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INVESTIGATION OF THE INFLUENCE OF ZINC OXIDE ON THERMAL DEGRADATION OF POLYCHLOROPRENE

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Thermal degradation of uncrosslinked chloroprene rubber in presence of different amount of zinc oxide has been investigated. It has been found that the quantity of zinc oxide has an important influence on the character, temperature, the rate of destruction and thermal stability. It concerns especially the first stage of degradation connected mainly with elimination of chlorine.

Ealier study of the thermal destruction of vulcanized and not vulcanised rubber containing chlorine [1] and the investigation of the influence of metal oxides on the degradation [2] have shown that zinc oxide causes considerable changes in the course of degradation of these polymers especially polychloroprene

In the literature there are only a few works concerning the degradation of polymers in the presence of metals. The works are usually connected with the thermal stability of olefine polymers and polyacrylates concerning their oxidation process [3-5].

It has been found that the majority of metals - zinc among others - chemically connected with polymer, or mechanically added (also in the form of oxides and salts) mostly as impurities, generally influenced badly on the thermal stability of polymers. Only in the case of acryl styrene copolymers it has been observed that zinc improves their stability [6].

In the case of polymers containing chlorine, metal oxides are used as ingredients of cross-linking systems (e.g. ZnO, MgO, Pb_2O_3 [7, 8]) or fire inhibitors for instance phosphorus or aluminium and antimony trioxides [9]. The degradation is connected with the evolution of HCl. In the presence of metal or its compounds HCl reacts, forming chloride which volatilizes or makes a non-volatile layer on the surface of polymer.

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Benbow and Cullis [10] have found that volatile chlorides form as reaction product with Zn, Bi, Cd, Cu, Pb, Mo oxides and Sb_2O_3 [11] and compounds phosphorus [9] non-volatile. Papers published on thermal investigations of chlorine containing polymers mainly concern polyvinyl chloride [11, 12]. Simon and his co-workers [11] have found that Zn and Mo oxides considerably decrease temperature and accelerate the degradation of PVC, while Al_2O_3 does not cause any important changes.

Our ealier studies concerning polychloroprene [1, 2] have shown that only ZnO has an important influence on the thermal degradation of polychloroprene. Serious changes in the character and temperatures of destruction mainly in the stage of dehydrochlorination have been found.

The present study is to see the influence of quantity of the introduced zinc oxide on thermal destruction of unvulcanised polychloroprene.

The changes of thermal stability and the parameters of degradation such as temperature, quantity, and the rate of forming volatile and solid products of destruction at the temperatures up to 550° in the atmosphere of inert gas, and also carbon and mineral residue have been analysed.

Experimental

Materials and test methods

The mixtures of polychloroprene Skypren B-30 with zinc oxide in the quantities 0, 2, 3, 4, 5, 7.5, 10, 15 and 20 parts ZnO phr have been studied. The mixtures prepared on a laboratory open mill were pressed at the temperature of 105 deg C into plates of 1 mm thick.

The investigations were carried out in a Perkin-Elmer TGS-1 Thermobalance in a nitrogen atmosphere at the rate of heating being 10 deg/min, up to temperature 550° using 5 mg samples. Undecomposed in nitrogen organic residue so called carbon residue after coolig to 300° was subjected to oxy-thermal degradation in the air up to complete decomposition, i.e. up to 600-700°.

Results and discussion

Thermogravimetric curves TG and DTG of tested CR/ZnO mixtures and CR without ZnO are presented in Fig. 1.

As the thermograms show, polychloroprene degradation undergoes in two main stages - the first characterized by $T_{\max}$ 376° is mainly connected with the process of dehydrochlorination; the other one - $T_{\max}$ 452° - mostly with destruction of macromolecules. It has been stated [1, 13] that in the first stage about 95 % chlorine split off in the form of HCl, while the remaining chlorine splits off in the second stage together with the destruction of polymer chains.

In the presence of ZnO the liberated HCl reacts with oxide, forming $ZnCl_2$. Important changes in the process of polychloroprene degradation can be observed. These changes (Fig. 1, Table 1) concern mainly the first stage of destruction and first of all change the degradation character: single stage of dehydrochlorination becomes transformed in the presence of ZnO in two steps occurring at a much lower temperature.

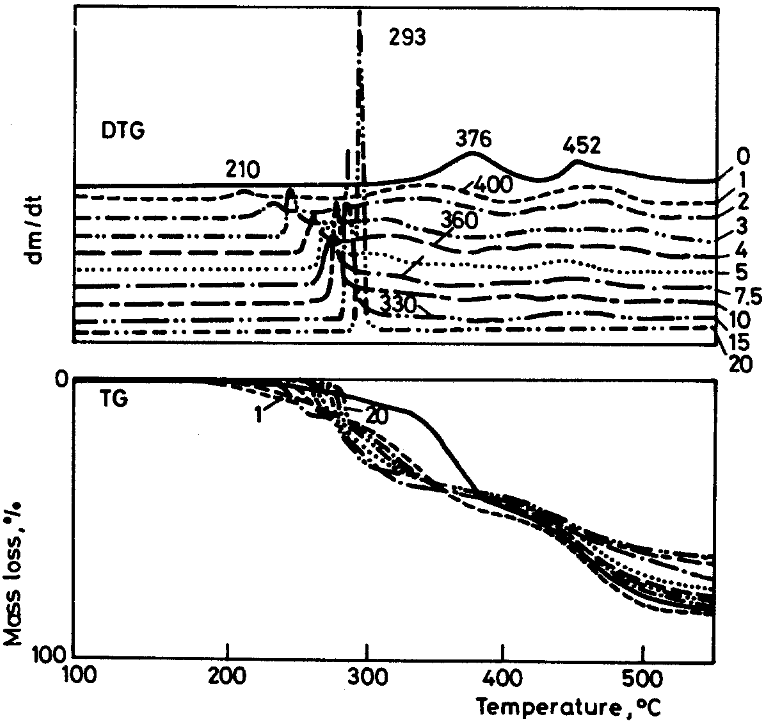

Fig. 1 TG and DTG curves of polychloroprene Skypren B-30 and its mixtures with the quantities 1, 2, 3, 4, 5, 7.5, 10, 15 and 20 p/100 p of polymer

Table 1 Degradation and destruction parameters of the mixtures CR/ZnO. The analysis of I stage connected with dehydrochlorination

ZnO content phr	I stage degradation						Total weight loss in I stage,	Weight loss at 300°C,	$T_{I/II}$,
		I' step			I'' step				
	T_5,	$T_{I'max}$,	Weight loss	dm/dt max	$T_{II''max}$,	Weight loss,			
	°C	°C	%	% m/min	°C	%	%	%	°C
0.0	280				376	43.0	43.0	6.0	
1.0	230	210	1.5	1.5	345	41.0	42.5	16.0	220
2.0	240	228	3.5	4.5	330	37.5	41.0	17.0	235
3.0	245	245	7.0	10.0	310	33.0	40.0	19.0	250
4.0	255	258	8.5	11.5	310	29.0	38.0	21.0	260
5.0	265	268	12.0	15.0	310	24.0	36.0	23.0	270
7.5	268	270	14.0	20.5	310	21.5	35.5	24.5	273
10.0	275	276	19.0	32.4	310	14.0	33.0	27.0	280
15.0	282	286	21.5	53.0	310	9.5	31.0	26.5	288
20.0	285	293	23.0	98.0	-	7.5	30.0		295

Table 2 Degradation and destruction parameters of the mixtures CR/ZnO. The analysis of II stage degradation connected with decomposition of the main chain structure

ZnO content phr	T_{IImax} °C	Weight loss, %	Total weight loss at 550°C, %	Zn loss in relation		Carbon residue at 550°C %	Mineral residue (ash), %
				to test, %	to added ZnO, %		
0	452	40.0	83.0			17	0.1
1.0	465	36.5	79.0	0.29	30	20.2	0.8
2.0	(425) 460	37.5	78.5	1.06	54	20.5	1.0
3.0	(390) 460	38.0	78.0	1.71	58	20.7	1.3
4.0	(395) 460	38.6	76.6	2.44	63	21.9	1.5
5.0	450	38.5	74.5	2.86	60	23.5	2.0
7.5	(396) 450	32.5	70.0	4.57	65	27.5	2.5
10.0	(405) 445	32.0	65.0	6.19	68	32.0	3.0
15.0	460	30.0	61.0	9.3	69	35.2	3.8
20.0	-	25.5	55.5	12.2	73	40.0	4.5

The content of ZnO has a significant influence upon the course of the process. With 1 phr of ZnO only important changes have been observed. There are: considerable worsening of thermal stability expressed by T_5 (decrease of 50°) a decrease of temperatures of the consecutive destruction phases, and a transformation of the dehydrochlorination stage into two steps, with T_{max} of the first step 210° and the second step 347°.

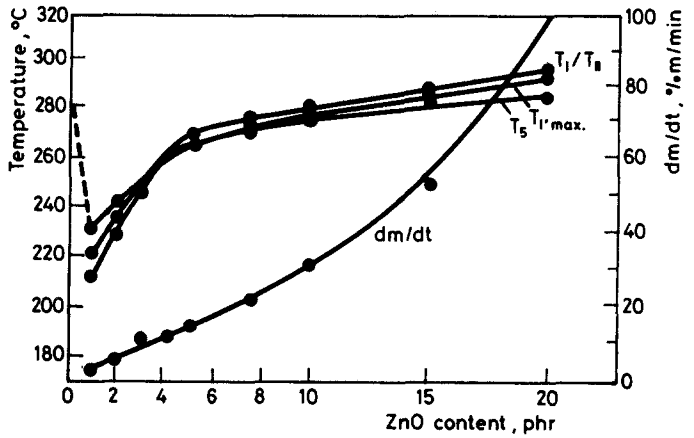

Fig. 2 Thermal parameters of the I stage of dehydrochlorination T_5, $T_{I'max}$, $T_{I/II}$ and dm/dt

The loss of weight in these steps proceeds at a small rate (about 1-2 % m/min) and it is considerably different - in the first step only 1.5 % while in the second one 41 %. The summarized value is a little lower than in the case of CR containing no oxide (43.0 %), in spite of a higher molecular weight of $ZnCl_2$ than HCl.

The analysis of the destruction stage of polymer macromolecules (Table 2, Figs 1-3) in the presence of 1 phr ZnO has shown that this stage also begins at a lower temperature $T_{I/II}$ of about 25° and is characterized by a smaller loss of weight.

The total loss of weight in the whole temperature range (up to 550°) is also smaller than in the absence of ZnO. The growth of carbon residue means that the quantity of solid decomposition products increases simultaneously.

As the content of ZnO in the range of 1-20 parts phr grows, the increase of the temperature of the initial degradation as well the thermal stability can be observed. The temperature T_5 increases from 230 to 285°. The temperature of the first step ($T_{I\max}$) of dehydrochlorination (Figs 1-3) systematically increases from 210 to 293°. These changes are accompanied by the loss of weight from 1.5 to 23 % and by the rate of the loss of weight from 1.5 to 98 % m/min.

It means a clear acceleration of the polychloroprene degradation in this step connected with the formation of increasing quantity of volatile destruction products. A similar phenomenon of the acceleration in the initial phase of degradation has been observed in the case of PVC, in the presence of stabilizers containing zinc [12].

In the second step of the stage of dehydrochlorination, together with the increasing of ZnO content (Table 1, Figs 1-3), an opposite relationship has been observed, namely the shifting of this step to the lower temperatures, which is characterized by a fall in the temperature of the peaks DTG ($T_{II\max}$), the temperature of the degradation termination T_{KII}, and also by a systematic decrease of the loss of weight.

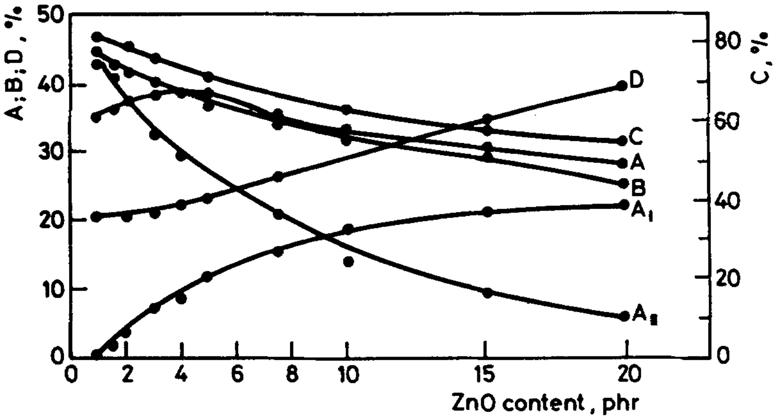

Fig. 3 The influence of the content of ZnO in CR on weight loss (A, B, C) and carbon residue (D)
A - I stage of dehydrochlorination (A_1+A_2); A_1 - the first step of I stage;
A_2 - the second step of I stage; B - II stage of destruction of macromolecules;
C - A+B; D - carbon residue at 550°C

The influence of ZnO in the second stage of degradation connected with the destruction of polymer chains (Table 2, Figs 1-3) is small in comparison with the stage of dehydrochlorination. Only a certain irregularity of destruction characteristic could be observed on the curves DTG, at a small rate of loss of weight (below 2 % m/min). Furthermore, a widening of the destruction range as a result of the decrease of the initial temperature of the second stage $T_{I/II}$ from about 400 to 330° with the increase of the content of ZnO, has been observed.

The total loss of weight in both stages of destruction in a nitrogen atmosphere up to the temperature of 550°, it means in the stages of dehydrochlorination and the polymer chains destruction, shows decreasing values (Table 2, Fig. 3), which indicates a diminishing total quantity of volatile destruction products. Simultaneously increase content of the carbon residue forming the solid decomposition products.

As the quantities of ZnO in ZnO/CR mixtures increase, the residue of mineral ingredients after thermal and oxythermal destruction increases also, from 0.1 to 4.5 % (Table 2, Fig. 4), ZnO being the main component of the residue. It means that not the whole quantity of the ZnO has reacted with the HCl (in spite of the surplus chlorine in polychloroprene), but only the quantity of ZnO being a difference between the introduced quantity and the quantity remaining after the destruction. This difference grows from 30 to 73 % of introduced ZnO.

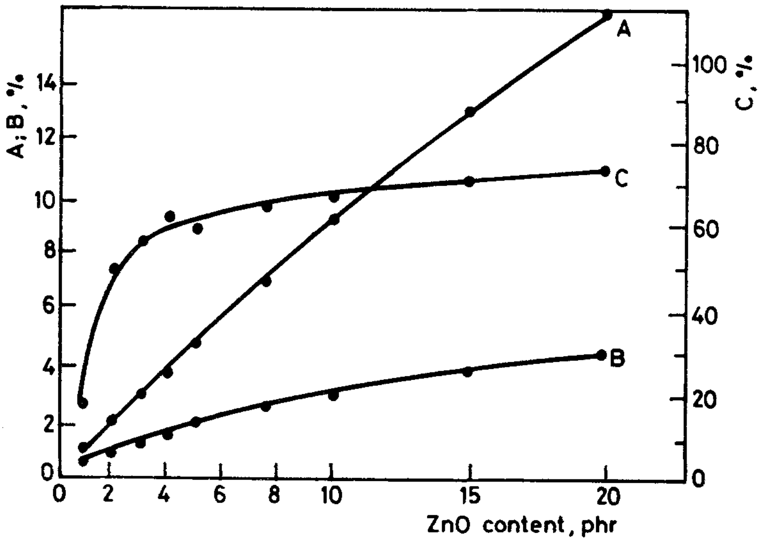

Fig. 4 The influence of the content of ZnO in CR on mineral residue and ZnO loss. A - introduced content ZnO; B - mineral residue (ash); C - ZnO loss

Conclusion

The influence of zinc oxide quantity on the thermal degradation of polychloroprene using the dynamic thermogravimetric method has been studied. It has been found that the quantity of ZnO has an important influence on the observed effects and can change especially the first stage of degradation associated with dehydrochlorination. These changes concern the character, temperature and the rate of destruction as well as a significant change of polychloroprene thermal stability.

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Zusammenfassung — Es wurde der thermische Abbau unvernetzten Chloroprenkautschuks in Gegenwart verschiedener Mengen Zinkoxid untersucht.

Es zeigte sich, daß die Zinkoxidmenge auf Charakter, Temperatur und Geschwindigkeit der Zersetzung sowie auf die Wärmebeständigkeit einen entscheidenden Einfluß ausüben. Dies betrifft besonders den ersten Schritt der Zersetzung, in dem hauptsächlich Chlor eliminiert wird.