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Experimental Toxicology of Pyrolysis and Combustion Hazards

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Data are presented on the acute toxicity (mortality only) of the thermal degradation products of polymers obtained by two methods of degradation. One system utilized a slowly increasing temperature (5°C/min) and gradual degradation of the polymer with the rats being exposed to degradation products as they were evolved. In this system the more toxic polymers included wool, polypropylene, poly(vinyl chloride), and urethane foam. The second system utilized conditions of rapid combustion and exposure of rats to the total products of combustion for a period of 4 hr. In this system the more toxic materials included red oak, cotton, acrylonitrile–butadiene–styrene (ABS), and styrene–acrylonitrile.

It is of interest to note that the natural product wool is among the least toxic under these rapid combustion conditions and among the most toxic under slow pyrolysis conditions. Other materials also vary in the comparative toxicity of their thermal degradation products, depending upon the conditions of degradation and animal exposure. The two experimental techniques presented here may well represent the two extreme conditions of rapid combustion versus slow pyrolysis. Intermediate types of fire situations might be expected to result in relative acute toxicities somewhere between these two extremes.

This report deals with acute toxicity on the basis of mortality data only and does not include other parameters of toxicity such as organ weights and histopathology.

The continued increase in the use of polymeric materials for the manufacture of commercial and household products has been associated with attempts to assess hazards arising from combustion of these materials. Such polymers are involved not only in home and industrial fires but are also present in waste burned in large-scale municipal incinerators. The toxicity of combustion products of plastics was studied by Berger et al. as early as 1947 (*1*). Since that time, a large number of publications have appeared concerning the toxicity of specific polymers using a variety of thermal degradation procedures (*2–6*). In reviewing these and other studies, it is quite apparent that each procedure for the thermal degradation of polymers and for the exposure of animals to degradation products is individually designed to simulate a different "real-life" situation proposed by the investigator. Thus, at the moment, no standard conditions have been developed for this kind of study. Although certain guidelines could perhaps be developed, it is unlikely that standard procedures will be adopted, and it is doubtful that such standardization would contribute materially to our understanding of this complex problem. Such a variety of factors will affect the rate of thermal decomposition as well as the nature of the products formed both in real life and laboratory situations, that at least for the time being, each such study must be evaluated individually. Factors which may affect the outcome of toxicological studies include the following: (1) the physical nature of the polymer (whether it is burned as a sheet, chunk, or powder); (2) conditions of pyrolysis with respect to the atmosphere (maximum oxy-

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gen supply, low oxygen supply, or nitrogen atmosphere); (3) heating conditions (rate of temperature increase, and whether or not flaming occurs); (4) dilution and cooling of the air stream (usually necessary in animal studies), which will in turn affect condensation of materials in the airstream and on the walls of the exposure chambers; (5) animal exposure techniques (animals completely within the exposure chamber, animals with only the nose in the pyrolysis airstream, length of exposure period); (6) animal species (mice, rats, guinea pigs, rabbits, or monkeys); (7) biological data taken (mortality data, tissue pathology, biochemical measurements, behavioral testing, or chemical analysis of tissues).

Any experimental procedure utilized to study the toxicity of pyrolysis products of polymeric materials is certain to be somewhat artificial. As a rule, the combustion products are cooled before animals are exposed, preventing the inhalation of hot gases. Although chamber air temperature may be elevated, it probably does not correspond well with ambient temperature in actual fire situations. Asphyxia, due to lack of oxygen, is usually prevented in experimental studies by the use of chambers of relatively large volume.

The present study is an attempt to accumulate comparative toxicity data for a number of polymeric materials. It is realized that such a study is markedly influenced by the factors previously discussed and that as a result such data must be examined primarily on a comparative basis. Two thermal degradation and animal exposure systems were utilized. One involves the slow thermal degradation of the polymer (dynamic chamber) and the second involves rapid combustion (static chamber).

Materials and Methods

The samples were obtained from an industrial source and represent commercial production of the polymeric materials. Samples utilized in this study represent basically the pure polymer without the addition of fire retardants. Natural materials including wool, cotton (unbleached muslin), and red oak were purchased from local sources. The only flame-retarded sample was the nylon 66 used in the blood thiocyanate studies.

Male Sprague-Dawley rats, weighing approximately 250 g, were utilized throughout the study. Animals were maintained on an *ad libitum* diet of commercial rat pellets and water except during the actual exposure period.

Static Chamber

Groups of animals (usually 15) were exposed to the combustion products of the sample in a 1500-liter stainless steel chamber. Polymers were subjected to combustion in a Vycor tube wrapped with resistance wire. Combustion temperature was usually reached in 1–2 min and elevated temperature (700°C) maintained for a total period of 6–10 min. At the end of this time only a relatively small ash usually remained. Animals were kept in the static chamber and exposed to the combustion products, both vapors and particulate matter, for a period of 4 hr. At the end of this time, the chamber was evacuated and the animals removed. Five animals were normally sacrificed immediately after exposure, and blood samples collected for carboxyhemoglobin determinations. Tissue samples were also taken at this time for histological examination. After an additional 24–36 hr, an additional five animals were sacrificed for blood and tissue studies. Seven days later the remaining five animals were sacrificed and examined for residual effects of the exposure. To determine the approximate LC_{50} for a particular polymer, groups of 15 animals were exposed in the static chamber to the combustion products of increasing quantities of the polymer being studied. These animals were observed for 7 days after exposure for the determination of delayed mortality.

Dynamic Chamber

In this system the sample was decomposed in a ceramic boat placed in a combustion furnace programmed for increasing temperature (5°C/min). This programming technique was previously described by Boettner and Weiss (*4*). Temperature was measured in the combustion boat by thermocouple and was found to reach a maximum of approximately 700°C after 140 min, at which time pyrolysis was essentially complete. During pyrolysis, 1 liter of air/min passed over the decomposing polymer. This pyrolysis airstream was cooled and diluted by the addition of 2 liters of air/min

prior to entry into the animal exposure chamber. The chamber used for exposure of animals to the thermal degradation products under these conditions was essentially a Pyrex glass tube with small side chambers constructed in such a manner that only the rat's nose was inserted into the airstream during the decomposition process.

The two exposure conditions described above were obviously quite different. In the static chamber the animals are exposed to the total products of combustion for a period of 4 hr. In the dynamic chamber system animals are exposed to the thermal degradation products only during the time in which they are being released from the polymer, since the airstream carries the gases past the exposed animal and out into the exhaust system. Thus, in the dynamic system animals may be exposed to a specific decomposition product for only a relatively short time. Another essential difference in the two systems is that in the static chamber when flaming occurs, volatile organics produced from the decomposing polymer are likely to be burned. In the dynamic exposure system the slow thermal decomposition of the polymer is normally not accompanied by flaming. Thus the animals are exposed to all of the gases released during degradation, in sequential order, whether they are combustible or not.

Concentrations of CO, HCl, HCN, and NO_x were monitored in both exposure chambers.

Results

The data presented here relate primarily to comparative mortality and to the effects of burning conditions on toxicity and related parameters.

Figure 1 shows the 0 to 100% mortality ranges in the static chamber for a series of polymers and natural products. The bottom of the bar represents the largest amount of material burned that produced zero mortality while the top of the bar represents the amount of material burned which produced 100% mortality. A discontinuity at the top of the bar indicates that 100% mortality had not been reached with the degradation of the largest amount of that material used. It may be noted, first of all, that there is considerable overlap in the mortality data. Two natural products, cotton and red oak, were the most toxic polymers

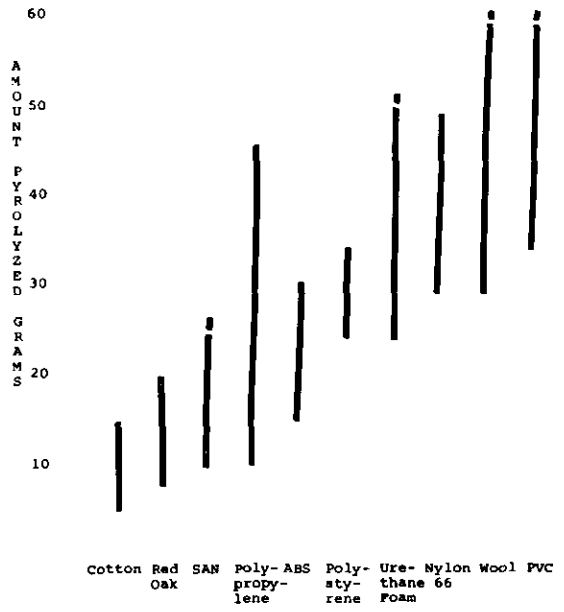

FIGURE 1. Zero to 100% mortality range in static chamber system. Bottom of the bar represents the largest amount burned which produced no deaths; top of bar is smallest amount which produced 100% mortality (15 rats per group).

when studied under static chamber conditions. With nylon, wool, and poly(vinyl chloride), no mortalities occurred in the static chamber when 30 g of the material was burned. Some of the possible reasons for the pattern of relative toxicity seen in this figure will be discussed in the subsequent section.

Figure 2 shows similar data indicating 0 to 100% mortality following the pyrolysis of varying amounts of polymers in the dynamic chamber system. The actual amounts burned here are considerably less than those used in the static chamber because of differences in procedure and the small size of the dynamic exposure system. The first obvious impression that one has with this data is that it appears to be largely the reverse of the toxicity data seen in Figure 1. Wool, which was among the least toxic materials in the static chamber system, appears to be the most toxic material when studied under dynamic chamber conditions of slow thermal decomposition. Similarly, the other two natural products, cotton and red oak, which were the most toxic materials in the static chamber, are now found to be among the less toxic polymers in the dynamic chamber. A similar but not so marked reversal of toxicity

Nylon, however, appears to be an exception, since it ranks among the least toxic polymers under both methods of decomposition and animal exposure.

The degradation of 10 g of polyurethane foam with and without flame in the static chamber resulted in high mortality under nonflaming conditions but no mortality under flaming conditions. This demonstrates quite clearly the importance of thermal degradation conditions on the overall toxicity of the products of combustion.

Since the production of cyanide from thermal decomposition of polyurethane foam could be an important factor in toxicity, a study of plasma thiocyanate levels under smoldering and flaming conditions is pertinent. It is interesting to note that with both polyurethane foam and nylon the major production of cyanide and the resulting elevated levels of plasma thiocyanate were found in animals exposed during flaming conditions of polymer degradation. Control and exposed animals had approximately the same plasma thiocyanate levels when the polymers were degraded under smoldering conditions.

It appears that under various conditions of thermal degradation of polymers there are many trade-offs in products of combustion versus toxicity. For example, under smoldering conditions with polyurethane foam, carbon monoxide production is greater than under flaming situations; however, cyanide production is less.

Although the exposure atmosphere may be extremely complex, these types of studies on the toxicity of thermal decomposition products of polymers may provide some information concerning the relative toxicity of a series of polymers and allow one to identify individual polymers which may have an unusually high toxicity. In addition, comparative data of this type may also aid in decisions concerning the appropriate use of fire retardants which in general tend to decrease flaming and increase smoldering of sample.

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