SAND2006-5192C

DEVELOPMENT OF RATE EXPRESSIONS FOR POLYMER DECOMPOSITION REACTIONS*

Kenneth L. Erickson
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

Organic polymer materials are used frequently in structures and transportation systems. Polymer materials may provide fuel for a fire or be damaged catastrophically due to an incident heat flux. Modeling the response of such structures and systems in fire environments has important applications in safety and vulnerability analyses. The decomposition chemistry of the organic polymer materials is an important factor in many analyses. To provide input to numerical models for hazard and vulnerability analyses, the thermal decomposition chemistry of organic polymers is being experimentally investigated using TGA-FTIR, GC-FTIR, infrared microprobe (IRMP), and DSC. Both TGA-FTIR and DSC experiments are done with unconfined and partially confined samples. Unconfined samples are used to examine initial decomposition reactions. Partially confined samples are used to examine reversible and secondary reactions. This paper discusses phenomena pertinent to using the aforementioned techniques to develop rate expressions for polymer decomposition reactions, and an example illustrating development of rate expressions for decomposition of poly(methyl methacrylate) (PMMA) is given.

KEY WORDS: Characterization, 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 as a result of an incident heat flux. Modeling the response of such structures and systems in fire environments has important applications in safety and vulnerability analyses. The decomposition chemistry of the organic polymer materials is an important factor in many cases. Specific applications include predicting the flux of volatile species to a flame region, predicting the extent of thermally induced mechanical damage in structural composite materials, determining the toxicity of evolved gases and vapors, modeling liquefaction and flow of decomposing materials, particularly foams, and characterizing char formation. To provide input to numerical models for hazard and vulnerability analyses, the thermal decomposition chemistry of organic polymers is being experimentally investigated using TGA-FTIR, TDS-GC-FTIR, infrared microprobe (IRMP), and DSC. Unconfined samples are used to examine initial decomposition reactions. Partially confined samples are used to examine reversible and secondary reactions. The objective of these investigations utimately is to develop a library of decomposition mechanisms and kinetics that is <u>based on the chemical functional</u> groups occurring in a variety of polymers.

---

* Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Several coupled physical and chemical phenomena occur during polymer decomposition. Fundamental phenomena include heat transfer, mass transfer, chemical reaction mechanisms and kinetics, evolution of the molecular weight distribution of the decomposing material, liquefaction and flow, and char formation. Mass transfer occurs in both condensed and gas phases and in the form of vaporization across the interface between condensed and gas phases. Liquefaction can occur as a result of melting or dissolution of larger polymer fragments by low molecular-weight decomposition products. Flow can occur due to the force of gravity or to a fluid-phase pressure gradient, which can result in bulk volumetric expansion of the condensed phase.

The manner in which the above phenomena impact the decomposition process will depend on the thermal and physical boundary conditions that are imposed on the decomposing polymer by the configuration of the engineered system or structure. The relative importance of the phenomena will depend on the engineered system and thermal environment resulting from fire. In most cases, reaction mechanisms and kinetics would be an important factor, and rate expressions would be needed in numerical models for hazard and vulnerability analyses.

In the following discussion, three examples of polymer decomposition with coupled phenomena are discussed for three significantly different types of thermal and physical boundary conditions that could be involved in hazard and vulnerability analyses. Reactions mechanisms and kinetics are pertinent to all three examples. Next, common decomposition reactions and the development of rate expressions are discussed, and a specific example illustrating development of rate expressions for decomposition of PMMA is given. Finally, some comments are given regarding the range of applicability of rate expressions obtained by the described methods.

2. PHYSICAL AND CHEMICAL PHENOMENA

Three examples that illustrate the interactions between physical and chemical phenomena, as well as effects of thermal and physical boundary conditions are briefly described below. The same physical and chemical phenomena are common to all three examples, but the degree to which the phenomena impact the bulk behavior of the material differs between the examples.

First, consider a burning polymer material as shown schematically in Fig. 1. In this case, temperatures are relatively high; rates of mass transfer of volatile species to a bulk gas-phase are relatively rapid, and the amount of liquid that forms is relatively small and rapidly vaporizes. Essentially, a solid-to-gas transformation occurs, and depending on the initial material, char formation could occur. In the flame region, the organic vapors react with oxygen to release energy, part of which is transferred back to the burning polymer material and promotes further decomposition and flame propagation.

Next, consider a polymer, or polymer foam, that is heated in an oxygen lean container as shown schematically in Fig. 2. The heat flux is orthogonal to the gravity vector. Combustion does not occur. The rate of mass transfer of volatile species away from the condensed phase is relatively slow, so that the low molecular weight organic species can act as a “solvent” for polymer fragments. As the molecular weights of the polymer fragments decrease, and the concentration of the “solvent” increases, the condensed-phase forms a fluid phase that flows due to gravity and would accumulate in the bottom of the container. The rate of flow would depend on the effective viscosity of the fluid, which depends on the molecular weight distribution of the polymer fragments, the relative amount of solvent, and the temperature.

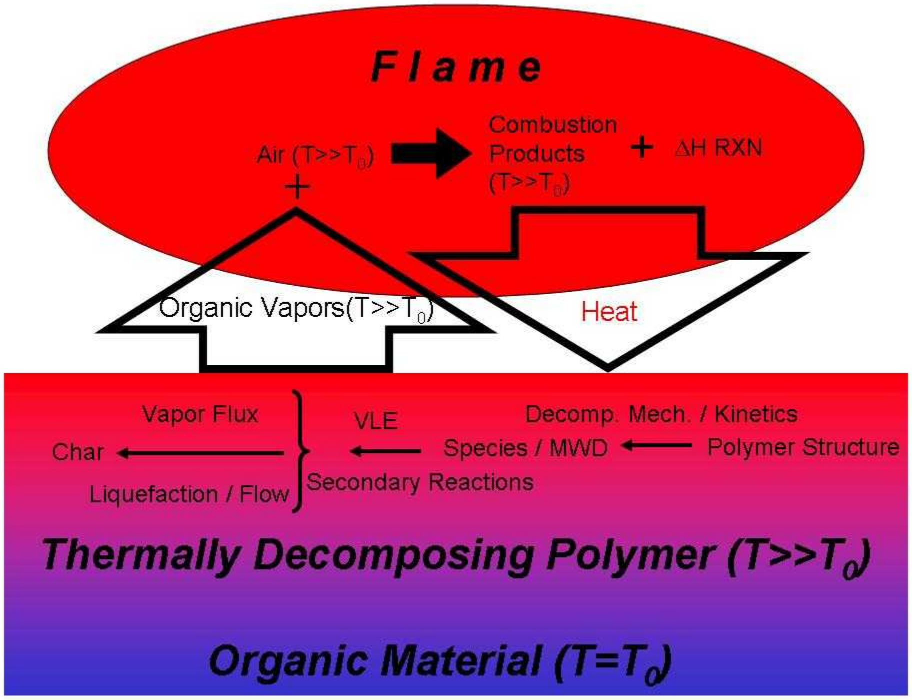


Fig. 1. Schematic diagram illustrating phenomena pertinent to a burning polymer material.

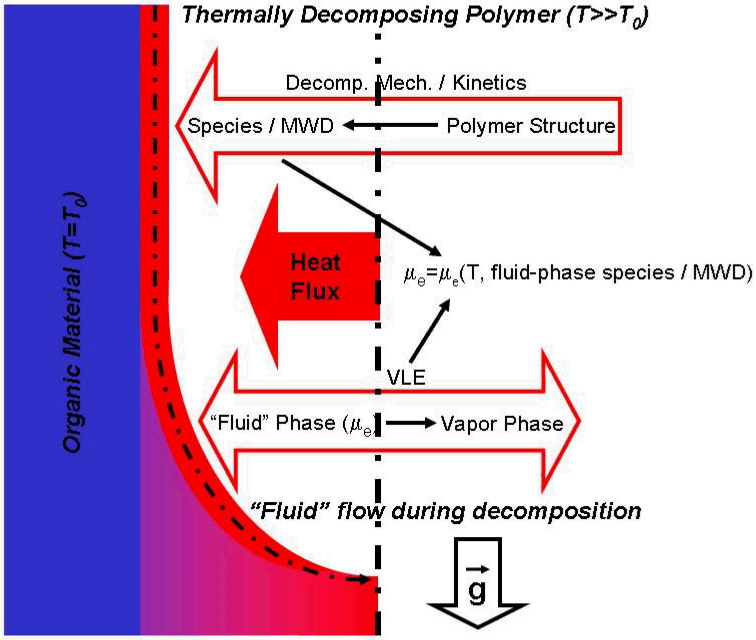


Fig. 2. Schematic diagram illustrating phenomena pertinent to liquefaction and flow due to gravity.

Finally, consider the case in which "significant" fluid accumulation occurs in the bottom of a container as shown in Fig. 3. As the liquid decomposes, gas/vapor bubbles form in the fluid. As decomposition proceeds, the pressure in the bubbles increases and causes the bubbles to expand. If the container is vented, a pressure gradient develops between the container and ambient. This results in the complicated flow of a reacting two-phase (vapor-liquid) material. The phenomena controlling bulk flow of the decomposing material are coupled and include interfacial phenomena, as well as chemical kinetics, vapor-liquid equilibria (VLE), and the effective viscosity μ_e of the two-phase material.

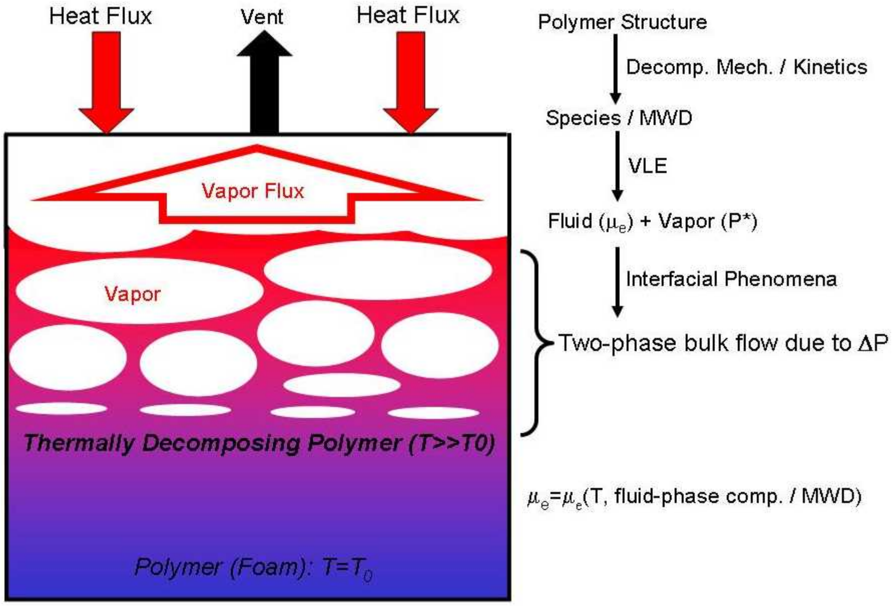


Fig. 3. Schematic diagram illustrating phenomena pertinent to two-phase flow or expansion.

Some applications involving engineered systems and heating scenarios similar to the examples in Figs. 1-3 have been described elsewhere (1-5). Those applications include predicting the flux of volatile species to a flame region, predicting the extent of thermal damage in foams, and modeling liquefaction and flow of decomposing materials, particularly foams. It should also be noted that if the examples in either Fig. 2 or Fig. 3 involved an oxygen environment, and if the organic material were burning, the physical situation would be much more complicated.

3. REACTION MECHANISMS

Thermal decomposition of organic polymers basically involves making small molecules from very large molecules. The chemical species that form depend strongly on: (1) The initial chemical structure of the polymer, (2) the corresponding chemical decomposition mechanisms and kinetics, and (3) the thermal boundary conditions. In some cases, the physical boundary conditions, such as confinement in closed or vented containers, also influence decomposition.

The initial chemical structure of the polymer is essentially a network of atoms connected by chemical bonds between the atoms. During thermal decomposition, the original polymer network is destroyed by bond scission and a variety of chemical species evolve. Bond scission can occur by: (1) De-polymerization, (2) random scission at particular chemical moieties, or (3) a combination of de-polymerization and random scission. De-polymerization yields a monomer plus the polymer chain reduced by one monomer unit. Random bond scission, which is the most common scission mode, involves breaking bonds at random locations in the polymer chain or network (6). Random scission yields a molecular-weight distribution of decomposition products that consist of polymer fragments consisting of one or more repeating units and molecular species that represent some portion of a repeating unit. The distribution of decomposition products is a fundamental characteristic of polymers that decompose by random scission.

Decomposition of poly(methyl methacrylate) (PMMA) is an example of de-polymerization (6).

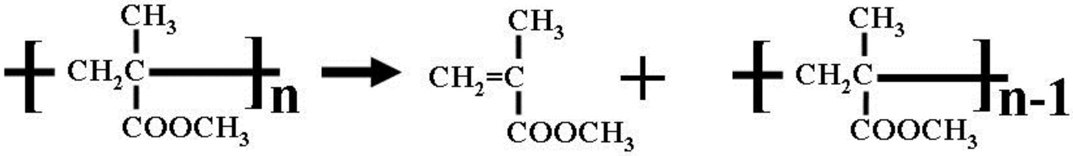


Fig. 4. Schematic representation of PMMA decomposition.

The decomposition of epoxy polymers (6-8) is an example of random scission, which occurs in the bisphenol A moiety, rather than between monomer units of the epoxy resin and the curing agent. The decomposition of a common type of epoxy polymer is illustrated in Fig. 5.

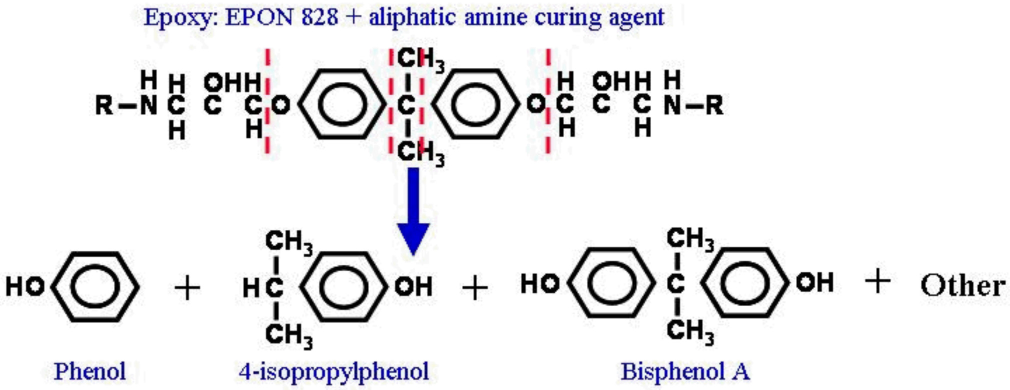


Fig. 5. Schematic representation of epoxy polymer decomposition.

Common molecular species that form during random bond scission include: (1) Inorganic and organic small molecules such as CO, CO_2, H_2O, CH_4, C_2H_2, CH_2O, etc; and (2) relatively low-molecular weight, volatile organic molecules, such as benzene, toluene, xylenes, phenols, siloxanes, di-isocyanates, aliphatic and aromatic amines, aldehydes, ketones, ethers, etc.

The evolution of molecular species generally requires scission of at least two bonds adjacent to the moiety that evolves as a volatile molecular species. However, in some cases, scission of only one bond is random. For example, initial bond rupture may be accompanied by radical decomposition reactions (9) evolving products such as CO, CO_2, and CH_2O. In this case, a single break in the polymer chain results in the evolution of a low-molecular weight decomposition product. Ring compounds formed from linear segments also may be eliminated from polymer chains during random scission. Examples include the elimination of cyclopentanone (7) from adipate moieties and the elimination of cyclic siloxanes (5) from polymers containing linear siloxane moieties. The ring formation may be a variation of radical decomposition or pyrolytic elimination (9), in which a single break in the polymer chain results in evolution of a cyclic decomposition product

Random chain scission can involve competing forward reactions, reversible reactions, and secondary reactions in which decomposition products or polymer fragments recombine or react to form different polymers, the decomposition of which proceeds by different mechanisms and kinetics. The decomposition of toluene diisocyanate (TDI)-based polyurethanes (7, 8) is an example of decomposition involving competing forward reaction, reversible reaction, and recombination to form a different polymer moiety. These reactions are illustrated in Fig. 6.

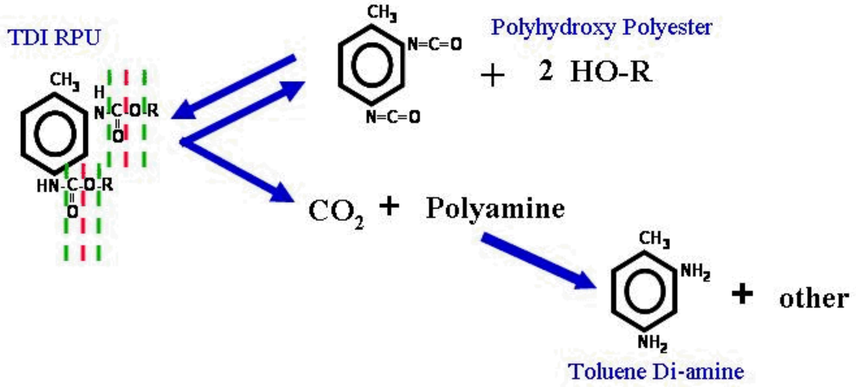


Fig. 6. Schematic representation of TDI-based polyurethane decomposition.

During decomposition of polyurethanes based on polyhydroxy polyesters, ester interchange reactions (10) will also cause formation of new polymer units. Char formation is another class of reactions that can involve formation of new polymer units, as well as polycyclic moieties.

In addition to chain or network breaking reactions, thermal decomposition can involve non-network-breaking reactions that evolve low molecular weight molecules such as H_2, H_20, and CH_4. The evolutions of H_2 and CH_4 from the bisphenol A moiety during epoxy decomposition are examples of non-network breaking reactions (6).

As mentioned previously, the physical behavior of the decomposing material depends strongly on the thermal and physical boundary conditions surrounding the polymer, as well as highly coupled physical and chemical phenomena that include thermal decomposition mechanisms and kinetics. In general, all polymer decomposition will, to varying degrees, involve the following: (1) Release of low-molecular weight inorganic gases and organic vapors that will exert pressure under confinement and can serve as fuel in a fire environment, (2) a decomposing condensed phase that will tend to form a liquid or fluid-like phase, a solid char, or both fluid-like phase and solid char.

The tendency to form a fluid-like phase depends on the dynamic interaction between the low-molecular weight organic species and the polymer fragments. The low-molecular weight species act as solvents for the polymer fragments. The tendency for the condensed-phase to liquefy, and the effective viscosity of the fluid-like phase, depend on the temperature, the molecular weight distribution of the polymer fragments, and the ratio (mass, mole, or volume) of low molecular weight organic species to polymer fragments in the condensed phase. In turn, the ratio of low molecular weight species to polymer fragments is determined by the physical boundary conditions of the system (vented versus confined) and the vapor-liquid equilibria (VLE) for the low-molecular weight species and polymer fragments.

The tendency to form char also depends on the dynamic interaction between the low-molecular weight organic species and the polymer fragments. However, secondary reactions that occur in the decomposing condensed phase and interactions with "inert" materials are the more important considerations.

4. REACTION RATE EXPRESSIONS

4.1 Common Experimental Methods One of the most common laboratory-scale methods for obtaining rate data for thermal decomposition of polymers is thermal gravimetric analysis (TGA). Small, typically mg-size, samples are heated according to a predetermined program. The sample mass and temperature of the "sample thermocouple" are recorded as a function of time. A variety of techniques can be employed to determine the chemical species evolving from the decomposing polymer. TGA coupled with Fourier transform infrared spectroscopy (FTIR) or TGA coupled with mass spectrometry (MS) can provide quasi-real-time chemical analysis of evolved decomposition products. However, when multiple species evolve concurrently, the analysis of spectra can be difficult. A variety of intermittent sampling techniques can be used to obtain samples for subsequent separation and chemical analysis by GC-FTIR, GC-MS, LPC-MS, GPC, etc. Differential scanning calorimetry DSC can provide data for enthalpy changes accompanying decomposition, as well as additional data for developing reaction rate expressions. Simultaneous thermal analysis (STA) provides both TGA and DSC analyses simultaneously from the same sample. Condensed-phase residues can be analyzed by several techniques including IR microprobe (IRMP) and nuclear magnetic resonance (NMR). Unfortunately, no single experimental technique can provide all needed information.

4.2 Approaches for Developing Rate Expressions The development of rate expressions from data obtained using the techniques mentioned above involves several considerations. Though often annoying, the available time, funds, and resources, both personnel and equipment, usually dictate the scope of the experimental investigation. Intended applications for rate expressions, such as the predictions needed from numerical models supporting hazard analyses, and model uncertainties will indicate the detail needed, as well as the complexity not needed, in the rate expressions. A reasonable "rule of thumb" might be that the level of detail examined experimentally and incorporated into rate expressions should be at a level consistent with, or greater than, the overall level of detail in a given model. Some models and applications will require more detail than others. The level of detail that can legitimately be pursued will often be dictated by how much is known about the chemical structure and morphology of the polymer material. The details of polymer formulation and structure are often proprietary, and manufacturers are reluctant to release information.

With the above issues in mind, the approaches for developing rate expressions from TGA results can be divided into two categories: (1) Expressions based on sample mass and first order decomposition and (2) expressions based on chemical decomposition mechanisms associated with the chemical functional groups in the polymer structure.

Expressions based on sample mass and first order decomposition require the least amount of data and information about the polymer material. However, these rate expressions may not provide sufficient detail for modeling thermal and physical boundary conditions significantly different from those in the experiments used to evaluate parameters. The basic approach is to assume an irreversible reaction that is first order in polymer mass and has a rate constant of the Arrhenius form. Temperature-dependent rate constants are then evaluated by an optimization procedure that determines the parameter values providing the best fit to experimental data. If TGA results indicate multiple decomposition mechanisms, multiple first order expressions can be used.

Rate expressions based on chemical decomposition mechanisms associated with the chemical functional groups in the polymer structure are potentially much more useful. However, the work involved can be substantial, particularly if the intended application requires calculating the molecular weight distribution in the decomposing polymer.

First, information regarding the chemical structure of the polymer is required. Representative structures can be postulated based on the details of the polymer synthesis (constituents, proportions, and sequence of preparation), if available. When synthesis details are not available, product specifications and material safety data sheets will usually provide some information. Total chemical analysis for C, H, N, and O can readily provide additional data. If appropriate, attempts can be made to reverse engineer the polymer. However, reverse engineering is generally time consuming and difficult. Furthermore, improper handling of the experimental data could result in issues over disclosure of proprietary information.

Next, the mechanisms that control decomposition must be identified. These are derived from the representative polymer structure, TGA and DSC results, observed vapor-phase and condensed-phase decomposition products, and any other pertinent information. Generally, insufficient data are available to develop mechanisms in terms of multi-step, elementary reactions. Instead overall reactions for formation of stable scission products are postulated. In formulating rate expressions, these reactions usually are assumed to be first order with respect to the moieties in the functional groups involved in bond scission. Similarly, reversible and secondary reactions are represented by over-all reactions that are assumed to be first order in each of the moieties participating in recombination. Parameters in the rate expressions are then evaluated based on rate data from TGA and data for evolution of decomposition products as a function of time. If decomposition is sufficiently complicated, developing a physically realistic set of reaction mechanisms may be untenable. Evaluating parameters that have physical significance under conditions significantly different from those in the experiments used to determine the parameter values may also be untenable. If the molecular weight distribution in the decomposing polymer is important in the intended application, then statistical techniques must be incorporated into the development of rate expressions. This can involve substantial issues that are beyond the scope of this paper.

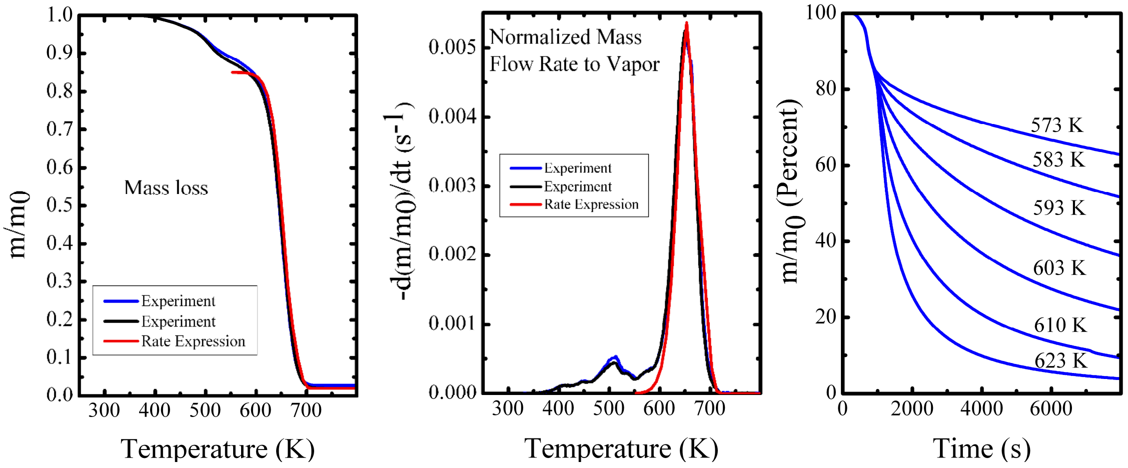
4.3 Example: PMMA Decomposition The thermal decomposition of PMMA (MW=100.1; normal boiling point = 373.5 K) was investigated previously (4) using TGA-FTIR in experiments with powdered samples (about 4.5 mg each) in open platinum pans. The powder was prepared from sheet PMMA using a fine-pitch file to produce powder particles having characteristic dimensions on the order of 0.1 mm. Powdered samples were used to reduce heat and mass transfer effects during decomposition, so that the TGA data primarily reflect the rate of chemical reaction controlling decomposition. Two programmed-heating schemes were used. "Temperature-ramp" experiments involved heating the samples at constant rates to temperatures at which complete decomposition had occurred. "Isothermal" experiments involved heating the samples at a constant rate (0.33K/s) to selected temperatures that were then held constant for prescribed time intervals, during which most decomposition occurred.

Analysis of the FTIR spectra from the TGA experiments indicated that methyl methacrylate (MMA) was the only significant decomposition product that evolved during all of the experiments and is consistent with previously reported results (6). Evolution of only the monomer from its polymer indicated that decomposition occurred by step-wise de-polymerization, rather than by random scission. Decomposition was essentially non-charring. The masses of solid residues that remained after heating to about 873 K were about two percent, or less, of the original sample masses.

The development of rate expressions for the decomposition of PMMA is illustrated below. The de-polymerization decomposition mechanism was determined from the TGA-FTIR results. Rate expressions were formulated, and rate constants were determined using the data from the isothermal experiments. The Arrhenius expression for the reaction rate constant was evaluated, and the rate expression was used to predict the results of the temperature-ramp experiments.

Rate expressions were based on the principle that the rate of de-polymerization of a polymer having a weight average molecular weight $<M_w>$ would depend on the number of polymer chains and the rate at which each chain evolves monomers. The shortest chains would be consumed first, and the longest chains consumed last. In general, the rate of monomer evolution would depend on the fraction of the original mass of material remaining, although probably not directly proportional to the fraction remaining. However, first-order reaction mechanisms are attractive with respect to simplicity in data analysis and modeling complicated systems.

Data from temperature-ramp and "isothermal" TGA experiments are shown below in Fig. 7. The two distinct peaks in the derivative curve from the temperature-ramp experiments in Fig. 7b indicate at least two decomposition regimes. In Fig 7a, about 15 percent mass loss occurs between 473 and 573 K. The remaining mass evolves into the vapor phase between about 573 and 623 K. The analyses below focus on temperatures of 573 K and above, where most decomposition occurs. The isothermal TGA experiments were done with constant temperatures of 573, 583, 593, 603, 613, and 623 K. Partial results are shown in Fig. 7c. Typical temperature histories from the temperature-ramp and isothermal TGA-FTIR experiments are shown in Fig. 8.



(a) (b) (c)

Fig. 7. TGA results: (a) m/m_o versus temperature from replicate temperature-ramp experiments (0.33 K/s), (b) $d(m/m_0)/dt$ versus temperature from the replicate temperature-ramp experiments (0.33 K/s), and (c) m/m_o versus time at constant temperatures from 573 K to 623 K.

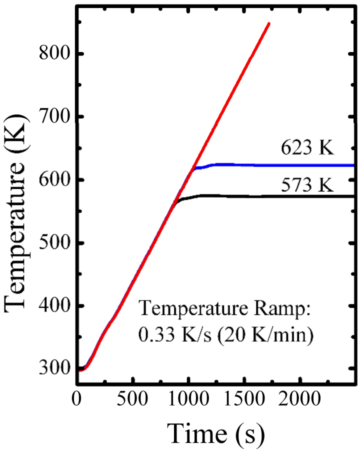


Fig. 8. Typical temperature histories from temperature-ramp and isothermal experiments.

Initial attempts to describe isothermal decomposition using a single first-order rate expression failed to represent adequately the data at longer times. The rate constants that fit the data at early times predicted faster mass loss than was observed in the experimental data at later times. This would be consistent with the longest polymer chains requiring relatively longer time to decompose completely. Good agreement with the experimental data was obtained by assuming that the total mass m of the polymer consisted of a mass m_1 of shorter chains, a mass m_2 of longer chains, and a mass m_3 that evolves at temperatures less than 573 K. Assuming that the intrinsic rate of the "unzipping" reaction is independent of the polymer chain, then polymer decomposition is described by

$$\frac{dm}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt} + \frac{dm_3}{dt} = -k_1 m_1 - k_2 m_2 + \frac{dm_3}{dt} = -k_1 m_1 - \langle \alpha \rangle k_1 m_1 + \frac{dm_3}{dt} \tag{1}$$

For $T \geq 573\,\mathrm{K}$, $m_3 \approx 0$, and Eq. 1 has the solution

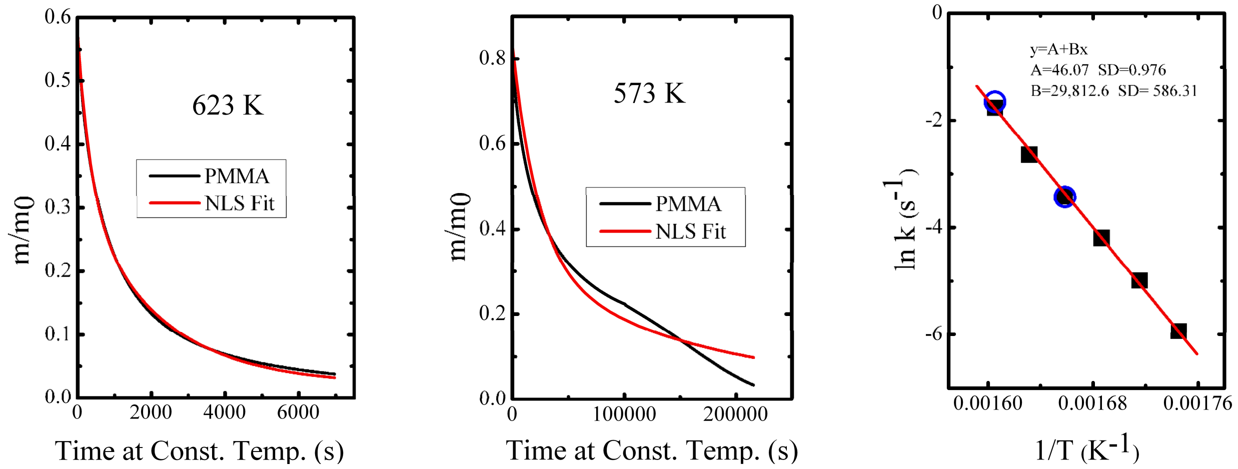
$$\frac{m}{m_0} = \left(\frac{m_{1_0}}{m_0}\right)\exp\left(-k_1 t\right) + \left(\frac{m_{2_0}}{m_0}\right)\exp(-\langle\alpha\rangle k_1 t) = A_1 \exp\left(-k_1 t\right) + A_2 \exp(-\langle\alpha\rangle k_1 t) \qquad (2)$$

where k_1 denotes the rate constant for the "unzipping" reaction; $\langle\alpha\rangle$ is an average empirical parameter that represents the ratio of the number of longer polymer chains to the number of shorter chains, and subscript 0 denotes the value at time $t = 0$.

The constants $\langle\alpha\rangle$, $A_1 = m_{1_0}/m_0$, and $A_2 = m_{2_0}/m_0$, as well as values of $k_1(T)$, were evaluated by iterative nonlinear regressions analyses of the data from each of the isothermal TGA experiments. Regression analyses were based on Eq. 2 modified to account for the solid residue

$$m/m_0 = A_1 \exp\left(-k_1 t\right) + A_2 \exp(-\alpha k_1 t) + 0.02 \qquad (3)$$

where $A_1 + A_2 + 0.02 = 0.85$. Regression results are illustrated by the red lines in Figs 9a and 9b.



(a) (b) (c)

Fig. 9. (a) Comparison of regression results and experimental data for isothermal experiment at a temperature of 623 K, (b) comparison of regression results and experimental data for isothermal experiment at a temperature of 573 K, and (c) Arrhenius plot based on results from isothermal TGA experiments.

The agreement between experimental and calculated results for temperatures of 583, 593, 603 and 613 K was similar to the agreement shown for 623 K in Fig. 9a. The agreement between results for 573 K, shown Fig. 9b, was somewhat poorer, probably due to some overlap with the decomposition mechanism that occurs between 473 and 573 K. The resulting values for $\langle\alpha\rangle$, $A_1 = m_{1_0}/m_0$, and $A_2 = m_{2_0}/m_0$, were 0.153, 0.53, and 0.30, respectively. A plot of $\ln k_1$ versus reciprocal temperature $1/T$ is shown in Fig. 9c. A linear least squares fit gave the following Arrhenius expression: $k_1(T) = k_1^0 \exp\left(-Q_1/RT\right)$, where $k_1^0 = 1.71x10^{18}\,\mathrm{s}^{-1}$, and $Q_1/R = 29{,}800\,\mathrm{K}$.

At temperatures above 573 K, the values of m/m_0 observed in the temperature-ramp TGA experiments are determined by decomposition of the polymer chains represented by m_1 and m_2. Values of m/m_0 can be predicted from Eq. 1, using the Arrhenius expression for $k_1(T)$, which has the solution

$$\frac{m}{m_0} = A_1 \exp\left\{-\int_0^t k_1[T(t')]dt'\right\} + A_2 \exp\left\{-\int_0^t \langle\alpha\rangle k_1[T(t')]dt'\right\} \tag{4}$$

Since the temperature history $T(t)$ is known, the integral in Eq. 4 can be evaluated numerically. The red lines in Figs. 7a and 7b show values of m/m_0 and $d(m/m_0)/dt$, respectively, from Eq. 4 that were calculated using the Arrhenius expression for $k_1(T)$. Values of m/m_0 predicted from Eq. 4 were increased by 0.02 to account for char formation. The agreement between experimental and predicted values is quite good.

5. DISCUSSION

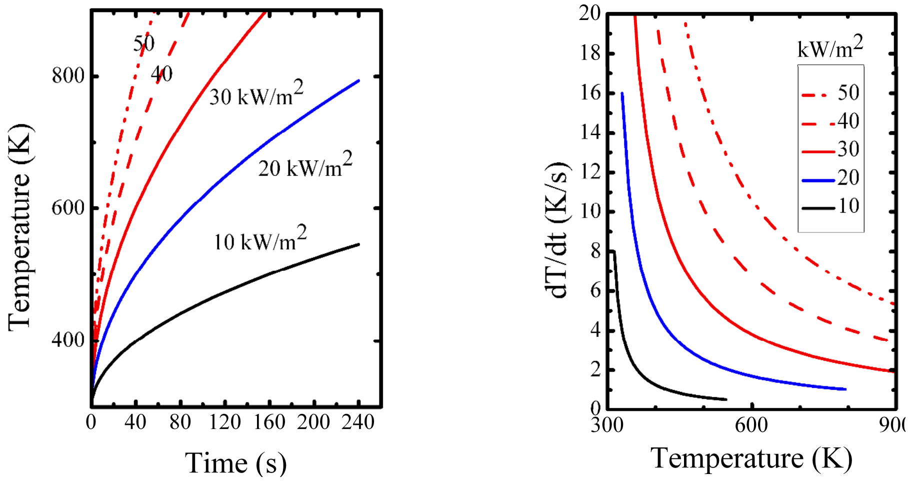
In addition to the issue of the molecular weight distribution of polymer fragments during random scission, the effect of heating rate on the relative rates of competing decomposition reactions is also extremely important. This is particularly true when the decomposing polymer is directly exposed to a substantial heat flux. For example, consider a constant heat flux $F_{x=0}$ to the surface of a semi-infinite solid that is initially at uniform temperature T_0 and has constant heat capacity c, thermal conductivity k, and density ρ. The temperature at the surface and the surface heating rate dT/dt are given, respectively, by (11)

$$T(x=0,t) = \left(\frac{2F_{x=0}}{\sqrt{\pi\rho ck}}\right)\sqrt{t} \tag{7a}$$

and

$$\frac{dT}{dt} = \left(\frac{F_{x=0}}{\sqrt{\pi\rho ck}}\right)\frac{1}{\sqrt{t}} \tag{7b}$$

The surface temperature continually increases with time, and the heating rate decreases with time. Figure 10a shows temperature as a function of time for incident heat fluxes of 10, 20, 30, 40 and 50 kW/m^2. The initial temperature was chosen as 298 K. Values for c, k, and ρ were respectively, 2200 J/KgK, 0.19 W/mK, and 1190 Kg/m^3. Figure 10b shows heating rate as a function of the temperatures shown in Fig. 10a.



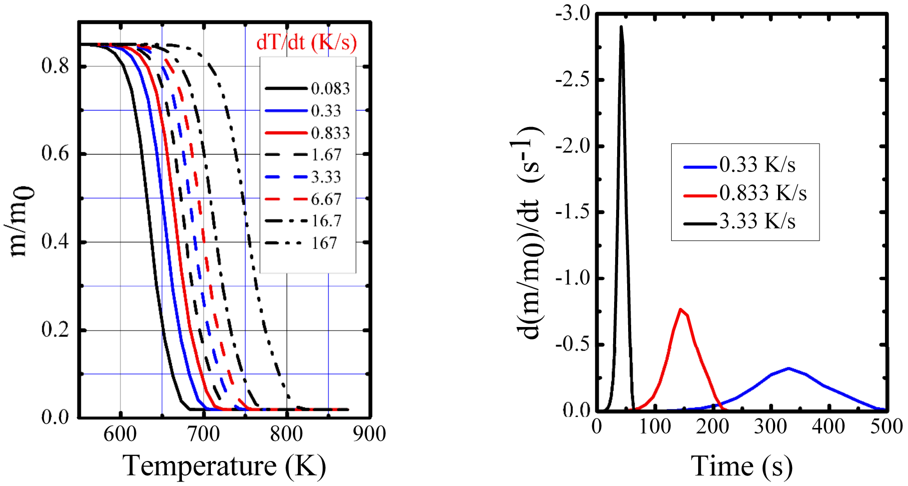
(a)

(b)

Fig.10. (a) Temperature (above 298 K ambient) versus time as a function of incident heat flux and (b) heating rate versus temperature as a function of incident heat flux.

If energy is consumed by endothermic reaction, the surface temperature will reach a steady-state value, because the rate at which energy (per unit area) is absorbed by endothermic reaction and vaporization cannot exceed the heat flux to the surface. The temperature given by Eq. 7a will begin to approach steady values when the corresponding rate of decomposition becomes significant.

To examine the effect of heating rate, Eq. 4 was used to calculate values of m/m_0 versus temperature for PMMA samples subjected to several heating rates that ranged from 0.083 to 167 K/s (5 K/min to 10,000 K/min). Temperature gradients in the samples were assumed to be negligible. The resulting mass loss curves are shown in Fig. 11a. Some representative derivative curves showing the rate of mass loss are shown in Fig. 11b. As the heating rate increases, the curves shift toward slightly higher temperatures. This shift occurs because at higher heating rates, the sample is at each temperature for shorter time intervals than at lower heating rates, and less mass evolves at each temperature. Therefore, as the heating rate increases, the curves shift toward slightly higher temperatures. The shift is relatively small because the rate of reaction increases rapidly with temperature. At sufficiently high heating rates, additional decomposition reactions may become significant, and vaporization of polymer fragments may occur. Either or both of these processes will alter the manner in which the decomposition curves behave with heating rate. The effect of heating rate on decomposition has been discussed in detail by Shlensky (12).



(a) (b)

Fig.11. Decomposition versus heating rate: (a) m/m_0 versus temperature as a function of heating rate, and (b) $d\left(m/m_0\right)/dt$ versus time as a function of selected heating rates.

6. CONCLUSIONS AND RECOMMENDATIONS

Several coupled physical and chemical phenomena occur during polymer decomposition. Fundamental phenomena include heat transfer, mass transfer, chemical reaction mechanisms and kinetics, evolution of the molecular weight distribution of the decomposing material, and liquefaction and flow. Reaction mechanisms and kinetics should be determined from small-scale experiments that minimize temperature gradients in samples and control mass transfer effects so that competing and reversible reactions can be studied under different conditions.

Often, insufficient data will be available to determine the mechanisms and kinetic controlling decomposition of complex co-polymers. In developing rate expressions for these cases, care should be taken to avoid placing unwarranted physical significance on results and introducing unwarranted complexity. The minimum number of rate expressions and parameters should be used that are consistent with the level of detail in the over-all model for the system. For complicated systems, rate expressions will be strictly valid only for the range of conditions used to develop the expressions. Extrapolations are reasonable only if coupled phenomena are accounted for adequately. For example, pressure increase in a closed container depends on the initial decomposition products, as well as subsequent reactions that can include high-temperature cracking of carbon-carbon bonds to yield low-molecular weight gases.

Acknowledgments The author gratefully acknowledges the considerable technical assistance provided by John Oelfke and Ted Borek of Sandia National Laboratories.

7. REFERENCES

1. T. Y. Chu, M. L. Hobbs, K. L. Erickson, et al, Proceedings of 1999 SAMPE '99 - 44th International SAMPE Symposium & Exhibition, Long Beach, CA, May 24-27, 1999."

2. M. L. Hobbs, K. L. Erickson, and T.Y. Chu, Polymer Degradation and Stability, **69**, 47 (2000).

3. B.E. Vembe, V.F. Nicolette, and K. L. Erickson, Proceedings of International Technical Conference: Computational Simulation Models in Fire Engineering and Research, hosted by the University of Cantabria (Spain), October 2004, ISBN 84-8102-383-3.

4. V. F. Nicolette, K. L. Erickson, and B. E. Vembe, Proceedings of Interflam 2004, 10th International Conference on Fire Science and Engineering, Edinburgh, Scotland, July 5-7, 2004, Interscience Communications Ltd. London, 1257-1268 (2004).

5. K. L. Erickson, S. M. Trujillo, K. R. Thompson, A. C. Sun, M. L. Hobbs, and K. J. Dowding, Computational Methods in Materials Characterization, WIT Press, Southhampton, 217-242 (2003).

6. A. Ravve, Principles of Polymer Chemistry, 2nd Ed., Kluwer Academic / Plenum Publishers, New York, pp. 581-616 (2000).

7. K. L. Erickson, Proceedings of SAMPE 2006, Long Beach, Ca, April 30 – May 5, 2005.

8. K. L. Erickson, Proceedings of NATAS 2006, Bowling Green, KY, Aug 5-9, 2006.

9. J. March, Advanced Organic Chemistry, John Wiley & Sons, New York, pp. 186-195, 1006-1110 (1992).

10. P. J. Flory, Principles of Polymer Chemistry, Cornell University press, Ithaca, New York, pp.87-91 (1971).

11. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in solids*, 2nd Ed., Oxford University Press, 1959, p. 75.

12. O. F. Shlensky, L. N. Aksenov, and A. G. Shashkov, Thermal Decomposition of Materials: Effect of Highly Intensive Heating, Elsevier, Amsterdam (1991).