JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 1955–1958 (1975)

Radiation Yield of Hydrogen Chloride in the Poly(vinyl Chloride) Foils Irradiated by Accelerated Electrons

W. SZYMAŃSKI and G. ŚMIETAŃSKA, *Institute of Chemistry, Nicholas Copernicus University, 87-100, Toruń, Poland*

Synopsis

The G_{HCl} values of PVC foils, containing 18% of dioctylphthalate, irradiated with accelerated electrons were studied after addition of various amounts of the stabilizers: (I) ethylene glycol bis-β-aminocrotonate, (II) calcium/zinc laurate + epoxy compounds, (III) calcium/zinc stearate, (IV) dioctyltin bis(octylthioglycolate). The effect of stabilization turned out to be very good, especially when stabilizer I was used. In the case of soft PVC foils in contact with water, elution of hydrogen chloride occurs. This creates difficulties in preparing PVC foils sterilized radiatively for medical purposes, especially if the foils are expected to be in contact with water.

INTRODUCTION

The problem of finding good stabilizers for poly(vinyl chloride) (PVC) exposed to ionizing radiation is still far from being solved. This is especially true in the case of PVC sterilized radiatively for medical purposes.

The stabilization of PVC degraded thermally or by light has been discussed in numerous papers. From the results of these studies as well as from the investigations of the mechanism of the radiolysis of PVC, one can infer that most of the inhibitors of the thermal and optical destruction of PVC can serve as stabilizers in the case of radiational degradation. This point of view has been presented by several authors[1–5] who examined well-known PVC stabilizers under the conditions of γ-irradiation. Attempts also have been made to use classical electron acceptors[6] as stabilizers. Apart from these possibilities endeavors are being made[7–13] to create new, radiationally stable, crosslinked poly(vinyl chloride) resin compositions.

In our previous investigations we studied the radiation yield of HCl in pure poly(vinyl chlorides)[14] and the stabilizing effect of some inhibitors on PVC foils exposed to γ^{60}Co rays.[15] In the latter work we achieved in the PVC–dioctylphthalate (DOP)–calcium/zinc laurate–epoxy system an appreciable decrease of the G_{HCl} value: it was over 3 without the stabilizer, 1.61 if 0.5% of the stabilizer was added, and 0.55 with 1% of the stabilizer. In the PVC–DOP–ethylene glycol bis-β-aminocrotonate system the result was even better, the G_{HCl} values being 0.43 and 0.26 for 0.5 and 1% of the stabilizer, respectively.

In the present paper we present the results of the investigations of some systems irradiated by electron beams. Although it is to be expected that as com-

pared with the γ-radiation the accelerated electrons will not deteriorate the PVC foil, the importance of the latter radiation source for sterilizing purposes makes a study of its effects desirable.

EXPERIMENTAL

The Preparation of Samples

The foil samples were prepared of a Polish-made commercial S-68P PVC and other suitable ingredients with the use of a fluidization mixer and a rolling mill. The samples were placed in closed cells on a transporter and were irradiated by sweeping 10-MeV electron beams from a linear electron accelerator LAE 13-9. The intensity of the beam was 9 μA. The dose rate determined with a PVC foil dosimeter amounted to 0.5 Mrad/sec. The average dose was 3 Mrad.

The Measurements

The irradiated cells were blown through with nitrogen and the emanating HCl was quantitatively absorbed in water. In some experiments the HCl was extracted from the samples directly in water. The amount of HCl was determined potentiometrically with a silver–chlorosilver electrode system using an agar-agar–KNO_3 salt bridge.

RESULTS AND DISCUSSION

In the PVC–DOP–stabilizer system we used, with 18% of DOP, the following stabilizers: (I) ethylene glycol bis-β-aminocrotonate, (II) calcium/zinc laurate + epoxy compounds, (III) calcium/zinc stearate, and (IV) dioctyltin bis(octylthioglycolate).

The dependence of the G_{HCl} values on the amount of the stabilizer (in %) is presented in Figure 1. The uncertainties of the position of the experimental points were computed by the method described in Ref. 16.

The effect of the stabilization is especially good in the case of stabilizer I.

The situation deteriorates when the concentration of dioctylphthalate is increased up to 30%, that is, for soft foils. For such systems we have performed the measurements adding to the samples epoxidized soybean oil, epoxide resin, and stabilizers I, II, and III in various proportions with the total of the stabilizers not exceeding 2%. The G_{HCl} never dropped below 0.5, changing from 0.5 to 0.7 with an appreciable dispersion of results.

In addition, the G_{HCl} values were dependent on whether the HCl was obtained by a direct extraction in water or as a result of a blowing of the samples with nitrogen. In the former cases the G_{HCl} values were higher by 75—125%. These differences were also observed when different stabilizers, such as barium/cadmium laurate (stabilizer V) were used, as well as after addition of hydroxybenzophenone or thiocarbamate derivatives.

However, no differences in the G_{HCl} values caused by different methods of obtaining HCl were observed in PVC foils containing 18% DOP. Therefore we conclude that this effect is due to the "loose" structure of soft foils.

In order to verify our conclusion the radiation yield of HCl in PVC–DOP mixtures with stabilizers was studied. The samples were mixed in a fluidization mixer but foils were not prepared. In this way we obtained a system that we

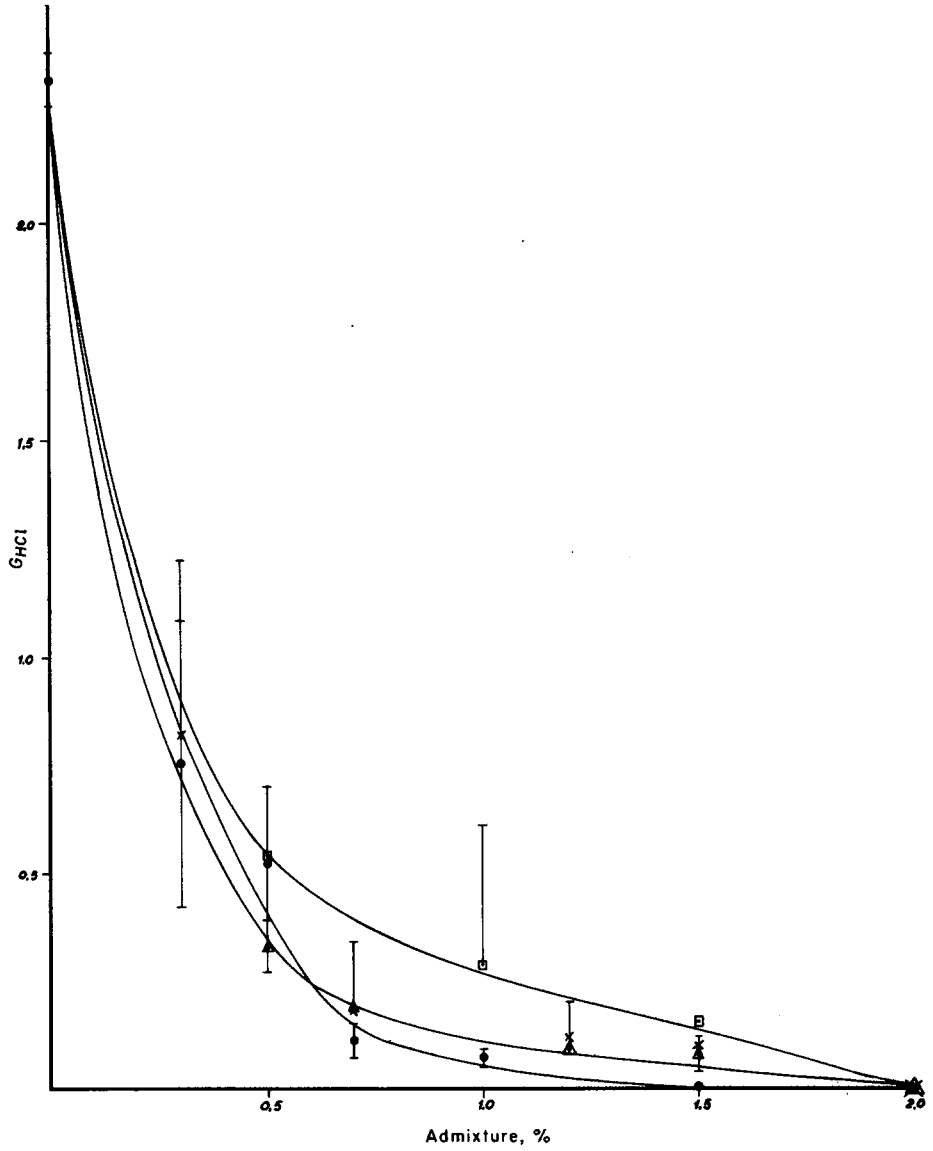

Fig. 1. G_{HCl} versus the stabilizer admixture (%): (⊙⊙⊙) stabilizer I, (△△△) stabilizer II, (×××) stabilizer III, (⊡⊡⊡) stabilizer IV.

thought to be a good approximation of a PVC foil with an ideally "loose" structure.

The mixtures were irradiated in the usual manner and the HCl was obtained by two different methods: (*a*) the cells were blown through with nitrogen for 24 hr and the hydrogen chloride was absorbed in water, (*b*) the cells were broken in water and remained there for 24 hr at which point the solution was filtered.

In both cases the amount of HCl was determined by the same, usual method. The results are presented in Table I.

It is seen that aside from the effect of the stabilizer there is a very appreciable extraction of HCl, perhaps together with the stabilizer, in systems with loose

TABLE I
The Yield of Hydrogen Chloride (G_{HCl}) for PVC Mixtures

Amount[a] of admixtures, %			G_{HCl}	
DOP	Epoxidized soybean oil	Stabilizers	Method A	Method B
0	0	0	16.60	17.15
18	0	0	8.3	9.0
18	0	0.3, stabilizer I	9.3	—
18	0	0.5, stabilizer I	—	11.8
18	0	0.7, stabilizer I	3.1	10.7
18	0	1.0, stabilizer I	—	9.8
18	0	1.5, stabilizer I	0	9.3
18	0	2.0, stabilizer I	0	8.2
18	0	2.0, stabilizers I + III	—	10.1 ± 1.3
30	0	0	11.8	—
30	3	0	1.4	—
30	3	2.0, stabilizer III	0.07 ± 0.02	—
30	3	0.5–2.0, stabilizer V	0.08 ± 0.06	—
0	0	0.3–2.0, stabilizer I	—	15.3 ± 1.0

[a] The complement to 100% gives the amount of PVC. For the description of methods a and b see text.

structure. Therefore it seems very difficult to obtain good soft PVC foils, especially those which must be in contact with liquids, sterilized radiatively for medical purposes.

References

1. M. N. Shteding and V. L. Karpov, *Vysokomol. Soedin.*, **4**, 1806 (1962).
2. V. L. Kabaivanov and S. I. Khadzhidocheva, *Plaste Kautsch.*, **17**, 478 (1970).
3. V. L. Kabaivanov and S. I. Khadzhidocheva, *Muanyag Gumi*, **7**(10), 337 (1970).
4. S. I. Khadzhidocheva and V. L. Kabaivanov, *Mitt. Chem. Forschungsinst. Wirt. Oesterr. Oesterr. Kunststoffinst.*, **27**(1), 29 (1973).
5. S. V. Krylova, A. E. Kulikova, Yu. V. Ovchinnikov, and S. M. Berlyant, *Plast. Massy*, **1**, 16–18 (1973).
6. B. V. Kotov and L. Zaloudkova, *Dokl. Akad. Nauk SSSR*, **159**(3), 640 (1964).
7. F. Suzuki, Jap. Patent, 72 40,702 (Oct. 14, 1972).
8. K. Kojima, Jap. Patent, 72 20,239 (Sept. 28, 1972).
9. V. I. Dakin, Z. S. Egorova, and V. L. Karpov, *Plast. Massy*, **6**, 37–38 (1973).
10. K. Nishio, T. Sasaki, K. Araki, and M. Fukushima, Jap. Patent, 73 22,136 (March 20, 1973).
11. Y. Kanaya, T. Ogawa, K. Araki, and T. Sasaki, Jap. Patent, 73 31,244 (Apr. 24, 1973).
12. F. F. Sukhov and N. A. Slovokhotova, *J. Polym. Sci. C*, **42**, 147 (1973).
13. W. A. Salmon and L. D. Loan, *Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem.*, **13**(1), 452 (1972).
14. W. Szymański, I. Lerke, and G. Śmietańska, *Nukleonika*, **19**, 323 (1974).
15. W. Szymański and G. Śmietańska, *Nukleonika*, submitted for publication.
16. R. B. Dean and W. J. Dixon, *Anal. Chem.*, **23**, 636 (1951).

Received August 5, 1974