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Effect of Ambient Oxygen Concentration on Thermal Decomposition of Organic Polymers

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INTRODUCTION

Organic polymers are used frequently in structures and transportation systems. To provide input to numerical models for hazard and vulnerability analyses involving fire environments, thermal decomposition of several organic polymers in atmospheres of nitrogen and atmospheres of varying concentrations of oxygen in nitrogen have been investigated using TGA-FTIR, GC-FTIR, DSC, and infrared microprobe. Results from earlier investigations of polymer decomposition in nitrogen atmospheres were used to determine decomposition mechanisms and to develop rate expressions for use in numerical simulations. Materials studied included poly(methyl methacrylate) (PMMA), poly(diallyl phthalate) (DAP), poly(vinyl chloride) (PVC), polycarbonate (PC), poly(phenylene sulphide) (PPS), several polyurethanes, and several epoxies.[1-5]

In fire environments with oxygen, polymer materials may provide fuel for sustaining the fire. In inert environments, polymer materials may be damaged catastrophically by the incident heat flux from an adjacent fire. Hazard and vulnerability analyses can involve a variety of scenarios in which oxygen may or may not be readily available to interact with thermally decomposing polymer materials. Therefore, in the work described below, the effect of oxygen concentration on thermal decomposition of the materials mentioned above, as well as additional materials, has been investigated. Experiments were done with samples in atmospheres of nitrogen, air, or intermediate mixtures of oxygen in nitrogen. Some initial results comparing decomposition of selected polymers in N_2 and air atmospheres were reported previously.[6]

EXPERIMENT

The experimental techniques used to examine thermal decomposition have been discussed in detail previously.[1-6] Most of the experimental data discussed below were obtained by thermal gravimetric analysis (TGA) with simultaneous evolved gas analysis by Fourier transform infrared spectroscopy (FTIR). The furnace purge gas exhaust from the TGA (TA Instruments Model 2950) was connected by a heated stainless steel transfer line to the TGA interface module of the FTIR spectrometer (Nicolet Magna 750). The purge gas was UHP nitrogen, air, or intermediate mixtures of UHP oxygen in UHP nitrogen flowing at 50 to 60 ml/min. The transfer line temperature was set at 300° C. The TGA-FTIR interface module in the auxiliary experiment compartment of the FTIR spectrometer also was maintained at 300° C. The spectrometer provided concurrent chemical analysis of evolved gases. Multiple spectra were collected and averaged over consecutive 30-second intervals to provide average spectra as a function of time. However, the spectra acquired represented the superposition of the spectra from all gas phase constituents. When multiple species contributed overlapping signals, the interpretation of spectra and identification of decomposition products was difficult.

Both differential scanning calorimetry (DSC) and simultaneous TGA-DSC (SDT) were used to examine enthalpy changes during decomposition. A TA instruments model 2920 DSC was used for temperature ranges from ambient to 600° C. A TA Instruments Q600 SDT was used for temperature ranges from 200 to 1200° C.

RESULTS

To varying degrees, the presence of oxygen appeared to alter the decomposition mechanisms in all of the materials studied. Generally, the initial stage of decomposition of each polymer in air proceeded similarly to the initial stage of decomposition in nitrogen. Small deviations between decomposition in nitrogen and air were noted with PMMA and DAP. However, with the exceptions of PMMA and PVC, decomposition of each polymer in air involved an intermediate stage in which oxygen appeared to react with the decomposing condensed phase to form a more thermally stable product. That product then decomposed slowly until the temperature increased sufficiently to substantially increase the rate of reaction between the condensed phase and oxygen. Samples were ultimately consumed by reaction with oxygen to form H_2O, CO, or CO_2. Such behavior was most pronounced with polymers that formed a substantial amount of carbonaceous char during decomposition in nitrogen atmospheres. In the case of polyurethanes, complete consumption did not occur until temperatures of 700° C or higher. Furthermore, experiments with dilute concentrations of O_2 in N_2 showed that formation of a transient thermally stable product and its subsequent reaction to gaseous products depended strongly on oxygen concentration in the purge gas in TGA-FTIR, DSC, and SDT experiments.

The effect of oxygen concentration is well illustrated by results from experiments with a rigid polyurethane (RPU) based on the polymeric form of methylene-4,4'diphenyl diisocyanate (PMDI) and polyhydroxy polyethers. The most pertinent results are summarized below.

Figure 1 shows residual mass ratio (ratio of instantaneous sample mass to initial sample mass) versus temperature from replicate TGA experiments that were done using a constant heating rate of 20° C/min. Results are shown from experiments using N_2, 1% O_2 (99% N2), 2% O_2 (98% N_2), or air as purge gas. Relative to experiments using N_2, the presence of O_2 had little effect on initial decomposition rates. However, an intermediate stage occurred in which oxygen appeared to react with the decomposing condensed phase to form a more thermally stable product having a much larger residual mass fraction than the char formed in experiments using nitrogen. Dilute concentrations of 1% and 2% oxygen also produce significant fractions of the intermediate thermally stable material. Ultimate reaction of the stable material to gaseous products is highly dependent on temperature and oxygen concentration in the purge gas.

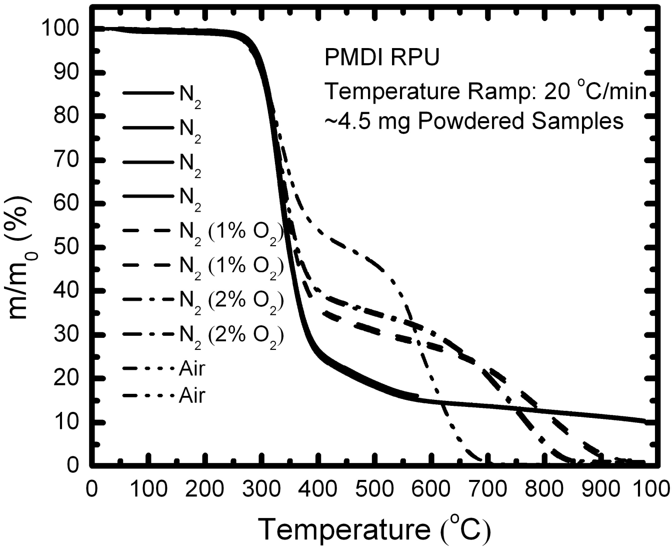

Figure 1. TGA results: residual mass ratio versus temperature.

Figure 2 shows rate of mass loss corresponding to one of the TGA experiments (Fig. 1) using N_2 purge gas and one of the experiments using air purge gas. Figure 3 shows the FTIR spectra corresponding to the maxima in the rate of mass loss results (Fig. 2) with N_2 and air purges at about 328° C. Figure 3 also shows the FTIR spectrum corresponding to the maximum at about 570° C in the air-purge results. The spectra at 328° C are similar. However, the large peak between about 2400 and 2100 cm^{-1} (due to overlapping CO_2 and isocyanate spectra) is relatively more intense in the spectrum obtained with air purge. The spectrum corresponding to about 570° C during the experiment with the air purge primarily shows a strong signal for CO_2 and a much weaker signal for CO.

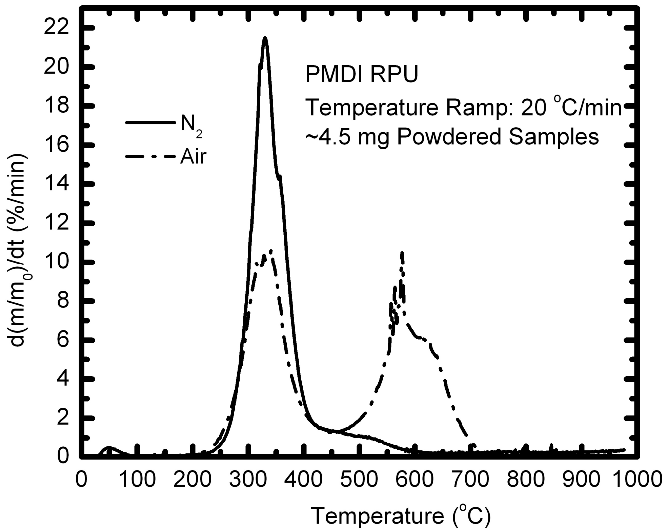

Figure 2. TGA Results: rate of mass loss versus temperature.

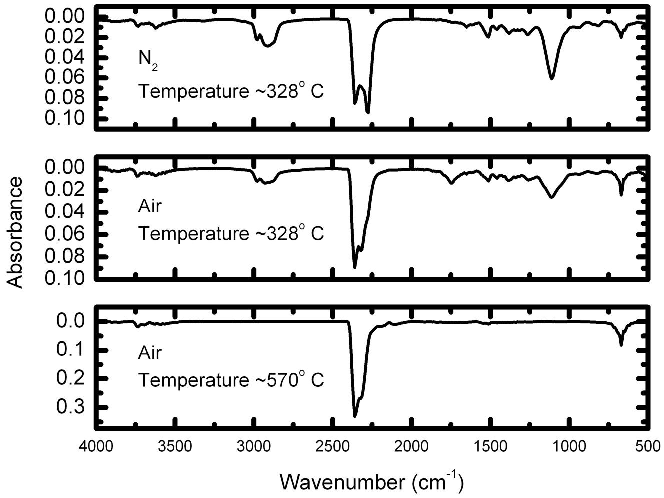

Figure 3. FTIR spectra corresponding to maxima in Fig. 2.

Figure 4 shows heat flow versus temperature from DSC and SDT experiments using N_2 or air for purge gas. DSC results obtained with N_2 for purge gas show endothermic behavior during decomposition. The DSC and SDT results obtained using air for purge show exothermic behavior during decomposition. Furthermore, as a function of oxygen concentration, the exothermic heat flow as a function of temperature appears to roughly correspond to the residual mass ratio (Fig. 1) as a function of temperature.

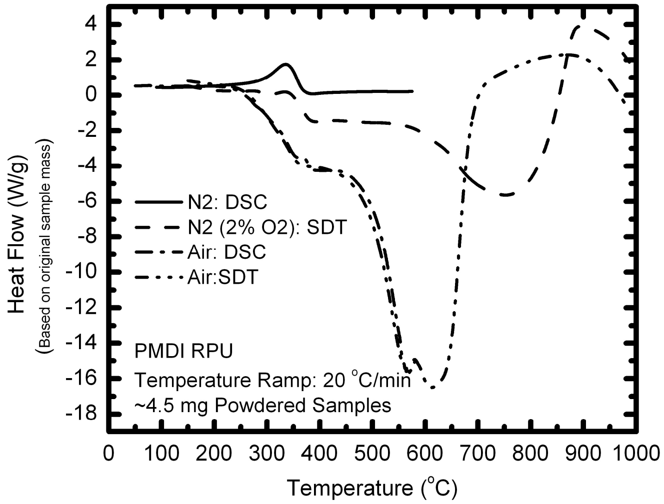

Figure 4. Heat flow (DSC and SDT) versus temperature.

DISCUSSION

To varying degrees, the presence of oxygen appeared to alter the decomposition mechanisms in all of the materials studied. Results from PMMA and DAP showed relatively little effect due to the presence of oxygen. However, results from materials that form significant char during decomposition in nitrogen showed much more significant effects. Decomposition mechanisms, particularly the formation of relatively thermally stable intermediate products, and subsequent reaction of those products to gaseous species depended strongly on temperature and oxygen concentration in the purge gas in TGA-FTIR, DSC, and SDT experiments.

With respect to system safety analyses, the extent to which chars or char-like materials form and subsequently react to gaseous products will depend on the availability of oxygen. Results indicate consistent decreases in the rate of char consumption as the oxygen concentration decreases and consistent decreases in alteration of decomposition mechanisms as the oxygen concentration decreases. Such trends are of interest in fire environments, since char layers can provide a resistance to heat transfer to the un-reacted polymer and can provide a resistance to mass transfer of decomposition products (fuel) to the vapor phase in a fire.

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