Synergistic Effect in Gamma-Irradiated Poly(vinyl Chloride) Hard Foils Stabilized by Plasticizer–Stabilizer Systems

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Synopsis

Changes in transparency and color as well as G_{HCl} values of hard PVC foils exposed to gamma radiation were investigated while using different amounts of the stabilizers ethylene glycol bis-β-aminocrotonate (I), calcium/zinc laurate + epoxy compounds (II), and magnesium/zinc stearate + sorbitol + epoxy compounds (III), and plasticizers dioctyl phthalate (DOP) (IV), dioctyl sebacate (V), propylene glycol polyadipate + octyl alcohol composition (VI), and diisotridecyl phthalate (VII). A strong synergistic effect was observed in systems containing both plasticizer and stabilizer. Best results were obtained for the I + II + IV, I + II + V, and I + III + V systems.

Introduction

It has been known for some time that PVC plasticizers have also a stabilizing effect. When epoxy groups were present in the plasticizers, this effect was usually explained by the familiar mechanism of stabilization by epoxy compounds, i.e., binding of HCl by the oxirane groups.[1] It was also established for these epoxy plasticizers that a synergistic effect occurs.[2] Some authors investigated the influence of the structure of the plasticizers on the thermal stability of the PVC composition, and aromatic compounds were most commonly used.[3] Occasionally, two similar compounds have different effects: either plasticizing or stabilizing, as is the case of the isocyanuric acid derivatives.[4] In most cases the plasticizers are used in polymeric PVC compositions, and their double action as stabilizers and plasticizers is not discussed by the authors, although it is obviously assumed. Many examples of that kind can be found in the current patent literature.

There are only few papers concerning PVC stabilization with respect to ionizing radiation that have any connection with the synergistic effect. Russian authors[5] have ascertained a positive effect of various stabilizers on the stability of dioctyl phthalate and dioctyl adipate during gamma irradiation. In another work,[6] after addition of a plasticizer, an increase in the radiation resistance of the PVC was noticed, which was attributed to the influence of the plasticizer on the radiation resistance of the organotin stabilizers used in the quoted work. However, it seems evident that in both cases we have a synergistic effect, the mechanism of which remains unknown. The effect of gamma irradiation on the stability of the PVC plasticizers was also studied, and the protective action of the phthalates was explained in general terms as a result of energy dissipation by the π-electron system.[7]

Unfortunately, it is not always possible to take advantage of the stabilizing effect of the plasticizers discussed above, because every plasticizer retains its

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plasticizing properties even if it is used as a stabilizer. Therefore, for useful solutions of the problem it is necessary to look for the optimal synergistic effect in systems containing classical stabilizers.

The experimental investigation of PVC foils resistant to inonizing radiation is quite important for several practical reasons. One of them is the search for soft foils appropriate for medical applications in the sense that contact with water would not result in extraction of hydrogen chloride. As we have shown in a preceding paper,[8] this is a very difficult problem because of the loose structure of the foil. Another practical problem is the production of hard PVC foils that would not change color upon irradiation and would be suitable for packing items to be sterilized by radiation.

We were able to determine the composition of foils satisfying the above requirements; and in the present paper we report the results of investigations that led to a patent claim[9] concerning the production of PVC wrapping foil resistant to ionizing radiation.

Experimental

The Preparation of Samples

All foil samples were prepared in the same way as described in our earlier papers.[8,10] In the present work we used the stabilizers ethylene glycol bis-β-aminocrotonate (I), calcium/zinc laurate + epoxy compounds (II), and magnesium/zinc stearate + sorbitol + epoxy compounds (III) and the plasticizers dioctyl phthalate (DOP) (IV), dioctyl sebacate (V), propylene glycol polyadipate + octyl alcohol (VI), and diisotridecyl phthalate (VII).

Foil samples were irradiated in an irradiation device PXM-γ-20 with ^{60}Co radiation. The average dose was 3 Mrad.

Measurements

The radiation yield of HCl, G_{HCl}, was measured by a standard method.[8,10] The transparency as well as the color of the foil were determined with the aid of a Colormaster Model V apparatus. The transparency T was determined according to the TGL 7196 norm as

$$T = 100 \left(\frac{w - s}{u_w - u_s}\right)^{1/2} \%$$

where w is the reflectance coefficient of a white plate covered with the foil, s is the reflectance coefficient of a black plate covered with foil, u_w is the reflectance coefficient of a white uncovered plate, and u_s is the reflectance coefficient of a black uncovered plate.

In the following we use the quantity $Tr = T^*/T_0$, with T_0 and T^* being the transparencies before and after irradiation, respectively, for the foil under investigation. Clearly, for a foil ideally resistant to irradiation one would get $Tr = 1$.

The color of the foil was determined in the Adams coordinate system.[11] For the evaluation of the total color difference E, we used in all cases the nonirradiated foil as the reference sample.

TABLE I
Transparency (*Tr*) and Total Color Difference (*E*) for PVC Soft Foils

Foil no.	Amount of admixture, % DOP	Stabilizers I + II	*Tr*	*E*	G_{HCl}
1	15	1.7	0.97	3.3	0.01
2	23	1.5	0.94	5.4	0.03 ± 0.01
3[a]	22	1.5	0.95	6.0	HCl undetectable
4[a]	22	2.0	0.97	2.7	HCl undetectable
5	0	2.0	—	65.9	0.02 ± 0.01

[a] Plus 2.2% epoxidized soybean oil.

RESULTS AND DISCUSSION

The standard commercial PVC wrapping foil is completely unsuitable for sterilization by radiation because of a strong discoloration upon irradiation. After irradiation of such a foil with 3 Mrad accelerated electrons, we found *Tr* = 0.10 and *E* = 69.3. The radiation yield G_{HCl} was 0.20 ± 0.09.

We have prepared samples of hard foils that contained neither DOP nor any other plasticizer using previously investigated compositions of stabilizers and varying the proportions of the remaining admixtures. It was found that in all cases a strong discoloration occurred after irradiation, regardless of whether gamma rays or accelerated electrons were used. The radiation yield G_{HCl} determined for these foils was relatively low, varying from 0.02 to 0.20.

However, an admixture of DOP plasticizer changes the situation drastically. In Table I we present data obtained with foils containing a DOP admixture. An inspection of these data leads to the following conclusions: (1) an admixture of DOP in quantities typical for soft foils stabilizes the color remarkably well; (2) above a certain DOP content (e.g., 15%), an additional increase in DOP content affects neither *Tr* nor *E*.

Therefore, we have investigated the influence of the DOP admixture, in quantities permissible for hard foils, without other addition to the PVC except for an 1.7–1.9% admixture of stabilizers I and II. In Figure 1 we give the results obtained for five samples (6–10). It is seen that the increase in T_r and decrease in *E* caused by the increase in DOP content from 0% to 10% are sufficiently strong to assure favorable results in the case of hard PVC foils, provided the composition

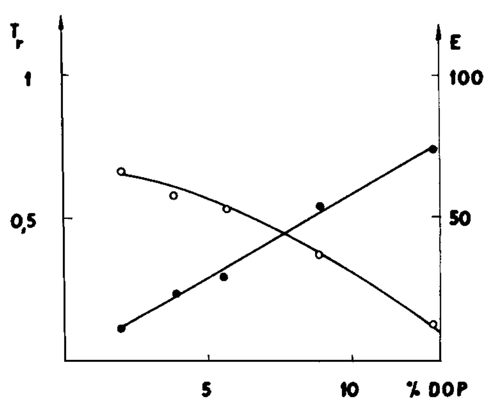

Fig. 1. Transparency *Tr* and total color difference *E* vs. plasticizer (DOP) admixture (%): (●●●) *Tr*; (○○○) *E*.

is chosen properly. The quantity of HCl liberated in samples 6–10 was below detection. The G_{HCl} was also vanishingly small in most subsequent experiments described in this paper (see Table II).

A series of experiments was performed with different hard foils containing different amounts of antioxidant (2,6-di-*tert*-butyl-*p*-cresol) and plasticizers. The results are given in Table II. One can note several regularities in this table: the optimal content of the plasticizer amounts to about 10 parts per 100 parts PVC. The DOP and dioctyl sebacate appear to be the best plasticizers (foils 30–40). The action of the plasticizer is synergistic, stabilizers I + II being optimal though I + III give favorable results, too. A single stabilizer does not show any synergistic effect with DOP (foils 41–45), and the lack of stabilization cannot be caused by the absence of antioxidant (the latter is also missing in foils 1–10). When the synergistic effect appears with the DOP and stabilizers I + II, the amount of the antioxidant has no effect on the optical properties of the irradiated foils (18–22).

Similarly, as in a majority of cases in which the synergistic effect takes place, we do not understand the real mechanism of that effect. In view of the presented data it is clear that it is strong enough to minimize the stabilizing action of the antioxidant. An attempt to answer the question concerning the origin of the synergic effect of the plasticizers as well as attempts to explain its mechanism

TABLE II
Transparency (*Tr*) and Total Color Difference (*E*) for PVC Hard Foils

Foil	Amount of admixture, %					
no.	Plasticizer	Stabilizer	Antioxidant	*Tr*	*E*	G_{HCl}
11–13	—	1.5, stab. I + III	2.4	0.50	38.7	
14–17	4.6, DOP	1.5, stab. I + III	2.3	0.73	20.1	0
18	4.6, DOP	1.8, stab. I + II	1.4	0.63	33.3	0
19	4.6, DOP	1.8, stab. I + II	1.8	0.81	15.5	0
20	4.6, DOP	1.8, stab. I + II	2.3	0.71	22.3	0
21, 22	4.5, DOP	1.8, stab. I + II	2.7	0.78	18.9	0
23	4.6, DOP	1.3, stab. I + III	2.3	0.69	21.5	0
24	4.6, DOP	1.8, stab. I + III	2.3	0.71	21.3	0
25	4.6, DOP	2.2, stab. I + III	2.3	0.79	16.9	0
26	6.3, DOP	1.4, stab. I + III	1.8	0.77	19.3	0
27	6.3, DOP	1.8, stab. I + II	1.8	0.79	17.2	0
28	7.2, DOP	1.4, stab. I + III	1.8	0.70	24.3	0
29	8.8, DOP	1.4, stab. I + III	1.8	0.81	16.1	0
30	8.8, DOP	1.8, stab. I + II	1.8	0.88	10.8	0
31, 32[a]	8.7, DOP	1.7, stab. I + II	1.7	0.92	13.6	0
33	4.6, plast. V	1.5, stab. I + III	2.3	0.67	24.3	0
34	8.8, plast. V	1.4, stab. I + III	2.2	0.88	8.9	0
35	4.6, plast. V	1.8, stab. I + II	1.8	0.32	24.4	0
36	8.8, plast. V	1.8, stab. I + II	1.8	0.92	6.6	0
37	4.6, plast. VI	1.8, stab. I + II	1.8	0.47	38.8	0
38	8.8, plast. VI	1.8, stab. I + II	1.8	0.78	16.8	0
39	4.6, plast. VII	1.8, stab. I + II	1.8	0.49	26.3	0
40	8.8, plast. VII	1.8, stab. I + II	1.8	0.42	12.7	0
41	9.1, DOP	0.3, stab. III	0	0.04	68.2	2.61 ± 0.72
42	9.0, DOP	0.6, stab. III	0	0.09	69.4	1.70 ± 0.69
43	9.0, DOP	1.1, stab. III	0	0.16	65.2	0.13 ± 0.09
44	9.0, DOP	1.4, stab. III	0	0.13	63.6	0.12 ± 0.14
45	8.9, DOP	1.8, stab. III	0	0.14	57.2	0.14 ± 0.08

[a] Plus 1.3% epoxidized soybean oil.

TABLE III
Transparency (*Tr*) and Total Color Difference (*E*) for Final PVC Hard Foils

Foil no.	Plasticizer, %	Stabilizer, %	*Tr*	*E*
46	8.3, DOP	1.7, stab. I + II	0.92	6.2
47	8.5, plast. V	1.4, stab. I + III	0.89	9.1
48[a]	8.5, plast. V	1.7, stab. I + II	0.96	3.3
49[a]	8.5, plast. V	1.4, stab. I + III	0.97	2.3

[a] Calendered foils.

could be made by studying model compounds of the PVC, as was done in the case of classical stabilizers. In the present work, undertaken for practical purposes, we could not extend the investigation in that direction, but we intend to return to this interesting point in the future.

The final tests were performed with foils 31 and 34. The samples were prepared according to a whole recipe and processed for 5 to 16 min at temperatures ranging from 170° to 190°C. On the basis of the composition of samples leading to best results, calendered foils were prepared. For the calendered foils (48 and 49) we determined the tensile strength, the relative elongation, and the softening point as defined by Vicat, with the following results: 541 ± 21 kg/cm^2, 16.7 ± 3%, and 61.7 ± 3.5°C, respectively. The permeability coefficient[12] of air was also measured with the following results: 0.35×10^{-11} N cm^3/cm^2 sec cm Hg before irradiation, 0.30×10^{-11} after irradiation with an electron beam, and 0.28×10^{-11} after gamma irradiation. The permeability of steam was 0.036×10^{-9}, 0.042×10^{-9}, and 0.069×10^{-9} g cm/cm^2 sec, respectively. The final results, presented in Table III, are in our opinion completely satisfactory.

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