Kinetic Study of Effect of Irganox E Antioxidants on Thermal Degradation of Poly(Vinyl Chloride)

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The effect of three Irganox E-type antioxidants (E 17, E 120, and E 201), based on α-tocopherol, on poly(vinyl chloride) thermal degradation rate at 180 °C has been studied. Fifteen film samples, which consisted of suspension poly(vinyl chloride), lubricant, and antioxidant, were prepared. Four samples contained a Ca/Zn stabilizer system with an epoxy co-stabilizer and Irganox E 201. Degradation in real atmosphere was followed by continuous potentiometry. The time of thermal stability τ and gradient of degradation dn_{HCl}/dt values were evaluated from the measured kinetic curves. Values of τ in the case of samples containing Ca/Zn stabilizer system did not overlap 90 min, their colour stability is approximately 25—30 min. Calculations of the kinetic parameters have shown that the studied antioxidants from the Irganox E group do not cause the polyene sequences growth termination.

Thermally initiated degradation of polymers proceeds at higher temperatures even in the absence of oxygen. However, it generally runs in the presence of oxygen, in the real atmosphere. Thermal degradation takes place especially during processing of the plastics. On the other hand, oxidation of polymers may occur during every stage of their life cycle. Thermal oxidative processes of polymers generally correspond to a free radical chain reaction that involves initiation generating free radicals, propagation yielding hydroperoxides, branching, and termination eliminating free radicals from the system [1, 2]. Antioxidants may intervene in any step of the thermal oxidation. Primary antioxidants (sterically hindered phenols and secondary aromatic amines) act through a chain transfer and termination. They are radical traps for oxy and especially peroxy radicals [3]. Secondary antioxidants (esters of thiodipropionic acid and phosphites) interfere with the autooxidation process at the initiation and/or chain-branching step [1].

Thermal degradation of poly(vinyl chloride) (PVC) manifests itself by dehydrochlorination (DHC) and autooxidation. DHC leads to the formation of conjugated polyene sequences (of 1 to 25 double bonds) [4]. This complex chain reaction is called zipper elimination. The exact mechanism – radical, ionic or molecular – of DHC is still a matter of study. Polyene sequences with 6—7 and more conjugated double bonds absorb visible light and consequently they are responsible for the discoloration of the polymer [5]. In the presence of oxygen, the typical radical chain oxidation reactions are observed. Thermooxidative degradation of PVC leads to polymer mass decrease that can affect

the mechanical properties [1]. To prevent autooxidation of PVC both primary and secondary antioxidants may be used. The addition of phenolic antioxidants to PVC reduces the loss of hydrogen chloride on thermal treatment [6, 7]. This shows the contribution of phenolic antioxidants to the stabilization of PVC.

In our previous paper [8] the influence of two synthetic antioxidants from the sterically hindered phenol group – Irganox 1010 and Topanol CA – was studied. We have also studied the behaviour of tocopherol acetate [9] and have found that this substance has the same capability to terminate the growth of polyene sequences as Irganox 1010. The benefits of α-tocopherol (natural α-tocopherol is the component of Vitamin E), which is one of nature's most effective antioxidants, are well known in healthcare, cosmetics or food industries. It is an excellent antioxidant in polypropylene and polyethylenes (HDPE, LDPE) [10]. This work deals with the study of the influence of three antioxidants on the basis of α-tocopherol, 2,5,7,8-tetramethyl-2-(4′,8′,12′-trimethyltridecyl)chroman-6-ol: Irganox E 17, E 120, and E 201, on DHC rate.
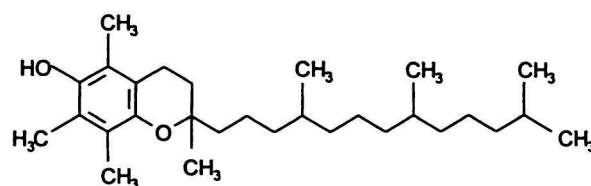
α-tocopherol

Table 1. Composition of the Samples

Sample	m_{PVC}/g	$m_{Wax\ E}$/g	$m_{Antioxidant}$/g	Type	$m_{\alpha\text{-tocopherol}}$/g
1	50	0.250	0.000	—	0.000
2	50	0.250	0.250	E 17	0.113
3	50	0.250	0.500	E 17	0.225
4	50	0.250	0.750	E 17	0.338
5	50	0.250	1.000	E 17	0.450
6	50	0.250	1.250	E 17	0.563
7	50	0.250	0.250	E 120	0.046
8	50	0.250	0.500	E 120	0.092
9	50	0.250	0.750	E 120	0.138
10	50	0.250	1.000	E 120	0.184
11	50	0.250	1.250	E 120	0.230
12	50	0.250	0.250	E 201	0.230
13	50	0.250	0.500	E 201	0.460
14	50	0.250	0.750	E 201	0.690
15	50	0.250	1.000	E 201	0.920
16	50	0.250	1.250	E 201	1.150

Sample	m_{PVC}/g	$m_{Wax\ E}$/g	m_{CaO}/g	m_{ZnSt}/g	m_{Edenol}/g	$m_{ethyl\ acetoacetate}$/g	$m_{E\ 201}$/g
17	50	0.250	1.000	0.125	1.000	0.500	0.500
18	50	0.250	1.000	0.125	1.000	0.500	1.000
19	50	0.250	1.000	0.139	1.000	0.500	1.000
20	50	0.250	1.000	0.125	0.500	0.500	1.000

EXPERIMENTAL

We prepared 15 specimens (Table 1) with PVC and antioxidant (0.5 %, 1 %, 1.5 %, 2 %, and 2.5 %) for the antioxidant action study. The specimens contain powdered suspension PVC Slovinyl S-621 and the following additives: Wax E (lubricant, montan wax, which does not affect stability and degradation rate of the polymer) and Irganox E antioxidants produced by Ciba. Irganox E 17 is a dry white powder containing $(\pm)$-α-tocopherol ($M_r = 430.72$) on a polyolefin carrier, content of tocopherol is (45 ± 3) %. Irganox E 120 is a clear, yellow to amber liquid containing min. 18.4 % of $(\pm)$-α-tocopherol. Irganox E 201 is a yellow to brownish viscous liquid (assay min. 92 %). We have also prepared 4 specimens with Irganox E 201 and Ca/Zn stabilizer system for the comparison of their thermal and colour stability with analogous specimens containing Irganox 1010 [8]. These specimens consist of PVC Slovinyl S-622 and the following additives: Wax E, powdered CaO (purity 99 %), zinc stearate (ZnSt, purity 99 %), ethyl acetoacetate (purity 99 %), Edenol D-81 (epoxy-soya oil, $M_r = 935$, epoxy-oxygen content 6.3—7 %, produced by Henkel Plastics & Coatings Technology), and Irganox 201.

The mixtures were mixed for 2 min at room temperature using standard laboratory mixing device to obtain maximum possible homogeneity and then calendered for 4 min at the temperature 170 °C to get 0.2—0.3 mm thick films.

Degradation of the samples in real atmosphere was monitored at the temperature 180 °C. Since hydrogen chloride is the only degradation product at this tem-perature, the degradation could be followed by the detection of the evolved HCl. It is absorbed in $AgNO_3$ solution and the decrease of Ag^+ concentration is continuously monitored by the electrode system – silver working electrode vs. reference saturated calomel electrode [11]. Colour stability of the samples at 180 °C was studied using the material heat resistance tester TOM model 204.

RESULTS AND DISCUSSION

The basic information obtained from the kinetic curves (Figs. 1 and 2) are the time of thermal stability τ and the gradient of the evolved HCl dn_{HCl}/dt (all quantities of the evolved HCl were converted to 0.2 g of the specimen) shown in Table 2. The time of thermal stability is the length of time elapsing before a significant amount of HCl evolves from the sample. Gradient dn_{HCl}/dt represents the slope of the approximately linear ascending part of the kinetic curve. Values of the gradient enable simple degradation rate comparison and reflect inhibition or catalytic effects of the additives or compounds formed by degradation. As we expected, the studied antioxidants do not considerably affect τ-values. Their effect on the degradation rate was surprising. Contrary to tocopherol acetate [9] or sterically hindered phenols Irganox 1010 and Topanol CA studied in [8] Irganox E antioxidants do not decrease the rate of the polymer degradation. The higher the quantity of the antioxidant, the higher the degradation rate (gradient dn_{HCl}/dt), except samples 11 and 16 compared with 10 and 15, respectively. This trend is also present, if we consider the gradients vs.
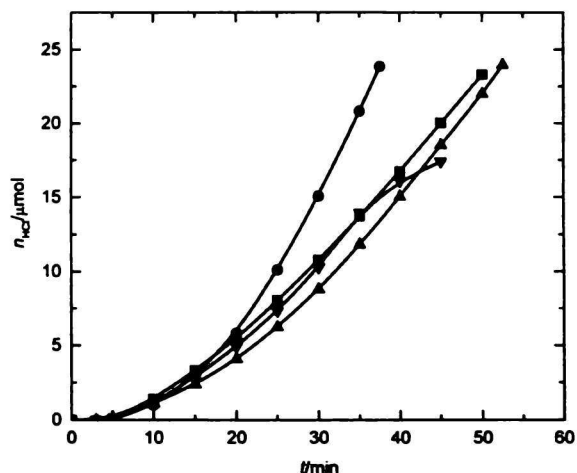
Fig. 1. Kinetic curves of PVC degradation of samples *1* (■), *3* (▲), *5* (●), and *7* (▼).
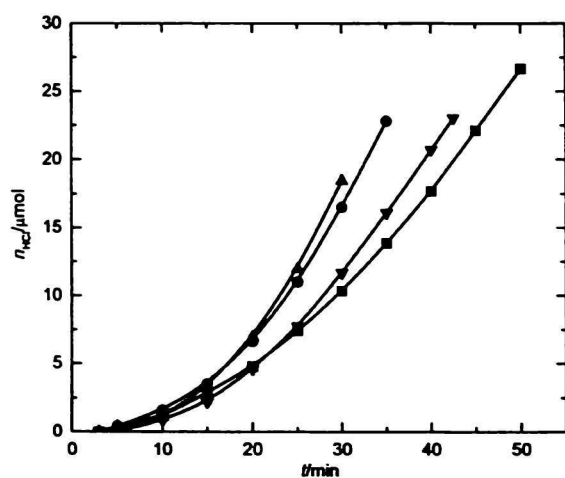

Fig. 2. Kinetic curves of PVC degradation of samples *11* (▼), *12* (■), *14* (●), and *16* (▲).

quantity of tocopherol in the samples (Fig. 3).

The rise of the antioxidant quantity (samples *17* and *18*) does not influence the τ, but the gradient value significantly grows – its value is about 80 % higher. As we expected, comparison of the sample *18* with *19* shows that the rise of ZnSt amount causes the increase of τ. The observed value of the time of thermal stability of the sample *20* reached 55 % of that found for the sample *18*. It confirms a strong influence of Edenol D-81 on this Ca/Zn stabilizer system performance.

Colour stability of the samples *17—20* does not exceed 25—30 min. Colour change of these samples takes place faster than changes of the analogous samples containing Irganox 1010. Sample colour gradually changes from yellow to dark brown.

To judge the ability of α-tocopherol (Irganox E 201) to terminate the growth of polyene sequences during polymer degradation and to compare the ob-
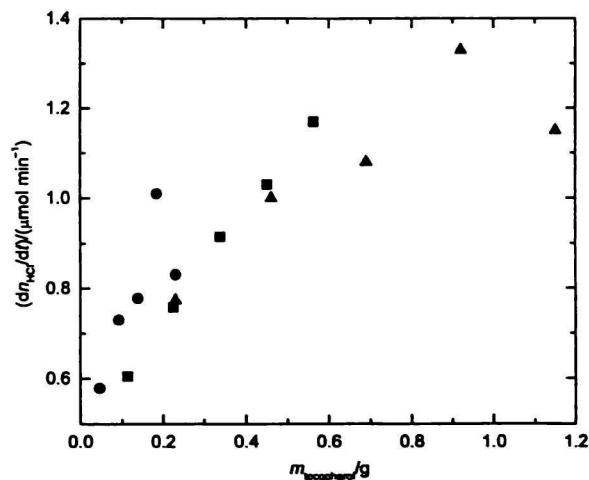

Fig. 3. The degradation gradient *vs.* α-tocopherol content in 50 g of PVC. ■ Irganox E 17, ● Irganox E 120, ▲ Irganox E 201.

Table 2. Thermal Stability τ and Gradient dn_{HCl}/dt

Sample	τ/min	$(dn_{HCl}/dt)/(\mu mol\ min^{-1})$
1	9	0.595
2	11	0.605
3	14	0.758
4	14	0.915
5	15	1.03
6	11	1.17
7	12	0.579
8	13	0.730
9	14	0.778
10	15	1.01
11	15	0.831
12	15	0.774
13	15	1.00
14	14	1.08
15	16	1.33
16	14	1.15
17	76	0.712
18	78	1.29
19	89	1.08
20	43	0.962

tained results with kinetic parameters of Irganox 1010 [8], we used the kinetic model for an additive acting as a weak HCl trapper on the basis of the following reaction scheme

$$PVC \xrightarrow{k_1} dePVC + HCl$$
$$antioxidant + HCl \xrightarrow{k_2} product$$
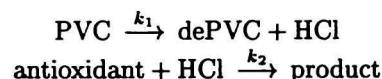
where dePVC means the dehydrochlorinated polymer. In the reaction scheme the autocatalytic effect of eliminated HCl is not considered because in such thin films the autocatalytic effect is negligible [12]. The effective rate constant k_2 includes all types of the interaction between HCl and the antioxidant (except chem-

ical reaction). Using the rate constants of initiation k_i, propagation k_p, and termination k_t of the polyene sequences, the effective rate constant k_1 can be expressed [13]

$$k_1 = k_i \left(1 + \frac{k_p}{k_t}\right)$$

Growth rate of the polyene sequences in the polymer in the presence of antioxidant can be expressed

$$dZ/dt = k_i(1 - x) - k_t Z - k_{Ao} X_{Ao} Z$$

where Z means relative mole fraction of polyenes, x degradation degree (the mole ratio of the evolved HCl and monomer links in the polymer specimen), and k_{Ao} rate constant expressing the contribution of the antioxidant to the polyene sequences termination. DHC rate can be expressed using a steady-state condition by the following formula

$$dx/dt = k_i \left[1 + \frac{k_p}{k_t + k_{Ao} X_{Ao}}\right](1 - x)$$

The relative mole fractions of components are designated as follows: X_1 – calculated conversion of DHC, X_2 – splitting-off HCl in polymer, X_3 – double bonds in polymer, X_{Ao} – antioxidant, and X_{prod} – product. We used the relative mole fractions for the calculations to get around difficulties stemming from the nonisochoric course of the degradation.

As soon as the degradation starts, no HCl can be detected because it accumulates in the polymer (and can be trapped by the components of the stabilizer system, if it is present in the plastic) and the X_2 value rises. HCl evolves from the polymer and can be detected when the mole fraction X_2 has reached a critical value X_c.

Kinetic equations for the above-described reaction scheme are as follows

1. $X_2 < X_c$

$dX_1/dt = 0$

$dX_2/dt = k_1(1 - X_3) - k_2 X_2 X_{Ao}$

2. $X_2 = X_c$

$dX_1/dt = k_1(1 - X_3) - k_2 X_2 X_{Ao}$

$dX_2/dt = 0$

$dX_3/dt = k_1(1 - X_3)$

$dX_4/dt = -(k_2 + k_{Ao})X_2 X_{Ao}$

The system of the differential equations was solved using the least-squares method with Powell's algorithm and the results were confirmed by simplex fit. The computation results are shown in Table 3. These results show that Irganox E 201 causes twenty-ninefold rise of the k_p/k_t ratio in comparison with Irganox 1010. k_{Ao}/k_t ratio shows a negligible contribution of Irganox E 201 to the polyene sequences termination. The trapping ability of Irganox E 201, as it could be anticipated, is negligible, too.

Table 3. Kinetic Parameters for the Samples Containing Irganox E 201 and Irganox 1010

Antioxidant	k_i/min^{-1}	k_p/k_t	k_{Ao}/k_t	k_2/min^{-1}
α-Tocopherol (E 201)	2×10^{-6}	88	0.13	9.3
Irganox 1010	2×10^{-6}	3	50	134

CONCLUSION

The action of three Irganox E antioxidants has been studied. Irganox E 201 has also been studied as a component of the Ca/Zn composite stabilizer system to judge the effect of the antioxidant on the performance of the stabilizer system.

The studied antioxidants negatively affect the PVC degradation rate. Degradation of the majority of the specimens containing Irganox E antioxidants ran significantly faster than the degradation of the pure polymer. The time of thermal stability of the samples stabilized with Ca/Zn system and containing Irganox E 201 reached lower values than in the case of using Irganox 1010. Calculation performed for Irganox E 201 showed an inability of Irganox E antioxidants to terminate the polyene sequences growth.

REFERENCES

1. Gugumus, F., *Oxidation Inhibition in Organic Materials*, Vol. 1, pp. 65—67. CRC Press, Boca Raton, 1990.
2. Pospíšil, J. and Nešpůrek, S., *Polym. Degrad. Stab. 49*, 99 (1995).
3. Wolf, R. and Kaul, B. L., *Ullmann's Encyclopedia of Industrial Chemistry A20*, 463 (1992).
4. Bacaloglu, R. and Fisch, M., *Polym. Degrad. Stab. 47*, 33 (1995).
5. Titow, W. V., *PVC Plastics. Properties, Processing, and Applications*, p. 105. Elsevier Publishers, New York, 1990.
6. Andreas, H., in *Plastics Additives.* (Gächter, R. and Müller, H., Editors.) P. 193. Carl Hanser Verlag, Munich, 1984.
7. Wypych, J., *Polyvinyl Chloride Degradation.* Elsevier, Amsterdam, 1985.
8. Kovařík, P., Klein, E., and Valko, L., *Chem. Pap. 51*, 245 (1997).
9. Klein, E., Kovařík, P., and Valko, L., *Chem. Listy 92*, 922 (1998).
10. Pospíšil, J., *Polym. Degrad. Stab. 39*, 103 (1993).
11. Vymazal, Z., Czakó, E., Meissner, B., and Štepek, J., *Plasty Kauc. 11*, 260 (1974).
12. Oremusová, J., Šimon, P., Valko, L., and Kovařík, P., *Chem. Pap. 43*, 721 (1989).
13. Šimon, P. and Valko, L., *Polym. Degrad. Stab. 29*, 263 (1990).