

A Numerical Model of Bubbling Thermoplastics

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Introduction

Thermoplastic materials such as polypropylene (PP), polyethylene (PE), and polystyrene (PS) are widely used in household furnishings, and therefore constitute a large fraction of the fuel load during a fire. The combustible gases generated during polymer decomposition contribute directly to the growth and intensity of the fire. In order to accurately predict the development of a fire and when or even whether flashover will take place, therefore, it is critical to determine the rate at which gases are released from these materials. The tendency of thermoplastic materials to bubble during intense heating has a profound effect on this process.

The behavior of thermoplastic materials during pyrolysis and combustion is highly complex. As the temperature rises, the molecules in a thermoplastic solid become increasingly mobile, until the material becomes a viscoelastic fluid. Chemical bond breaking reduces the average molecular weight of the polymer, further reducing the viscosity. Eventually, the polymer fragments are small enough to constitute gas molecules. The gas does not escape instantaneously but diffuses through the surrounding material, collecting within any bubbles that have nucleated within the polymeric melt. The bubbles transport the volatile gases at a rate that is dictated by bubble dynamics. Upon reaching the surface, the bubbles may not release their gases immediately but instead develop a thin film that takes time to drain and rupture. The result is an insulating layer that reduces the transport of heat into the interior, thus slowing the gasification. As they burst, the bubbles may expose a larger region near the surface to chemical attack from the surrounding gases (such as oxygen) due to entrainment and, for highly viscous melts, to the distortion of the surface geometry.¹

A numerical model of the pyrolysis of a thermoplastic sample including effects of bubble dynamics is described. The model combines nucleation, growth, migration, and bursting of individual bubbles with a finite element model that solves a one-dimensional equation for the temperature field of a one-fluid mixture. Energy calculations include surface losses due to radiation and convection, conductive heat transfer through the condensed material, and the chemistry of gasification.

Thermal Model

The model geometry is a rectangular solid constrained in x- and y-directions, with gravity acting in the negative z-direction. A steady heat flux is applied from above, and the sample is insulated on its lower surface. The sample consists of two components, polymer and gas, both

of which are treated as fluids. The transformation of the polymer from a solid to a melt as the temperature rises above the glass temperature is handled through changes in the polymer viscosity. Densities of polymer and gas are defined as $\rho_p = M_p/V_p$ and $\rho_g = M_g/V_g$ respectively, and the local volume fractions are $\phi_p = V_p/V$ and $\phi_g = V_g/V$, where $V = V_p + V_g$ is the total volume. The sum of local volume fractions is equal to one, and the initial conditions are $\phi_p = 1$ and $\phi_g = 0$.

Mass is exchanged from polymer to gas through a chemical reaction which can be described by the Arrhenius expression

$$\dot{m} = \rho_p \phi_p B \exp(-E / RT), \quad (1)$$

where B and E are the pre-exponential constant and activation energy for the gasification reaction and R is the universal gas constant. The one-dimensional mass balance equations are

$$\text{Polymer:} \quad \frac{\partial \rho_p \phi_p}{\partial t} + \frac{\partial}{\partial z} (\rho_p \phi_p W_p) = -\rho_p \phi_p B \exp(-E / RT) \quad (2)$$

$$\text{Gas:} \quad \frac{\partial \rho_g \phi_g}{\partial t} + \frac{\partial}{\partial z} (\rho_g \phi_g W_g) = +\rho_p \phi_p B \exp(-E / RT), \quad (3)$$

where W_p and W_g are velocities of polymer and gas respectively, and the total mass density is $\rho^* = \rho_p \phi_p + \rho_g \phi_g$. The polymer and gas velocities are determined by bubble dynamics rather than through the usual continuum momentum equations such as the Navier-Stokes equation for fluids or Darcy's law for porous media.

From the internal energy equation, the equation for temperature is:

$$(\rho c_p)^* \left(\frac{\partial T}{\partial t} + W^* \frac{\partial T}{\partial z} \right) + H_v \rho_p \phi_p B e^{-E/RT} = \frac{\partial}{\partial z} \left(k^* \frac{\partial T}{\partial z} \right), \quad (6)$$

where H_v is the heat of vaporization, $(\rho c_p)^* = (\rho c_p)_p + (\rho c_p)_g$ for the mixture, k^* is the effective thermal conductivity, and velocity is $\rho^* W^* = \rho_p \phi_p W_p + \rho_g \phi_g W_g$.

For numerical solution, the sample is divided vertically into a number of elements. The finite element method, which allows for large changes in element size from one timestep to the next, is employed to determine the vertical temperature profile. This provides the environment for bubble behavior.

Bubble Dynamics

Nucleation: Research suggests that homogeneous nucleation, in which thermal fluctuations give rise to clusters of gas molecules over a critical size for bubble formation, is adequate for describing bubble nucleation in polymer foams. The classical molecular theory describes the nucleation rate J in terms of an Arrhenius expression,

$$J = MB \exp(-\Delta F_{cr} / k_B T) \quad (7)$$

where M is the number of molecules per unit volume of the liquid phase, B is a frequency factor, k_B is Boltzmann's constant, and ΔF_{cr} is the free energy change required to form the

critical bubble. Modifications of this theory to include other important factors such as the presence of macromolecules, the degree of supersaturation, and the gas diffusivity have improved the model, although predicted bubble population densities are still off by a few orders of magnitude.²

Bubble nucleation is also affected by the presence of elastic stresses, which lower the free energy required for critical cluster formation. Deformation of macromolecules surrounding a growing bubble may experience such elastic stresses, causing the formation of small satellite bubbles near a primary bubble.³ Such secondary nucleation may be responsible for the “frosted” appearance of some bubbles formed within burning PMMA.⁴

Bubble growth: The rate of gas generated due to polymer degradation at a given temperature can be described by the Arrhenius expression in equation (1). Given this chemical model, the quantity of gas produced in a given time increment within a given volume can be treated as a known quantity. The question that then arises is how to properly distribute these gases into nearby bubbles, and whether some gas remains as individual molecules dispersed throughout the polymer melt.

A recent model of diffusion-induced bubble growth in viscoelastic liquids brackets the growth rate between a lower bound of growth in a Newtonian fluid and an upper bound of diffusion-controlled growth, in which bubble radius increases as the square-root of time.⁵ Fluid elasticity was found to have far greater impact than nonlinear fluid rheology. Secondary nucleation due to elastic stresses could cause much larger apparent bubble growth rates, with reports of “flashlike” devolatilization of the neighborhood of a growing bubble.³ The current model makes the assumption that all gases produced in an element during a timestep are distributed to bubbles within the element.

Migration: The bubbles in this sample experience forces due to gravity and temperature gradients that propel them through the polymer melt. Because both surface tension and viscosity are strong functions of temperature, the forces are due to surface tension gradients (Marangoni force) and viscosity gradients. The translation velocity is

$$W = -\frac{2(\rho_p - \rho_g)gR^2}{9\mu} + 2R\dot{R}\left(-\frac{d \ln \mu}{dT}\right)\frac{\partial T}{\partial z} + \frac{R}{3\mu}\left(-\frac{d \ln \sigma}{dT}\right)\frac{\partial T}{\partial z} \quad (8)$$

where R is the bubble radius and \dot{R} the bubble growth rate.

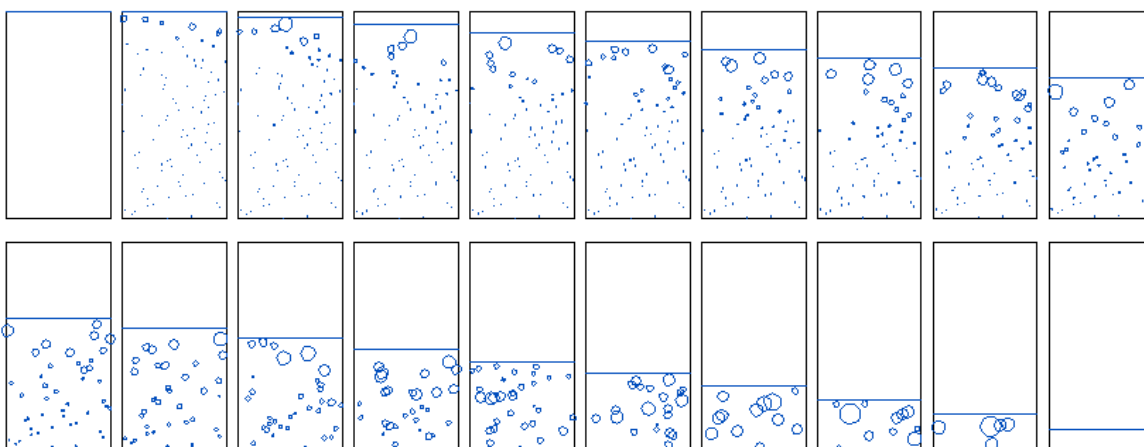
As a bubble approaches the surface of the melted polymeric sample, the surface deforms. This causes the bubble to slow until it reaches a fixed final position at which drainage and bursting occur.⁶ A multiplicative factor incorporates this deceleration as a function of distance from the surface.

Coalescence and bursting: Bubble coalescence involves three stages: approach, thin-film drainage, and instability leading to rupture. (Bursting may be considered as coalescence with a bubble of infinite radius). The third stage is very rapid, and most research has concentrated on understanding the rate of drainage. The presence of a surface-active agent, or surfactant, can make the difference between coalescence on the order of milliseconds and on the order of hundreds of seconds. Long thin-film drainage times are related to immobility of the liquid-gas

interface and to the formation of a dimple in the film profile. Coalescence times for pure liquids and liquids containing surfactants have been predicted based on fluid and interface properties.⁷ An accurate analysis for combusting thermoplastics, however, also needs to take into account the degradation of polymer in the thin film, which will considerably speed the process. For the current model, it is simply assumed that bubbles coalesce whenever they overlap. The effects of bursting are explored through a time delay for each bubble.

Results

A time sequence showing pyrolysis of a PMMA sample is shown here. This example assumes a fixed initial distribution of bubble nucleation sites and bubble bursting as soon as the surface is touched.



More elaborate submodels of bubble nucleation and bursting processes result in significant changes on mass loss rate.

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² Vrentas, J.S. and Duda, J.L., "Molecular Diffusion in Polymer Solutions," AICHE J. 25:1-24 (1979).

³ Yarin, A.L., Lastochkin, D., Talmon, Y., and Tadmor, Z., "Bubble Nucleation During Devolatilization of Polymer Melts," AICHE J. 45:2590-2605 (1999).

⁴ Olson, S.L., "Buoyant Low Stretch Stagnation Point Diffusion Flames Over a Solid Fuel," doctoral thesis for Dept. of Mech. And Aero. Eng. at Case Western U. (1997).

⁵ Venerus, D.C., Yala, N., and Bernstein, B., "Analysis of Diffusion-Induced Bubble Growth in Viscoelastic Liquids," J. Non-Newt. Fluid Mech., 75:55-75 (1998).

⁶ Chi, B.K. and Leal, L.G., "A Theoretical Study of the Motion of a Viscous Drop toward a Fluid Interface at Low Reynolds Number," J. Fluid Mech. 201:123-146 (1989).

⁷ Li, D. and Liu, S., "Coalescence between Small Bubbles or Drops in Pure Liquids," Langmuir, 12:5216-5220.