Stabilization of Gamma-Irradiated Poly(vinyl Chloride) by Epoxy Compounds. II. Production of Hydroperoxides in Gamma-Irradiated PVC–Stabilizer Mixtures

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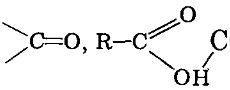
Synopsis

The concentration of hydroperoxides, produced in the process of radiolysis, was studied in γ-irradiated PVC samples with 4% admixture of four epoxy stabilizers: diglycidyl ether of 2,2-bis(4-hydroxy-3-methyl phenyl)propane (I), styrene oxide (1,2-epoxy ethyl benzene) (IV), epoxidized ricinus oil (VI), and epoxidized soybean oil (Drapex 6.8.) (VII). The results indicate that the process of radiation oxidation occurs in two stages. Only the stabilizers with benzene ring demonstrate the antioxidative action. The stabilizers VI and VII do not act as the antioxidants, and, moreover, as a consequence of their plasticizing properties, they facilitate the penetration of the oxygen to polymer. The epoxy groups have no influence upon the oxidation process, in the case of compounds VI and VII.

INTRODUCTION

The role of the oxygen in the process of the radiation destruction of polymers consists of the production of peroxidized polymer,[1] of the production of hydroperoxides and peroxides, and of the formation of crosslinks. The PVC irradiated in an oxygen atmosphere undergoes, mainly the process of degradation.[2] This degradation by oxygen results in slight changes of the color on account of the reactions of the oxygen with conjugated double bonds.[3]

The formed peroxidic radicals pass into carbonyl or hydroxyl groups,[4] such as ROOH, ROH,  $>C{=}O$, $R{-}C(=O)OH$ CO, and, to a lesser degree, into CO_2.[5]

The appearance of two different kinds of peroxiradicals and one of hydroperoxide was ascertained.[6] 60% of peroxiradicals decay at 20°C in atmospheric oxygen at a half-time $t_{1/2} \cong 3$ h, and 40% of them are relatively stable at room temperature and decay at 56°C in vacuum with $t_{1/2} \cong 40$ h. The hydroperoxide ROOH decays at 50°C in vacuum with $t_{1/2} = 650$ h.

The radiation–oxidation process is essential for the radiolysis of PVC; thus it seemed necessary to investigate the influence of epoxy stabilizers upon this process. In our complicated system (of PVC with stabilizers) the use of such methods as IR and EPR was difficult; therefore, we have been limited to the determination of the amount of produced hydroperoxides only.

In the present paper (Part II) the stabilizers I and IV were chosen from the

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compounds with aromatic ring and stabilizers VI and VII from the group of linear stabilizers. The enumeration of stabilizers is the same as in Paper I of the cycle.

EXPERIMENTAL

The samples were irradiated in the RHM-γ-20 irradiation unit in an oxygen flux of 50 cm^3/min. The admixture of a stabilizer was 4% in all cases. In terms of moles of oxirane groups per mole of PVC monomer units (mu) the admixture is as follows: Stabilizer I, 1.03×10^{-2}; IV, 1.55×10^{-2}; VI, 0.34×10^{-2}; VII, 0.96×10^{-2}.

The determination of the stable hydroperoxides was based on the reduction by Fe^{++} ions in acid medium and on the spectrophotometric measurements of the concentration of Fe^{+++} ions in the form of thiocyanate complex.[6] The absorption spectra were made in the region of 330–600 nm. The extinction was obtained from the difference between the absorption maximum at 520 nm and minimum at 390 nm. The assumed[7] absorption coefficient was $\epsilon = (7.46 \pm 0.21) \times 10^5$ $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

The results are presented in the form of the amount of hydroperoxides (mol ROOH/g PVC) and in the form of the radiation yield of the formation of hydroperoxides, G_{ROOH}. The rate of the formation of hydroperoxides is taken as $d[ROOH]/d[t \cdot I]$, where t = time and I = dose rate (mol $\times 10^5$/g PVC·Mrad).

RESULTS AND DISCUSSION

The results of the measurements for the pure PVC are drawn in Figure 1. The results of investigations of the mixtures of PVC with stabilizers I, IV, VI, and VII are presented in Figures 2–5, respectively.

As can be seen from the dependence of the amount and the rate of formation of the hydroperoxides vs. irradiation dose, the process of radiation oxidation occurs in two stages. Each stage corresponds to a linear equation [ROOH] =

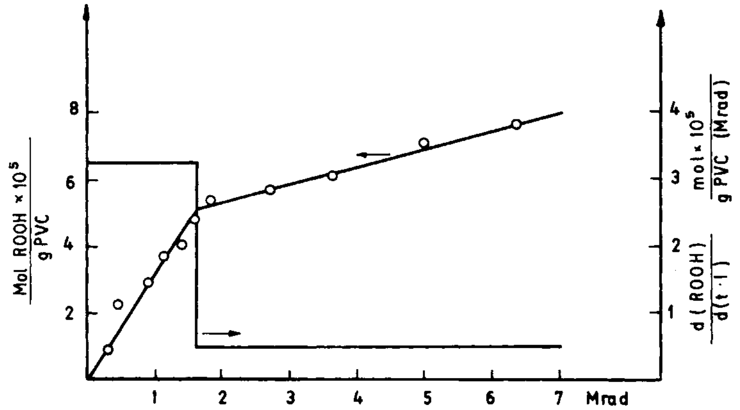

Fig. 1. The amount of formed hydroperoxides (mol ROOH $\times 10^5$/g PVC) and the rate of the formation (mol $\times 10^5$/g PVC·Mrad) vs. γ-irradiation dose, for the pure PVC. Dose rate 4.73×10^{17} $eV \cdot cm^{-3} \cdot min^{-1}$.

TABLE I
Kinetic Data of Formation of Hydroxyperoxides in γ-Irradiated PVC–Stabilizer Mixtures

System	Duration of first stage (Mrad), Constant *a* (mol ROOH/ g PVC)	Constant in second stage (mol ROOH/ g PVC)	Rate of process in first stage (mol ROOH/ g PVC· Mrad)	Rate of process in second stage (mol ROOH/ g PVC· Mrad)	Radiation yield G_{ROOH} in first stage	Radiation yield G_{ROOH} in second stage
PVC	0–1.62 0	3.25×10^{-5}	3.14×10^{-5}	0.6×10^{-5}	30.27	4.82
PVC + I	0–0.85 -0.95×10^{-5}	2.5×10^{-5}	4.12×10^{-5}	0.6×10^{-5}	39.76	5.79
PVC + IV	0–3		6.12×10^{-5}	0	59.01	
PVC + VI	0–1.6 0	3.5×10^{-5}	3.15×10^{-5}	0.97×10^{-5}	30.77	9.35
PVC + VII	0–1.6 0	3.35×10^{-5}	3.05×10^{-5}	0.98×10^{-5}	29.45	9.40

$kD + a$, where D designates the dose of the irradiation (time × dose rate). The data for the constant value of a in both stages, the rate of the formation of the hydroperoxides, and their radiation yield G_{ROOH} are collected in Table I.

The data concerning the mixture of PVC with stabilizer I as compared with those of the pure PVC indicate that stabilizer I is a moderate antioxidant. In this case a little induction period of about 0.2 Mrad (2 kGy) appears, and the amount of the formed hydroxyperoxides diminishes by 28% for the dose of 3 Mrad (30 kGy) and by 19% for the dose of 6 Mrad (60 kGy). It happens as a consequence of the considerable shortening of the rapid first stage, although the rate of oxidation and the yield G_{ROOH} is, relative to pure PVC, greater for both stages.

In the case of styrene oxide (stabilizer IV) the mechanism of inhibition of the oxidation reaction of polymer is markedly different. In spite of the appearance of an induction period, of about 0.25 Mrad (2.5 kGy), the amount of ROOH in

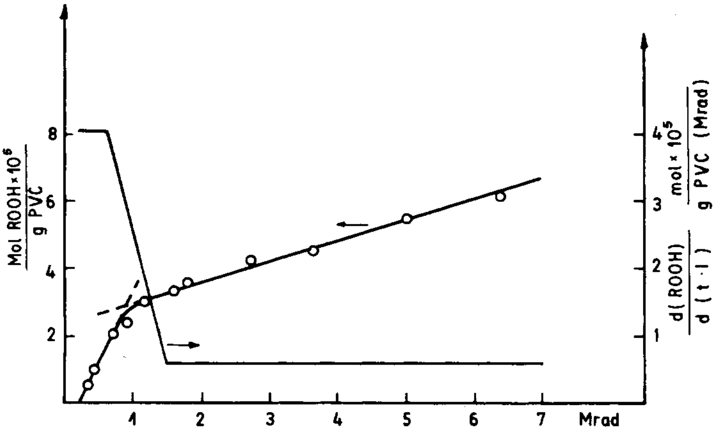

Fig. 2. The amount of formed hydroperoxides (mol ROOH × 10^5/g PVC) and the rate of the formation (mol × 10^5/g PVC·Mrad) vs. γ-irradiation dose, for PVC with 4% of stabilizer I admixture. Dose rate 4.73×10^{17} eV·cm^{-3}·min^{-1}.

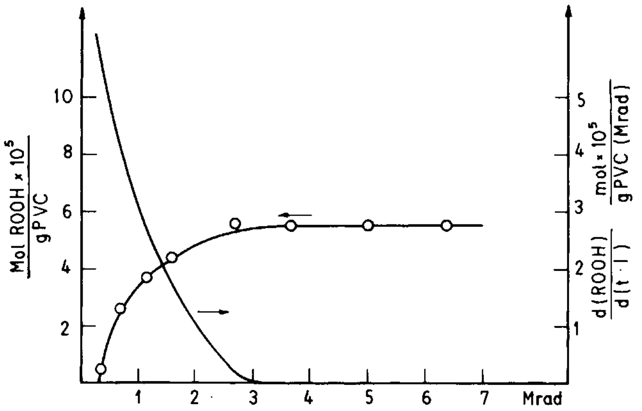

Fig. 3. The amount of formed hydroperoxides (mol ROOH × 10^5/g PVC) and the rate of the formation (mol × 10^5/g PVC·Mrad) vs. γ-irradiation dose, for PVC with 4% of stabilizer IV admixture. Dose rate 4.73 × 10^{17} eV·cm^{-3}·min^{-1}.

the first stage is greater than in pure PVC. The value of G_{ROOH} is also very high. However, already after absorption of the dose of 1.5 Mrad (15 kGy) the stabilizer IV proves to be an effective antioxidant and the effectivity of the stabilization process increases with the dose.

The both linear stabilizers VI and VII do not act as the antioxidants. In the first stage, its duration, the rate of the oxidation process and the amount of hydroperoxides are the same as for the pure PVC. In the second stage an acceleration of the process, in relation to pure PVC, occurs and the radiation yields of ROOH production are almost doubled.

As it seems, when we have to do with the plasticizing action of our stabilizers VI and VII, this result helps to explain the two-stage process of oxidation.

In the first stage the attack of oxygen on these fragments of PVC macromol-

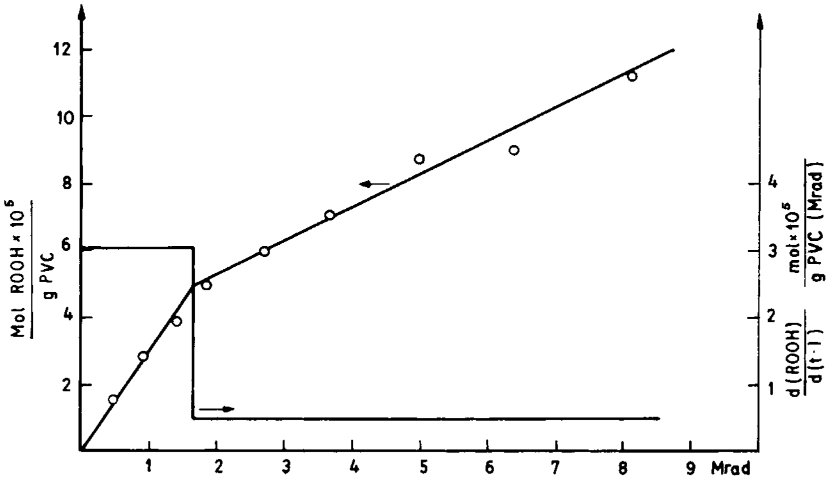

Fig. 4. The amount of formed hydroperoxides (mol ROOH × 10^5/g PVC) and the rate of the formation (mol × 10^5/g PVC·Mrad) vs. γ-irradiation dose, for PVC with 4% of stabilizer VI admixture. Dose rate 4.73 × 10^{17} eV·cm^{-3}·min^{-1}.

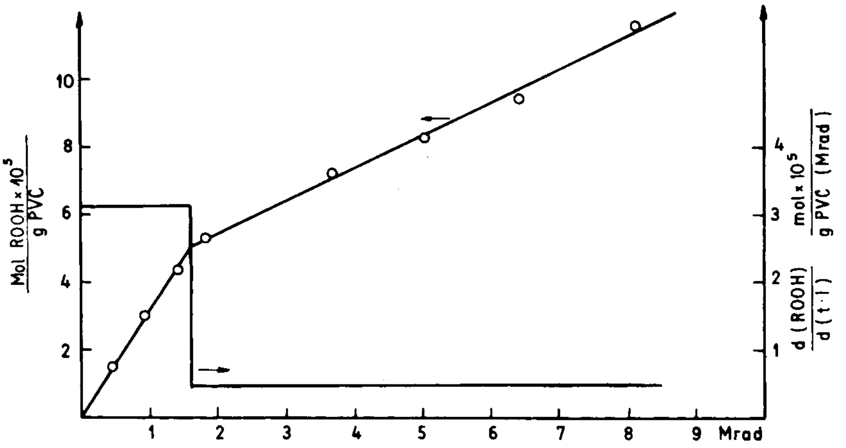

Fig. 5. The amount of formed hydroperoxides (mol ROOH × 10^5/g PVC) and the rate of the formation (mol × 10^5/g PVC·Mrad) vs. γ-irradiation dose, for PVC with 4% of stabilizer VII admixture. Dose rate 4.73 × 10^{17} eV·cm^{-3}·min^{-1}.

ecule, in which initiation of radiation decomposition occurs, and the propagation of the chain oxidation reaction are essential. As the result we obtain the great yields G_{ROOH}, which exceed the radiation yields of the HCl.

In the second stage the reaction of chain oxidation persists. On the one hand, this reaction can be inhibited by the processes of termination of the chain and, on the other hand, is propagated by the diffusion of oxygen to a polymer. The action of stabilizers VI and VII in the second stage consists probably of the facilitation of the penetration of the oxygen to a polymer, as a consequence of their plasticizing properties.

The first stage, where the quantitative process of radiolysis is identical for the pure PVC and for the mixtures with the stabilizers VI and VII, is, most probably, independent on the diffusion of the oxygen to a polymer. In this way stabilizers VI and VII do not affect directly the process of oxidation, independently of the concentration of the epoxy groups.

Landler and Lebel[8] stated that the catalytic effect of HCl onto the thermal decomposition of products of the ozonization of PVC occurred. Then in our case the amount of epoxy groups should have an influence on the peroxidation rate. As it is seen from our results, this process is not taking place for the stabilizer VI and VII. Such an effect is possible when we observe the behavior of styrene oxide (IV) in comparison with glycide ether (I). The stabilizer IV is less effective than the I, having a much greater extent of epoxy oxygen in IV; moreover, in the first stage the free epoxy groups are still present in the system. Independently from the question as to whether the catalytic effect of HCl has a significant meaning when the HCl is removed continuously from material, we conclude that in our case the antioxidative action demonstrate only the presence of the benzene rings, which was said above.

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