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INVESTIGATION OF THE INFLUENCE OF METAL OXIDES ON THE THERMAL DEGRADATION OF CHLORINE-CONTAINING POLYMERS BY THERMOGRAVIMETRY

T. Kleps and *M. Piaskiewicz*

INSTITUTE OF RUBBER INDUSTRY, PIASTÓW BY WARSAW,
POLAND

The influence of oxides of zinc, magnesium, antimony and aluminium on the thermal degradations of polychloroprene, chlorinated polyethylene and epichlorhydrin homopolymer has been investigated. The investigations showed that these metal oxides can change the thermal stabilities and degradation processes of chlorine-containing polymers. A considerable acceleration of the dehydrochlorination of these polymers was found in the presence of zinc oxide.

Polymers containing chlorine atoms in their molecules are marked by specific physico-chemical features and by the different character of their thermal degradation.

The cross-linked polymers display high resistance to hydrocarbon solvents, oils, benzine and other chemicals, and they have good mechanical and thermal features. When heated, they undergo degradation and decomposition, with the evolution of chlorine as hydrogen chloride and the formation of volatile organic products of decomposition. In the case of thermal degradation in an atmosphere without oxygen, solid products of decomposition are formed as well.

The dehydrochlorination of hydrocarbon polymers containing chlorine takes place in a stage prior to the destruction of the polymer chains.

In the case of epichlorhydrin polymers, containing C—O groups in their chains, the evolution of hydrogen chloride is accompanied by the simultaneous decomposition of the chains. Detailed investigations of the degradation of these polymers were reported earlier [1–3].

In the present work, the process of thermal degradation of chlorine-containing polymers has been investigated in the presence of metal oxides in practical use as cross-linking substances in compound and rubber goods, for example zinc and magnesium oxide, or fire inhibitors such as Sb_2O_3.

There are many well-known publications on investigations of the influence of metal oxides on the oxidation of olefin polymers [4]. As concerns polymers

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containing chlorine, investigations have been published on the influence of stabilizers such as zinc and cadmium stearates on the thermal degradation of polyvinyl chloride [5].

Experimental

Materials and investigation methods

Various chlorine-containing polymers commonly used in rubber technology were investigated. They are listed in Table 1.

The polymers and their mixtures with the oxides of zinc, magnesium, antimony and aluminium in a proportion of 5 parts/100 parts of polymer were investigated.

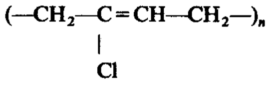
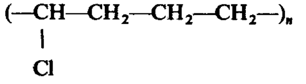
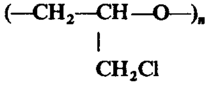
Thermal degradation was carried out in a nitrogen atmosphere in a Perkin–Elmer TGS–1 Thermobalance at a heating rate of 10 deg/min up to 550°, using 5 mg samples. The non-volatile residue in nitrogen was next heated in air to full decomposition.

Results and discussion

The TG and DTG thermogravimetric curves are presented in Figs 1–3, and the degradation parameters in Table 2.

These data show that the various metal oxides have different effects on the degradation of the polymers investigated. The greatest changes were observed in the presence of zinc oxide in the stage connected with the evolution of hydrogen chloride.

Table 1 Characteristics of polymers

Type of polymer	Chemical formula	Trade name	Chlorine content in polymer, %
Polychloroprene (CR)	 $(-CH_2-\underset{\underset{Cl}{\mid}}{C}=CH-CH_2-)_n$	Skypren B–30	37
Chlorinated polyethylene (CP)	 $(-\underset{\underset{Cl}{\mid}}{CH}-CH_2-CH_2-CH_2-)_n$	CPE 42–13	42
Epichlorhydrin homopolymer (CO)	 $(-CH_2-\underset{\underset{CH_2Cl}{\mid}}{CH}-O-)_n$	Hydrin 100	38

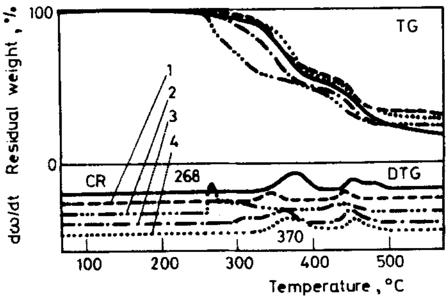


Fig. 1 TG and DTG curves of polychloroprene Skypren B–30 (CR) and its mixtures with metal oxides and trioxides. 1. CR-MgO, 2. CR-ZuO, 3. CR-Sb_2O_3, 4. CR-Al_2O_3

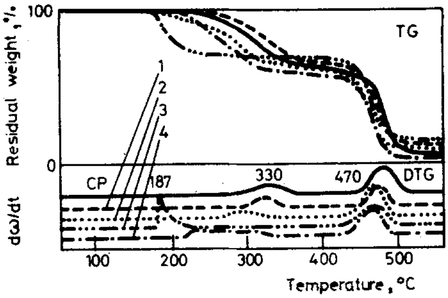


Fig. 2 TG and DTG curves of chlorinated polyethylene CPE 42–13 (CP) and its mixtures with metal oxides and trioxides. 1. CP-MgO, 2. CP-Al_2O_3, 3. CP-ZnO, 4. CP-Sb_2O_3

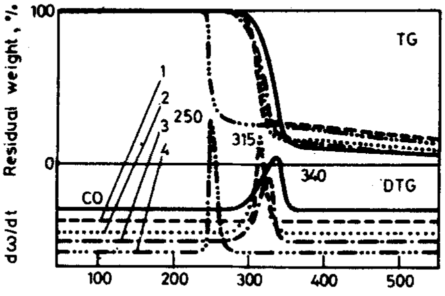


Fig. 3 TG and DTG curves of epichlorhydrin homopolymer Hydrin 100 (CO) and its mixtures with metal oxides and trioxides. 1. CO-MgO, 2. CO-Al_2O_3, 3. CO-Sb_2O_3, 4. CO-ZnO

Table 2 Degradation parameters of polymers and their mixtures with metal oxides in a nitrogen atmosphere

Type of sample	Initial temperatures of degradation, °C		Degradation stage I associated with main dehydrochlorination		Degradation stage II associated with decomposition of main chain structure
	T_0	T_2	$T_{\max DTG}$, °C	$dw/dt_{\max}$, % wt/min	$T_{\max DTG}$, °C
Skypren B-30 (CR)	180	233	376	8.0	450
CR-ZnO	222	260	268	15.0 3.0	435
CR-MgO	196	280	361	8.6	440
CR-Sb_2O_3	165	240	362	8.0 3.0	450
CR-Al_2O_3	180	238	370	8.0	454
Chlor. polyethylene (CP)	210	243	330	5.0	482
CP-ZnO	177	184	187	10.0	475
CP-MgO	228	258	314	4.4	472
CP-Sb_2O_3	214	224	238	5.0 2.0	470
CP-Al_2O_3	184	200	300	4.4	470
Hydrin 100 (CO)	280	290	340	29.0	—
CO-ZnO	244	246	250	56.6	—
CO-MgO	292	299	315	40.6	—
CO-Sb_2O_3	235	280	327	28.6	—
CO-Al_2O_3	260	282	320	32.0	—

Zinc oxide

For all the polymers, regardless of the chemical structure, ZnO caused a considerable decrease of the temperature of degradation in the stage connected with the liberation of hydrogen chloride, and a great increase of the destruction rate. Furthermore, in the case of polychloroprene, distinct increases of the temperatures demonstrating the thermal stability (T_0 and $T_{2\%}$) and a change of the degradation character were also observed. The otherwise single-stage of liberation of HCl was transformed into two stages in the presence of ZnO. These took place at different rates, the first one with a rapidly rising rate, and the second one with a considerably reduced rate of destruction. This demonstrates a change in mechanism of polychloroprene dehydrochlorination in the presence of ZnO.

Magnesium oxide

Improved that thermal stability of the investigated polymers, without causing radical changes in the process of further degradation, except for a rise in the rate of destruction of epichlorhydrin homopolymer.

Antimony trioxide

With polychloroprene and chlorinated polyethylene caused a change in the character of the degradation. As for the mixture of polychloroprene with ZnO, this involved transformation of the single dehydrochlorination stage into a double stage, with different rates of destruction. Furthermore, a small decrease in stability and a fall in the temperature of hydrogen chloride liberation were observed.

Aluminium trioxide

Caused a lowering of the thermal stabilities of chlorinated polyethylene and epichlorhydrin homopolymer, without causing other changes in the processes of degradation of the investigated polymers.

The investigations carried out showed that metal oxides can change the thermal stabilities and the processes of degradation of polymers, by altering the mechanisms of the reactions. This problem is currently the subject of further investigations.

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Zusammenfassung — Es wurde der Einfluß von Zink-, Magnesium-, Antimon- und Aluminiumoxid auf den thermischen Zerfall von Polychloropren, chloriertem Polyäthylen und Epichlorhydrin-homopolymeren untersucht. Die Untersuchungen zeigen, daß diese Metalloxide die thermische Stabilität und die Zersetzungsprozesse von chlorhaltigen Polymeren verändern können. In Gegenwart von Zinkoxid wurde eine bedeutende Beschleunigung der Dehydrochlorierung dieser Polymere festgestellt.

Резюме — Исследовано влияние оксидов цинка, магния, сурьмы и алюминия на термический распад гомополимеров полихлоропрена, хлорированного полиэтилена и эпихлоргидрина. Исследования показали, что оксиды металлов могут изменять термоустойчивость и процесс распада хлорсодержащих полимеров. В присутствии оксида цинка наблюдалось значительное ускорение процесса дегидрохлорирования полимеров.