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# THERMAL DECOMPOSITION OF POLYMERS IN NITROGEN AND IN AIR*

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## ABSTRACT

To provide input to numerical models for hazard and vulnerability analyses, thermal decomposition of eight polymers has been examined in both nitrogen and air atmospheres. Experiments have been done with poly(methyl methacrylate), poly(diallyl phthalate), Norwegian spruce, poly(vinyl chloride), polycarbonate, poly(phenylene sulphide), and two polyurethanes. Polymers that formed a substantial amount of carbonaceous char during decomposition in a nitrogen atmosphere were completely consumed in an air atmosphere. However, in the case of polyurethanes, complete consumption did not occur until temperatures of $700^{\circ}$ C or higher. Furthermore, to varying degrees, the presence of oxygen appeared to alter the decomposition processes in all of the materials studied.

KEY WORDS: Thermal Analysis, Degradation, Polymer

## 1. INTRODUCTION

Organic polymer materials are used frequently in structures and transportation systems. Polymer materials may provide fuel for a fire or be damaged catastrophically by an incident heat flux. To provide input to numerical models for hazard and vulnerability analyses, thermal decomposition of several organic polymers is being investigated using a variety of experimental techniques. These include TGA-FTIR, GC-FTIR, infrared microprobe (IRMP), and DSC. 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, thermal decomposition of several polymers has been examined in both nitrogen and air atmospheres.

The role of polymer decomposition in fire dynamics was discussed by Drysdale (1). Applications of thermal decomposition in fire analyses involving polymer materials in an air environment were discussed by Nicolette, et al (2) and Vembe, et al (3). Applications of thermal decomposition in systems safety analyses involving polymer materials in a nitrogen environment were discussed by Erickson, et al (4), Sun, et al (5), Hobbs, et al (6), and Chu, et al (7).

This paper discusses results from experiments, involving nitrogen or air atmospheres, that have been done with eight polymers: poly(methyl methacrylate) (PMMA), poly(diallyl phthalate)

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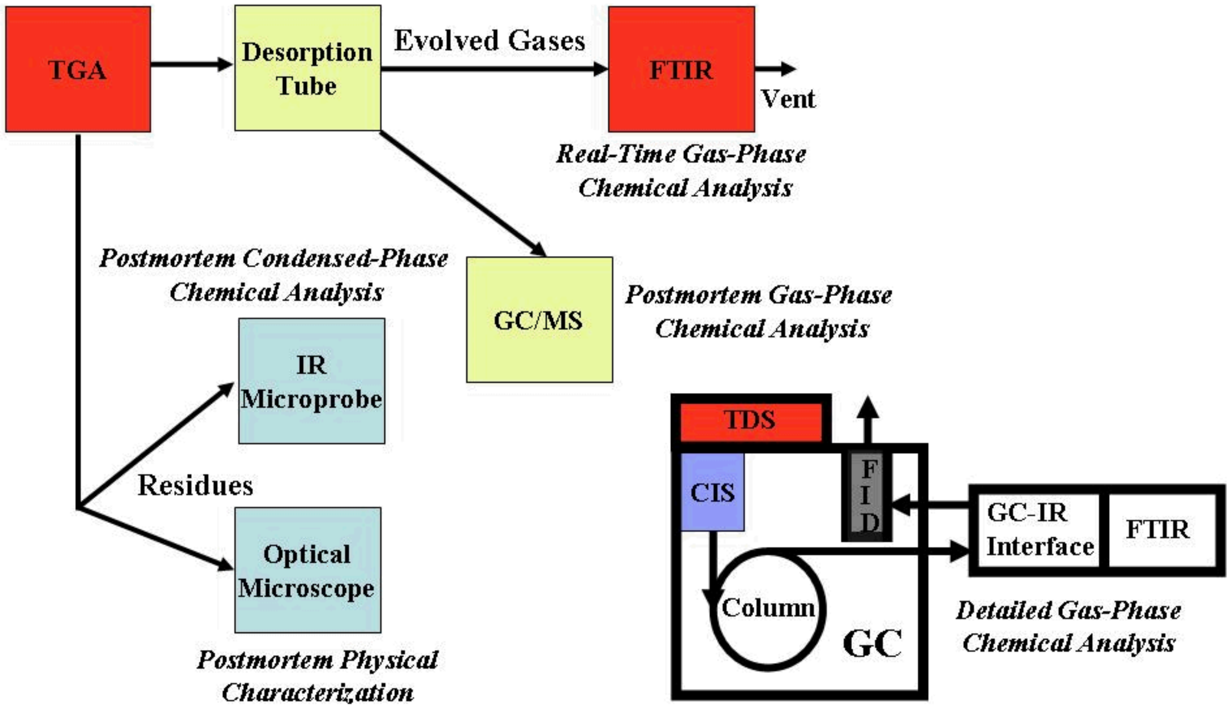
(DAP) with glass fiber reinforcing, Norwegian spruce, poly(vinyl chloride) (PVC), the polycarbonate Lexan®, the poly(phenylene sulphide) Fortron®, and two polyurethanes. One polyurethane (denoted by MDI RPU) was based on methylene-4,4'diphenyl diisocyanate (MDI) and polyhydroxy polyethers. The other polyurethane (denoted by PMDI RPU) was based on polymeric diisocyanate (PMDI) and polyhydroxy polyethers. The experimental techniques are described first. Then results from TGA experiments with each of the materials in nitrogen or air atmospheres are discussed and compared. Results from complementary FTIR and GC-FTIR experiments are briefly summarized. Inclusion of a complete discussion of the FTIR and GC-FTIR results is beyond the scope of this paper and is deferred to a later publication. Furthermore, thermal decomposition of PMMA in nitrogen atmospheres was previously discussed in detail (2), and thermal decomposition of DAP, Fortron®, MDI RPU, and PMDI RPU in nitrogen atmospheres was discussed in detail by Erickson (8-10).

## 2. EXPERIMENT

Much of the experimental data for thermal decomposition were obtained using a thermal gravimetric analyzer (TGA) as shown schematically in Figure 1a.



(a) (b)

Fig. 1. Schematic diagram of TGA-FTIR analysis and complementary methods: (a) TGA-FTIR and (b) TDS-GC-FTIR.

The furnace purge gas exhaust of the TGA (TA Instruments Model 2950) was usually connected by a heated stainless steel transfer line to the TGA interface module of the Fourier transform infrared (FTIR) spectrometer (Nicolet Magna 750). The purge gas was UHP nitrogen or house air 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. The spectra acquired represented the superposition of the spectra from all of the gas phase constituents. When multiple species contribute overlapping signals, the interpretation of spectra and identification of decomposition products is difficult.

To obtain additional gas phase analyses, the technique illustrated schematically in Figure 1b was used. A thermal desorption system, TDS (Gerstel TDS 4), served as a small, temperature-programmable tube furnace. Samples were placed in an aluminum boat that was placed in an empty desorption tube in the TDS. As the sample was heated, the decomposition products were removed by the carrier gas, UHP helium, and were quenched and retained in the cryogenic injection system, CIS (Gerstel CIS 2). After sample heating was complete, the CIS was rapidly heated (12° C/s), and the decomposition products were injected onto the capillary column of the gas chromatograph. Carrier gas was monitored in the GC-IR interface module, and FTIR spectra were collected similarly to the TGA-FTIR experiments. However, spectra were averaged over shorter, 3- to 6-second, intervals. From the GC-IR interface, the carrier gas flowed through the flame ionization detector (FID) and was then vented.

The TGA-FTIR experiments discussed below were done with small, about 4- to 5-mg, samples that were heated in an unconfined sample pan configuration. The unconfined configuration consisted of samples in open platinum pans and was used to examine initial decomposition mechanisms under conditions that minimize effects of mass transfer and reversible and secondary reactions. Samples of PMMA, DAP, Lexan®, MDI RPU, and PMDI RPU were powders prepared by grinding or filing. Samples of PVC, Fortron®, and Norwegian spruce were thin wafers.

In previous work (8-10) involving nitrogen atmospheres, a partially confined sample configuration also was used. This configuration consisted of sealed hermetic aluminum pans (TA Instruments) having lids with circular orifices as small as 60 μm and was used to examine the effects of any reversible or secondary reactions that would result from limiting mass transfer of the decomposition products away from the sample. On occasion, residues from the experiments were examined with the infrared microprobe (IRMP) and optical microscopy. Also, an alternative technique (Figure 1a) based on desorption tube sampling and subsequent GC-mass spectrometry analysis was used.

## 3. RESULTS

Results from the TGA experiments discussed below were all obtained using a constant heating rate of 20° C/min. The duration of the experiment depended on the thermal stability of the polymer. At least two replicate experiments with each polymer were done in nitrogen and in air.

TGA results from PMMA are shown in Figure 2. The fraction (%) of the initial sample remaining ($m/m_0$) is shown as a function of temperature. The rate of mass loss (%/min), or derivative curve [$d(m/m_0)/dt$ versus temperature] for selected samples in nitrogen and in air atmospheres are shown in Figs. 3a and 3b, respectively.

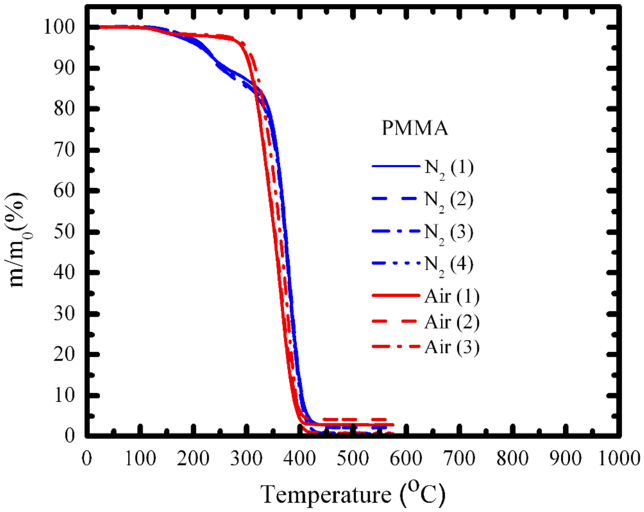
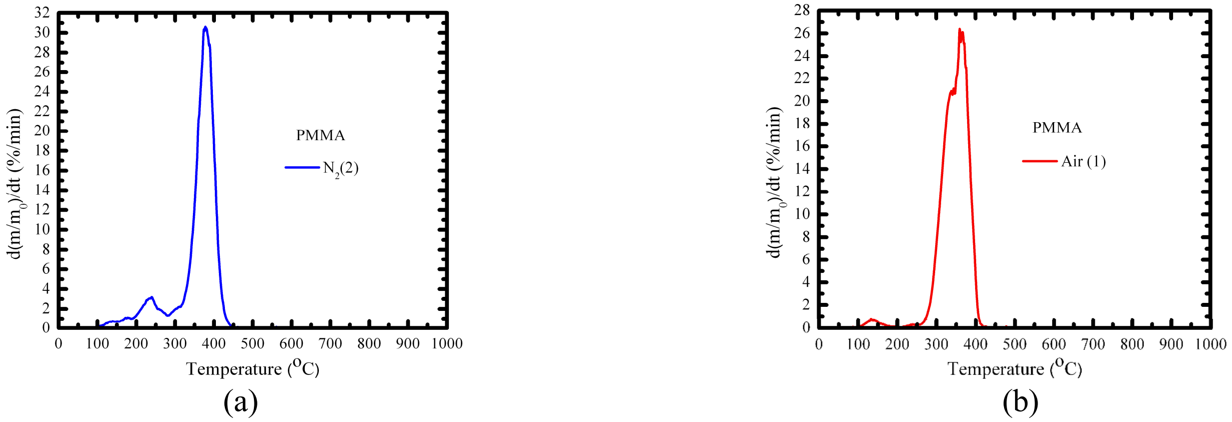


Fig. 2. Results from replicate TGA experiments with PMMA samples heated in nitrogen or air.



(a)

(b)

Fig. 3. Rate of mass loss from PMMA samples heated in (a) nitrogen or (b) air.

PMMA is a chain polymer and did not form appreciable char during decomposition in nitrogen atmospheres. FTIR spectra collected during TGA experiments and results from TDS-GC-FTIR experiments indicated that methyl methacrylate was the only major decomposition product (2) corresponding to the peaks in Fig. 3a. In air atmospheres, initial decomposition occurred at higher temperatures than in nitrogen. However, most decomposition occurred at slightly lower temperatures than in nitrogen atmospheres. FTIR spectra collected during TGA experiments indicated that a change occurred in the decomposition products corresponding to the large peaks in Figs. 3a and 3b. During decomposition in air (Fig. 3b), a substantial amount of $CO_2$ evolved, as well as methyl methacrylate. The FTIR spectra further indicated that methacrylate products other than methyl methacrylate may have formed.

TGA results from DAP are shown in Figs. 4 and 5. DAP is a highly cross-linked, highly aromatic polymer, which did not form appreciable char during decomposition in nitrogen atmospheres. The residue apparent in Fig. 4 is due to glass fiber reinforcing in the material studied. FTIR spectra collected during TGA experiments and results from TDS-GC-FTIR experiments indicated that phthalic anhydride was the primary decomposition product (9, 10) corresponding to the peak in Fig. 5a. During decomposition in air atmospheres, the rate of decomposition was somewhat faster relative to that in nitrogen until the value of $m/m_0$ was about 60% at 388° C. Decomposition of the remaining DAP was much slower than in nitrogen. FTIR spectra collected during TGA experiments indicated that for temperatures up to 400° C, phthalic anhydride was still the major decomposition product corresponding to the large peak in Fig 5b, but significant amounts of $H_2O$, CO, and $CO_2$ also evolved. At temperatures above 400° C, decomposition products were primarily $H_2O$, CO, and CO2, corresponding to the small peak in Fig. 5b.

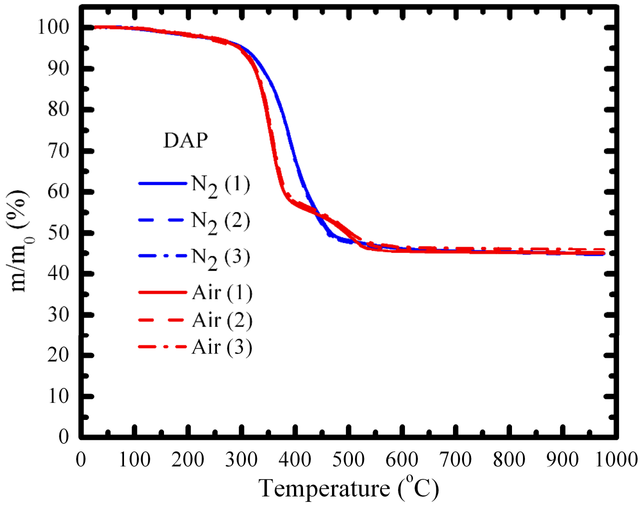
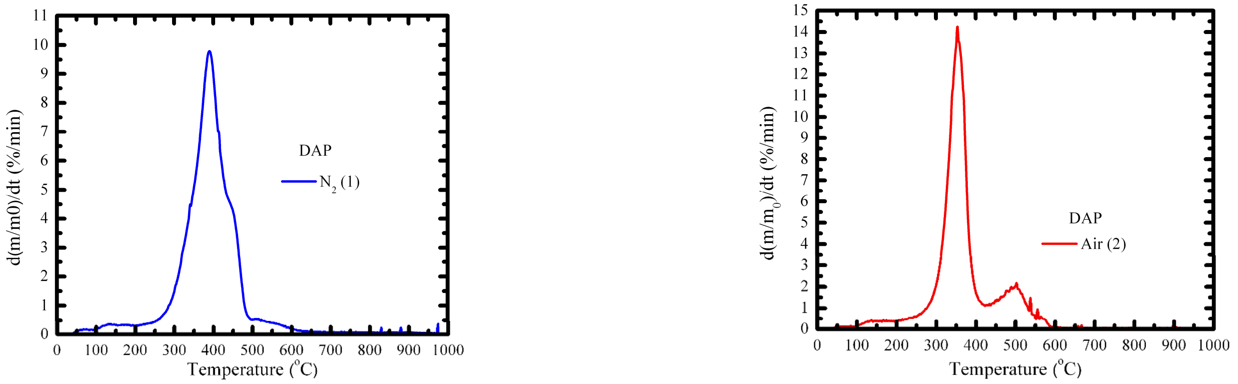


Fig. 4. Results from replicate TGA experiments with DAP samples heated in nitrogen or air.



(a)

(b)

Fig. 5. Rate of mass loss from DAP samples heated in (a) nitrogen or (b) air.

TGA results from PVC are shown in Figs. 6 and 7. PVC is a chain polymer, which formed carbonaceous char during decomposition in nitrogen atmospheres. Initial decomposition between temperatures of about 300° C and 320° C was rapid, corresponding to the left peak in Fig. 7a. The rate of decomposition slowed dramatically when $m/m_0$ reached about 40% at 370° C, and did not increase appreciably until temperatures of about 450° C. From about 450° C to 520° C, decomposition was relatively rapid, corresponding to the right peak in Fig. 7a. Above 520° C, the char that formed decomposed slowly. FTIR spectra collected during TGA experiments indicated that during initial decomposition, corresponding to the left peak in Fig.7a, the primary decomposition product was HCl. During subsequent decomposition, corresponding to the right peak in Fig 7a, the primary decomposition products were unsaturated hydrocarbons. In air atmospheres, the rate of decomposition was relatively similar to that in nitrogen, except that decomposition continued at temperatures above 520° C, and most of the sample was consumed. The residue appeared to be from additives in the PVC. FTIR spectra collected during TGA experiments indicated that during initial decomposition corresponding to the left peak in Fig.7b, the primary decomposition product was again HCL. During subsequent decomposition corresponding to the broad right peak in Fig 7b, the primary decomposition product was $CO_2$.

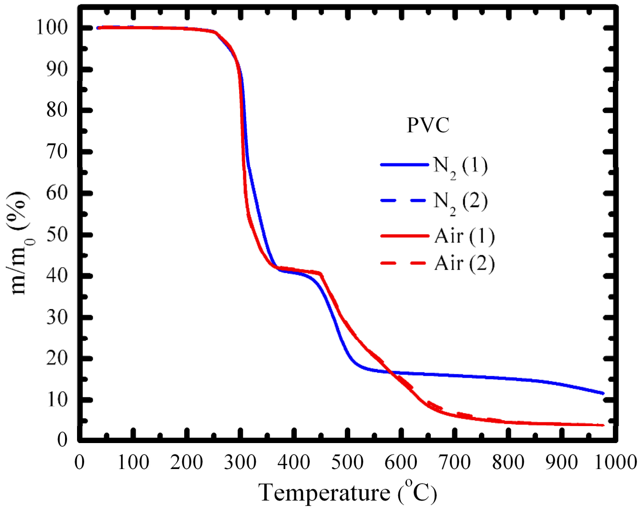
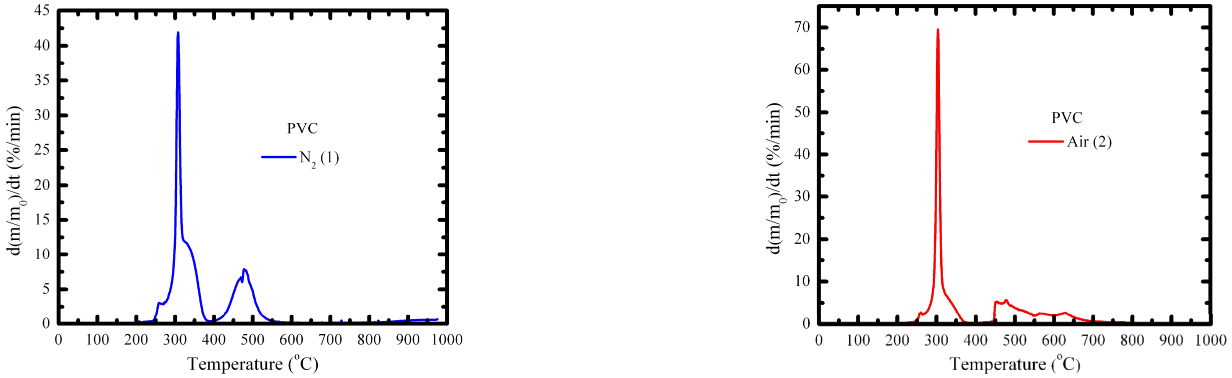


Fig. 6. Results from replicate TGA experiments with PVC heated in nitrogen or air.



(a) (b)

Fig. 7. Rate of mass loss from PVC samples heated in (a) nitrogen or (b) air.

TGA results from Norwegian spruce are shown in Figs. 8 and 9. Norwegian spruce is essentially a composite material consisting of chain polymers that are composed of aliphatic rings. Norwegian spruce formed significant char during decomposition in nitrogen atmospheres, as indicated by the slow decomposition that occurs between 400° C and 1000° C (Fig. 8). FTIR spectra collected during TGA experiments and results from TDS-GC-FTIR experiments indicated that the primary decomposition products, corresponding to the large peak in Fig. 9a, were low molecular weight carbonyl compounds and small amounts of $H_2O$, CO, and $CO_2$. During decomposition in air, the rate of decomposition was somewhat faster relative to that in nitrogen until the value of $m/m_0$ was about 30% at 370° C. The decomposition rate became significantly slower between about 370° C and 450° C. Above 450° C, the decomposition rate increased rapidly. FTIR spectra collected during TGA experiments indicated that for temperatures up to 400° C, corresponding to the left peak in Fig 9b, $H_2O$, CO, and $CO_2$ were the major decomposition products. Formaldehyde was also observed. At temperatures above 450° C, corresponding to the right peak in Fig 7b, the primary decomposition product was $CO_2$.

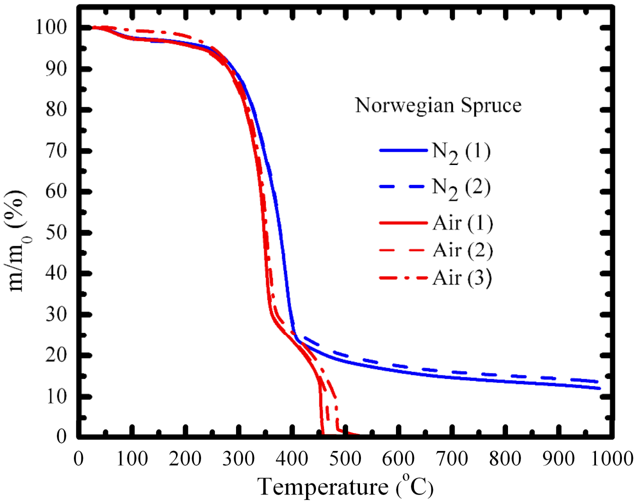
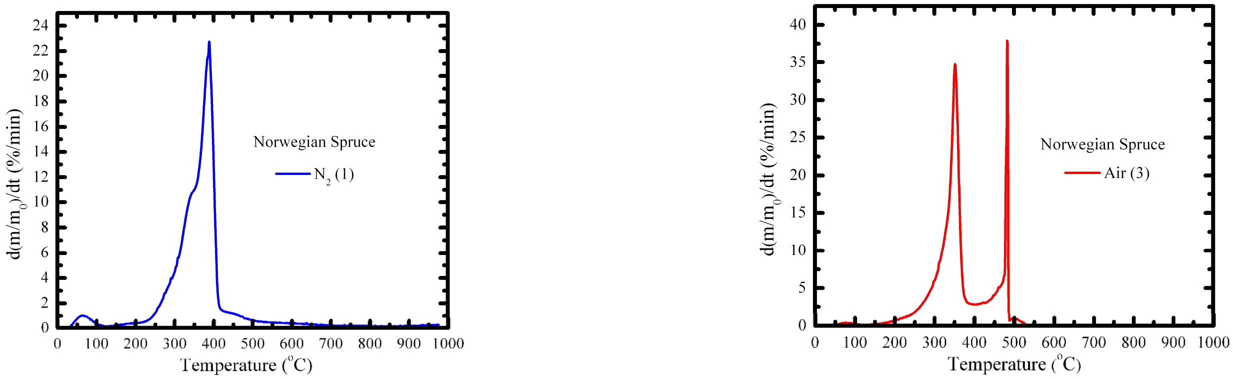


Fig. 8. Results from replicate TGA experiments with Norwegian spruce samples heated in nitrogen or air.



(a)

(b)

Fig. 9. Rate of mass loss from Norwegian spruce samples heated in (a) nitrogen or (b) air.

TGA results from Lexan® are shown in Figs. 10 and 11. Lexan® is a chain polymer containing aromatic rings. Lexan® formed significant amounts of char during decomposition in nitrogen atmospheres. Most decomposition occurred between 400° C and 550° C. The rate of decomposition slowed between 550° C and 600° C where $m/m_0$ reached a value of about 20%. FTIR spectra collected during TGA experiments indicated that major decomposition products were CO, $CO_2$, and phenolic compounds including bisphenol A. In air atmospheres, the rate of decomposition was very similar to that in nitrogen until $m/m_0$ reached a value of about 35% at 490° C. The rate of decomposition was somewhat slower between about 490° C and 550° C. At temperatures above 550° C, the rate of decomposition increased, and the sample was consumed. FTIR spectra collected during TGA experiments indicated that between 400° C and 500° C, corresponding to the first peak in Fig 11b, the major decomposition products were also CO, $CO_2$, and phenolic compounds including bisphenol A. However, $CO_2$ was more abundant than during decomposition in nitrogen. Between 500° C and 600° C, corresponding to the right peak in Fig. 11b, the only major decomposition product was $CO_2$.

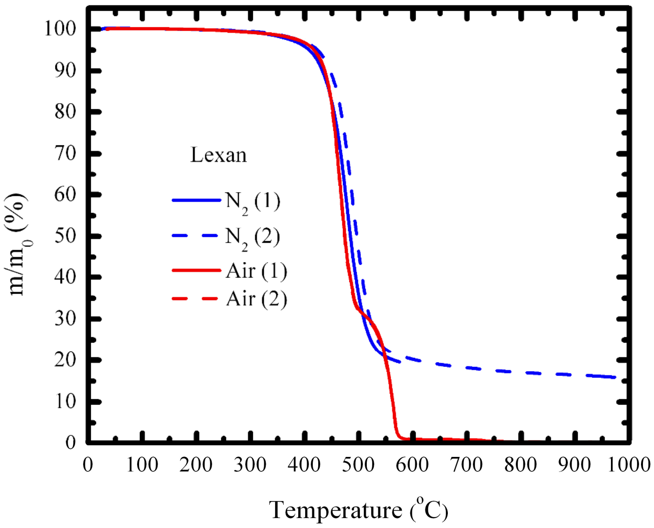
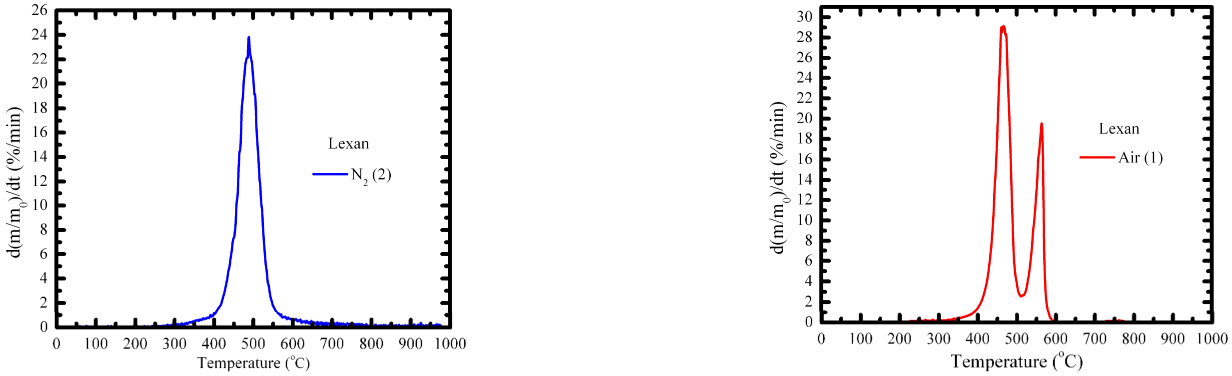


Fig. 10. Results from replicate TGA experiments with Lexan® samples heated in nitrogen or air.



(a) (b)

Fig. 11. Rate of Mass loss from Lexan® samples heated in (a) nitrogen or (b) air.

TGA results from Fortron® are shown in Figs. 12 and 13. Fortron® is a chain polymer containing aromatic rings. Fortron® formed significant amounts of char during decomposition in nitrogen atmospheres. Most decomposition occurred between 500° C and 580° C. The rate of decomposition slowed substantially as $m/m_0$ approached a value of about 40% at a temperature of about 580$^o$ C. FTIR spectra collected during TGA experiments indicated that the major decomposition products were phenylene sulfides. In air atmospheres, the rate of decomposition was almost identical to that in nitrogen until $m/m_0$ reached a value of about 60% at 550$^o$ C, where the rate of decomposition decreased. The rate of decomposition then increased as $m/m_0$ approached a value of about 50% at 600$^o$ C, and the sample was consumed as temperature increased. FTIR spectra collected during TGA experiments indicated that between 500$^o$ C and 550$^o$ C, corresponding to the left peak in Fig 13b, the major decomposition products were CO, $CO_2$, $SO_2$, and aromatic hydrocarbons. Between 600$^o$ C and 700$^o$ C, corresponding to the right peak in Fig. 11b, primary decomposition products were $CO_2$ (much more abundant) and $SO_2$.

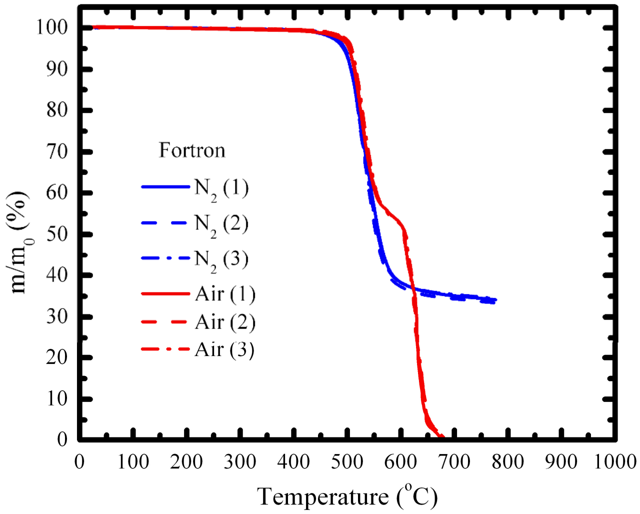
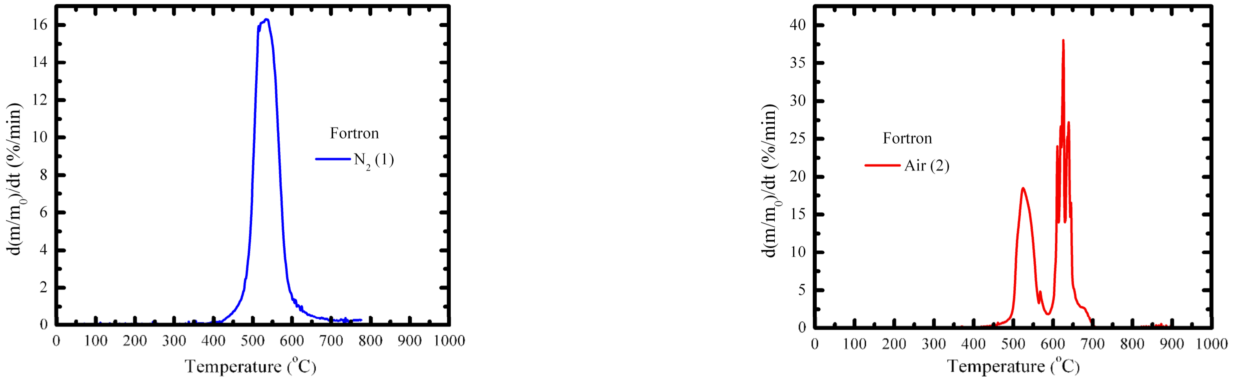


Fig. 12. Results from replicate TGA experiments with Fortron samples in nitrogen or air.



(a) (b)

Fig. 13. Rate of mass loss from Fortron samples heated in (a) nitrogen or (b) air.

TGA results from MDI RPU are shown in Figs. 14 and 15. MDI RPU is a cross-linked polymer containing aromatic rings. MDI RPU formed significant amounts of char during decomposition in nitrogen atmospheres. Decomposition occurred relatively rapidly between 250$^o$ C and 345$^o$ C. As $m/m_0$ approached a value of about 40% at 330$^o$ C, the rate of decomposition gradually decreased until $m/m_0$ approached about 20% at 600$^o$ C. Above 600$^o$ C, the char that had formed decomposed slowly. FTIR spectra collected during TGA experiments and TDS-GC-FTIR experiments indicated that the major decomposition products were isocyanates, $CO_2$, polyether fragments, and analines (8-10). In air atmospheres, decomposition proceeded almost identically to that in nitrogen until $m/m_0$ approached a value of about 60% at 325$^o$ C. The rate of decomposition then decreased, and relatively little decomposition occurred until $m/m_0$ approached a value of about 45% at 500$^o$ C. The rate of decomposition then increased, and decomposition proceeded more rapidly until $m/m_0$ approached a value of about 15% at 625$^o$ C. Decomposition then proceeded gradually until the sample was consumed at about 850$^o$ C. FTIR spectra collected during TGA experiments indicated that between 250$^o$ C and 345$^o$ C, corresponding to the left peak in Fig 15b, decomposition products were primarily $CO_2$ and polyether fragments. Isocyanates also appeared to evolve. At higher temperatures, corresponding to the center and right peaks in Fig. 15b, decomposition products were primarily CO and $CO_2$.

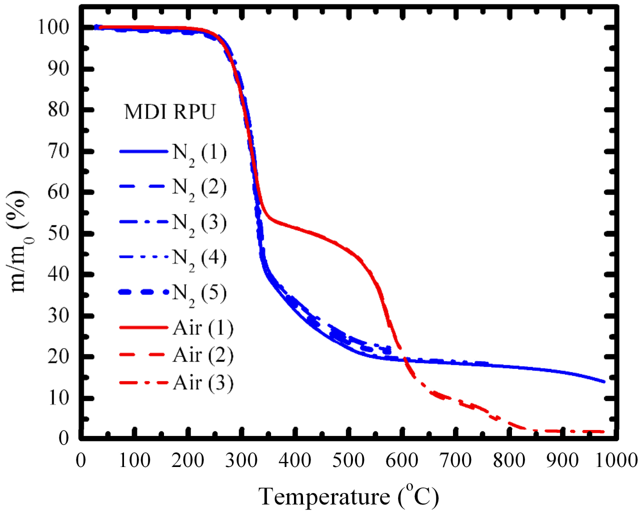
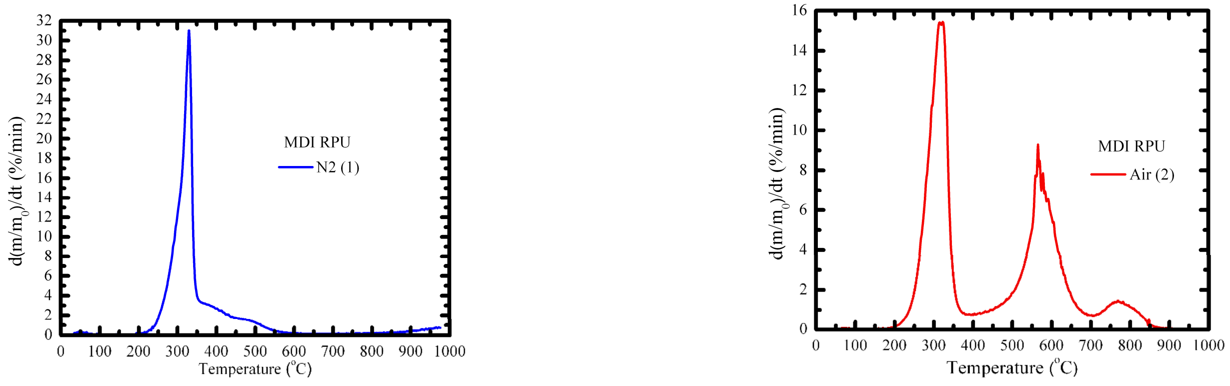


Fig. 14. Results from replicate TGA experiments with MDI RPU samples in nitrogen or air.



(a)

(b)

Fig. 15. Rate of mass loss from MDI RPU samples heated in (a) nitrogen or (b) air.

TGA results from PMDI RPU are shown in Figs. 16 and 17. PMDI RPU is a cross-linked polymer containing aromatic rings. PMDI RPU formed significant amounts of char during decomposition in nitrogen atmospheres. Decomposition occurred relatively rapidly between about 280° C and 395° C. As $m/m_0$ approached a value of about 28% at 395° C, the rate of decomposition began decreasing rapidly until $m/m_0$ approached about 15% at 600° C. Above 600° C, the char that had formed decomposed slowly. FTIR spectra collected during TGA experiments indicated that the major decomposition products were isocyanates, $CO_2$, polyether fragments, and analines. In air atmospheres, initial decomposition proceeded almost identically to that in nitrogen until $m/m_0$ approached a value of about 85% at 315° C. The rate of decomposition then decreased and was relatively slow between 400° C and 500° C where $m/m_0$ decreased from about 54% to 46%. Above 500° C, C The rate of decomposition increased, and the sample was consumed when the temperature reached 700° C. FTIR spectra collected during TGA experiments indicated that between 250° C and 400° C, corresponding to the left peak in Fig 17b, decomposition products were primarily $CO_2$ and polyether fragments, although some isocyanates appeared to be present. At higher temperatures, corresponding to the right peak in Fig. 17b, decomposition products were primarily CO and $CO_2$.

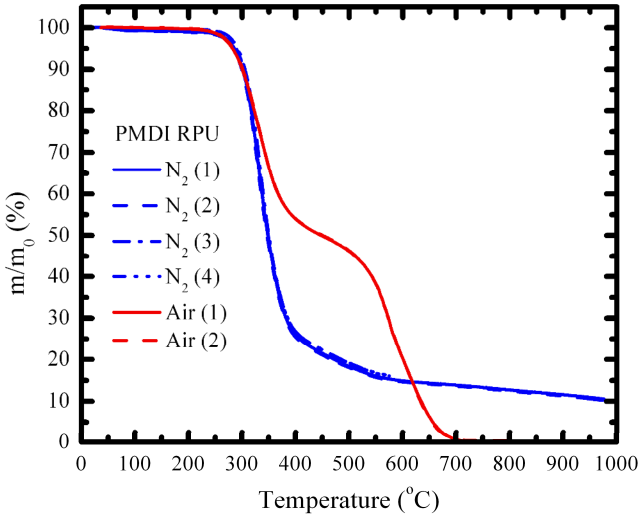


Fig. 16. Results from replicate TGA experiments with PMDI RPU samples heated in nitrogen or air.

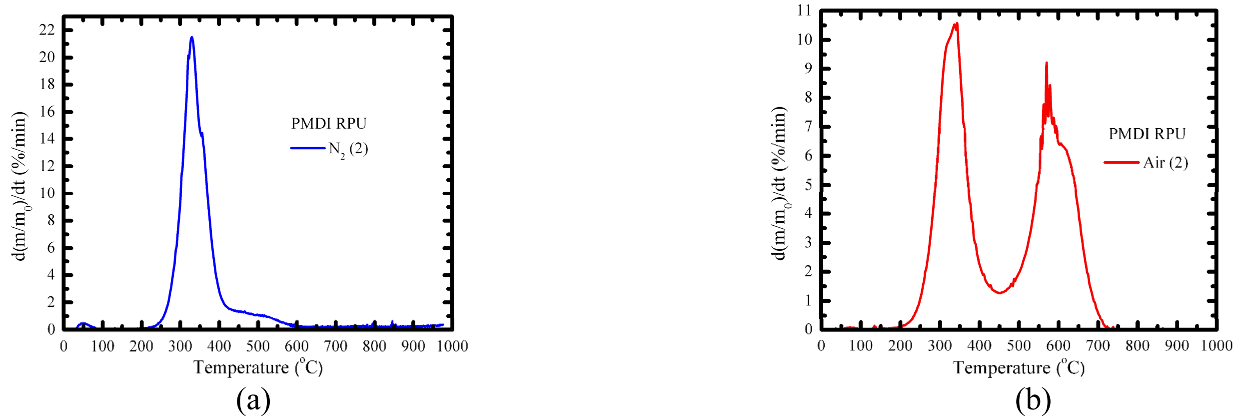
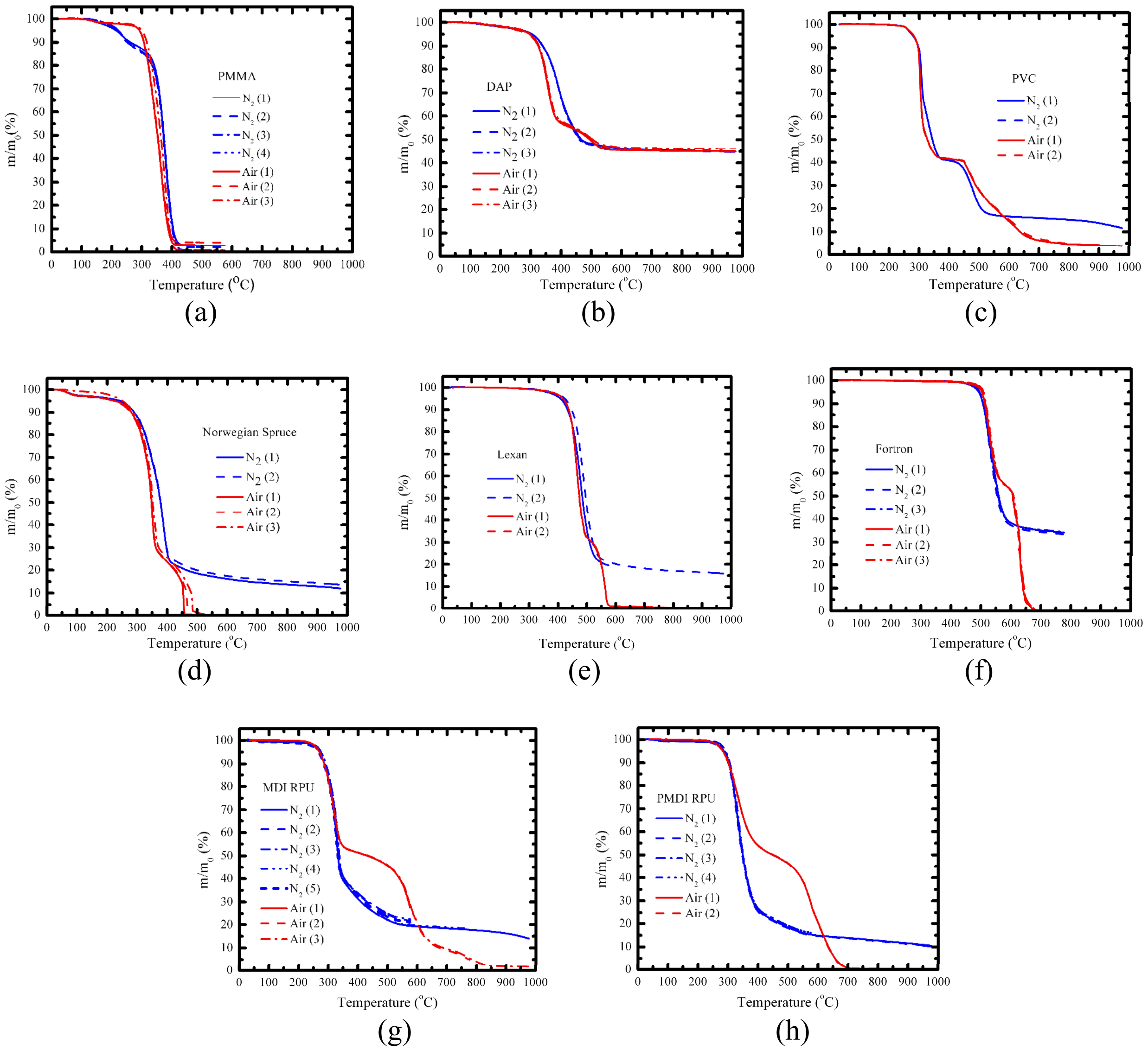


Fig. 17. Rate of mass loss from selected PMDI RPU samples heated in (a) nitrogen or (b) air.

# 4. DISCUSSION

For ease of reference, the TGA results from replicate experiments with each of the materials discussed above are shown in Fig. 18.



(a) (b) (c)

(d) (e) (f)

(g) (h)

Fig. 18. Comparison of results from replicate TGA experiments with each of the materials studied: (a) PMMA, (b) DAP, (c) PVC, (d) Norwegian spruce, (e) Lexan®, (f) Fortron®, (g) MDI RPU, and (h) PMDI RPU.

PMMA formed negligible char in nitrogen atmospheres. In air, initial decomposition of PMMA appears to have been delayed by interaction with oxygen. Most decomposition appeared to proceed at slightly lower temperatures than in nitrogen. However, additional data and analyses would be needed to determine if that difference were statistically significant. FTIR spectra indicated some change in decomposition products, particularly the presence of $CO_2$. The current data are insufficient for determining if the $CO_2$ evolved from reaction of oxygen with the condensed-phase PMMA, or if the $CO_2$ evolved from gas phase reaction of oxygen with methyl methacrylate in the heated transfer line and IR cell. As discussed below, results from the other polymers studied indicated that, to varying degrees, oxygen did interact with the condensed-phase materials.

DAP also formed negligible char during decomposition in nitrogen atmospheres, although a glass fiber residue remained in both nitrogen and air atmospheres. During decomposition in air atmospheres, the rate of decomposition was somewhat faster relative to that in nitrogen until the value of $m/m_0$ was about 60% at $388^o$ C. Decomposition of the remaining DAP was much slower than in nitrogen. At temperatures to $400^o$ C, phthalic anhydride was still the major decomposition product, but significant amounts of $H_2O$, CO, and $CO_2$ also evolved. At temperatures above about $400^o$ C, decomposition products were primarily $H_2O$, CO, and $CO_2$. These results suggest that interaction of oxygen with the decomposing DAP produced a more thermally stable, perhaps char-like, material that decomposed relatively slowly. Continued decomposition was due to further reaction with oxygen as temperature increased.

PVC formed significant char during decomposition in nitrogen atmospheres. Furthermore, two stages of char formation may have occurred. However, in air atmospheres, decomposition of PVC was very similar to that in nitrogen, except that decomposition continued at temperatures above $520^o$ C, and the samples were consumed except for a granular residue that is believed to be due to inorganic additives in the PVC.

Norwegian spruce, Lexan®, and Fortron® formed significant char during decomposition in nitrogen atmospheres. In air atmospheres, decomposition of a major fraction of the Norwegian spruce, Lexan®, and Fortron® samples was very similar to that in nitrogen, particularly in the case of Lexan® and Fortron®. In general, similar decomposition products were observed in both nitrogen and air atmospheres, except that more $H_2O$, CO, and $CO_2$ were observed in air. However, as the value of $m/m_0$ decreased, a prominent decrease in decomposition rate occurred and persisted over a moderate temperature range ($50^o$ C to $100^o$ C). This change occurred at values of $m/m_0$ that were somewhat greater than those at which the rate of decomposition rapidly decreased due to char formation in nitrogen atmospheres. As temperatures further increased, the decomposition rate increased rapidly, and samples were completely consumed. During the latter stages of decomposition the primary product was $CO_2$.

MDI RPU and PMDI RPU also formed significant char during decomposition in nitrogen atmospheres. In air atmospheres, decomposition of a major fraction of the MDI RPU and PMDI RPU samples also was very similar to that in nitrogen. In general, similar decomposition products were observed in both nitrogen and air atmospheres, except that more $CO_2$ was observed in air. Again, as the value of $m/m_0$ decreased, a prominent decrease in decomposition rate occurred. However, in the case of MDI RPU and PMDI RPU, the decrease in decomposition rate persisted over a relatively large temperature range ($150^o$ C to $200^o$ C), before increasing temperature caused an increase in decomposition rate, and the samples were completely consumed. This change occurred at values of $m/m_0$ that were substantially greater than those at which the rate of decomposition rapidly decreased due to char formation in nitrogen atmospheres. However, in air atmospheres, the decomposition rate at higher temperatures did not increase as rapidly as with Norwegian spruce, Lexan®, and Fortron®. During the latter stage of decomposition of PMDI RPU and PMDI RPU the primary products were CO and $CO_2$.

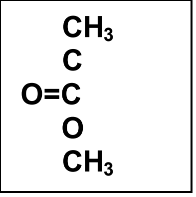
In summary, for the polymers studied, the most obvious difference between decomposition in nitrogen and decomposition in air occurred with materials that formed carbonaceous char in nitrogen atmospheres. During decomposition in air, the same materials essentially were consumed completely. However, other differences were apparent. Decomposition rates as a function of temperature were different in air atmospheres as opposed to nitrogen atmospheres. Some differences were small, but others were substantial. Furthermore, during decomposition in air, $H_2O$, CO, and $CO_2$ were observed in addition to the decomposition products that evolved during decomposition in nitrogen atmospheres. To varying degrees, oxygen interacted with the condensed-phase materials and altered the decomposition process. The current data are insufficient for determining to what extent $H_2O$, CO, and $CO_2$ were formed by reaction of oxygen with the condensed-phase material versus having been formed from gas phase reaction of oxygen with organic vapors in the heated transfer line and IR cell.

# 5. CONCLUSIONS AND RECOMMENDATIONS

Thermal decomposition of eight polymers has been examined in nitrogen and in air atmospheres. Experiments have been done with poly(methyl methacrylate), poly(diallyl phthalate), Norwegian spruce, poly(vinyl chloride), the polycarbonate Lexan®, the poly(phenylene sulphide) Fortron®, and two polyurethanes (MDI RPU and PMDI RPU). Polymers that formed a substantial amount of carbonaceous char during decomposition in a nitrogen atmosphere were completely consumed in an air atmosphere. However, in the case of polyurethanes, complete consumption did not occur until temperatures of $700^{o}$ C or higher. Furthermore, to varying degrees, the presence of oxygen appeared to alter the decomposition processes in all of the materials studied.

With the exception of PMMA and DAP, the initial stage of decomposition of each polymer in air proceeded similarly to that in nitrogen. With the exception 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 $CO_2$. However, current data are insufficient for determining to what extent $H_2O$, CO, and $CO_2$ were formed from reaction of oxygen with the condensed-phase material versus having been formed from gas phase reaction of oxygen with organic vapors in the heated transfer line and IR cell.

With respect to system safety analyses, the extent to which a carbonaceous char will or will not form will depend on the availability of oxygen. If char does form, it could provide a resistance to heat transfer to the un-reacted polymer. Formation of char also could reduce the flux of fuel to the vapor phase in a fire. Additional experiments to examine the effect of oxygen concentration on polymer decomposition would be of value in predicting whether or not char would form in a given situation. Also, complementary DSC experiments would provide data for enthalpy changes accompanying decomposition in both nitrogen and air. The effect of oxygen concentration and



$$\begin{array}{r} CH_3 \\ C \\ O{=}C \\ O \\ CH_3 \end{array}$$

acquisition enthalpy data corresponding to TGA-FTIR experiments would provide additional insight into decomposition mechanisms occurring in air, as well as in nitrogen atmospheres.

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