^{\circ} \text{ min}^{-1}$

perature range $230\text{--}410^{\circ}$ (DTG max at 330°). Chain destruction in the next stage takes place at a similar temperature mentioned above, the degradation of chloro-sulphonated polyethylene occurs in three stages. The first degradation stage, at $180\text{--}270^{\circ}$ appears in the DTG curve in the form of a flat peak and is related to the elimination of the SO_2Cl group. This finds confirmation in the absence of sulphur in samples heated to 300° .

There is no regular relation between the chlorine content of the polymer with ethylene chain structure and the temperature corresponding to the maximum degradation rate in the stage connected with elimination of hydrogen chloride.

Table 2

Degradation temperatures and weight loss of polymers degraded in nitrogen atmosphere

Type of polymer	Degradation temperatures, °C and weight loss of polymers, %							
	initial stage of decomposition		I degradation stage associated with the main hydrochlorination			II degradation stage associated with decomposition of the main chain structure		
	range of temperature, °C	weight loss, %	range of temperature, °C	T _{DTG} max, °C	weight loss, %	range of temperature, °C	T _{DTG} max, °C	weight loss, %
Polychloroprene:								
Skypren B-30	190-340	12.5	340-440	395	40.0	440-550	480	27.4
Butaclor MC-10	180-340	10.7	340-440	390	43.7	440-540	470	23.1
Polymers of epichlorhydrin:								
Hydrin 100	—	—	290-480	380	88.9	—	—	—
Hydrin 200	—	—	300-475	385	92.5	—	—	—
Hydrin 400	—	—	250-575	390	93.5	—	—	—
Polyethylene	—	—	—	—	—	310-530	495	99.5
Chlorinated polyethylene:								
	—	—	230-410	330	43	410-520	490	50.5
Chlorosulphonated polyethylene:								
Hypalon 20	180-270	7.4	270-415	355	53.6	415-525	485	55.4
Hypalon 40	180-270	5.0	270-420	365	40.7	420-520	490	49.8
Polyvinyl chloride	200-260	3.0	280-400	330	61.0	400-565	490	27.5

The chlorine content has no influence either on the destruction temperature of the hydrocarbon chain. For all investigated compounds the degradation temperature was about 490° (max of the peak in the DTG curve).

Polyvinyl chloride, with a similar chain structure although with a different segment length between the chlorine atoms and with a higher chlorine content undergoes thermal degradation in a very similar way to chlorinated polyethylene from the point of view of character and temperature distribution; the only difference is the higher rate of the first degradation stage.

Thermogravimetric curves of epichlorhydrin elastomers show different characteristics. Homopolymer, copolymer as well as terpolymer degradation proceeds in one stage, in a very narrow temperature range. High and well-developed peaks in the DTG curves, with max rate at about 390°, prove that the degradation occurs with high rate in the whole range.

The weight loss in the TG curves begins at about 300° for the homo- and the copolymer, and at 250° for the terpolymer.

The character of chloroprene rubber degradation does not show any deviation from that presented in the literature. The weight loss starts at 180-190° (about

11%, in comparison with 3–7% for the polymer with the ethylene chain structure) and proceeds very slowly up to 300°. No peak is observed in this range. The weight loss rate increases significantly in the range of the two main degradation stages connected with elimination of hydrogenchloride and hydrocarbon chain destruction, at 340–440° (DTG max at about 390°) and at 440–550° (DTG max at 470°), respectively.

As will be shown in the next part of the paper, the elimination of HCl from polychloroprene requires a much higher temperature than for the other polymers investigated.

Carbon residue

Pyrolysis of chlorine-containing polymers in a nitrogen atmosphere usually leads to the formation of a non-volatile residue, conventionally called the "carbon residue". Investigations of the composition of the residue after heating of certain polymers such as PVC [4, 5] and CR [1, 2] showed that it also contains some hydrocarbons with methylene groups.

Table 3 lists values obtained from curves of residues after thermal degradation of particular polymers at 550°, which are burned in air at 600–650°.

These data are different, depending on the chemical structure and the chlorine content of the polymers.

In polymers with similar chain structures the carbon residue increases with increase of the chlorine ratio. This finds confirmation in results obtained for Hydrin

Table 3

Carbon residues after thermal degradation of polymers at 550°C heated at a rate 20° min⁻¹ in nitrogen atmosphere

Type of polymer	Amount of chlorine weight, %	Carbon residue weight, %
Polychloroprene:		
Skypren B-30	33.7	20.1
Neopren WRT	37.2	24.6
Butaclor MC-10	34.2	22.5
Epichlorhydrin Polymers:		
Hydrin 100	35.6	11.1
Hydrin 200	24.0	7.5
Hydrin 400	23.7	6.5
Chlorinated Polyethylene	42.0	6.5
Chlorosulphonated Polyethylene:		
Hypalon 20	28.5	3.6
Hypalon 40	33.0	4.5
Polyvinyl Chloride	52.0	8.5

100, 200 and 400 and polymers of ethylene chain structure (3,6–8,5% residue for a chlorine content of 28.5–52%).

In the comparison of polymers with similar chlorine contents but different main chain structures, as for example polychloroprene (about 34% chlorine), epichlorohydrin homopolymer Hydrin 100 (35.6% chlorine) and chlorosulphonated polyethylene Hypalon 40 (33% chlorine), a distinct dependence between carbon residue and polymer structure can be observed.

The highest residue (20%) is given by polychloroprene, lower ones (6.5–11.5%) having ether groups in the chain, and the lowest ones (3.5–8.5%) polymers with ethylene main chain structures.

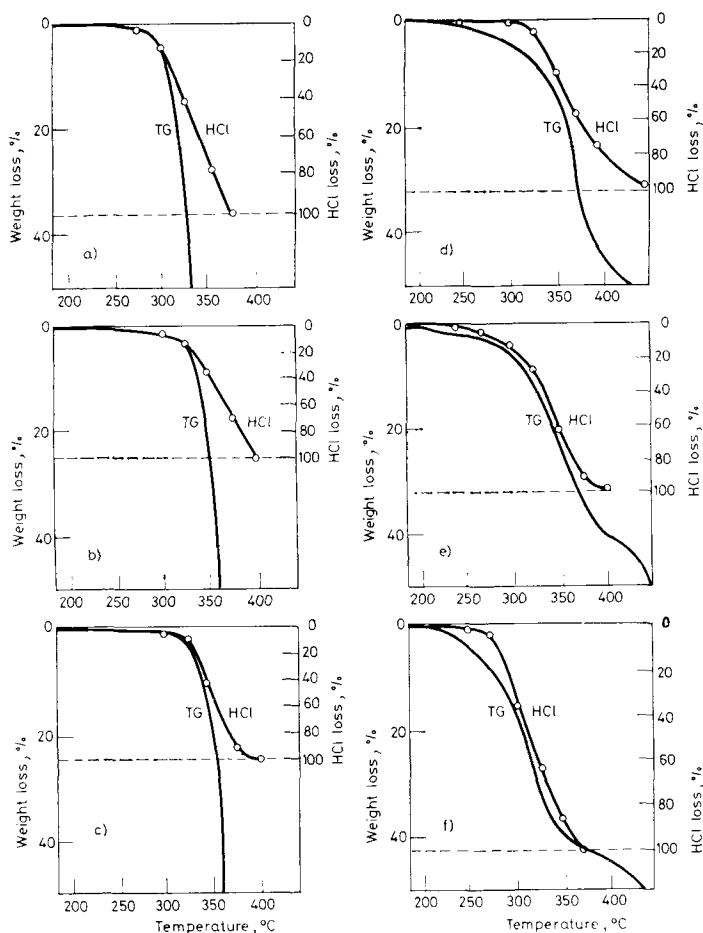


Fig. 3. Comparison of weight loss measured by TG and hydrogen chloride determined from titration data: a) Hydrin 100, b) Hydrin 200, c) Hydrin 400, d) Skypren B-30, e) Hypalon 40, f) Chlorinated polyethylene

In general, it can be stated that the quantity of non-volatile residue from the polymer investigated depends to a higher degree on the structure and the ratio of the number of hydrogen atoms to chlorine atoms than on the chlorine content of the polymer.

This problem is of fundamental importance in the quantitative analysis of chlorine-containing rubber vulcanizates, because the carbon residue can lead to errors in the evaluation of the ratio of particular components in the compounds (elastomer, carbon black).

Elimination of chlorine during heating in a nitrogen atmosphere

The quantities of chlorine (calculated as HCl) eliminated from the investigated polymers at various temperatures are presented directly in the thermal curves (Fig. 3) and in Table 4.

Table 4

Amount of hydrogen chloride evolved during programmed degradation up to various temperatures in nitrogen

Type of polymer	Trade-name	Weight loss in I degradation stage %	Calculated amount of HCl as % polymer	HCl as %
				250
Polychloroprene	Skyren B-30	42.0	34.7	0
Epichlorhydrin Polymers:	Hydrin 100	89.9	36.6	0
	Hydrin 200	92.5	24.7	0
	Hydrin 400	93.5	24.4	
Chlorosulphonated Polyethylene	Hypalon 20	36.0	29.0	1.5
	Hypalon 40	40.7	34.0	1.0
Chlorinated Polyethylene		45.0	43.3	0

Polymer chlorine at various temperature °C

275	300	325	350	375	400	450
	2.5	5.4	19.3	57.3	71.8	93.5
	5.6	13.2	41.9	75.3	99.5	
	2.5	12.6	30.2	64.2	100	
	1.7	5.9	41.4	95.0	100	
10.3	24.1	41.4	74.1	94.6	100	
6.0	14.8	31.0	60.0	92.8	100	
8.0	39.1	62.0	85.3	100		

Comparison of the data shows that the weight loss in the first, main degradation stage is usually higher, than the quantity of hydrogen chloride evolved. This is in agreement with literature data indicating that the elimination of HCl is connected with partial chain decomposition and the evolution of other volatile products. Further, in the case of epichlorhydrin rubbers, which degrade in one stage, distinct differences were observed between the general weight loss and the amount of HCl evolved.

With the exception of the initial period, the differences are the lowest for polymers with ethylene chain structure (chlorinated and chlorosulphonated polyethylene).

On the other hand, only in the case of epichlorhydrin elastomer is the initial weight loss connected directly with dehydrochlorination. In the remaining polymers it is preceded by a decrease in the TG curve, probably caused by the evolution of low molecular weight volatile products. It is especially distinct in the case of polychloroprene a weight loss of, (about 11 %) even at 180–300° not connected with dehydrochlorination).

The least stable is the bonding of chlorine in chlorinated polyethylene. The total evolution is complete by 370°. At this temperature the elimination amounts to about 93% for Hypalon, 64–75% for epichlorhydrin elastomers (the most stable in copolymer) and 57% for polychloroprene.

The diagram presenting the amount of evolved HCl as a function of temperature is nearly linear for chlorinated polyethylene and Hydrin, which may show that the reaction is not catalyzed by evolved hydrogen chloride. Similar data were obtained during an isothermal investigation of epichlorhydrin elastomers in an atmosphere of air [20].

In general, the temperature ranges as well as the relations between hydrogen chloride elimination and temperature are connected directly with the polymer structure and the mode of chlorine bonding.

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RÉSUMÉ — On a étudié, en atmosphère d'azote, la dégradation thermique des polymères contenant du chlore, utilisés dans la technologie du caoutchouc.

On a comparé les caractéristiques de la dégradation par thermogravimétrie, formation d'un résidu de carbone et élimination du chlore. On discute les différences observées dans la dégradation des polymères étudiés suivant leur structure.

ZUSAMMENFASSUNG — Die thermische Zersetzung von in der Kautschuk-Technologie verwendeten chlorhaltigen Polymeren wurde unter Stickstoff untersucht.

Die Charakteristika der Zersetzung durch die Thermogravimetrie, Kohlenrückstand und Chlorabspaltung wurden verglichen. Die in der Zersetzung der untersuchten Polymere in Abhängigkeit von ihrer Struktur beobachteten Unterschiede wurden diskutiert.

Резюме — Изучен в атмосфере азота термический распад хлоросодержащих полимеров, используемых в технологии резин. С помощью термогравиметрии были сопоставлены характеристики распада этих полимеров и оценены остаточный углерод и выделяющийся при этом хлор. Отмеченные различия в разложении исследованных полимеров обсуждены на основе их строения.