Kinetic Study of Action of Additives in Poly(Vinyl Chloride) Stabilizer Systems
II. Sterically Hindered Phenolic Antioxidants: Influence of Degradation Atmosphere

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The action of two antioxidants from the sterically hindered phenol group – Irganox 1010 and Topanol CA – and a composite stabilizer system based on calcium/zinc compounds has been studied. Fifty film samples with various amounts and combinations of additives have been prepared. The additives used were nontoxic, suitable for food packaging materials. Degradation in the inert nitrogen atmosphere has been followed potentiometrically. The time of thermal stability and the gradient of degradation degree dx/dt have been evaluated from the measured kinetic curves and a composite stabilizer system for long-time stabilization has been found. Calculations of the rate constants have shown ability of the antioxidants to terminate growth of polyene sequences and their weak ability to act as HCl trappers.

Due to low thermal stability of poly(vinyl chloride) (PVC) heat treatment brings about problems. Thermal degradation of PVC is a complex chain reaction forming conjugated polyene sequences [1] by HCl splitting off. Oxidative processes also decrease polymer length of life. The presence of oxygen causes increase of the degradation rate [2, 3].

PVC processing at the temperatures about 180 °C and applications of this polymer are impossible without additives, like stabilizers and antioxidants, since dehydrochlorination (DHC) starts above glass transition temperature [4].

A good stabilizer should prevent or disrupt the reactions in thermal DHC, especially bind HCl – the autocatalyst of DHC. Ca/Zn stabilizers are the most widely used nontoxic stabilizers, though they are not the most effective ones. In this work we have studied the action of two nontoxic, sterically hindered phenols – Irganox 1010, pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] and Topanol CA, 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane.

EXPERIMENTAL

For the study of the behaviour of samples by heat treatment in the inert nitrogen atmosphere, 50 specimens (composition of the most important samples is shown in Table 1) with powdered suspension PVC Slovinyl S-622 with various additives were prepared. Used additives: Wax E (lubricant, montan wax), powdered CaO (HCl trapper, component of the calcium/zinc stabilizer systems, purity 99 %), zinc stearate (ZnSt, to increase the colour stability, purity 99 %), rape oil (cold pressed low erucic oil, unstabilized, acid number (KOH) 1.1—1.3 mg g^{-1}, for better mechanical properties), ethyl acetoacetate (purity 99 %, for better mechanical properties), and antioxidants Irganox 1010 and Topanol CA. The mixtures were mixed for 2 min to obtain maximum possible homogeneity, then calendered for 3 min at processing temperature 180 °C and pressed to get 0.1 mm thick films. Since HCl is the only degradation product at 180 °C, the degradation could be followed by the detection of the evolved HCl. It was absorbed in AgNO$_3$ solution and the decrease of Ag$^+$ concentration was monitored with electrode system – silver working electrode *vs.* reference saturated calomel electrode.

RESULTS AND DISCUSSION

The basic information obtained from kinetic curves is the time of thermal stability τ and the gradient dx/dt. The time of thermal stability τ is the length of time elapsing before perceptible and measurable degradation develops. Here must be mentioned that degradation in an inert atmosphere runs markedly slower than degradation in a real atmosphere – the values of thermal stability duration are higher and gradients of degradation degree are lower [3]. Such high τ values are not possible without a strong synergism between additives.

Table 1. Composition of Several Samples, Time of Thermal Stability τ, and Gradient Values dx/dt

Sample	m_{PVC}/g	$m_{Wax\ E}/g$	m_{CaO}/g	m_{ZnSt}/g	$m_{rape\ oil}/g$	$m_{ethyl\ acetoacetate}/g$	$m_{Irganox}/g$	τ/min	$(dx/dt) \times 10^4/min^{-1}$
1	25	0.125	0.000	0.000	0.000	0.000	0.125	20	0.124
2	25	0.125	0.000	0.000	0.000	0.000	0.250	39	0.157
3	25	0.125	0.000	0.000	0.000	0.000	0.375	21	0.149
4	25	0.125	0.000	0.000	0.000	0.000	0.500	65	0.116
5	25	0.125	0.000	0.000	0.000	0.000	0.625	71	0.147
6	25	0.125	0.500	0.000	0.000	0.000	0.125	104	0.116
7	25	0.125	0.500	0.000	0.000	0.000	0.250	106	0.171
8	25	0.125	0.500	0.000	0.000	0.000	0.500	90	0.131
14	25	0.125	0.500	0.250	0.500	0.500	0.125	258	0.235
15	25	0.125	0.500	0.250	0.500	0.500	0.250	410	0.236
16	25	0.125	0.500	0.250	0.500	0.500	0.500	506	0.160

Sample	m_{PVC}/g	$m_{Wax\ E}/g$	m_{CaO}/g	m_{ZnSt}/g	$m_{rape\ oil}/g$	$m_{ethyl\ acetoacetate}/g$	$m_{Topanol}/g$	τ/min	$(dx/dt) \times 10^4/min^{-1}$
9	25	0.125	0.000	0.000	0.000	0.000	0.125	8	0.690
10	25	0.125	0.000	0.000	0.000	0.000	0.250	10	0.250
11	25	0.125	0.000	0.000	0.000	0.000	0.375	11	0.949
12	25	0.125	0.000	0.000	0.000	0.000	0.500	7	0.127
13	25	0.125	0.000	0.000	0.000	0.000	0.625	17	0.157
17	25	0.125	0.500	0.250	0.500	0.500	0.125	425	0.208
18	25	0.125	0.500	0.250	0.500	0.500	0.250	330	0.243
19	25	0.125	0.500	0.250	0.500	0.500	0.500	270	0.270
20	25	0.125	0.000	0.000	0.000	0.000	0.000	7	0.724

Table 2. Kinetic Parameters Calculated for Samples 1—5, 9—13

Sample	k_i/min^{-1}	k_p/k_t	k_{Ao}/k_t	k_2/min^{-1}	k_3/min^{-1}	Atmosphere
1—5	2.00×10^{-6}	3.00	50.0	108	4.96	Real
1—5	2.00×10^{-6}	5.27	19.0	56.2	5.77	Nitrogen
9—13	2.00×10^{-6}	3.30	55.8	84.8	25.8	Real
9—13	1.57×10^{-6}	5.88	22.8	51.6	18.8	Nitrogen

The results obtained suppose a weak HCl trapping by the antioxidants, CaO being a main HCl trapper. ZnSt and HCl reaction product – $ZnCl_2$ causes an increase of the rate of degradation after all ZnSt is consumed [5]. ZnSt with antioxidant has no stabilizing effect due to a $ZnCl_2$ catalytic effect in degradation, but in the presence of CaO a very strong stabilizing effect takes place. Rape oil and ethyl acetoacetate added for better mechanical properties do not significantly act as stabilizers, but in composite stabilizer systems a synergistic enhance between Ca/Zn system, antioxidant, and these two additives could be observed. τ and dx/dt values show that Irganox 1010 is a better HCl trapper than Topanol CA in the composite stabilizer system. This fact was confirmed for model samples by calculations of the effective rate constants of the antioxidant and HCl reaction with antioxidant as the only additive. A kinetic model has been proposed on the basis of the following reaction scheme [3]

$$PVC \xrightarrow{k_1} dePVC + HCl \qquad (A)$$

$$antioxidant + HCl \underset{k_3}{\overset{k_2}{\rightleftharpoons}} product \qquad (B)$$
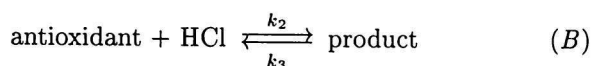
where dePVC means dehydrochlorinated polymer. This kinetic model considers the fact that HCl is not leaked out from the sample immediately after the beginning of the degradation, but only after reaching the critical amount of splitted off HCl in the sample. The model also proposes capability of the antioxidants to terminate the growth of polyene sequences (Table 2) [3, 6]. If we compare the values of kinetic parameters in nitrogen and real atmosphere, no significant difference between the initiation rate constant k_i values can be seen in different atmospheres. This could be expected, because the initiation of degradation is thermal and there is no influence of degradation atmosphere. A significant difference is in the k_{Ao}/k_t ratio (k_{Ao} describes the effect of antioxidant by growth of polyene sequences and k_t is the rate constant of termination of the polyene sequences growth). It may be ascertained from these values that the main action of antioxidant in inert atmosphere is termination of growth of sequences, which is confirmed also by the decrease of k_2 (rate constant of antioxidant and HCl reaction). In k_3 values there are not significant differences.
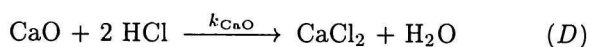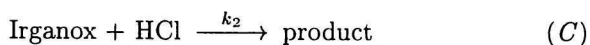
Analogous model has been proposed for samples containing CaO and Irganox 1010 (as a better HCl

Table 3. Kinetic Parameters Calculated for Samples *6—8*

Sample	k_1/min^{-1}	$k_{\text{CaO}}/\text{min}^{-1}$	k_2/min^{-1}	Atmosphere
6—8	3.93×10^{-5}	4960	185	Real
6—8	1.18×10^{-5}	2670	376	Nitrogen
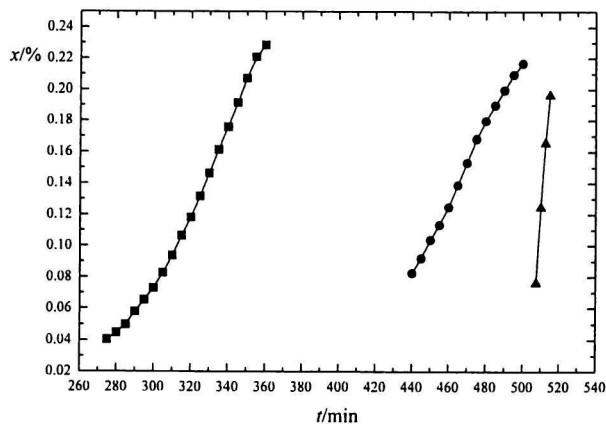
Fig. 1. Kinetic curves of PVC degradation of samples 14 (■), 15 (●), 16 (▲).
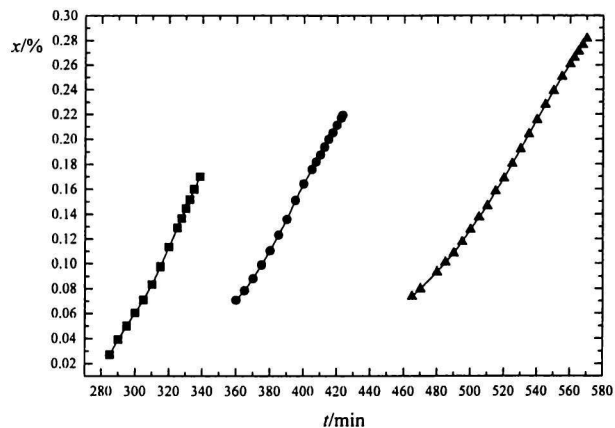
Fig. 2. Kinetic curves of PVC degradation of samples 17 (▲),18 (●), 19 (■).

trapper) to evaluate CaO trapping ability (k_{CaO}) and k_2 increase in the presence of CaO (Table 3). The model has been proposed on the basis of the following reaction scheme

$$\text{PVC} \xrightarrow{k_1} \text{HCl} + \text{dePVC} \qquad (A)$$

$$\text{Irganox} + \text{HCl} \xrightarrow{k_2} \text{product} \qquad (C)$$

$$\text{CaO} + 2\,\text{HCl} \xrightarrow{k_{\text{CaO}}} \text{CaCl}_2 + \text{H}_2\text{O} \qquad (D)$$

Comparison of k_1 confirms a lower DHC rate supposed in inert atmosphere. Absence of oxygen also may cause a lower k_{CaO} value. In an inert atmosphere a stronger synergism between CaO and Irganox 1010 can be observed – k_2 is two times higher in nitrogen atmosphere than its value in a real atmosphere.

CONCLUSION

A composite stabilizer system for long-time stabilization of PVC has been found (Figs. 1 and 2). The time of thermal stability varies from 250 to 500 min in inert (N_2) atmosphere. The composition of this sta-

bilizer system is: 2 % CaO, 1 % zinc stearate, 2 % rape oil, 2 % ethyl acetoacetate, and antioxidant in the range 0.5 %—2 %.

Main action of both antioxidants is termination of the growth of polyene sequences. Antioxidants are also weak HCl trappers. Irganox 1010 is more effective antioxidant than Topanol CA in the composite stabilizer systems.

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