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Influence of Stabilizers with Secondary Amine Groups on the Thermal and Thermo-oxidative Decomposition of Polyepichlorohydrin

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The thermal and thermo-oxidative destruction of epichlorohydrin elastomers, stabilized with secondary amine groups containing antioxidants has been studied, using TG and DSC methods, chromatographic and IR-spectrometric analysis of gaseous products of the destruction and also elementary analysis, gel-content and viscometric measurements on the polymers.

The elimination of chlorine atoms is not important in the process of polyepichlorohydrin destruction. Most important are the scission of the main chains, producing drastic decreases of the intrinsic viscosities of the polymers, and also the formation of carbonyl groups on the macromolecules. The first destruction step is accompanied by substantial changes of the molecular weights, the weight loss being not important.

The secondary amine-type stabilizers do not influence the thermal destruction, but have a good inhibiting activity on the thermo-oxidative destruction of polyepichlorohydrin, increasing the temperature at which this process occurs.

At relatively high temperatures (about 150°C) the secondary amines react with CH₂Cl groups of the polymer. In the case of difunctional aminic antioxidants these reactions yield crosslinked polymers.

KEY WORDS Polyepichlorohydrin, elastomers, thermal destruction, thermo-oxidative destruction, diamines, antioxidants, stabilizers, gel content, crosslinking.

INTRODUCTION

High molecular, amorphous polymers of epichlorohydrin, obtained by ionic-coordinate ring-opening polymerization are elastomers with high stability in fuels and mineral oils up to relatively high temperatures. These properties, as well as the good mechanical strengths caused a certain interest on the market for epichlorohydrin rubbers.

In a previous paper¹ were reported some results of the study of polyepichlorohydrin thermo-oxidative decomposition. Thus, it was established that HCl elimination does not characterize the process, consequently the breaks of C—Cl bonds are not important in the destruction mechanism. The process occurs through free-radical

intermediates, which are forming probably at the tertiary C-atoms. The thermal oxidation of polyepichlorohydrin is accompanied by the formation of carbonyl groups in the macromolecules.

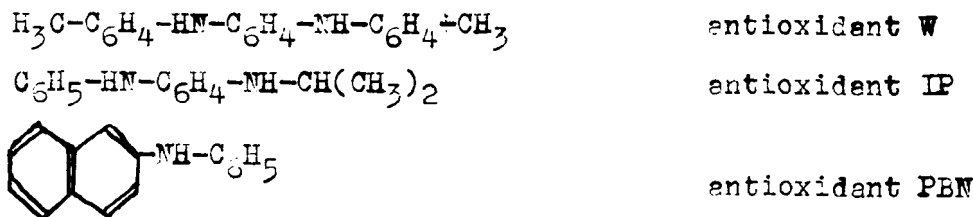
The epichlorohydrin rubbers have a higher stability at thermoxidation in comparison with the diene rubbers for general purposes, with nitrile rubbers and polychloroprenes. This stability may be more increased by using appropriate stabilizers. It was established that secondary amine groups-containing antioxidants are very effective for stabilizing polyepichlorohydrin.¹

The present work contains some new aspects of the thermal and thermoxidative destruction of epichlorohydrin elastomers and of the influence of secondary amine-type stabilizers on these processes.

EXPERIMENTAL

Epichlorohydrin rubber was obtained by ring-opening polymerization of epichlorohydrin in toluene solution, using a preformed catalyst TIBA:Et₂O:H₂O = 1:4:0.6 (molar ratios), between 20 and 60°C. The monomer concentration was 2 moles/l and the catalyst concentration was 40 milimoles TIBA/l. The polymer has $\bar{M}_v = 800,000$.

Four samples of this polymer, α —without antioxidant and β , γ , δ —with 1% stabilizer W, IP and PBN respectively were tested.



DSC measurements were run on 5×10^{-3} g samples, in air and argon atmosphere, using a Dupont 99° apparatus, in the temperature range 50–350°C, with a heating rate of 10°C/min.

TG measurements at 20 to 500°C were obtained using a MOM derivatograph Q-1500 in the same conditions as presented above.

There were also performed destructions under vacuum (10^{-2} mmHg) and in the presence of dried oxygen (2 moles/mole structural unit), in glass ampules. The gaseous products of the destruction were analyzed with a LKhM-8MD gas-chromatograph, having a $h = 1$ m, $d = 3$ mm column, filled with Parapack-Q (for CO₂), or with activated carbon (for CO, O₂, CH₄); column temperature 25°C, carrier gas-helium (60 ml/min), catarometric detector (at 120 mA).

The viscosities were measured at 25°C on cyclohexanone solutions, using an Ubbelohde viscometer. The gel contents of the samples were evaluated, too.

IR spectra of the gaseous products resulting from destruction processes were obtained on an IR-lo apparatus, in the wave number range 400–3700 cm⁻¹.

RESULTS AND DISCUSSIONS

During the thermal destruction of α , β and γ samples in vacuumed ampules (Table I) there was no weight loss after one hour at 175°C. The intrinsic viscosity of the unstabilized polymer (α) remained unchanged. In these conditions the polymers β and γ , containing *p*-phenylenediamine derivatives suffered a considerable cross-linking and an important increase of the viscosities of soluble fractions.

At higher temperatures (200 and 250°C) one observes some weight losses and drastic viscosity decreases up to the loss of polymeric feature for all three samples. By gas-chromatography was detected CO in the gaseous products of the destruction. In the same products the IR-spectra shown absorption peaks at 737 cm^{-1} (the bond C—Cl) and at 2700-3100 cm^{-1} (the bonds C—H in CH_2 and CH_3 groups), indicating the presence of chlorinated derivatives of inferior hydrocarbons.

The *p*-phenylenediamine antioxidants do not increase the thermal destruction of polyepichlorohydrin. On the contrary, one can observe at 200°C a higher decrease of the viscosity in the samples stabilized with such derivatives.

The results presented in Table II show that the destruction of the samples β and γ in the presence of oxygen, especially at 200°C, gives smaller amounts of CO + CO₂ than the sample α . This behavior confirms the inhibition of the thermoxidation by the secondary amines. As in the case of thermal destruction, the heating in oxygen of stabilized polymer samples produces at the beginning some cross-linking and the increase of viscosities of the soluble fractions. In the case of thermoxidative destruction, these phenomena occur at 150°C and with reduced intensities in comparison with the thermal destruction.

Even in conditions in which the destruction is up to losing the polymeric features, the changes of the elementary composition are not important (Table III). This fact indicates that the destruction occurs especially through scissions of the macromolecules, the elimination of small molecules having a reduced importance.

The differential thermogravimetric curves of the rubbers α , β and γ indicate the

TABLE I
The thermodecomposition in vacuum, 1 hr at different temperatures

Polymer sample	Temperature, °C	Weight loss, %	CO in the gaseous phase, moles/mole structural unit	$[\eta]$, dl/g	Gel content, %
α	20	—	—	2.25	0
	175	0	0	2.25	0
	200	1.9	traces	1.74	0
	250	4.9	0.001	—	0
β	20	—	—	2.02	0
	175	0	0	5.80	70.5
	200	2.0	traces	0.88	5.0
	250	4.9	0.001	—	0
γ	20	—	—	2.18	0
	175	0	0	11.60	85.0
	200	2.0	traces	0.12	0
	250	4.7	0.001	—	0

TABLE II
Thermooxidative decomposition, 1 hr at different temperatures

Polymer sample	Temperature, °C	Absorbed O ₂ , moles/mole structural unit	CO + CO ₂ in gaseous phase, moles/mole struct. unit	[η], dl/g	Gel content, %
α	20	—	—	2.25	0
	150	0	0	3.07	0
	175	0	0	1.36	0
	200	0.077	0.015	0.50	0
	250	0.100	0.053	—	0
β	20	—	—	2.02	0
	150	0	0	4.70	17.5
	175	0	0	1.10	0
	200	0.066	0.003	0.42	0
	250	0.133	0.026	—	0
γ	20	—	—	2.18	0
	150	0	0	6.32	14.8
	175	0	0	1.55	0
	200	0.057	0.005	0.53	0
	250	0.109	0.025	—	0

TABLE III
Elementary analysis of the samples, initial and after 1 hr of destruction

Polymer sample	Decomposition conditions	C, %	H, %	Cl, %	O, %
α	—	38.99	5.61	36.71	18.69
	250°C, vacuum	38.73	5.57	36.38	19.32
	250°C, oxygen	37.92	5.66	35.79	20.63
β	—	39.07	5.55	36.38	19.00
	250°C, vacuum	38.29	5.22	35.99	20.50
	250°C, oxygen	38.51	5.42	35.52	20.54
γ	—	39.55	5.56	36.17	18.72
	250°C, vacuum	38.89	5.53	35.84	19.74
	250°C, oxygen	38.33	5.72	35.84	20.11

beginning of the destruction at about 200°C in normal atmosphere (Figure 1) and at about 250°C under argon (Figure 2). The curves of the unstabilized polymer α are very similar to those of the stabilized samples β and γ. Taking into account the results which demonstrated the strong effect of secondary amines as stabilizers for polyepichlorohydrin,¹ the similarity of TG curves confirms that the elimination reactions have no importance in the studied process.

DSC curves under argon (Figure 3) show that the used stabilizers have no influence in the thermal destruction of epichlorohydrin rubbers. Up to 280°C the curves of stabilized and unstabilized polymers are identical and indicate an endotherm process, occurring with a rate which increases with the temperature. Over 280°C, the curves of stabilized samples show small exotherm peaks, which may be

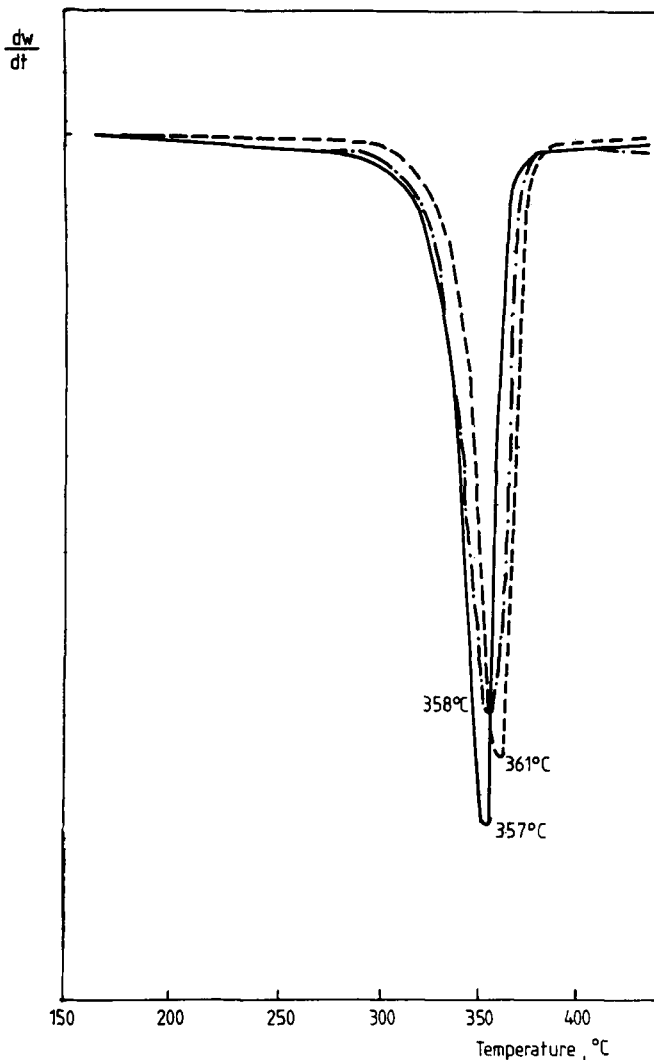


FIGURE 1 TG curves under normal atmosphere for the samples α (—), β (-----) and γ (-·-·-).

attributed to some reactions of the antioxidants, but the overall endotherm character of the process is conserved even in this case.

The influence of aminic antioxidants is clearly showed by the DSC curves in the air (Figure 4). The destruction of the unstabilized polymer begins at 212°C and occurs as a very rapid exotherm process. It seems to be probable for this process a chain mechanism through free radicals. The samples β and γ , which are stabilized with p-phenylenediamine derivatives begin to have modifications at 259 and 237°C, respectively. The first reactions are endotherm. The exotherm oxidation starts for both samples at 290°C. The endotherm part of the thermograms cannot be attributed to the destruction of the stabilizers: as one can observe in the Figure 5, the destruction of antioxidant W starts at 204°C, occurring as a strong exotherm process;

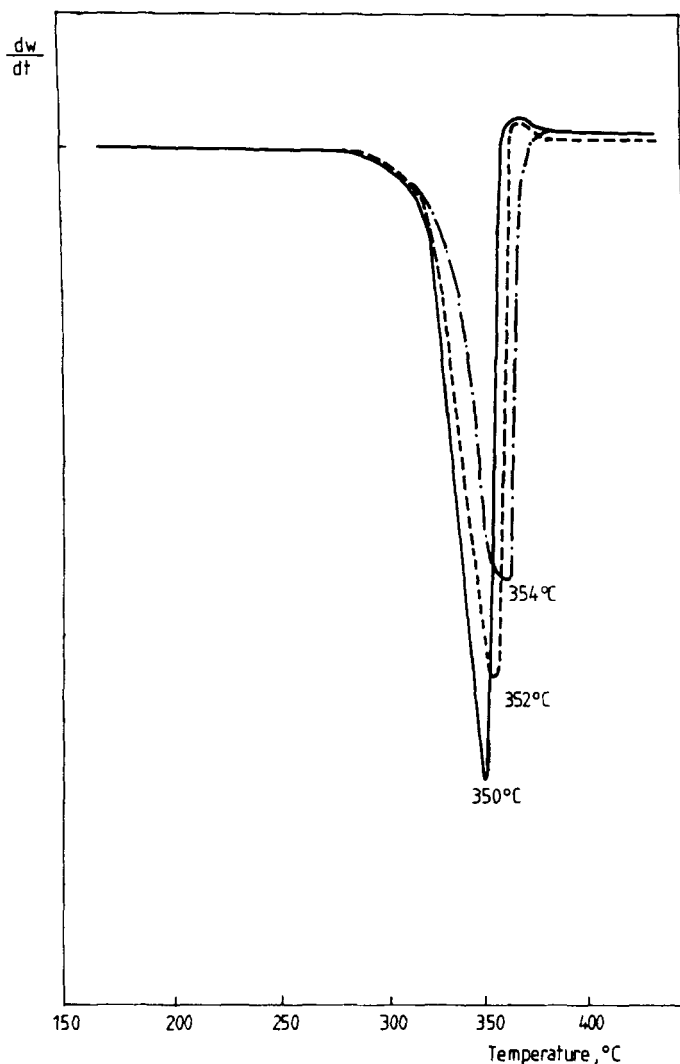
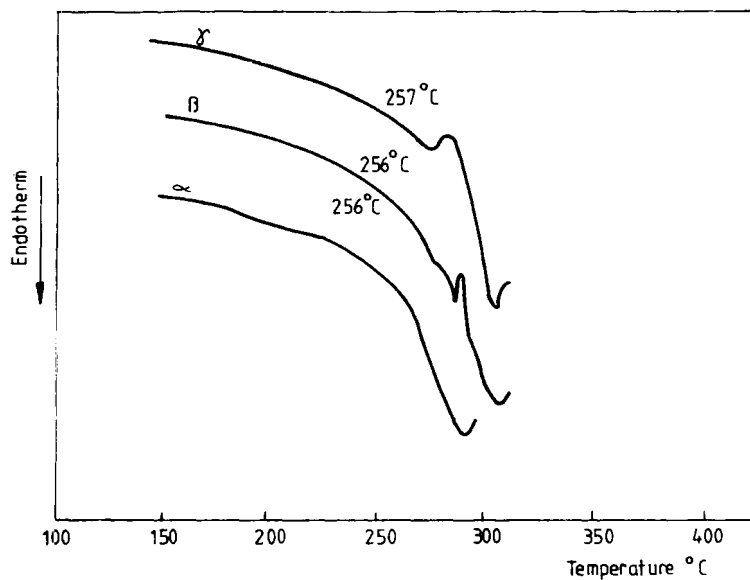
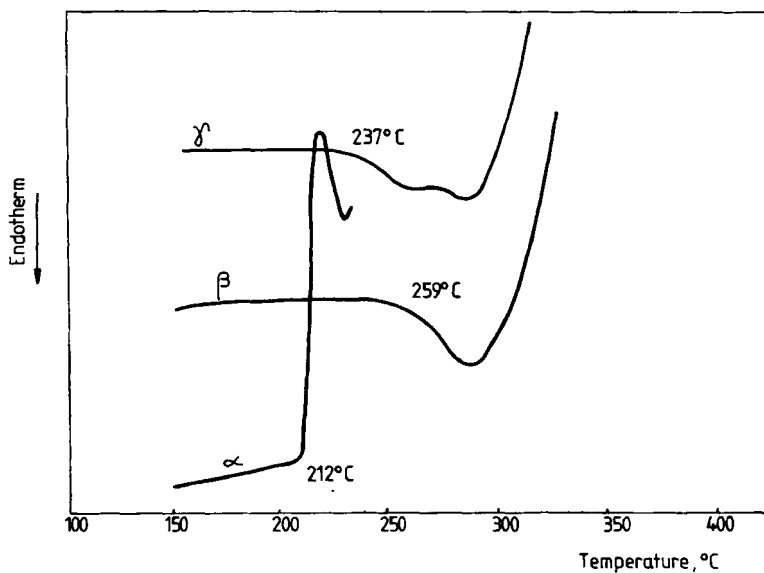


FIGURE 2 TG curves under argon atmosphere for the samples α (—), β (-----) and γ (-·-·-).

the IP antioxidant shows a weak exotherm reaction which occurs in the temperature range 200–228°C, then occurs an endotherm reaction up to 260°C, followed by a rapid exotherm oxidation. Consequently, the endotherm parts of the curves presented in Figure 4 for the β and γ samples may be attributed to some possible reactions between the polymer and the diamines used as stabilizers. This hypothesis is in accordance with the observed crosslinking too.

Comparing the DSC temperatures at which begin the modifications of the tested samples (Table IV), one observes that the unstabilized polymer begins to degrade at 212°C in the air and at 256°C under argon, the secondary amines do not modify the process in inert atmosphere, but in the air they increase these temperatures, tending to reach the limit represented by the thermal destruction.

FIGURE 3 DSC curves for α , β , γ samples under argon atmosphere.FIGURE 4 DSC curves for α , β , γ samples in air.

As one can see from the Figure 4, there is an evident difference between the endotherm parts of DSC curves at the thermoxidation of the polymers β and γ : in the case of the sample stabilized with W only one endotherm reaction occurs, but by using IP stabilizer take place two successive endotherm reactions. This experimental fact confirms the hypothesis that the endothermic parts of these curves

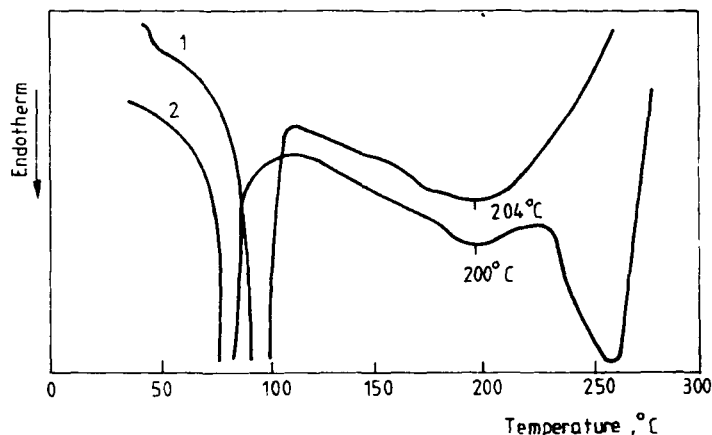


FIGURE 5 DSC curves for W (1) and IP (2) antioxidants.

TABLE IV

The starting temperatures of reactions (DSC data)

Polymer sample	Temperature, °C	
	Thermostoxidation process	Thermal Destruction
α	212	256
β	259	256
γ	237	257

represent the thermal effects of certain reactions between the polymer and the stabilizers: the W derivative is a symmetric one, having identical substituted NH groups, while IP antioxidant is asymmetric, its NH groups being different substituted and consequently having various reactivities.

We consider the reaction of the secondary aminic antioxidants with polyepichlorohydrin as occurring between the NH and CH₂Cl functions. By using difunctional antioxidants (the cases of W and IP), this reaction produces crosslinked structures:

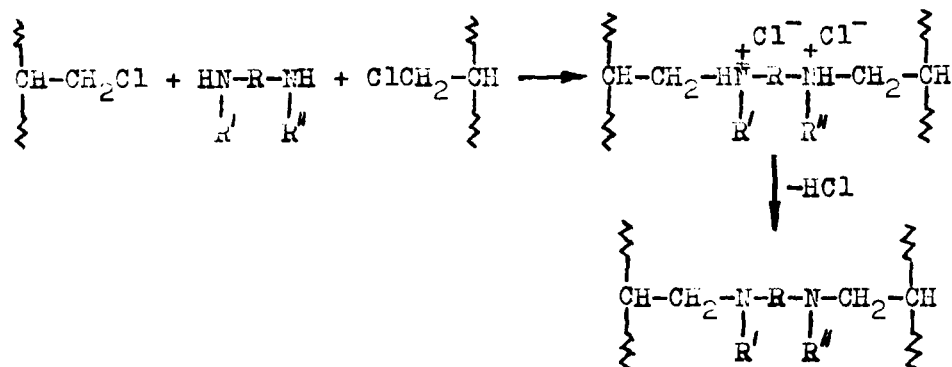


TABLE V

Thermal and thermoxidative decomposition of the sample δ , 1 hr

Destruction conditions	$[\eta]$, dl/g	Gel content, %
—	2.21	0
175°C, vacuum	2.22	0
150°C, oxygen	2.50	0
175°C, oxygen	1.58	0

Crosslinking of polyepichlorohydrin with reagents containing two or more NH groups (polyamines, polyureas) is mentioned by other authors too.²

A supplementary proof of such reactions is the fact that by using a monofunctional amine stabilizer (the sample δ), one can observe all the discussed phenomena (the antioxidant effect, DSC curve of the thermoxidation similar to those for the sample β), excluding gel-formation, which does'nt occur (Table V).

CONCLUSIONS

The thermal destruction of epichlorohydrin elastomers of homopolymeric type occurs without important elimination of HCl or other gaseous substances, the main reactions consisting in scissions of the macromolecules. Such reactions have an overall endotherm effect. The eliminations of gaseous and volatile destruction products became important only after the polymer lost his high-molecular feature. Secondary amines do not protect polyepichlorohydrin in the thermodestruction.

The thermoxidative destruction of unprotected polyepichlorohydrin occurs at lower temperature than the thermodestruction and has an intensive exotherm effect. The first step of this process is also dominated by breaking of macromolecules, without important elimination of gaseous and volatile products. Secondary amine antioxidants have a marked influence on this process, increasing the temperatures at which the destruction occurs.

Secondary amines are able to react with polyepichlorohydrin at high temperatures. Consequently, crosslinking may occur when diamine stabilizers are used.

References

1. M. Corciovei, F. Taran, T. Sărbu, G. Ivan, E. Dănilă, M. Giurginca and M. Chipară, *Intern. J. Polymeric Mater.*, **13**, 137 (1990).
2. Pat. USA 3,717,592 (CO8 G23/20), published 20.02.1973.