

RADIOLYTIC GAS PRODUCTION IN THE ALPHA PARTICLE DEGRADATION OF PLASTICS*

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ABSTRACT

Net gas generation due to alpha particle irradiation of polyethylene and polyvinyl chloride was investigated. Experiments were performed in an air environment at 30, 60, and 100°C. The predominant radiolytic degradation products of polyethylene were hydrogen and carbon dioxide with a wide variety of trace organic species noted. Irradiation of polyvinyl chloride resulted in the formation of HCl in addition to the products observed for polyethylene. For both plastic materials, a strong enhancement of net yields was noted at 100°C.

INTRODUCTION

The production of gas due to the interaction of high LET (alpha particle) ionizing radiation with homogeneous materials in transuranic (TRU) waste is potentially an important issue during both the initial storage and subsequent transportation to the Waste Isolation Pilot Plant (WIPP) site. Current guidelines provide for a period of up to 60 days where the normally vented shipping container will be sealed during transport from the waste generator site to the WIPP. An assessment of gas generation during this period is needed to demonstrate compliance for waste shipment.

The alpha particle degradation of polyethylene (PE) and polyvinyl chloride (PVC) has not been extensively studied. A number of studies have been performed, however, with low LET (gamma and beta particle) irradiation. Reviews of this work have been published elsewhere (1,2,3). For polyethylene, hydrogen gas ($G(\text{H}_2) = 3.5$ to 5.0 molec/100 eV) and lesser amounts of hydrocarbons are the radiolytically induced degradation products. For PVC (3), hydrogen and hydrochloric acid (up to 13 molec/100 eV) are observed. The replacement of beta and gamma ionizing radiation with alpha particles was expected to affect the relative amounts of products observed in low LET systems.

In this paper, the initial results of an ongoing study to investigate the dose rate, temperature and material-specific dependence of gas generation for polyethylene and polyvinyl chloride are presented. The data reported relate to the highest dose rate experiments in our test matrix. Ongoing work addresses the dose rate dependence and variability of our results on plastic material type. Tests are being conducted at temperatures up to 100°C to bound temperatures the waste packages may reach during shipping in sealed containers. Polyethylene and polyvinyl chloride are emphasized as these are common plastic materials used to package TRU waste.

EXPERIMENTAL

The polyethylene and polyvinyl chloride plastic materials were received from Westinghouse Savannah River Company (WSRC) and correspond to material they are currently using to package TRU waste. The initial environment in all the experiments was air at a relative humidity of $70 \pm 5\%$ at 21°C. Irradiations were performed in the glass-Teflon vessel shown in Fig. 1.

The plastic was cut into sheets approximately 6.1 cm x 6.1 cm and mounted 3 mm from an alpha particle source (233 $\mu\text{Ci}/\text{cm}^2$ Am-241 with a gold surface coating). The energy deposition rate of the foil was established by exposing the Am foil to ethylene gas (4) and measuring the buildup of hydrogen gas ($G[\text{H}_2] = 1.35$ molec/100 eV). The energy deposition rate measured for the foils we used was $1.0 \pm 0.05 \times 10^{12}$ MeV/h. No correction for attenuation by air in the air gap was made.

The foil-plastic assembly was placed in the irradiation vessel. The vessel was sealed, leak-checked, attached to a vacuum manifold and evacuated to < 10 mtorr. Water vapor was added to the vessel by expanding previously degassed liquid water into the vacuum manifold to a total water vapor pressure of approximately 14 torr. This was measured directly by an MKS Baratron Type 220 pressure gauge that was

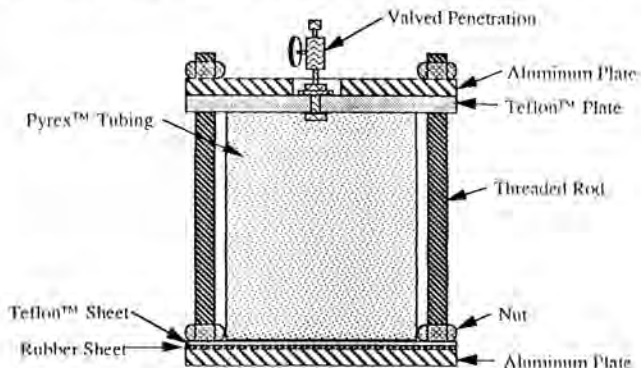


Fig. 1. Irradiation vessel.

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calibrated to NIST- traceable standards. A Panametrics hygrometer was also used to confirm that the pressure measured was due to water vapor and not air present in the system. Breathing air, $21.5 \pm 0.2\%$ O₂, $78.5 \pm 0.2\%$ N₂, and typically $<0.01\%$ carbon dioxide was added to the vessel to a total pressure of 760 ± 10 torr.

Once prepared, the vessels were placed in ovens at 30, 60, or 100°C and periodically removed to sample the gas phase. Gas analyses were performed by gas chromatography on a Varian model 3300 or 3400 gas chromatograph. Hydrogen analyses were performed using argon as the carrier gas and a thermal conductivity detector. Oxygen, nitrogen, and carbon dioxide were determined using a thermal conductivity detector with helium as the carrier gas. Trace organic composition was determined using a flame ionization detector with helium as the carrier gas. For PVC samples, a vessel rinse was made after test termination and analyzed for chloride content using ion chromatography. Both plastic materials used were weighed before and after irradiation to determine weight change.

ALPHA PARTICLE IRRADIATION OF POLYETHYLENE AND POLYVINYL CHLORIDE

A summary of gas phase analyses for the experiments performed is given in Table I. The resulting yield data is summarized in Table II.

Irradiation of Polyethylene

Polyethylene samples (two replicates) were irradiated at 30, 60, and 100°C for a duration of 33 days. The gas phase of the irradiated samples was analyzed at day 3, 7, 14, and 33. One of each replicate experiment was continued for an additional 40 days to more clearly establish the long term trends we were observing. A blank experiment with no alpha particle source present was also performed at each temperature.

The predominant radiolytic products noted were hydrogen and carbon dioxide. A plot of the concentration of both these species as a function of time is shown in Fig. 2 for 30, 60, and 100°C. Trace organic content was also observed to increase with both absorbed dose and temperature. In the gas phase, substantial oxygen depletion was observed at 100°C.

Hydrogen gas was produced at a rate that was linear with time (i.e., absorbed dose) at all temperatures. Hydrogen yield was 2.7 ± 0.2 molec/100 eV at 30°C, remained the same at 2.4 ± 0.2 at 60°C, and increased to 3.7 ± 0.7 at 100°C.

Carbon dioxide formation, due to radiolytic/thermal oxidation of carbon in the plastic, was not generated at a linear rate (see Fig. 1b). Accelerated formation of carbon dioxide was noted at longer irradiation times and elevated temperature. Approximate yields, calculated by a "forced" linear least-squares fit of the data, were 3.0 ± 0.4 , 3.3 ± 0.2 , and $11\text{-}35$ molec/100 eV at 30, 60, and 100°C, respectively.

The change in the weight of the plastic material is summarized in Table III. For all the polyethylene samples, a significant weight gain was noted. For a nominal initial weight of 0.7 g, approximately 0.003-0.004 g was gained after 33 days at the lower two temperatures. 0.05 and 0.09 g was gained after 73 days in the extended replicate experiments. At 100°C, weight gain was 0.02 g and 0.032 g after 33 and 73 day, respectively. This is a factor of 3-5 times higher than that observed at the lower temperatures.

The trace organic content of the gas phase was determined qualitatively for all experiments performed. Ten to fifteen distinguishable alkene/alkane peaks as well as acetone were identified. Total organic concentrations in the gas phase were ≤ 0.02 , ≤ 0.04 , and ≤ 0.3 mole% at 30, 60, and 100°C, respectively. The major products noted were ethane, ethylene, propylene, and acetone in all experiments. The organics noted are the result of coupled radiolytic-thermal effects since little organic buildup in the gas phase was evident in the blank experiments where no irradiation source was present.

The 30 and 60°C results compare well with existing literature (5-8) using low LET radiation as the source of ionizing radiation. The same major products were observed. The yield for hydrogen was somewhat lower than the values of 3.5 to 5.0 molec/100 eV typically reported in gamma/beta irradiation studies. Carbon dioxide was expected as a product because of the oxygen-containing atmosphere we utilized (6,8). In our experiments, we cannot differentiate between air oxidation of organics to carbon dioxide vs. direct oxidation of carbon in the plastic. The large weight gains noted are indicative of oxygen uptake in the system which was consistent with oxygen depletion we noted in the gas phase data and results reported by others (6,8).

The results reported herein do not entirely agree with alpha irradiation results published elsewhere (9). In our work, (1) carbon dioxide and hydrogen formation were approximately the same compared with a 98:0.6 ratio, (2) we saw essentially no temperature effect between 30 and 60°C, and (3) net yields were twice as high in our work. These results could be explained based on variability in the plastic material used. The effect of plastic variability is being addressed in our work as part of the ongoing matrix.

Irradiation of Polyvinylchloride

Two replicate samples of polyvinyl chloride plastic were irradiated at 30, 60, and 100°C. Blank experiments with this plastic were also performed at each temperature. Sampling of the gas phase was the same as done for the polyethylene samples. At 33 d, however, all tests were terminated so that a rinse for chloride could be done on all samples.

The major gaseous radiolytic products we observed were hydrogen, hydrogen chloride, and carbon dioxide. A plot of the hydrogen and carbon dioxide yields as a function of time is shown in Fig. 3 for 30, 60, and 100°C. The trace organic composition of the gas phase was complex and only qualitatively established.

The yield of hydrogen chloride was 0.3 ± 0.05 , 1.0 ± 0.1 , and 11 ± 0.4 molec/100 eV at 30, 60, and 100°C, respectively. These data fall within the range typically reported for HCl yield at room temperature (3). We did not establish the absorbed dose trend in these experiments since HCl was only measured at the end of the experiment. The strong temperature dependence noted is consistent with general results reported by others (3). These results however do not agree with other alpha irradiation studies (9) where no HCl production was reported.

Hydrogen production was linear with absorbed dose (see Fig. 2b) at all three temperatures investigated. Hydrogen yields measured were 0.78 ± 0.05 , 0.67 ± 0.04 , and 1.7 ± 0.2 molec/100 eV at 30, 60, and 100°C, respectively. The slight decrease noted between 30 and 60°C was nearly within experimental uncertainty and not considered significant. These

TABLE I

Bulk Composition of Gas Phase in Irradiated Polyethylene (PE) and Polyvinyl Chloride (PVC) Samples

Sample Description	Expt. #	Duration (days)	Mole % ^a			
			O ₂	N ₂	H ₂	CO ₂
PE @ 30°C	1	3	21.6	78.4	ND	0.011
		7	21.5	78.5	0.063	0.034
		14	21.1	78.8	0.048	0.081
		33	20.4	79.3	0.28	0.292
	2	3	ND ^b	ND	ND	ND
		7	21.5	78.5	0.074	0.014
		14	21.1	78.8	0.154	0.085
PVC @ 30°C	10	33	20.5	79.2	0.30	0.270
		3	21.6	78.4	ND	0.0090
		7	21.7	78.3	0.017	0.023
		14	21.3	78.7	0.032	0.042
	11	33	21.0	78.8	0.08	0.112
		3	ND	ND	ND	ND
		7	21.7	78.2	0.006	0.033
PE @ 60°C	27	14	21.3	78.7	0.029	0.031
		33	21.2	78.7	0.07	0.92
		3	21.7	78.3	ND	0.013
		7	22.0	78.0	0.064	0.036
	28	14	21.1	78.9	0.049	0.085
		33	20.0	79.7	0.23	0.31
		3	ND	ND	ND	ND
PVC @ 60°C	32	7	21.6	78.4	0.070	0.031
		14	21.2	78.8	0.123	0.073
		33	19.9	79.7	0.24	0.32
		3	21.6	78.4	ND	0.010
	33	7	21.5	78.4	0.021	0.021
		14	21.3	78.7	0.02	0.044
		33	21.0	78.8	0.064	0.12
PE @ 100°C	37	3	ND	ND	ND	ND
		7	22.0	78.0	0.012	0.031
		14	21.2	78.7	0.030	0.043
		33	21.0	78.9	0.068	0.119
	38	3	21.5	78.5	ND	0.039
		7	21.4	78.6	ND	0.068
		14	19.1	80.6	0.025	0.312
PVC @ 100°C	46	33	0.9	95.8	0.4	3.3
		3	ND	ND	ND	ND
		7	21.4	78.5	0.103	0.109
		14	19.5	80.2	0.214	0.294
	47	33	15.9	83.1	0.354	1.02
		3	ND	ND	ND	ND
		7	20.8	79.1	0.019	0.096
47	14	17.7	81.9	0.053	0.35	
	33	11.6	87.4	0.138	0.98	
	3	ND	ND	ND	ND	
	7	21.7	78.3	0.014	0.043	
	14	17.6	82.0	0.074	0.35	
		33	10.9	89.1	0.174	0.021

^aUncertainty is ± 0.3 for O₂, ± 0.3 for N₂, $\pm 10\%$ for CO₂ and H₂.^bND = Not determined.

TABLE II

Summary of "Best" Yield Values
(molec/100 ev)

Plastic	G(H ₂)	G(CO ₂)	G(HCl)
PE @ 30°C PVC @ 30°C	2.7 ± 0.2 0.78 ± 0.05	3.0 ± 0.4 0.98 ± 0.06	NA 0.3 ± 0.05
PE @ 60°C PVC @ 60°C	2.4 ± 0.2 0.67 ± 0.04	3.3 ± 0.2 1.2 ± 0.1	NA 1.0 ± 0.1
PE @ 100°C PVC @ 100°C	3.7 ± 0.7 1.7 ± 0.2	11 - 35 0.2 - 11	NA 11 ± 0.4

NA = not applicable.

TABLE III

Weight Change Data for Irradiated
PVC and PE Samples

Sample	Experiment	Weight Change, g*
PE @ 30°C, 33 d	2	+0.00335
PE @ 30°C, 73 d	1	+0.00496
PE @ 60°C, 33 d	28	+0.00447
PE @ 60°C, 73 d	27	+0.00958
PE @ 100°C, 33 d	38	+0.02023
PE @ 100°C, 73 d	37	+0.03208
PVC @ 30°C, 33 d	10	-0.00397
	11	-0.00321
PVC @ 60°C, 33 d	32	-0.00440
	33	-0.00636
PVC @ 100°C, 33 d	46	-0.05622
	47	-0.05534

*Uncertainty is ±0.00002 g.

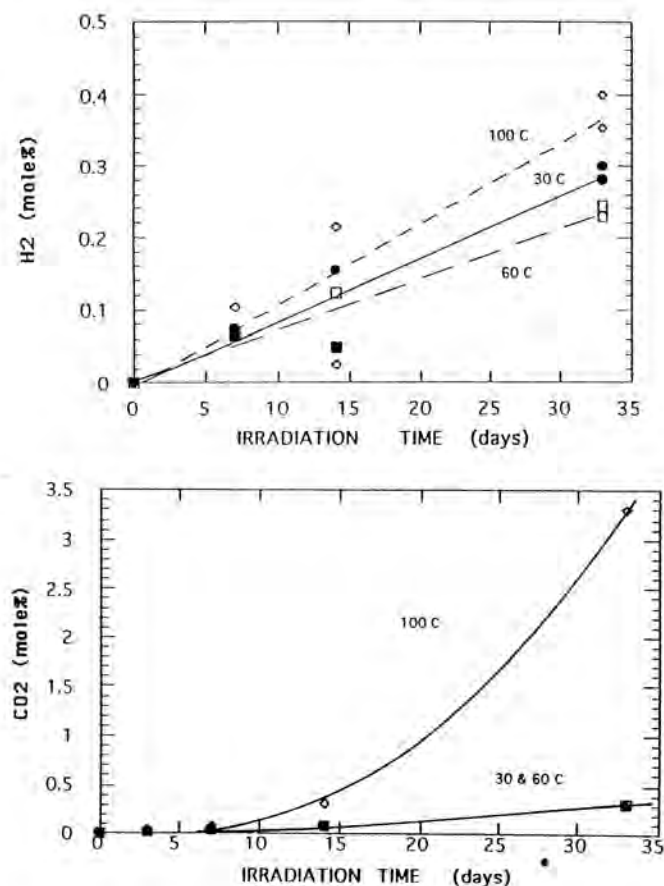


Fig. 2. Hydrogen and carbon dioxide formation as a function of time for polyethylene.

data compare with essentially no hydrogen production reported in the literature at room temperature for low LET systems (3).

Carbon dioxide yields were linear with absorbed dose at 30 and 60°C. Yields measured were 0.98 ± 0.06 and 1.2 ± 0.1 molec/100 eV, respectively. At 100°C, however, carbon dioxide concentration increased nonlinearly with absorbed dose and, in one case, was substantially depleted subsequent to its

initial buildup. In this experiment, the deposition of organic material on the vessel wall was also noted.

For all the PVC samples, irradiation resulted in weight loss. Average weight loss was 0.0036 g at 30°C, 0.005 g at 60°C, and 0.056 g at 100°C. Nominal initial weight was 1.5 g. As noted in the polyethylene samples, net change in the sample was greatly accelerated (by a factor of 10 in this case) at 100°C.

The trace organic content of the gas phase was similar to that observed for polyethylene. Net degradation was due to coupled radiolytic-thermal effects and increased with temperature. A shift to larger amounts of higher-molecular weight products was noted relative to the polyethylene experiments.

SUMMARY OF CONCLUSIONS

The alpha particle degradation of polyethylene and polyvinyl chloride was investigated. The yield of major products were identified (see Table II) as a function of temperature and plastic material. Overall plastic degradation was significantly enhanced at 100°C.

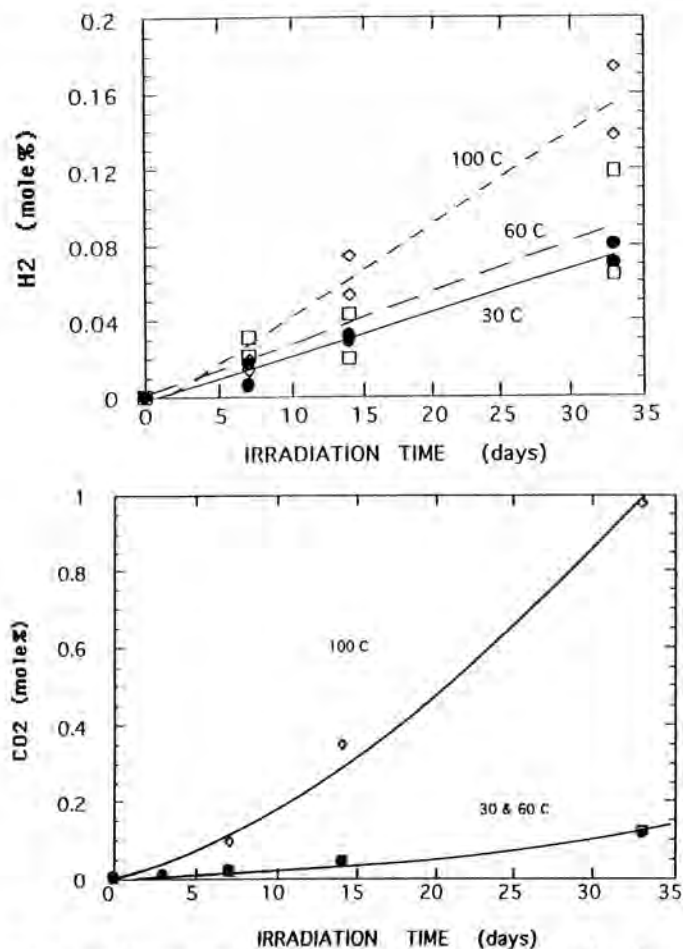


Fig. 3. Hydrogen and carbon dioxide formation as a function of time for polyvinyl chloride.

Irradiation of polyethylene plastic led to the formation of hydrogen, carbon dioxide and a wide variety of trace organics. $G(\text{H}_2)$ was between 2.4 and 3.7 molec/100 eV, and $G(\text{CO}_2)$ was 3.0 molec/100 eV to as high as 35 molec/100 eV. Accelerated radiation-induced decomposition of the plastic was noted at 100°C that results in increased weight gain and significant change in the gas phase composition.

For polyvinyl chloride, hydrogen chloride was also a predominant radiolytic product with hydrogen, carbon dioxide, and trace organics also observed. Yields obtained were $G(\text{H}_2) = 0.8$ to 1.7 molec/100 eV, $G(\text{CO}_2) = 0.2$ to 11 molec/100 eV, and $G(\text{HCl}) = 0.3$ to 11 molec/100 eV. All yields, as we observed in the case of polyethylene, increased significantly between 60 and 100°C.

ACKNOWLEDGMENTS

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