

Radiation-Induced Oxidative Degradation of Poly(vinyl Chloride)

EL-SAYED A. HEGAZY,* TADAO SEGUCHI,† and SUEO MACHI, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma-ken, 370-12 Japan*

Synopsis

Gas evolution and oxygen consumption in the γ -irradiation of PVC were studied. The gas evolution and the oxidative degradation are retarded by the presence of plasticizers and stabilizers. The $G(\text{HCl})$ and $G(\text{H}_2)$ are 8 and 0.24 for the irradiation of pure PVC under vacuum and 0.02 and 0.14 for that of plasticized PVC, respectively. Gas evolution increases in the presence of oxygen, specially for the pure PVC. The $G(-\text{O}_2)$ values for the pure and plasticized PVC are 30 and 12, respectively. The dependence of gas evolution and oxygen consumption on the oxygen pressure is more pronounced for the plasticized PVC than pure PVC because the oxygen diffusion is controlled.

INTRODUCTION

This report extends our work on the radiation effects on poly(vinyl chloride) (PVC) used for disposable medical supplies. The first report¹ deals with the study of radiation-induced oxidative degradation of isotactic polypropylene.

In the study of radiation chemistry of PVC, it is known that the oxidation processes take place in the presence of atmospheric oxygen during irradiation. Minsker et al.² reported that the oxidation during irradiation produces hydroperoxide groups. The formation of carbonyl groups in PVC³ increases up to a dose of 5 Mrad and then decreases at higher doses because the rate of oxidation is larger than that of HCl elimination at low doses. The G -value of HCl formation in the irradiation of PVC stabilized by epoxy compounds was studied by Lerke et al.,⁴ measuring HCl during irradiation with a pH meter. They found that $G(\text{HCl})$ increases sharply in the initial period of irradiation at low doses (1–1.5 Mrad) and that the $G(\text{HCl})$ is 28 at 6 Mrad and decreases with the amount of stabilizers.

The effect of plasticizers on the behavior of PVC in γ -irradiation was studied by Krylova et al.³ They reported that in PVC plasticizer systems, the plasticizer has a marked effect in reducing the radiation chemical changes, in which the plasticizer breaks down readily. There are few practical results concerning the effects of plasticizers and stabilizers in the radiation oxidation of PVC.⁴ The few articles published on the subject of irradiated epoxy compounds concern only practical methods of producing improved plastics.⁵

It is our aim to study the effect of such additives on the gas evolution and oxidative degradation in γ -irradiation of PVC, which is widely used for disposable medical supplies.

* Present address: National Centre for Radiation Research and Technology, Madinet Nasr, Cairo, Egypt.

† To whom all correspondence should be addressed.

EXPERIMENTAL

Materials. Pure PVC powder with average diameter 0.2 mm was supplied by the Sumitomo Chemical Co., Ltd. The plasticized PVC film with thickness of 0.4 mm was supplied by the Terumo Co., Ltd. The plasticized PVC contains the following additives:

Component	Ratio (phr)
PVC (degree of polymerization 1000)	100
Diocetyl phthalate	50
Epoxy oil (Dratex-6.8, Argus Chemical)	5
Ca-Zn Stearate compound (Mark 33, Adeka, Argus Chemical)	2

Irradiation. The samples were irradiated with ^{60}Co γ -rays under vacuum, in oxygen and in air at a dose rate of 1 Mrad/h at room temperature.

Analysis and measurements. Oxygen consumption and gas evolution were measured by gas chromatograph and mass spectrometer. The tensile properties were measured by an Instron. The apparatus and procedures were the same as in our previous study.¹

RESULTS AND DISCUSSION

Gas Evolution and Oxygen Consumption

Figure 1 shows the amounts of evolved gases from pure PVC irradiated under vacuum at room temperature. The amount of total gas increases with dose. HCl is the main product, and hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4) are observed as minor products. The formations of

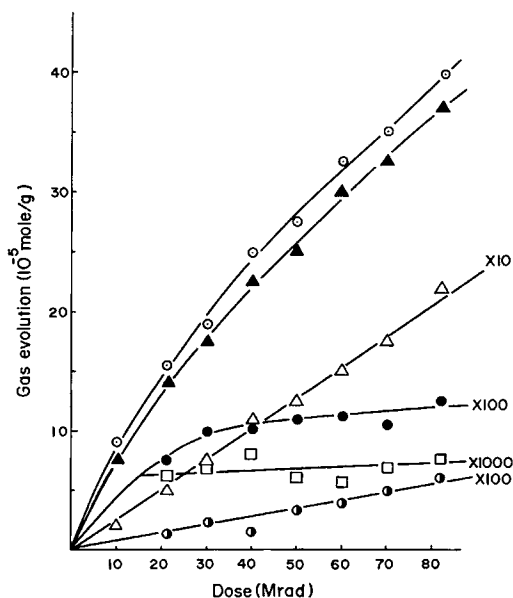


Fig. 1. Gas evolution vs. dose for pure PVC powder irradiated under vacuum at room temperature: (○) total gas; (▲) HCl; (△) H_2 ; (□) CH_4 ; (●) CO_2 ; (●) CO . $\times 10$, $\times 100$, and $\times 1000$, mean multiplication of observed values by 10, 100, and 1000, respectively.

H₂ and CO increase linearly with dose, but CO₂ and CH₄ level off above 30 Mrad. Upon irradiation the sample changed to yellow at low doses and to brown at higher doses. As the color is associated with conjugation, the more and the longer the conjugation sequences are, the darker the color becomes.

Figure 2 shows the amounts of evolved gases from the plasticized PVC irradiated under vacuum at room temperature. The amounts of total gases and HCl are very small until 20 Mrad, and then increase sharply at higher doses. The evolutions of H₂ and CH₄ increase linearly with dose, and the CO and CO₂ level off at higher doses.

The *G*-values for the evolved gases from pure and plasticized PVC irradiated under vacuum are listed in Table I. We can see that *G*(HCl) for the plasticized PVC is only 10% of the *G*(total) and less than *G*(H₂) below 20 Mrad. It is clear that *G*(total) and *G*(HCl) for the plasticized PVC are much smaller than for pure PVC at low doses.

The presence of stabilizers such as epoxy oil and Ca-Zn stearate compound effectively inhibit the gas evolution from PVC below 20 Mrad. The elimination of HCl from PVC is not prevented yet by the presence of such additives, but HCl is captured by the epoxy oil and Ca-Zn. These stabilizers are degraded by irradiation above 20 Mrad, and consequently the HCl and total gas evolution are increased sharply above 20 Mrad. Lerke and Szymanski⁴ reported that the evolved HCl was captured by the epoxy compounds. The compositions for the evolved gases, which were analyzed by mass spectrometer, are listed in Table II. The CO and CO₂ are formed due to the small amounts of residual oxygen in the samples after evacuation.

Figure 3 shows the amounts of oxygen consumption and gas evolution for pure PVC irradiated in oxygen with initial pressure of 500 torr as a function of dose.

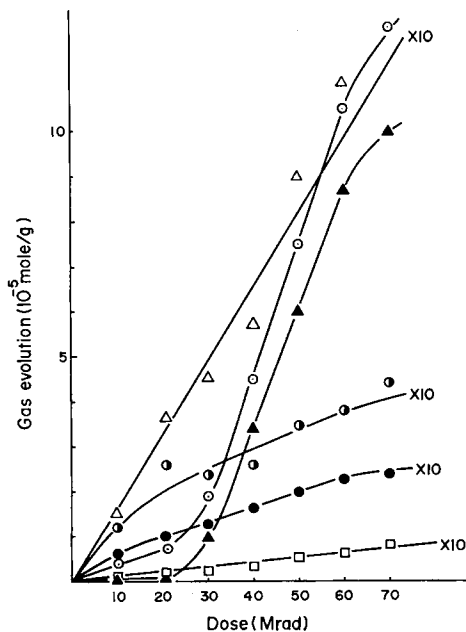


Fig. 2. Gas evolution vs. dose for plasticized PVC film irradiated under vacuum at room temperature. Symbols same as in Fig. 1.

TABLE I
G-Values of Evolved Gases for Pure PVC Powder and Plasticized PVC Film During Irradiation under Vacuum at Room Temperature

Dose (Mrad)	Pure PVC					Plasticized PVC						
	10	21	30	40	50	60	10	21	30	40	50	60
G(Total)	8.4	7.1	6.0	6.0	5.1	5.2	0.35	0.34	0.61	1.1	1.4	1.7
G(H ₂)	0.20	0.23	0.24	0.27	0.24	0.25	0.13	0.17	0.14	0.14	0.18	0.18
G(CH ₄) × 10 ³	—	2.8	2.4	1.9	1.2	0.7	16	10	10	10	10	10
G(CO) × 10 ²	—	0.5	0.6	0.3	0.6	0.6	12	13	8	6	7	6
G(CO ₂) × 10 ²	—	3.5	3.2	2.4	2.0	1.8	5	4	4	4	4	4
G(HCl)	8.2	6.8	5.7	5.7	4.8	4.9	0.03	0.03	0.33	0.83	1.1	1.4
G(C ₂ H ₆) × 10 ³	—	—	—	—	—	—	9	—	11	13	9	8

TABLE II
Relative Composition of Evolved Gases for Pure PVC Powder during Irradiation under Vacuum and in Oxygen at 300 torr by Mass Spectrograph

Component gas	Relative composition	
	40 Mrad under vacuum	20 Mrad in oxygen
HCl	100	100
CH ₄	0.06	0.10
CO	0.17	17.0
CO ₂	0.29	16.9
C ₂ H ₆	0.20	—
C ₂ H ₄	0.05	—
C ₃ H ₈	0.008	—
H ₂ O	0.5	1.1
O ₂ (residue)	—	56.8

The oxygen consumption and gas evolution increase linearly at low doses and level off at the higher doses. It is noted that the oxygen increases the evolution of HCl and CH₄ but H₂ decreases compared to irradiation under vacuum. The evolved gases detected by the mass spectrometer are listed in Table II. It has been reported that dehydrochlorination and oxidation occur simultaneously during the photoinduced degradation process of PVC in air.⁶⁻⁸

Figure 4 shows the amounts of oxygen consumption and gas evolution for the plasticized PVC irradiated in oxygen at initial pressure of 500 torr as a function of dose. The oxygen consumption and gas evolution increase linearly with dose until 50 Mrad. Table III shows that the evolved HCl increases in the presence of oxygen for both pure and plasticized PVC. The increase of HCl evolution in the presence of oxygen is more remarkable for the plasticized PVC than for the pure PVC. But the evolution of HCl is retarded by the additives in both presence

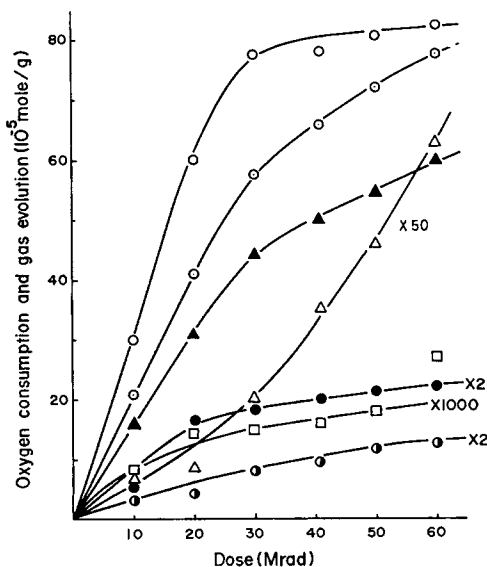


Fig. 3. Oxygen consumption and gas evolution vs. dose for pure PVC powder irradiated in oxygen at 500 torr at room temperature: (O) O₂ consumption. Other symbols same as in Fig. 1. ×2, ×50, and ×1000 mean multiplication of observed values by 2, 50, and 1000, respectively.

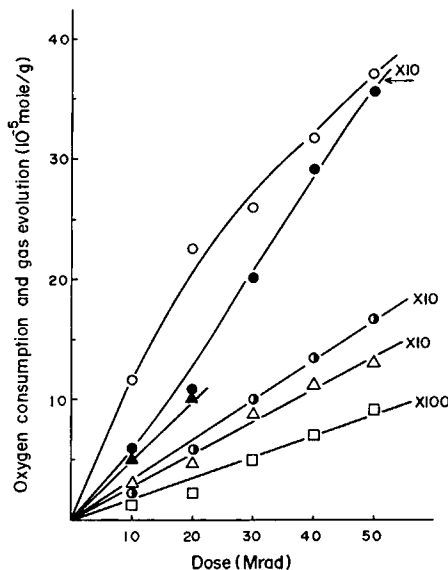


Fig. 4. Oxygen consumption and gas evolution vs. dose for plasticized PVC irradiated in oxygen at 500 torr at room temperature. Symbols same as in Fig. 3.

and absence of oxygen. Under these experimental conditions, the oxygen pressure in the sample tube decreases by the consumption during irradiation as shown in Table III.

The dependence of the oxygen consumption and gas evolution on the oxygen pressure was studied at 20 Mrad for pure and plasticized PVC, as shown in Figures 5 and 6. The oxygen consumptions for both pure and plasticized PVC increase with oxygen pressure and level off at the higher pressures. The evolutions of HCl and CO₂ show the same tendency as the oxygen consumption. The *G*-values for the oxygen consumption and evolved gases for pure and plasticized PVC are listed in Table IV. The *G*(-O₂) and *G*(HCl) for pure PVC level off at 400–500 torr, and for plasticized PVC, at 600–700 torr. This fact is due to the oxygen diffusion control in the plasticized PVC film samples.

Tensile Properties of the Irradiated PVC

The tensile properties were studied for only plasticized PVC because pure PVC is difficult to be molded into sheets. The changes in tensile strength (*T_b*) and percent elongation (*E_b*) at break for the plasticized PVC irradiated under different conditions (in air, in oxygen, and under vacuum) are shown in Figure 7. The *E_b* slightly increased upon irradiation under vacuum and decreased in air and in oxygen. The *T_b* was almost constant until 40 Mrad under vacuum, but decreased in air and in oxygen as the oxidation degradation occurred at higher doses above 20 Mrad. It has been reported that HCl accelerates the thermal and photodegradation of PVC^{8,9} and that the degradation is enhanced by the conjugated polyenes in the PVC chains. As mentioned above, the HCl evolution from the plasticized PVC increases sharply at doses above 20 Mrad under vacuum and is enhanced by the presence of oxygen. This is one of the reasons for the tensile property degrading above 20 Mrad. At low doses, a small change is ob-

TABLE III
G-Values of Gas Evolution and Oxygen Consumption for Pure PVC Powder and Plasticized PVC Film during Irradiation in Oxygen at Initial Pressure of 500 torr

Dose (Mrad)	Pure PVC					Plasticized PVC					
	10	20	30	40	50	60	10	20	30	40	50
$G(\text{Total})$	20	20	19	16	14	13	5.8	5.9	—	—	—
$G(\text{H}_2)$	0.14	0.11	0.13	0.16	0.18	0.20	0.27	0.20	0.29	0.26	0.25
$G(\text{CH}_4) \times 10^3$	7.3	7.0	4.8	3.8	3.5	4.4	13	11	16	17	18
$G(\text{CO})$	1.4	1.0	1.3	1.1	1.1	1.0	0.23	0.27	0.33	0.33	0.32
$G(\text{CO}_2)$	2.5	3.6	2.9	2.3	2.1	1.8	0.57	0.52	0.64	0.71	0.70
$G(\text{HCl})$	16	15	14	12	11	10	4.7	5.0	—	—	—
$G(-\text{O}_2)^a$	28.5	29.0	25.0	18.0	16.0	13.3	11.3	11.0	8.4	7.5	7.2
$P(\text{O}_2)$, torr ^b	308	274	1.1	1.0	0.7	—	428	367	351	305	266

^a Oxygen consumption.

^b Remaining oxygen pressure after irradiation.

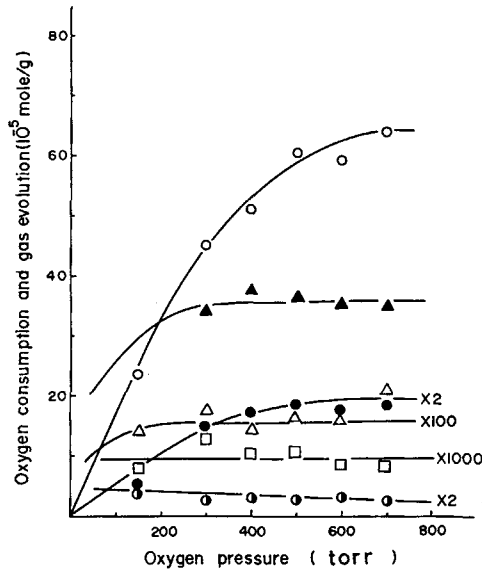


Fig. 5. Oxygen consumption and gas evolution vs. oxygen pressure for pure PVC powder irradiated in oxygen up to 20 Mrad at room temperature. Symbols same as in Fig. 3.

served for both T_b and E_b in air, in oxygen and under vacuum, as shown in Figure 8.

These results may indicate that the dioctyl phthalate inhibits effectively the degradation at low doses up to 20 Mrad. At higher doses, the dioctyl phthalate is decomposed and the T_b and E_b slowly decrease. As the dioctyl phthalate acts as the radiation energy transfer agent, main-chain scission of PVC is retarded.

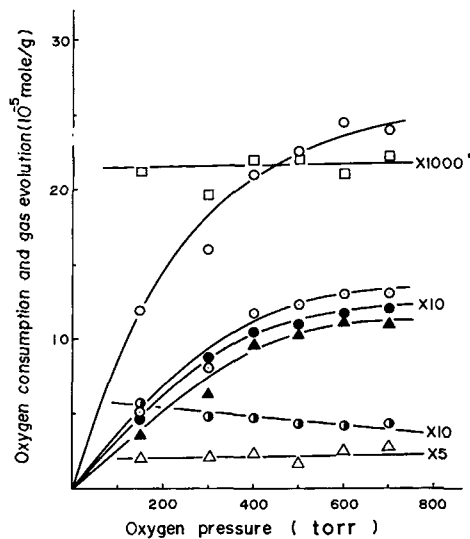


Fig. 6. Oxygen consumption and gas evolution vs. oxygen pressure for plasticized PVC irradiated in oxygen up to 20 Mrad. Symbols same as in Fig. 3.

TABLE IV
G-Values of Gas Evolution and Oxygen Consumption for Pure PVC Powder and Plasticized PVC Film Irradiated Up to 20 Mrad at Various Oxygen Pressures

Initial oxygen pressure (torr)	Pure PVC					Plasticized PVC				
	150	300	400	500	700	150	300	400	500	700
G(Total)	10	21	23.5	20.3	22.0	2.4	3.9	5.6	5.9	6.3
G(HCl)	8.0	17	19	15	17	1.7	3.0	4.7	5.0	5.3
G(H ₂)	0.07	0.08	0.06	0.08	0.08	0.2	0.2	0.2	0.19	0.24
G(CH ₄) × 10 ³	4	6	5	5	4	10	9	10	10	10
G(CO)	0.98	0.5	0.7	0.6	0.7	0.24	0.23	0.23	0.21	0.21
G(CO ₂)	1.2	3.2	3.7	4.3	4.1	0.24	0.41	0.50	0.52	0.58
G(-O ₂) ^a	11.3	22	25	29	31	6	8	10	11	12
P(O ₂) torr ^b	0.3	1.2	42	173	208	73	191	261	367	438
					249					556

^a Oxygen consumption.

^b Remaining oxygen pressure after irradiation.

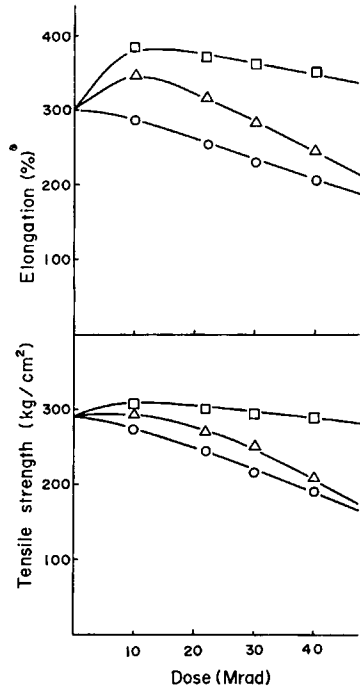


Fig. 7. Tensile strength and percent elongation at break vs. dose for plasticized PVC irradiated at room temperature: (\square) irradiated under vacuum; (Δ) irradiated in air; (\circ) irradiated in oxygen at 650 torr.

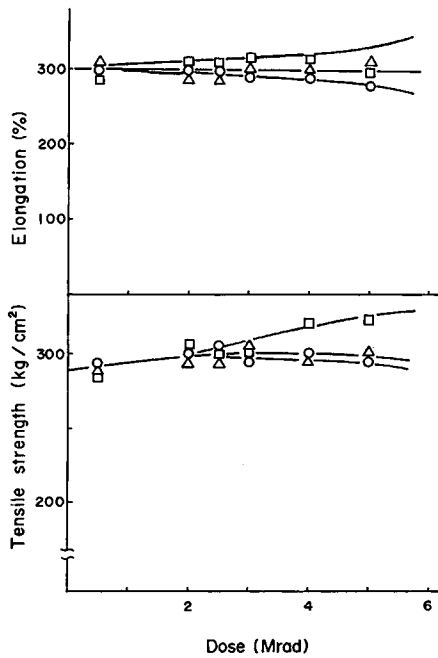


Fig. 8. Tensile strength and percent elongation at break vs. dose for plasticized PVC irradiated at low dose. Symbols same as in Fig. 7.

CONCLUSIONS

The gas evolution and oxygen consumption of γ -irradiated pure and plasticized PVC were investigated. For pure PVC, $G(\text{HCl})$ is about 8 under vacuum and 16 in oxygen at low doses. The $G(\text{H}_2)$ is 0.24 under vacuum and 0.13 in oxygen. The evolution of CO , CO_2 , and CH_4 was increased in the presence of oxygen. The oxygen consumption in pure PVC was dependent on the oxygen pressure; $G(-\text{O}_2)$ was about 30 above 500 torr of oxygen.

On the other hand, $G(\text{HCl})$ for the plasticized PVC is only 0.02–0.03 up to 20 Mrad under vacuum and about 5 in oxygen. Oxygen markedly increases the formation of HCl , H_2 , CH_4 , CO , and CO_2 . The stabilizers retarded effectively the gas evolution and oxidative degradation of PVC. The $G(-\text{O}_2)$ for the plasticized PVC is about 12, and the dependence on oxygen pressure is more remarkable than for pure PVC due to the oxygen diffusion control in the film samples. The degradation of mechanical properties of the plasticized PVC are well retarded by the plasticizers and stabilizers; T_b and E_b are scarcely changed until 20 Mrad in air, oxygen and vacuum.

The authors are grateful to Mr. K. Arakawa of their institute for his help with the mass spectrography. El-Sayed A. Hegazy wishes to thank Prof. Dr. Abd-El-Gawad Rabie of the Faculty of Science, Ain Shams University, Egypt, and Dr. A. M. Desouky and Assistant Prof. Dr. A. A. El-Milligy of the National Centre for Radiation Research and Technology, Cairo, for their guidance and encouragement.

References

1. E. A. Hegazy, T. Seguchi, K. Arakawa, and S. Machi, *J. Appl. Polym. Sci.*, **26**, 1361 (1981).
2. K. S. Minsker and G. T. Fedoseyeva, *Destruktsiya i Stabilizatsiya Polyvinylchloride*, Khimiya, Moscow, 1972.
3. S. V. Krylova, Yu. V. Ovchinnikov, A. Ye. Kulikova, L. I. Pavlinov, and T. M. Lyutova, *Polym. Sci. USSR*, **21**, 749 (1979).
4. I. Lerke and W. Szymanski, *J. Appl. Polym. Sci.*, **21**, 2067 (1977).
5. R. Y. Mixer and D. B. Parkinson, Report MADC-TR-56-534, 1957.
6. G. P. Mack, *Mod. Plast.*, **31**, 150 (1953).
7. J. Petit and G. Zaitoun, *C.R. Acad. Sci., Ser. C*, **256**, 2610 (1966).
8. A. L. Scarbrough, W. L. Keller, and P. W. Rizzo, *Nat. Bur. Stand. Circ. No. 525*, 1953, p. 95.
9. R. F. Boyer, *J. Phys. Colloid Chem.*, **51**, 80 (1947).

Received December 1, 1980

Accepted February 3, 1981