

### *Aerosol Production from Heated Polymers*

Certain aspects of polymer behavior can be observed with the aid of aerosol measuring instruments. For instance, the temperature at which a polymer emits fragments of itself whose aggregates can be detected as condensation nuclei has been measured. The phenomenon by which a polymer produces a condensation aerosol upon being heated is called thermoparticulate production (TP<sup>2</sup>).<sup>1</sup> The behavior of many polymers depends, in part, on the gaseous atmosphere surrounding the polymer. That the gaseous environment influences the thermal degradation of polymers is well known.<sup>2</sup> Investigators have usually chosen a simple inert atmosphere in studies of polymer degradation (e.g., high vacuum, helium, argon, or nitrogen). Some<sup>3-5</sup> have investigated the reactions of gases such as nitrogen dioxide (NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) with various polymers. Such investigations have led to information about the nature of the polymers. More generally, it is clear that the investigation of the interaction between the gaseous environment and various polymers will lead to a better understanding of both the gases and polymers used.

I have chosen to study the thermoparticulate interaction because of the great sensitivity of thermoparticulate analysis compared with other analytical techniques. Using the General Electric Condensation Nuclei Counter<sup>6</sup> (GECNC), the number concentration of condensation nuclei larger than 10<sup>-7</sup> cm radius can be continuously observed with a mass flow rate down to 10<sup>-14</sup> g/sec (10<sup>-9</sup> g/day). In contrast, spectroscopy in the UV, visible, and IR regions requires between micrograms and milligrams of sample.

The qualitative result that stimulated the pursuit of this Ph.D. research<sup>7</sup> is that the presence of certain gases will enhance the production of aerosol as a function of the identity and concentration of the reactant gas, the identity, thickness, and history of the polymer, the composition of the carrier, and the operating temperature.

There exist unusual conditions under which TP<sup>2</sup> is depressed, rather than enhanced, by the addition of carbon monoxide. The materials tested included polystyrene-2-ethylhexylacrylate (PS2EHA), poly(vinyl chloride) (PVC), and paraffin wax (PW). Combinations of nitrogen, oxygen, and water vapor were tested as carrier components in order to determine the carrier composition that maximized the enhancement of TP<sup>2</sup>. The reactant gases used in this study can be divided into two groups on the basis of optimum carrier composition. A simple nitrogen carrier was optimum for the enhancing effect of chlorine, nitrogen dioxide, ammonia, hydrogen sulfide, and ethylene, while a mixture of nitrogen and oxygen as carrier was optimum for the effect of carbon monoxide, sulfur dioxide, and nitric oxide.

The most effective gas in enhancing TP<sup>2</sup> (of those tested) was chlorine, which was also the most reactive gas tested. Among the three nitrogen oxides tested, NO<sub>2</sub>, NO, and N<sub>2</sub>O, the order of decreasing ability to enhance TP<sup>2</sup> was the same as the order of decreasing oxygen-to-nitrogen ratio in the gas molecules. For chlorine and ethylene concentrations ranging over about two orders of magnitude, there is a linear relationship between the logarithm of the signal-to-noise ratio and the logarithm of concentration. The wide range for the slope of this linear relation from experiment (0.4 to 3) surrounds the theoretically derived value of 1. The noise is the aerosol concentration produced thermally and the signal is the concentration with reactant gas enhancement. The duration of exposure of the reactant material to the reactant gas for durations between 1 and 10 sec has only a slight influence on the resulting signal-to-noise ratio for ethylene but a great influence for chlorine.

Paraffin wax requires less thermal energy for the onset of TP<sup>2</sup> compared to PS2EHA and PVC, probably because the short molecules of the former are more easily broken into fragments short enough to escape from the surface. Successive cycles of heating PW to the onset of TP<sup>2</sup> causes very little change in the onset temperature because of the

ability of the liquid PW to renew its surface continuously by convection. In contrast, the inability of PS2EHA to renew its surface yields an onset temperature that increases upon successive heating. As the weakest links are severed, more thermal energy is required to break the remaining links. PVC has a decrease of onset temperature for the first five heating cycles before it exhibits the same behavior as the PS2EHA. The initial decrease with PVC is probably due to the initial evolution of HCl.

The minimum detectable concentration of reactant gas parallels the variation of the onset temperature. When the average link (or bond) strength is low, less thermal energy is required to break links and the onset temperature is low. Also, it is easier for reactive gas molecules to break links, resulting in a low minimum detectable concentration (or high sensitivity).

Successive heating cycles can lead to greatly prolonged lifetime of the phenomenon of reactant gas-induced enhancement of TP<sup>2</sup>, where the lifetime of a reactant material is defined as the time interval during which the signal-to-noise ratio from a constant concentration of reactant gas exceeds 2.

From diffusion measurements, it is concluded that the thermally produced condensation nuclei have an equivalent diffusion radius larger than 0.1 micron, while the chlorine-produced nuclei have an equivalent diffusion radius about  $5 \times 10^{-3}$  micron. Both types of nuclei are uncharged.

Certain combinations of reactant gas, reactant material, and carrier composition depress TP<sup>2</sup> (i.e., signal-to-noise ratio less than unity). No tested explanation is available, but the reactant gas carbon monoxide that depressed TP<sup>2</sup> is the only reactant gas tested that could conceivably bind up broken polymer linkages with its carbonyl form.

The theory developed to explain TP<sup>2</sup> enhancement by reactant gases is based on chemical reaction between the reactant gas and reactant molecules at those links that have been most weakened by thermal agitation. Successive scissioning of the reactant molecules finally leads to molecular fragments short enough (and volatile enough) to escape from the reactant surface. These fragments aggregate to form the detected condensation nuclei.

It seems that the development of gas detectors can follow the more complete understanding and control of the phenomenon of the enhancement of TP<sup>2</sup> from a solid or liquid polymer by reactant gases. Also, thermoparticulate analysis may become more helpful to the analysis of materials, especially the analysis of polymers. Polymer chemists have the great problem of determining the best parameters for the characterization of polymers. The dependence of TP<sup>2</sup> on temperature, the gaseous environment, and the reactant polymer may lead to helpful polymer characterizations.

I thank the National Air Pollution Control Administration and State University of New York at Albany for fellowship support, the Office of Naval Research under Contract N 000-14-69-C-0043 for equipment, and Professor Volker A. Mohnen, Dr. Vincent J. Schaefer, and Dr. Douglas Bird for guidance.

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Received December 22, 1970

Revised February 19, 1971

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