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# THE PREDICTION OF TOXIC ATMOSPHERES FROM DECOMPOSING POLYMERS

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**ABSTRACT:** The generation of carbon monoxide from polymethyl methacrylate and polyethylene, and of hydrogen chloride from polyvinyl chloride, was calculated. Calculations were made for various amounts of polymer evolving gaseous products into a 60 $ft^3$ compartment.

## INTRODUCTION

THE PREDICTION OF the amounts of polymeric materials which could be safely exposed to a fire situation in a closed compartment requires a knowledge of the amounts of toxic gases which can be generated from a specific quantity of polymer under particular conditions of exposure. The concentration of toxic gases at any point in time is a function of the quantity of polymer originally present, and of the conditions of temperature and oxygen concentration to which it is exposed.

This paper presents the results of calculations using a computer program to calculate equilibrium compositions of gases from the decomposition of polymethyl methacrylate, polyethylene, and polyvinyl chloride.

## COMPUTER PROGRAM

The Aerotherm equilibrium program [1] computes the equilibrium composition and temperature for a chemical system whose initial composition and thermodynamic properties are known. Specifically, the input to the program contains the elemental composition of at most four reactant species (air is counted as a single species) and their enthalpies of formation. The input also contains the elemental composition of all possible product species, gaseous or condensed, their heats of formation and their heat capacities as a function of temperature. The final pressure must also be specified. From these data, the program calculates the equilibrium composition and temperature of the system, the temperature corresponding to the adiabatic flame temperature in the case of a combustion reaction.

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## POLYMETHYL METHACRYLATE

Our model assumes that polymethyl methacrylate (PMMA) is first pyrolyzed to give the gaseous monomer [2]. The latter then reacts with varying amounts of oxygen in air to give the equilibrium combustion products (Table 1). The pyrolysis kinetics provide the rate-determining step, the rate constant being taken from Madorsky [2]. The carbon monoxide concentrations produced in a 60 $ft^3$ closed compartment by the pyrolysis and burning of 10, 20, and 50 g quantities of PMMA are shown in Tables 2 to 4 and in Figures 1 to 3.

The individual figures correspond to PMMA combustion in air with oxygen/PMMA monomer mole ratios of 2:1, 5:1, and 6:1. In each case, curves of CO concentration as a function of time are given for PMMA pyrolysis temperatures ranging from 340 to 400°C. Higher pyrolysis temperatures generally increase the rate of production of CO, with the 60°C temperature interval corresponding to a 50-fold rate increase for the case of a 2:1 mole ratio of oxygen to PMMA monomer. The latter case produces the most toxic effects in terms of CO generation. For 10 g PMMA, the maximum concentration possible is close to 6,000 ppm; this concentration is almost reached in 2 min with a pyrolysis temperature of 400°C (Figure 1). For the same 2:1 ratio, the pyrolysis and combustion of 50 g PMMA at a pyrolysis temperature of 340°C produces nearly 9,000 ppm CO, the lower temperature being more than compensated for by the larger amount of PMMA and the longer time.

Less CO is produced at the higher oxygen/PMMA ratios (Figures 2 and 3). The maximum concentration possible for 10 g PMMA is about 2,200 ppm CO for a ratio of 5:1, and 700 ppm for a ratio of 6:1. With the 5:1 ratio, the CO concentration

*Table 1. Combustion of Polymethyl Methacrylate (PMMA) in Air.*

| Moles oxygen/mole PMMA monomer | 2 | 5 | 6 |
|---|---|---|---|
| Equilibrium composition (mole fractions) | | | |
| carbon monoxide (CO) | 0.273 | 0.060 | 0.016 |
| carbon dioxide ($CO_2$) | 0.030 | 0.119 | 0.140 |
| water ($H_2O$) | 0.030 | 0.130 | 0.121 |
| hydrogen ($H_2$) | 0.212 | 0.012 | 0.003 |
| oxygen ($O_2$) | 0.000 | 0.000 | 0.007 |
| nitrogen ($N_2$) | 0.455 | 0.675 | 0.705 |
| hydroxyl (OH) | 0.000 | 0.001 | 0.003 |
| nitric oxide (NO) | 0.000 | 0.000 | 0.003 |
| Moles CO/mole PMMA monomer | 4.5 | 1.7 | 0.5 |
| Temperature, °K. | 1181 | 2235 | 2278 |

*Table 2. Generation of Carbon Monoxide from Polymethyl Methacrylate Oxygen/PMMA Monomer Ratio 2:1 — Compartment Volume 60 ft³*

| Temperature °C. | Time min | CO Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PMMA | 20 g PMMA | 50 g PMMA |
| 340 | 1 | 403 | 803 | 2,015 |
| | 2 | 784 | 1,568 | 3,920 |
| | 5 | 1,770 | 3,540 | 8,850 |
| | 10 | 3,012 | 6,024 | 15,060 |
| | 20 | 4,497 | 8,994 | 22,485 |
| | 50 | 5,768 | 11,536 | 28,840 |
| 350 | 1 | 772 | 1,544 | 3,860 |
| | 2 | 1,426 | 2,852 | 7,130 |
| | 5 | 2,982 | 5,964 | 14,910 |
| | 10 | 4,466 | 8,932 | 22,330 |
| | 20 | 5,578 | 11,156 | 27,890 |
| | 50 | 5,934 | 11,868 | 29,670 |
| 360 | 1 | 1,428 | 2,816 | 7,040 |
| | 2 | 2,477 | 4,954 | 12,385 |
| | 5 | 4,402 | 8,804 | 22,010 |
| | 10 | 5,542 | 11,084 | 27,710 |
| | 20 | 5,910 | 11,820 | 29,550 |
| | 50 | 5,940 | 11,880 | 29,700 |
| 370 | 1 | 2,376 | 4,752 | 11,880 |
| | 2 | 3,802 | 7,604 | 19,010 |
| | 5 | 5,477 | 10,954 | 27,385 |
| | 10 | 5,904 | 11,808 | 29,520 |
| | 20 | 5,940 | 11,880 | 29,700 |
| 380 | 1 | 3,641 | 7,282 | 18,205 |
| | 2 | 5,049 | 10,098 | 25,245 |
| | 5 | 5,887 | 11,774 | 29,435 |
| | 10 | 5,940 | 11,880 | 29,700 |
| 390 | 1 | 4,889 | 9,778 | 24,445 |
| | 2 | 5,756 | 11,512 | 28,780 |
| | 5 | 5,940 | 11,880 | 29,700 |
| 400 | 1 | 5,673 | 11,346 | 28,365 |
| | 2 | 5,928 | 11,856 | 29,640 |
| | 5 | 5,940 | 11,880 | 29,700 |
| maximum | | 5,940 | 11,880 | 29,700 |

*Table 3. Generation of Carbon Monoxide from Polymethyl Methacrylate Oxygen/ PMMA Monomer Ratio 5:1 – Compartment Volume 60 ft³*

| Temperature °C. | Time min | CO Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PMMA | 20 g PMMA | 50 g PMMA |
| 340 | 1 | 152 | 304 | 760 |
| | 2 | 296 | 592 | 1,480 |
| | 5 | 668 | 1,336 | 3,340 |
| | 10 | 1,136 | 2,272 | 5,680 |
| | 20 | 1,696 | 3,392 | 8,480 |
| | 50 | 2,175 | 4,350 | 10,875 |
| 350 | 1 | 291 | 582 | 1,455 |
| | 2 | 547 | 1,094 | 2,735 |
| | 5 | 1,125 | 2,250 | 5,625 |
| | 10 | 1,685 | 3,370 | 8,425 |
| | 20 | 2,104 | 4,208 | 10,522 |
| | 50 | 2,238 | 4,476 | 11,190 |
| 360 | 1 | 531 | 1,062 | 2,655 |
| | 2 | 934 | 1,868 | 4,670 |
| | 5 | 1,660 | 3,320 | 8,300 |
| | 10 | 2,090 | 4,180 | 10,450 |
| | 20 | 2,229 | 4,458 | 11,145 |
| | 50 | 2,240 | 4,480 | 11,200 |
| 370 | 1 | 896 | 1,792 | 4,480 |
| | 2 | 1,434 | 2,868 | 7,170 |
| | 5 | 2,066 | 4,132 | 10,330 |
| | 10 | 2,227 | 4,454 | 11,135 |
| | 20 | 2,240 | 4,480 | 11,200 |
| 380 | 1 | 1,373 | 2,746 | 6,865 |
| | 2 | 1,904 | 3,808 | 9,520 |
| | 5 | 2,220 | 4,440 | 11,100 |
| | 10 | 2,240 | 4,480 | 11,200 |
| 390 | 1 | 1,844 | 3,688 | 9,220 |
| | 2 | 2,171 | 4,342 | 10,855 |
| | 5 | 2,240 | 4,480 | 11,200 |
| 400 | 1 | 2,139 | 4,278 | 10,695 |
| | 2 | 2,236 | 4,472 | 11,180 |
| | 5 | 2,240 | 4,480 | 11,200 |
| maximum | | 2,240 | 4,480 | 11,200 |

*Table 4. Generation of Carbon Monoxide from Polymethyl Methacrylate Oxygen/ PMMA Monomer Ratio 6:1 — Compartment Volume 60 ft³*

| Temperature °C. | Time min | CO Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PMMA | 20 g PMMA | 50 g PMMA |
| 340 | 1 | 46 | 92 | 230 |
| | 2 | 89 | 178 | 445 |
| | 5 | 200 | 400 | 1,000 |
| | 10 | 341 | 682 | 1,705 |
| | 20 | 509 | 1,018 | 2,545 |
| | 50 | 653 | 1,306 | 3,265 |
| 350 | 1 | 87 | 174 | 435 |
| | 2 | 161 | 322 | 805 |
| | 5 | 338 | 676 | 1,690 |
| | 10 | 506 | 1,012 | 2,530 |
| | 20 | 632 | 1,264 | 3,160 |
| | 50 | 672 | 1,344 | 3,360 |
| 360 | 1 | 159 | 318 | 795 |
| | 2 | 286 | 562 | 1,425 |
| | 5 | 499 | 998 | 2,495 |
| | 10 | 628 | 1,256 | 3,140 |
| | 20 | 669 | 1,338 | 3,345 |
| | 50 | 673 | 1,346 | 3,365 |
| 370 | 1 | 269 | 538 | 1,345 |
| | 2 | 431 | 862 | 2,155 |
| | 5 | 620 | 1,240 | 3,100 |
| | 10 | 669 | 1,338 | 3,345 |
| | 20 | 673 | 1,346 | 3,365 |
| 380 | 1 | 412 | 824 | 2,060 |
| | 2 | 572 | 1,144 | 2,860 |
| | 5 | 667 | 1,334 | 3,335 |
| | 10 | 673 | 1,346 | 3,365 |
| 390 | 1 | 554 | 1,108 | 2,770 |
| | 2 | 652 | 1,304 | 3,260 |
| | 5 | 673 | 1,346 | 3,365 |
| 400 | 1 | 643 | 1,286 | 3,215 |
| | 2 | 671 | 1,342 | 3,355 |
| | 5 | 673 | 1,346 | 3,365 |
| maximum | | 673 | 1,346 | 3,365 |

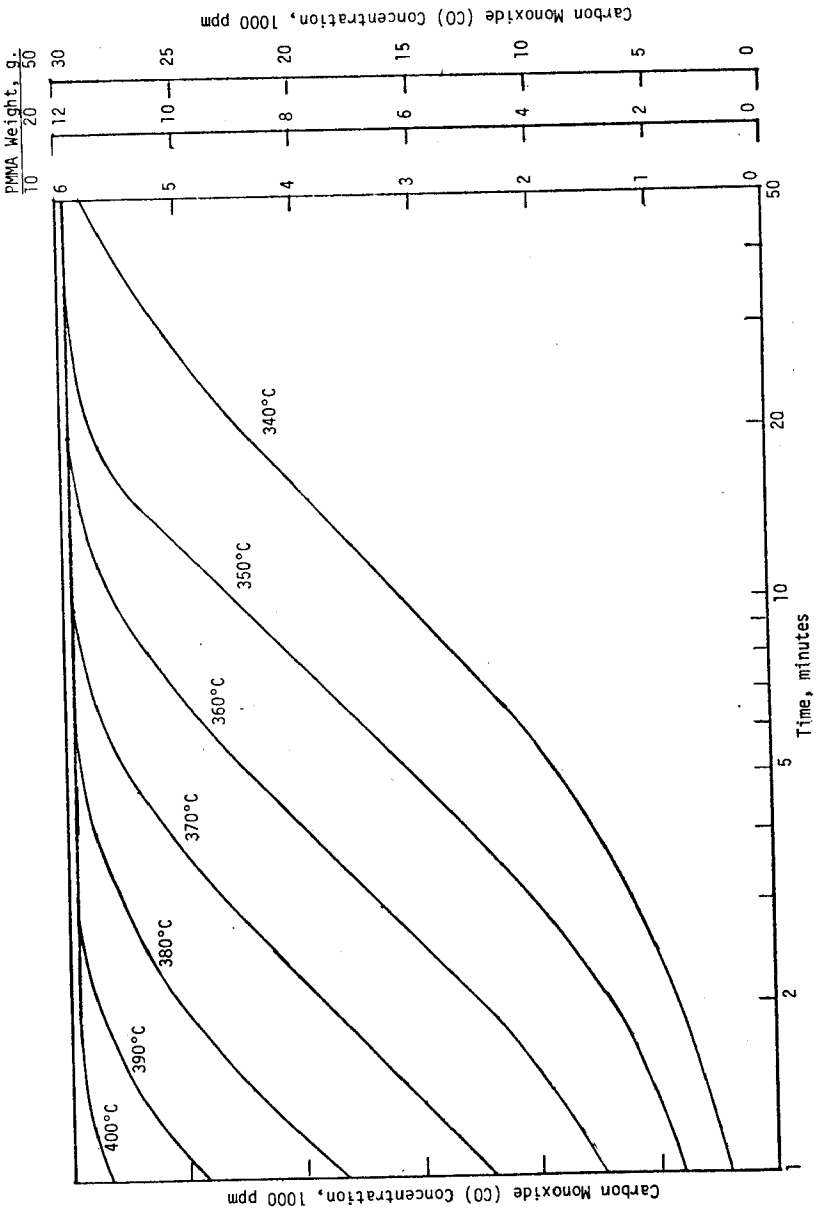


*Figure 1. Generation of Carbon Monoxide from Polymethyl Methacrylate (2:1 $O_2$/PMMA).*

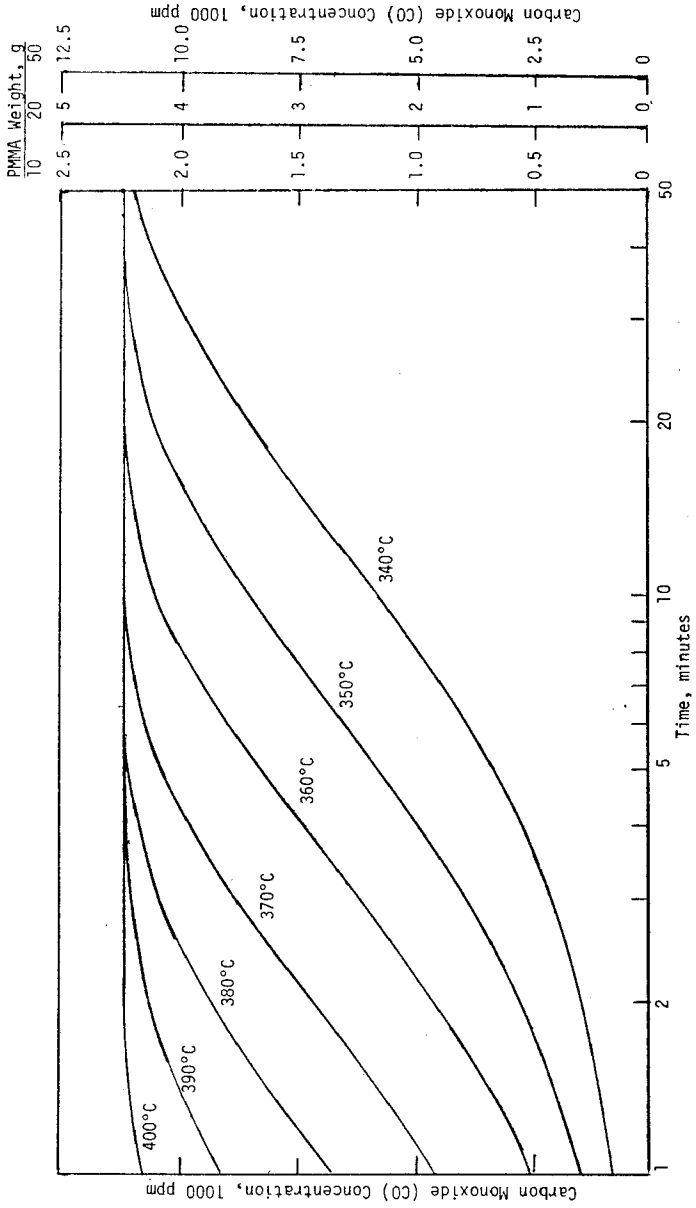


*Figure 2. Generation of Carbon Monoxide from Polymethyl Methacrylate (5:1 $O_2$/PMMA).*

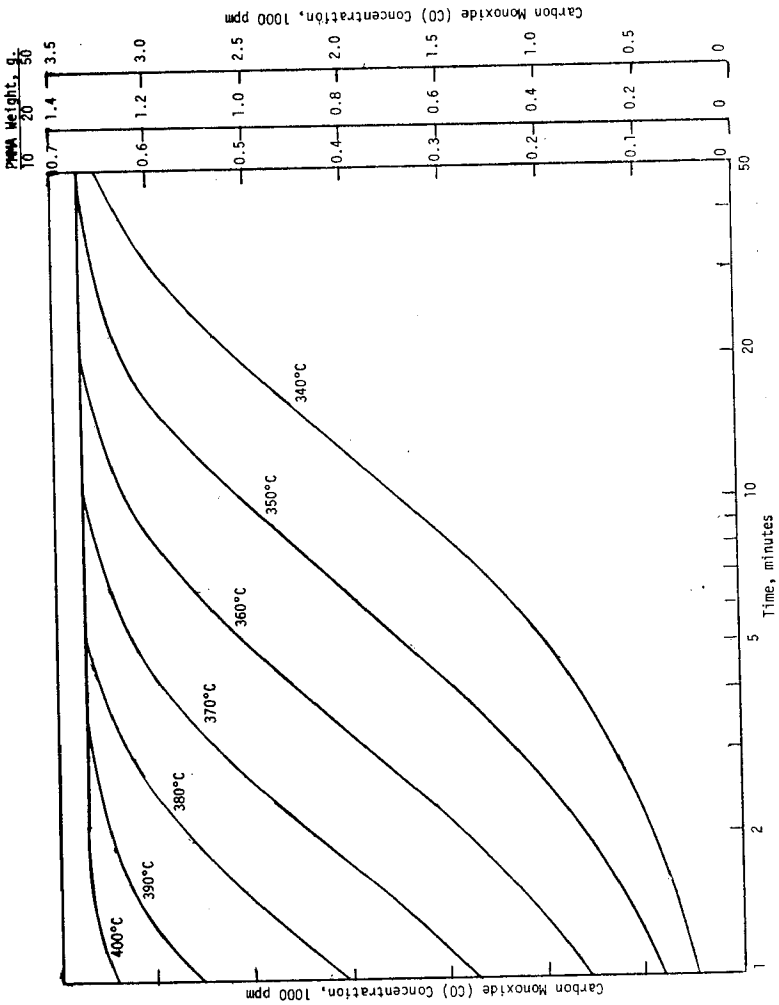


*Figure 3. Generation of Carbon Monoxide from Polymethyl Methacrylate (6:1 $O_2$/PMMA).*

reaches 3,000 ppm only with a 50 g quantity of PMMA. With increasing availability of oxygen the toxic threat decreases, but the temperature and hence the thermal threat increase.

## POLYETHYLENE

In the case of polyethylene, the situation is more complicated, at 600°C, there are four major volatile decomposition products, with 60 per cent of the volatile material being monomeric ethylene [3]. At lower temperatures there is a wide range of products with very little or no ethylene [2]. Nevertheless, we have carried out calculations for a model in which ethylene is the only decomposition product at all temperatures. The main effect of this assumption is to make the calculated equilibrium temperatures somewhat too high. The calculated equilibrium compositions (Table 5) will still reflect correctly the trend produced by the varying carbon/oxygen ratio. The rate constant for the pyrolysis of linear polyethylene was taken from the work of Wall [4].

The carbon monoxide concentrations produced in a 60 $ft^3$ closed compartment by the pyrolysis and burning of 10, 20, and 50 g quantities of polyethylene are shown in Tables 6 and 7 and in Figures 4 and 5.

The individual figures correspond to oxygen/polyethylene monomer ratios of 1:1 and 3:1. The temperatures are higher than in the case of PMMA, ranging from 470 to 530°C. Carbon monoxide concentrations are given as a function of time for polymer weights of 10, 20 and 50 g. The maximum CO concentrations in a 60 $ft^3$

*Table 5. Combustion of Polyethylene (PE) in Air.*

| Moles oxygen/mole PE monomer | 1 | 3 |
|---|---|---|
| Equilibrium composition (mole fractions) | | |
| carbon monoxide (CO) | 0.257 | 0.020 |
| carbon dioxide ($CO_2$) | 0.000 | 0.109 |
| water ($H_2O$) | 0.000 | 0.122 |
| hydrogen ($H_2$) | 0.257 | 0.004 |
| oxygen ($O_2$) | 0.000 | 0.009 |
| nitrogen ($N_2$) | 0.485 | 0.726 |
| hydroxyl (OH) | 0.000 | 0.004 |
| nitric oxide (NO) | 0.000 | 0.005 |
| Moles CO/mole PE monomer | 2.0 | 0.3 |
| Temperature, °K. | 1420 | 2370 |

*Table 6. Generation of Carbon Monoxide from Polyethylene Oxygen/PE Monomer Ratio 1:1 – Compartment Volume 60 ft³.*

| Temperature °C. | Time min | CO Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PE | 20 g PE | 50 g PE |
| 470 | 1 | 498 | 996 | 2,490 |
| | 2 | 969 | 1,938 | 4,845 |
| | 5 | 2,239 | 4,478 | 11,195 |
| | 10 | 3,951 | 7,902 | 19,755 |
| | 20 | 6,236 | 12,472 | 31,180 |
| | 50 | 8,785 | 17,570 | 43,925 |
| 480 | 1 | 931 | 1,862 | 4,655 |
| | 2 | 1,759 | 3,518 | 8,795 |
| | 5 | 3,809 | 7,618 | 19,045 |
| | 10 | 6,076 | 12,152 | 30,380 |
| | 20 | 8,230 | 16,460 | 41,150 |
| | 50 | 9,350 | 18,700 | 46,750 |
| 490 | 1 | 1,655 | 3,310 | 8,275 |
| | 2 | 3,019 | 6,038 | 15,095 |
| | 5 | 5,841 | 11,682 | 29,205 |
| | 10 | 8,051 | 16,102 | 40,255 |
| | 20 | 9,208 | 18,416 | 46,040 |
| | 50 | 9,406 | 18,812 | 47,030 |
| 500 | 1 | 2,822 | 5,644 | 14,110 |
| | 2 | 4,797 | 9,594 | 23,985 |
| | 5 | 7,826 | 15,652 | 39,130 |
| | 10 | 9,142 | 18,284 | 45,710 |
| | 20 | 9,397 | 18,794 | 46,985 |
| | 50 | 9,406 | 18,812 | 47,030 |
| 510 | 1 | 4,487 | 8,974 | 22,435 |
| | 2 | 6,829 | 13,658 | 34,145 |
| | 5 | 9,039 | 18,078 | 45,195 |
| | 10 | 9,387 | 18,774 | 46,935 |
| | 20 | 9,406 | 18,812 | 47,030 |
| 520 | 1 | 6,434 | 12,868 | 32,170 |
| | 2 | 8,465 | 16,930 | 42,325 |
| | 5 | 9,378 | 18,756 | 46,890 |
| | 10 | 9,406 | 18,812 | 47,030 |
| 530 | 1 | 8,174 | 16,348 | 40,870 |
| | 2 | 9,246 | 18,492 | 46,230 |
| | 5 | 9,406 | 18,812 | 47,030 |
| maximum | | 9,406 | 18,812 | 47,030 |

*Table 7. Generation of Carbon Monoxide from Polyethylene Oxygen/PE Monomer Ratio 3:1 — Compartment Volume 60 ft³.*

| Temperature °C. | Time min | CO Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PE | 20 g PE | 50 g PE |
| 470 | 1 | 75 | 150 | 375 |
| | 2 | 146 | 292 | 730 |
| | 5 | 336 | 672 | 1,680 |
| | 10 | 593 | 1,186 | 2,965 |
| | 20 | 936 | 1,872 | 4,680 |
| | 50 | 1,318 | 2,636 | 6,590 |
| 480 | 1 | 140 | 280 | 700 |
| | 2 | 264 | 528 | 1,320 |
| | 5 | 572 | 1,144 | 2,860 |
| | 10 | 912 | 1,824 | 4,560 |
| | 20 | 1,235 | 2,470 | 6,175 |
| | 50 | 1,403 | 2,806 | 7,015 |
| 490 | 1 | 249 | 498 | 1,245 |
| | 2 | 453 | 906 | 2,265 |
| | 5 | 876 | 1,752 | 4,380 |
| | 10 | 1,208 | 2,416 | 6,040 |
| | 20 | 1,382 | 2,764 | 6,910 |
| | 50 | 1,411 | 2,822 | 7,055 |
| 500 | 1 | 424 | 848 | 2,120 |
| | 2 | 720 | 1,440 | 3,600 |
| | 5 | 1,174 | 2,348 | 5,870 |
| | 10 | 1,372 | 2,744 | 6,860 |
| | 20 | 1,410 | 2,820 | 7,050 |
| | 50 | 1,411 | 2,822 | 7,055 |
| 510 | 1 | 673 | 1,346 | 3,365 |
| | 2 | 1,025 | 2,050 | 5,125 |
| | 5 | 1,356 | 2,712 | 6,780 |
| | 10 | 1,408 | 2,816 | 7,040 |
| | 20 | 1,411 | 2,822 | 7,055 |
| 520 | 1 | 965 | 1,930 | 4,825 |
| | 2 | 1,270 | 2,540 | 6,350 |
| | 5 | 1,407 | 2,814 | 7,035 |
| | 10 | 1,411 | 2,822 | 7,055 |
| 530 | 1 | 1,226 | 2,452 | 6,130 |
| | 2 | 1,387 | 2,774 | 6,935 |
| | 5 | 1,411 | 2,822 | 7,055 |
| maximum | | 1,411 | 2,822 | 7,055 |

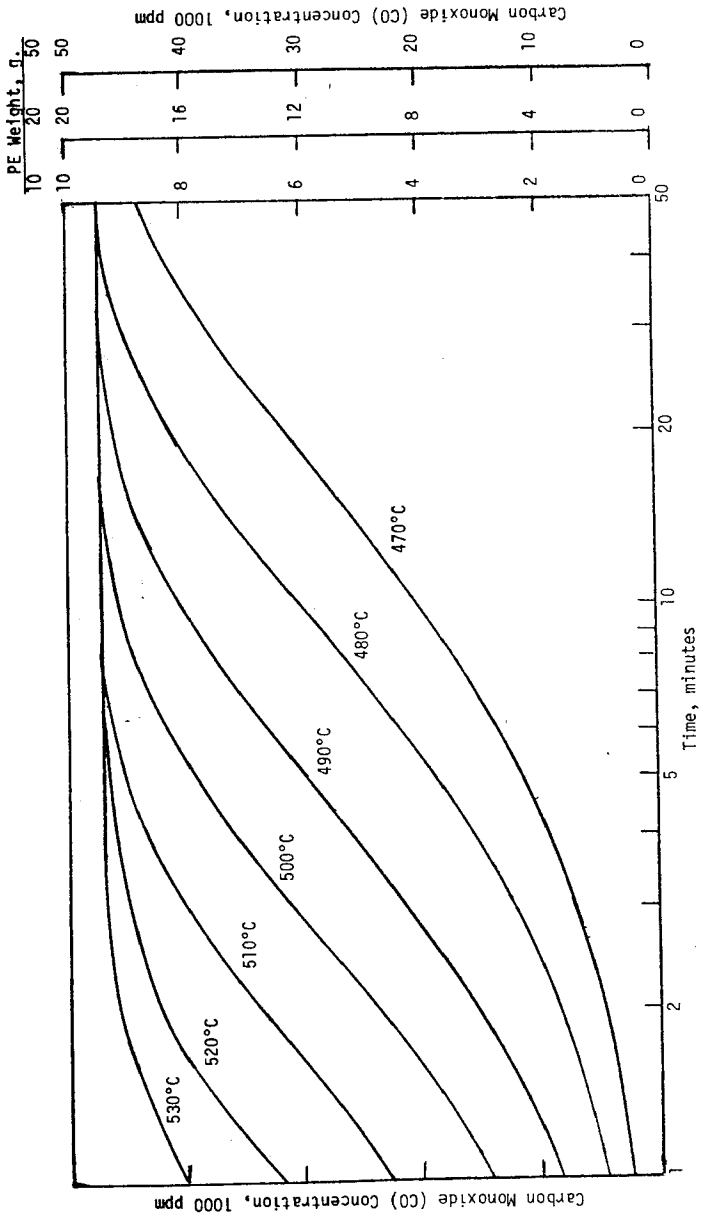


*Figure 4. Generation of Carbon Monoxide from Polyethylene (1:1 $O_2$/PE).*

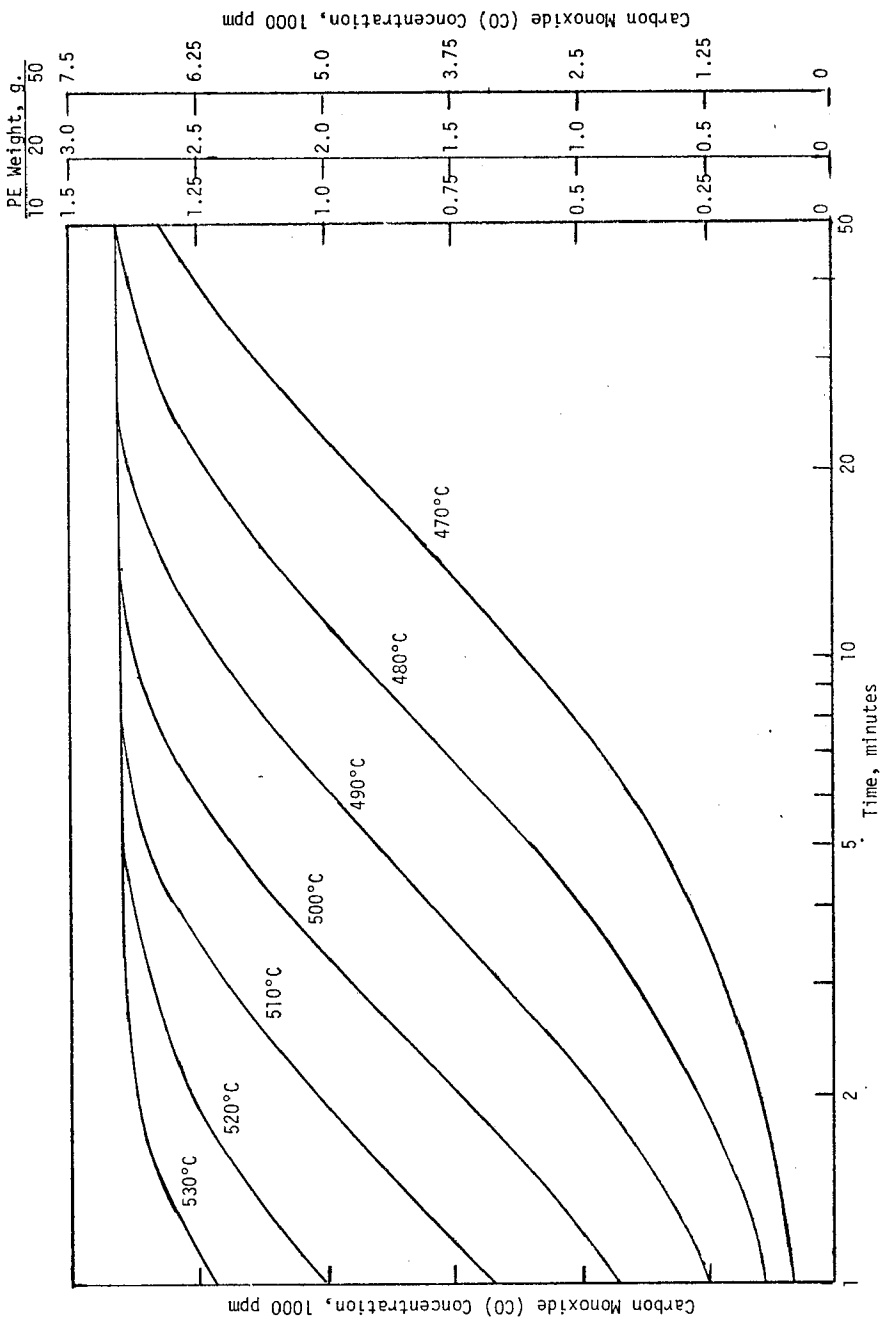


*Figure 5. Generation of Carbon Monoxide from Polyethylene (2:1 $O_2$/PE).*

*Table 8. Generation of Hydrogen Chloride from Polyvinyl Chloride: Compartment Volume 60 ft³.*

| Temperature °C. | Time min | HCl Concentration, ppm | | |
|---|---|---|---|---|
| | | 10 g PVC | 20 g PVC | 50 g PVC |
| 240 | 1 | 16.5 | 33 | 82.5 |
| | 2 | 33 | 66 | 165 |
| | 5 | 82.5 | 165 | 413 |
| | 10 | 165 | 330 | 825 |
| | 20 | 339.5 | 679 | 1,698 |
| | 50 | 1,382 | 2,764 | 6,910 |
| 250 | 1 | 30.2 | 60.5 | 151 |
| | 2 | 60.5 | 121 | 303 |
| | 5 | 151.5 | 303 | 758 |
| | 10 | 306 | 612 | 1,530 |
| | 20 | 751 | 1,502 | 3,755 |
| | 50 | 2,006 | 4,013 | 10,033 |
| 260 | 1 | 55 | 110 | 275 |
| | 2 | 110 | 220 | 550 |
| | 5 | 275 | 550 | 1,375 |
| | 10 | 588 | 1,177 | 2,943 |
| | 20 | 1,502 | 3,005 | 7,513 |
| | 50 | 2,108 | 4,216 | 10,540 |
| 270 | 1 | 96 | 192 | 480 |
| | 2 | 192 | 384 | 960 |
| | 5 | 481 | 962 | 2,405 |
| | 10 | 1,086 | 2,173 | 5,433 |
| | 20 | 2,004 | 4,009 | 10,023 |
| | 50 | 2,110 | 4,220 | 10,550 |
| 280 | 1 | 166.5 | 333 | 833 |
| | 2 | 333.5 | 667 | 1,668 |
| | 5 | 880 | 1,760 | 4,400 |
| | 10 | 1,794 | 3,587 | 8,968 |
| | 20 | 2,089 | 4,178 | 10,445 |
| | 50 | 2,110 | 4,220 | 10,550 |
| 290 | 1 | 280.5 | 561 | 1,403 |
| | 2 | 561 | 1,122 | 2,805 |
| | 5 | 1,473 | 2,946 | 7,365 |
| | 10 | 2,065 | 4,130 | 10,325 |
| | 20 | 2,110 | 4,220 | 10,550 |
| 300 | 1 | 470 | 939 | 2,348 |
| | 2 | 939 | 1,878 | 4,695 |
| | 5 | 1,938 | 3,877 | 9,692 |
| | 10 | 2,108 | 4,216 | 10,540 |
| | 20 | 2,110 | 4,220 | 10,550 |
| maximum | | 2,110 | 4,220 | 10,550 |

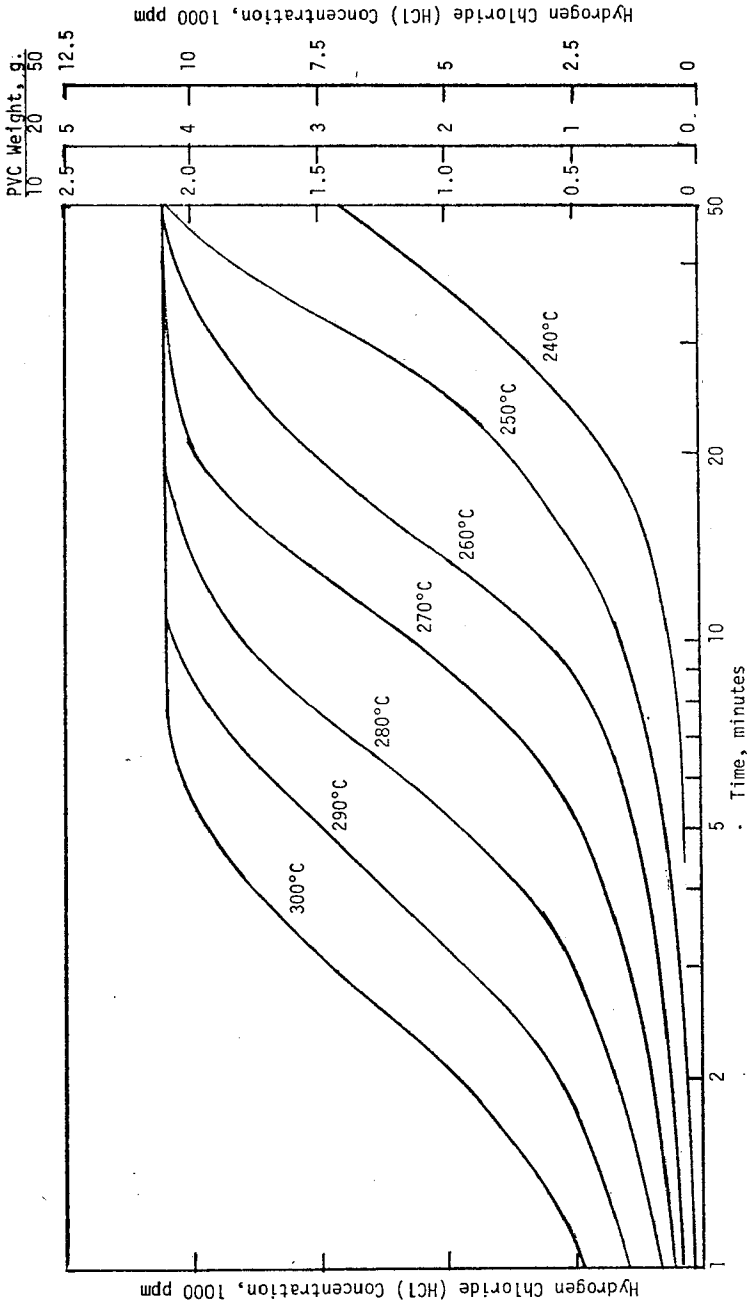


*Figure 6. Generation of Hydrogen Chloride from Polyvinyl Chloride.*

chamber produced by a 10 g quantity of polyethylene are about 9,400 ppm for the 1:1 ratio, and 1,400 ppm for the 3:1 ratio. In many respects, the behavior of polyethylene is analogous to that of PMMA. A similar pattern may be expected for any polymer which pyrolyzes to give volatile hydrocarbon products.

## POLYVINYL CHLORIDE

The behavior of polyvinyl chloride (PVC) differs from that of polymethyl methacrylate and polyethylene in that the toxic gas produced is hydrogen chloride instead of carbon monoxide, and pyrolysis alone is sufficient to produce the toxic gas without the necessity for combustion.

The hydrogen chloride (HCl) concentrations in a 60 $ft^3$ closed compartment produced by pyrolysis of PVC at temperatures ranging from 240 to 300°C are shown in Table 8 and in Figure 6. HCl concentrations are shown as a function of time for 10, 20, and 50 g quantities of PVC. The maximum possible HCl concentration produced by 10 g PVC is about 2,100 ppm.

The rate equations for the dehydrochlorination of PVC were taken from the work of Taliamini and Pezzin [5].

## CONCLUSIONS

Small differences in pyrolysis temperature in a temperature region that is critical for a particular polymer can result in substantial changes in toxic gas generation. This critical temperature is approximately 360°C for polymethyl methacrylate, 500°C for polyethylene, and 270°C for polyvinyl chloride.

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