

## Chapter 15

# Physical Modeling of Intumescent Fire Retardant Polymers

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Intumescent chemical systems are designed to swell into a thick, robust foam upon exposure to heat, protecting the underlying material from fire by providing a physical barrier to heat and mass transfer. The mechanisms determining the fire-resistant properties of these materials are not well understood. Various approaches to modeling intumescent behavior are reviewed. A three-dimensional model that incorporates physical and chemical phenomena at the scale of a single bubble is described.

The fire resistant capabilities of intumescent materials, which respond to heat by swelling into an insulating char of thickness between 5 and 100 times that of the original material, are well known and widely applied. These materials provide thermal protection to the underlying surface through the absorption of heat by endothermic chemical reactions and through the insulating properties of the final char. Flame spread is inhibited through mechanisms common to other charring materials. The closed foam structure inhibits the transport of volatiles to the environment and the transport of oxygen to unburned regions beneath the char (1), and the retention of mass in the char limits further involvement of the underlying materials in the fire.

The first commercial patent for a foaming fire retardant system was issued to Tramm in 1938 (2). A variety of coating formulations, in the forms of paints and mastics, have been developed and put into commercial use starting in the 1950's (3). The increasing use of organic polymers, which are highly flammable in their natural state, has encouraged the development of intumescent additive systems (4-10). Current research on this topic has been boosted by concerns regarding traditional halogen-based fire retardants, which tend to generate obscuring, toxic, and corrosive smoke during a fire (11). Intumescent coatings have been reviewed by Vandersall (12) and Kay et al. (13), and additive systems have been reviewed by Camino et al. (14,15).

Applications of intumescent fire retardants cover a wide range. Intumescent paints are used for protection in hazardous situations on aircraft carriers and off-shore

oil platforms (16). They may be applied to bring landmark buildings up to current fire protection codes (17). In the construction industry, intumescent coatings for structural steel provide structural integrity during a fire and are less messy to install than alternative fire protection systems that must be sprayed into place (18,19). The expanded foam provides a physical barrier to smoke and fire when intumescent material is used in the form of strips applied to edges of doors. Penetration seals consisting of intumescent mastics, putties, and collars restore protection for fire walls breached by holes for cables and pipes (20,21).

Mechanistic studies have provided a general understanding of the chemical and physical processes that must occur for intumescence to take place. When subjected to a high heat flux, the rising temperature within an intumescent material puts into motion the following sequence of events. First, an inorganic acid, typically stored in the form of a salt, is released. The acid dehydrates a carbon-rich polyhydric compound, in preparation for the eventual formation of a solid char. This reaction may be catalyzed by an organic amine or amide. The intumescent mixture melts. At a temperature corresponding to the proper viscosity an endothermic chemical reaction generates gases. The gases diffuse into small bubbles with diameter typically on the order of 10-60 microns, resulting in the formation of a foam. The material then solidifies through cross-linking into a thick multicellular char.

Careful design is required to ensure that the above events occur in the proper order and with the proper timing. Intumescent chemical formulations are often complicated, requiring a carefully matched set of components (12,15) and attention to the effects of other chemicals in the mixture, which may be synergistic or antagonistic to the desired fire retardant properties (22-24). The timing of chemical events is critical to the protective qualities of the final char. Of particular importance is the decomposition of the blowing agent with respect to the melt viscosity. If gasification takes place when the melt viscosity is too high, bubble growth will be strongly opposed, and the gas will tend to diffuse through the mixture without generating bubbles. If the molten polymer is too fluid, i.e. the melt viscosity is too low, the bubbles will be large, resulting in a fragile and ineffective char. A uniform, fine, close-celled foam structure is highly desirable as an endpoint for these materials due to the need for long-lasting physical integrity and the improved insulating properties of such structures.

The empirical approach that has characterized the development of intumescent coatings and additives has resulted in the successful design of a number of chemical formulations. Further development efforts would be considerably aided, however, by an improved understanding of the fundamental physical and chemical mechanisms responsible for intumescent behavior and its fire protection capabilities. The chemical reactions responsible for the various steps in the gasification and charring processes have been studied in detail for some common intumescent mixtures (25,26). The foaming process and its effects on heat transfer are complex, and few models have been developed to investigate the physical aspects of intumescence.

### **Heat Transfer Modeling**

Since thermal protection is the main purpose of intumescent materials, several models have been developed to study the effects of intumescence on heat transfer to the underlying surface. These have been primarily one-dimensional in nature, and concentrate on the effects of swelling on the thermal properties of a coating.

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**Penetration Seal Model.** In order to investigate the heat transfer for the specialized geometry of an intumescent penetration seal, a simple numerical three-dimensional model was developed by Pehrson and Barnett (32). The penetration through a floor above a furnace is modeled as an annular space bounded by the cylindrical concrete wall of the hole and by a cylindrical pipe. The pipe is not necessarily centered in the hole; in fact, the most severe exposure is expected to occur for the pipe in contact with the side of the hole. The intumescent caulk of even initial thickness forms an upper wall for the annular space. The caulk is divided into a regular array of rectangular control volumes, each of which multiply into a specified number of new char elements when a sufficient amount of heat is absorbed. Finite difference calculations solve the heat transfer problem, which includes radiation, convection, and conduction through both pipe and concrete materials. Temperature as a function of time is predicted at locations within the caulk and along the concrete and pipe walls. These plots show rough qualitative agreement with thermocouple measurements taken in full-scale tests of floor assemblies. Limitations of the model due to the control volume approach, the simple representation of intumescent expansion, and the difficulty of obtaining accurate thermal property data for the intumesced char are acknowledged.

### Physical Modeling

Although the heat transfer models discussed above have given insights into some of the mechanisms by which intumescent materials provide fire protection, none attempt to understand the basic mechanisms that cause swelling. Attempts to optimize fire resistant properties would greatly benefit from improved understanding of the fundamental phenomena of intumescent foam development and its sensitivity to material properties, chemistry, and fire conditions. Models that focus on the mechanisms of swelling and bubble formation are found in the literature on foam fabrication, gasification of heated thermoplastics, and softening coal pyrolysis.

**Foam models.** Because of its commercial importance, considerable effort has gone into understanding the evolution of thermoplastic structural foams. Bubbles are typically introduced during injection molding by dissolving a gas into the polymer melt at high pressures. When the solution enters the mold, a sudden decrease in pressure results in a supersaturated state, and bubbles nucleate and grow. The morphology that develops during fabrication determines the uniformity and physical properties of the final product. Many models have been developed to characterize bubble nucleation and growth in the manufacturing environment.

Early models of bubble growth in a supersaturated solution address the problem of a single bubble growing in a fluid of infinite extent (33-35). Given an initial cavity that exceeds a critical size (34), the bubble growth process is driven by diffusion opposed by elastic and surface tension forces at small radii and by viscous forces. Inertial terms may be neglected in foam calculations. Street et al. (36) includes variations in gas concentration and temperature with radial distance from the bubble, and includes mass, momentum, and energy conservation.

Amon and Denson introduced the concept of a cell model (37), in which the bubble grows in a sphere containing a specified amount of fluid, which forms a concentric shell around the bubble. Figure 2 provides a schematic of this model. This

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**One-dimensional Models.** The one-dimensional models that have been developed to investigate intumescent behavior apply the equations of energy and mass conservation to some variation of the geometry illustrated in Figure 1. In this schematic the thickness of virgin material and char layers and the location of the pyrolysis zone are functions of time, and each layer is assigned its own values of thermodynamic parameters.

The earliest model of this kind was developed by Cagliostro et al. (27) to investigate the sensitivity of backwall temperature to swelling behavior and material properties. The model replaces thermal conductivity  $k$  in a standard ablation model with an "effective" thermal conductivity  $k/E$ , where  $E(y,t)$  is an expansion factor relating the original position  $y$  of a point in the intumescent layer to its position during and after swelling. Assuming an empirical form for  $E$ , lower backwall temperatures are attained for rapid expansion, greater coating thickness, thicker expansion, and endothermal heat of reaction. For model parameters obtained from experiment, prediction of behavior is found to be accurate within 20%. A similar approach has been taken by Zverev et al. (28).

Anderson and Wauters (16) use the pyrolysis zone between virgin material and char to represent the active region of intumescent behavior. This model assumes an expansion factor similar to that proposed by Cagliostro et al., but also takes into account the velocity at each point. The velocity is zero within the virgin material, constant within the char, and a function of the expansion factor and mass loss rate within the pyrolysis zone. Heating of the substrate and radiative losses at the surface are also included. Given empirical curves of mass loss and thermodynamic parameters as functions of temperature, comparisons of the predicted substrate temperature with experiment suggest that a better understanding of the expansion factor is necessary.

In accordance with experimental evidence that the region in which intumescence takes place is thin relative to the coating thickness, a frontal model was developed by Buckmaster et al. (29). In this model the pyrolysis zone is reduced to a thin front, across which material properties, velocity, and temperature gradient are discontinuous. The temperature at the front is assumed fixed at a specified critical value. The problem reduces to a Stefan problem that is readily solved numerically. Results of this model show that, in qualitative agreement with experiment, the temperature of the substrate tends to level off as the front traverses through the intumescent coating, followed by a rapid temperature increase. This trend in temperature is attributed to the convection associated with the expansion, which counters the conductive flux of heat. The temperature plateau is lengthened by endothermicity of the chemical reactions. The frontal model is compared with experimental results in a paper by Anderson et al. (30).

Effects of the insulating properties of the intumescent char were studied using a simple thermal resistance model by Anderson, et al. (31). Thermal conductivities of samples were estimated from temperature vs. time data and compared to values computed assuming a porous material that can be represented by layers of solid and trapped gas. The authors conclude that the likely cause of low thermal conductivity for an intumescent char is gases that are trapped within the char.

All of these one-dimensional models rely on empirical information about the amount and rate of expansion. Their scope is limited to heat transfer, and they are not capable of supplying insights into the swelling process itself.

approach enables the consideration of bubbles separated from their neighbors by a thin film and adds the important factor of depletion of the dissolved gas. Use of the cell model as a building block for the study of macroscopic foam behavior is demonstrated in a later paper (38). In this investigation, the melt temperature, bulk foam pressure, and fraction of solidified foam are inputs, and the bulk foam density and bubble size distribution are calculated.

The cell model is used by Arefmanesh et al. (39) to study the size distribution and density variations during foam fabrication by taking into account the flow velocity of the melt. As the developing foam fills a narrow elongated mold, the bubbles are assumed to be transported with the same velocity as the melt. Larger bubbles are predicted close to the melt front than near the inlet gate, in agreement with experiment. Heat transfer from the sides of the mold has been added to this model (40) through the dependence of viscosity and other material properties on temperature.

Many foam models take into account the viscoelastic properties of the polymeric melt. Non-Newtonian effects have been determined to be most important in the early stages of bubble growth (36, 40, 41).

An intumescent foam differs from the structural foams treated by the above models in that the concentration of gas in the melt surrounding a bubble derives from chemical reactions rather than from the expansion of dissolved gases. The gasification chemistry is highly dependent on temperature, whose large spatial variations must also be taken into account.

**A Model of Thermoplastic Gasification.** When subjected to an incident heat flux, non-charring thermoplastic materials form a molten layer. Temperatures above the boiling point of the monomer may be attained at locations within the material. In addition to vaporization occurring at the surface, therefore, gasification occurring in-depth frequently results in bubbles that transport volatiles to the surface. There, (unlike during intumescence) the bubbles burst and release gases to the environment. The resulting increase in steady-state surface regression rate was studied by Wichman (42) using a theoretical model that describes the evolution of bubble number distribution. The model includes bubble nucleation, translation driven by the temperature gradient, and growth. Results of this model demonstrate the insulating properties of the bubbles by showing that their presence increases the temperature gradient in the melt. The regression rate is shown to be determined by a balance among the surface heating rate, the rate of heat absorption in the interior of the melt, and the rate at which the monomer forms bubbles.

**Models of Softening Coal Pyrolysis.** The transport of volatiles from the interior of coal particles by bubbles is of significant importance in the pyrolysis process. Coal melts and often swells when heated, and several models have been developed to better understand the effects of bubbles on coal pyrolysis behavior, such as weight loss and changes in mechanical properties.

Attar (43) concentrates on bubble nucleation, modifying classical bubble nucleation theory to account for the accumulation of gases due to a chemical reaction. The nucleation rate is found to be controlled by the viscosity of the coal melt, and the critical gas concentration for homogeneous nucleation to take place is determined.

A model developed by Oh et al. (44) explores the effects of pressure, particle diameter and temperature, and heating rate on tar yields, weight losses, swelling ratio, and plasticity. This model assumes isothermal spherical coal particles, in accordance

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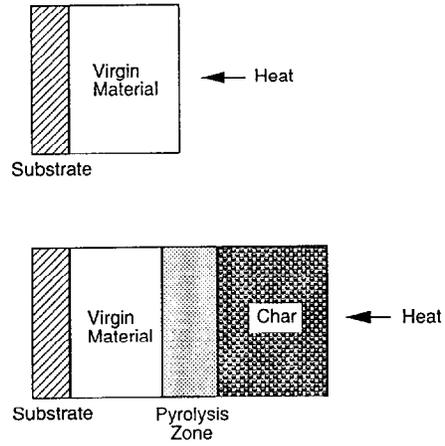


Figure 1. Typical one-dimensional model for an intumescent coating: Initial configuration (top) and configuration during swelling process (bottom).

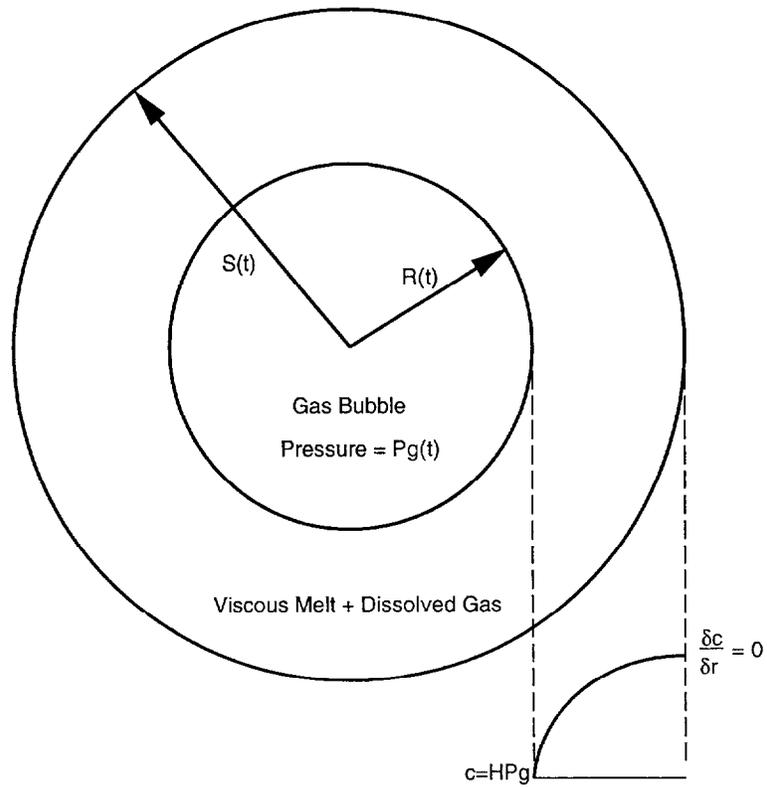


Figure 2. Schematic of cell model for foam analyses.

The number of bubbles that will be included in this model is far too high to consider solving the equations of mass, momentum, and energy exactly, meeting all boundary conditions. The approach taken is to consider the behavior of a single bubble in a fluid containing a temperature gradient, as pictured in Figure 3. A simple description of the physics and chemistry, either as an analytical solution or a lookup table, is sought for the individual bubble. It is then presumed that the total field in the melt can be reasonably approximated as a summation of the individual fields. This is strictly valid only for bubbles far apart compared to their radius, although insight into intumescent behavior is expected even at larger bubble sizes. When the bubbles are sufficiently large, and/or solidification has taken place, the bubbles no longer move independently and the material behaves like a foam.

The basic components of the three-dimensional model are bubble growth, hydrodynamics, and heat transfer. The current status and direction for each of these submodels are discussed below. A more complete description of the mathematics will be published in the near future (Butler, K. M., Baum, H. R., and Kashiwagi, T. *Fire Safety Science, Proceedings of the Fifth International Symposium*, in press.).

**Bubble Growth Submodel.** The growth rate of bubbles in the intumescent material depends on the chemistry of the decomposition of the blowing agent and on the physical properties of the gas and surrounding melt. As in foam fabrication, bubble growth is primarily due to diffusion of gas, although the gas is generated from chemical decomposition rather than supersaturation. In the model, the number and locations of nucleation sites are provided as inputs. When the temperature at the position of one of these sites reaches the value at which decomposition begins, as determined by the three-dimensional heat transfer calculations, growth is initiated. Currently, the intumescent model uses a simple analytic expression for the bubble growth rate  $\dot{R}$  in a supersaturated fluid from early work by Epstein and Plesset (33):

$$\dot{R} = DS \left( \frac{P_0}{P_c} - 1 \right) \left[ \frac{1}{R} + \frac{1}{(\pi Dt)^{1/2}} \right],$$

where  $R$  is radius,  $t$  time,  $D$  the diffusion coefficient,  $S$  the gas solubility,  $P_0$  the initial supersaturation pressure, and  $P_c$  the minimum critical pressure for bubble inflation. Growth is triggered instantaneously instead of being driven by chemical kinetics. This is a place holder for a more sophisticated submodel currently under development and based on the cell model for foams. The critical factors to be included in this submodel include viscous resistance to bubble expansion, reaction chemistry, depletion of the blowing agent, and solidification.

**Hydrodynamics Submodel.** Each expanding bubble experiences forces due to gravity, to gradients of viscosity and surface tension over its surface due to the local temperature gradient (46), and to the motions of other bubbles. The problem can be simplified by setting the velocity in the melt surrounding the bubble equal to the sum of a radial expansion field plus a velocity field due to translation. The Reynolds number,  $Re = \rho U(2R) / \mu$ , with translation velocity  $U$ , melt viscosity  $\mu$ , and melt density  $\rho$ , is very small for these bubbles. A small Reynolds number is consistent with an assumption that the bubble remains spherical. With the additional assumption

with observed sizes on the order of 70  $\mu\text{m}$  in diameter and a heating rate of 1000  $^{\circ}\text{C}/\text{s}$ . Equations are derived to track the number of bubbles of a given size, allowing for bubble growth due to diffusion, chemical reactions within the bubble, changes in pressure, and coalescence, and to maintain the mass balance for gas and decomposable polymers (metaplast) in the molten coal. The mass balance includes depletion of the metaplast. Buoyancy is neglected due to the high melt viscosity, and the gas is released when the bubble boundary intersects the particle surface. Physical properties of the melt, gases, and metaplast are entered into the model using empirical correlations. Initiation of the bubbles is assumed to take place at pore sites in the original solid coal. Unlike Attar's work, these calculations indicate that bubble nucleation is not a rate-limiting process. The model predicts that the bubble size distribution is relatively uniform throughout the particle. Depletion of the metaplast results in resolidification of the melt. Predictions of weight loss, swelling, yields of tar, gases, and metaplast, and sensitivity to various parameters are in good qualitative agreement with experiment.

These models of softening coal pyrolysis include the chemistry of gasification and solidification, phenomena that are also important in intumescence. However, their direct applicability is limited by the differences in geometry, size, and heat transfer between the small, isothermal coal spheres and the extended intumescent layers containing high thermal gradients.

### Three-dimensional Model of Intumescence

Clearly, intumescent materials present considerable difficulties to modellers. As demonstrated by the one-dimensional heat transfer models, swelling is central to their fire protective capabilities, and a fundamental understanding of the mechanisms that cause expansion is important. Unlike foams and softening coals, temperature gradients and heat transfer play a central role in intumescent behavior. In particular, the effect of the growing bubbles on the temperature field cannot be neglected. The sizes of nearby bubbles may be quite different due to the large temperature gradients within the intumescent melt.

In an attempt to address these factors, a three-dimensional model that incorporates bubble and melt hydrodynamics, heat transfer, and chemical reactions is currently under development (45). In this model, the intumescent system is represented as a highly viscous incompressible fluid containing a large number of expanding bubbles. The bubbles obey equations of mass, momentum, and energy on an individual basis according to the values of local parameters, and their collective behavior is responsible for the swelling and fire retardant properties of the material.

Initially, the sample is in the shape of a rectangular solid containing a large number (up to 10,000) of infinitesimally small bubble nucleation sites randomly distributed throughout the volume. A specified heat flux is applied to the upper surface of the sample and the energy equation is solved to determine the temperature field in the sample. When the temperature at a given nucleation site exceeds the degradation temperature of the blowing agent, gas is produced, and the bubble begins to grow. Both viscosity and surface tension are functions of temperature, and the strong temperature gradient plus gravity cause migration of the expanding bubble. The presence of the bubble, with thermal conductivity an order of magnitude lower than that of the surrounding melt, distorts the temperature field, as do the endothermic chemical reactions that generate the gas.

that the expansion velocity is much greater than the translation, the flow field around a solitary bubble can be described analytically by a simple Stokes equation driven by a force due to the viscosity gradient. The polymeric melt is not expected to be free of surface-active contaminants, so internal circulation is assumed to be absent, and the force due to surface tension gradients is neglected. The translation velocity of the bubble through the melt is determined by calculating the terminal velocity resulting from a balance of forces on the bubble, and is given by

$$U = -\frac{2}{3} R \dot{R} \frac{\partial \ln \mu}{\partial T} G - \frac{2}{9} \frac{\Delta \rho g R^2}{\mu} ,$$

where  $G = dT/dz$  is the local temperature gradient at the bubble,  $\Delta \rho$  is the difference between melt and bubble density, and  $g$  is acceleration due to gravity. Here gravity is taken to act in the  $z$ -direction. For thermal gradients at an angle to gravity, the translation velocity is given by a vector sum. The total velocity field, shown in Figure 4, is similar to the field determined by Sadhal and Ayyaswamy (47) for a slowly moving evaporating drop.

To handle the intumescent problem, the motion of a large number of bubbles must be determined. A simple summation of individual flow fields provides a reasonable approximation for the total flow field if the spacing between bubbles is large compared with their size. This assumption is most accurate, of course, at small times, although the tendency of expansion velocity fields to cancel each other improves the validity of this assumption at later times. The addition of image bubbles beneath the lower surface of the sample maintains a no-flux boundary condition.

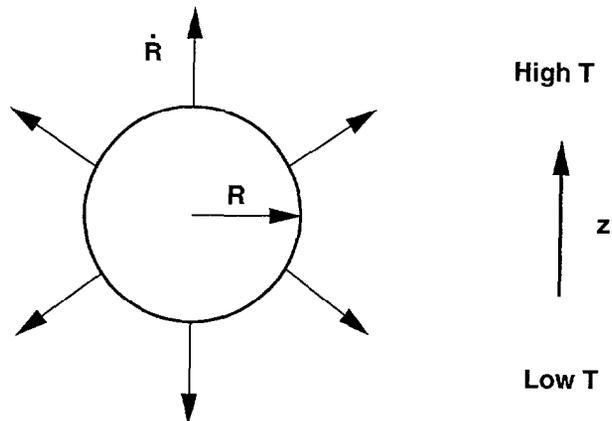
The outer surface of the intumescent sample is forced upward by the sum of forces from the bubbles expanding within the melt. As a first approximation for the surface properties of the intumescent material, the bubbles are assumed to be retained by the sample. The upper surface therefore stretches to prevent bubbles from bursting and releasing gases to the exterior. The polymeric melt changes shape only in response to bubble growth and movement, and is assumed to be sufficiently viscous that gravity and other forces have negligible effect on the melt itself.

The variation of viscosity with temperature is currently estimated by the WLF equation for polymer melts (48),

$$\ln \mu = 13 - \frac{17.44 (T - T_g)}{51.6 + (T - T_g)} ,$$

where  $T_g$  is the glass temperature of the polymer melt. This relationship can be readily modified within the model to include other important factors such as molecular weight.

**Heat Transfer Submodel.** Upon exposure to the heat flux from a fire, the temperature within the intumescent sample rises, triggering gasification reactions at locations progressively farther from the outer surface. By adding a simple one-dimensional model of heat transfer through a slab to bubble growth and hydrodynamics submodels, the progress of nucleation and the bubble size distribution



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42. Wichman, I. S. *Comb. & Flame* **1986**, *63*, 217-229.
43. Attar, A. *AIChE J.* **1978**, *24*, 106-115.
44. Oh, M. S.; Peters, W. A.; Howard, J. B. *AIChE J.* **1989**, *35*, 775-792.
45. Butler, K. M.; Baum, H. R.; Kashiwagi, T. *Proceedings of the International Conference on Fire Research and Engineering*; Orlando, FL, 10-15 Sept. 1995; pp. 261-266.
46. Young, N. O.; Goldstein, J. S.; Block, M. J. *J. Fluid Mech.* **1959**, *6*, 350-356.
47. Sadhal, S. S.; Ayyaswamy, P. S. *J. Fluid Mech.* **1983**, *133*, 65-81.
48. Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Amer. Chem. Soc.* **1955**, *77*, 3701.
49. Jeffrey, D. J. *Proc. R. Soc. Lond. A* **1973**, *335*, 355-367.
50. Batchelor, G. K. *Ann. Rev. Fluid Mech.* **1974**, *6*, 227-255.
51. Lee, Y.-M.; Haji-Sheikh, A.; Fletcher, L. S.; Peterson, G. P. *J. Heat Trans.* **1994**, *116*, 17-27.

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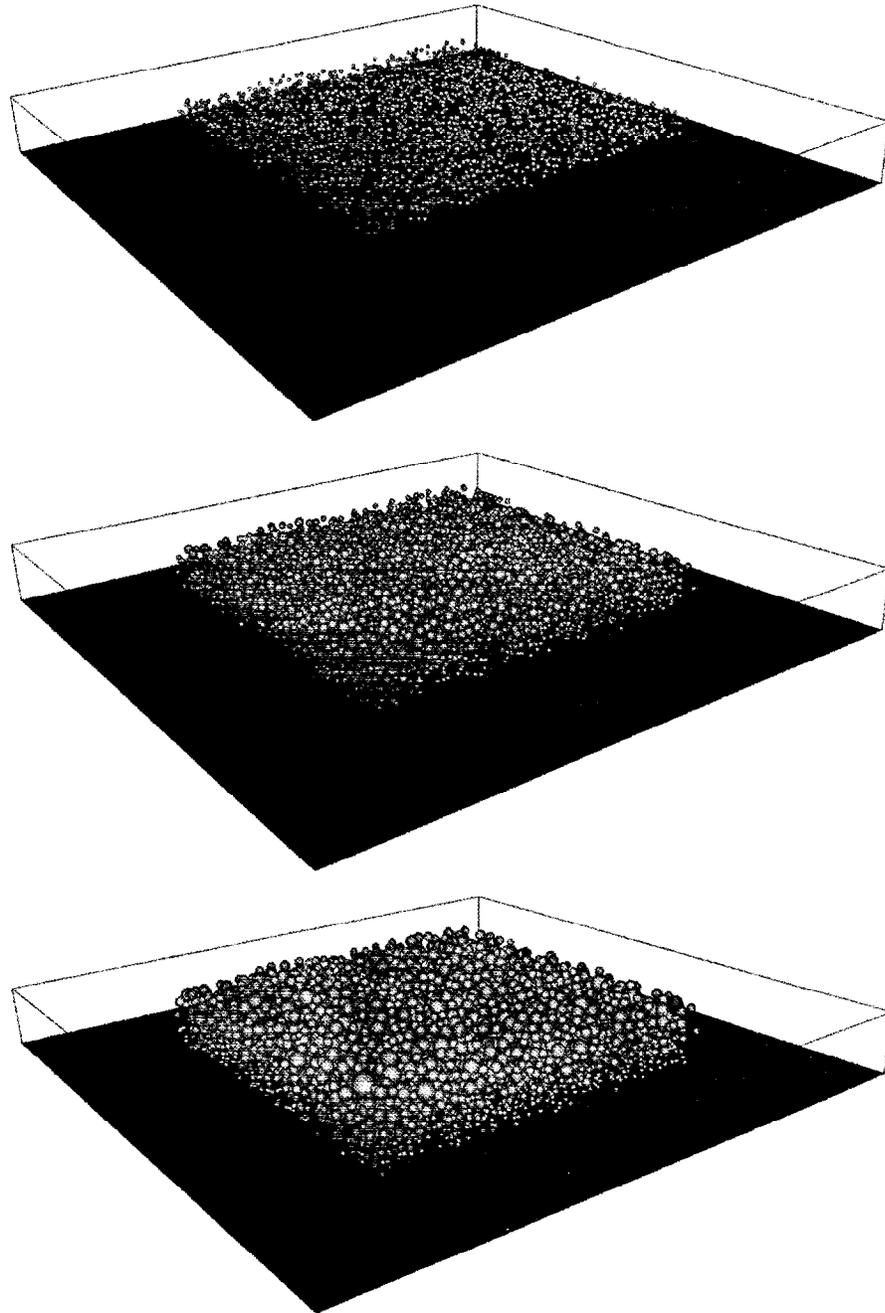


Figure 6. Perspective views of bubble development corresponding to the final three times illustrated in Figure 5.

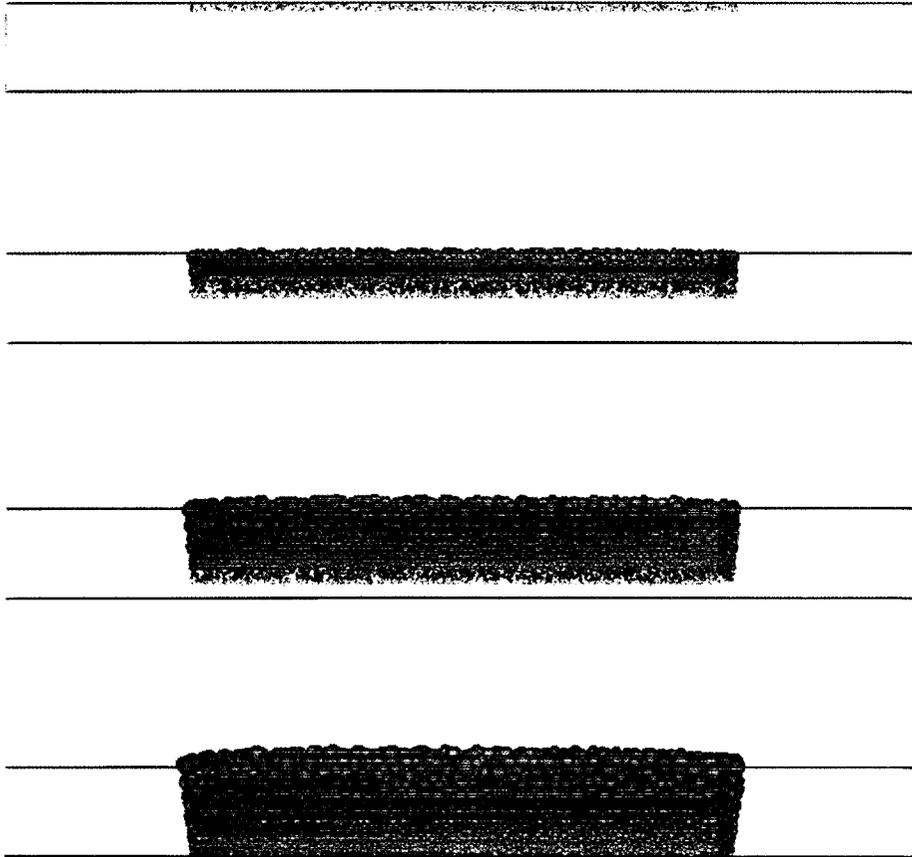


Figure 5. Development of 10,000 bubbles with time as a heat flux is applied to the upper surface of a volume whose initial dimensions in centimeters are  $10 \times 10 \times 1$ . The bubbles are randomly distributed in the central  $6 \times 6 \times 1$  region. As the internal temperature increases, nucleation occurs progressively deeper in the melt.

may be observed. Figures 5 and 6 illustrate the behavior of the model over time for a computer run in which the central region is randomly seeded with 10,000 bubble nucleation sites.

In order to capture the thermal mechanisms responsible for the fire resistance of intumescent materials, the effects of the bubbles on heat transfer must be included. One-dimensional models have identified two important mechanisms: the endothermal chemical reactions that absorb heat during gasification, and the insulating properties of the final char.

Efforts to determine the transport of heat through a suspension of particles, such as composites, have focused on the determination of an effective thermal conductivity (49-50). Although the particles may be randomly distributed, statistical homogeneity is assumed. This does not describe the intumescent problem, in which an intumescent "front" is observed to move through the material. Bubble nucleation and growth are strongly dependent on local temperature, which is in turn dependent on the locations and sizes of bubbles closer to the heat source.

To investigate this problem, therefore, we again consider the single expanding spherical bubble in a uniform background temperature gradient as shown in Figure 3. In the intumescent melt, we can safely assume that the timescale for thermal diffusion is much shorter than the timescales for bubble expansion and translation. The solution to the transient energy equation is therefore well approximated by the solution of the Laplace equation with boundary conditions that account for a background temperature gradient and for continuity of temperature and heat flux at the surface of the sphere. If the endothermal chemical reaction is introduced as a heat sink at the bubble surface, then the temperature field in the surrounding fluid is identical to that from the sum of a dipole singularity plus a source:

$$T = Gz + Gz \frac{R^3}{r^3} \left( \frac{1-\alpha}{2+\alpha} \right) + \frac{\dot{q}'' R^2}{kr} ,$$

where  $G$  is the local temperature gradient,  $r$  the radial distance from the center of the sphere,  $k$  the thermal conductivity of the melt,  $\alpha = k_s/k$  the ratio of the thermal conductivity of the sphere to that of the melt, and  $s$  the heat source. This analytical solution may be summed over multiple bubbles (45).

Figure 7 shows the temperature contours in the neighborhood of a sphere centered in each plot. The temperature increases in the positive  $z$ -direction. The results of thermal conductivity differences between the sphere and the surrounding fluid are illustrated in Figures 7a and b. In (a), the sphere is highly conductive, with thermal conductivity of the sphere ten times that of its surroundings. The temperature of this sphere is nearly uniform. In (b), the sphere represents a bubble, with thermal conductivity an order of magnitude less than the surrounding fluid. Figures 7c and d shows the effect of a heat source and a sink, respectively, on the surface of the sphere, representing exothermal and endothermal chemical reactions. Note that for the case of a bubble with endothermicity, combining Figures 7b and d, the temperature in the region directly beneath the bubble is decreased as expected.

As in the case of the velocity field, a reasonable approximation to the total temperature field is obtained by summation of the individual fields if the separation of multiple bubbles is larger than their radii.

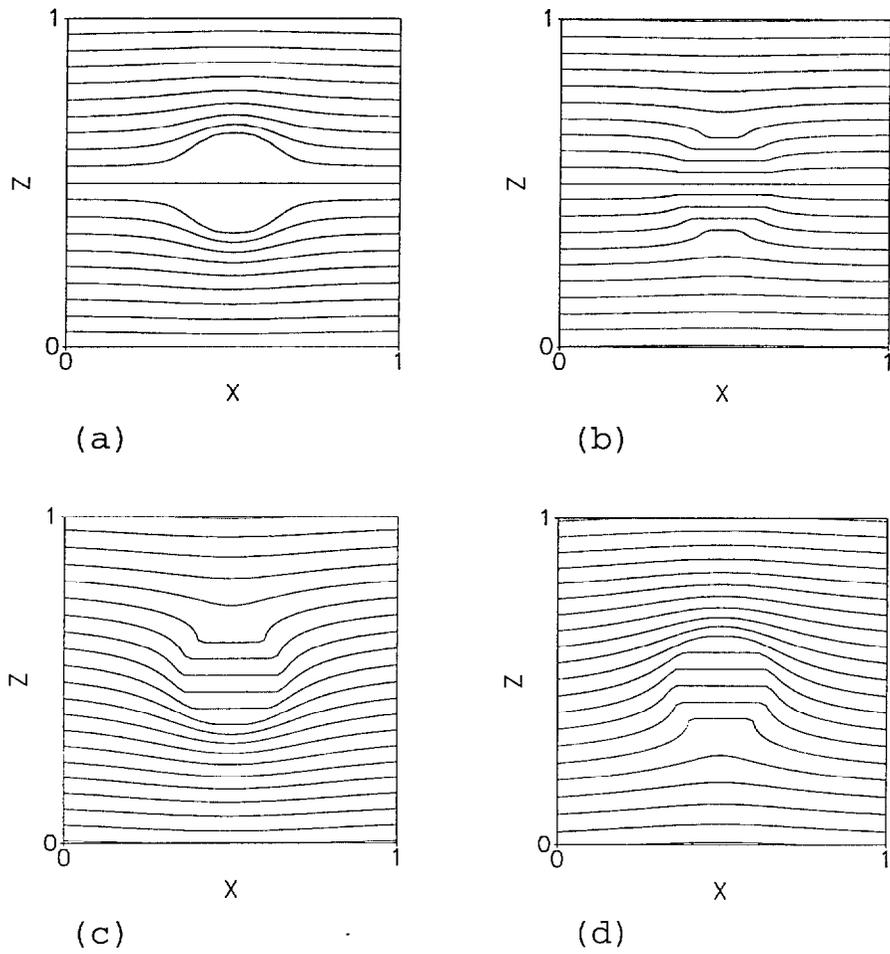


Figure 7. Temperature contours for single bubble in a fluid of infinite extent. The background temperature increases in the positive  $z$ -direction. The bubble is a) a thermal conductor, b) a thermal insulator, c) a heat source, and d) a heat sink.

- for Hazard Prevention; Nelson, G. L., Ed.; ACS Symposium Series 599; American Chemical Society: Washington, DC, 1995; pp. 76-90.
10. Lewin, M.; Endo, M. In *Fire and Polymers II; Materials and Tests for Hazard Prevention*; Nelson, G. L., Ed.; ACS Symposium Series 599; American Chemical Society: Washington, DC, 1995; pp. 91-116.
  11. Pagliari, A.; Cicchetti, O.; Bevilacqua, A. In *Flame Retardants '92; 5th International Conference*; London, England, 22-23 Jan. 1992; Elsevier Applied Science: New York, NY, 1992; pp. 41-52.
  12. Vandersall, H. L. *J. Fire & Flamm.* **1971**, *2*, 97-140.
  13. Kay, M.; Price, A. F.; Lavery, I. *J. Fire Ret. Chem.* **1979**, *6*, 69-91.
  14. Camino, G.; Costa, L. *Polym. Deg. & Stab.* **1988**, *20*, 271-294.
  15. Camino, G.; Costa, L.; Martinasso, G. *Polym. Deg. & Stab.* **1989**, *23*, 359-376.
  16. Anderson, C. E.; Wauters, D. K. *Int'l Engrg. Sci.* **1984**, *22*, 881-889.
  17. Harp, D. W. *Techn. & Conserv.* **1981**, *6*, 30-31.
  18. Allman, F. *Bldg. Control* **1987**, *24*, 32-33.
  19. Sakumoto, Y.; Yamaguchi, T.; Okada, T.; Yoshida, M.; Tasaka, S.; Saito, H. *J. Struct. Eng.* **1994**, *120*, 1103-1121.
  20. Becker, W. *Fire and Mat.* **1991**, *15*, 169-173.
  21. Hulin, K. *Fire Surveyor* **1993**, *22*, 12-15.
  22. Scharf, D.; Nalepa, R.; Heflin, R.; Wusu, T. *Fire Safety J.* **1992**, *19*, 103-117.
  23. Levchik, S. V.; Levchik, G. F.; Camino, G.; Costa, L. *J. Fire Sci.* **1995**, *13*, 43-58.
  24. Bourbigot, S.; Le Bras, M.; Bréant, R.; Trémillon, J.-M.; Delobel, R.; *Fire & Mat.* **1996**, *20*, 145-154.
  25. Camino, G.; Costa, L.; Trossarelli, L. *Polym. Deg. & Stab.* **1984**, *6*, 243-252.
  26. Camino, G.; Martinasso, G.; Costa, L.; Gobetto, R. *Polym. Deg. & Stab.* **1990**, *28*, 17-38.
  27. Cagliostro, D. E.; Riccitiello, S. R.; Clark, K. J.; Shimizu, A. B. *J. Fire & Flam.* **1975**, *6*, 205-221.
  28. Zverev, V. G.; Isakov, G. N.; Nesmelov, V. V.; Nazarenko, V. A. *Intl. J. Polym. Mat.* **1993**, *20*, 91-99.
  29. Buckmaster, J.; Anderson, C.; Nachman, A. *Intl. J. Engng. Sci.* **1986**, *24*, 263-276.
  30. Anderson, C. E., Dziuk, J., Mallow, W. A. and Buckmaster, J., *J. Fire Sci.* **1985**, *3*, 161-194.
  31. Anderson, C. E.; Ketchum, D. E.; Mountain, W. P. *J. Fire Sci.* **1988**, *6*, 390-410.
  32. Pehrson, R.; Barnett, J. R. *J. Fire Prot. Engr.* **1996**, *8*, 13-30.
  33. Epstein, P. S. and Plesset, M. S., *J. Chem. Phys.* **1950**, *18*, 1505-1509.
  34. Gent, A. N.; Tompkins, D. A. *J. Appl. Phys.* **1969**, *40*, 2520-2525.
  35. Prosperetti, A.; Plesset, M. S. *J. Fluid Mech.* **1978**, *85*, 349-368.
  36. Street, J. R.; Fricke, A.L.; Reiss, L. P. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 54-64.
  37. Amon, M.; Denson, C. D. *Polym. Eng. & Sci.* **1984**, *24*, 1026-1034.
  38. Amon, M.; Denson, C. D. *Polym. Eng. & Sci.* **1986**, *26*, 255-267.
  39. Arefmanesh, A.; Advani, S. G.; Michaelides, E. E. *Polym. Engr. & Sci.* **1990**, *30*, 1330-1337.
  40. Arefmanesh, A.; Advani, S. G. *Polym. Engr. & Sci.* **1995**, *35*, 252-260.
  41. Ramesh, N. S.; Rasmussen, D. H.; Campbell, G. A. *Polym. Engr. & Sci.* **1991**, *31*, 1657-1664.

## Discussion

The physical and chemical behavior of intumescent fire retardant materials in the presence of a fire is highly complex. Although some questions about their heat transfer properties may be answered by relatively simple one-dimensional models, a better understanding of the complex mechanisms behind intumescence requires a modeling approach that considers fundamental physical and chemical processes. Many scientific fields can contribute to this problem. In addition to the literature on intumescent heat transfer, foams, bubbling thermoplastic materials, and softening coal pyrolysis discussed in this chapter, modeling of intumescent behavior can also benefit from research in such areas as bulk properties of suspensions and porous media, N-body simulations, and char behavior.

This modeling effort seeks an improved understanding of the mechanisms leading to intumescence and of the sensitivity of intumescent characteristics to various physical and chemical parameters. Pursuit of these insights in cooperation with developers of intumescent systems is expected to contribute to the further development of this important category of fire-resistant materials.

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## References

1. Bertelli, G.; Camino, G.; Marchetti, E.; Costa, L.; Casorati, E.; Locatelli, R. *Polym. Deg. & Stab.* **1989**, *25*, 277-292.
2. Tramm, H.; et al., U.S. Patent 2,106,938; Feb. 1938; assigned to Ruhrchemie Aktiengesellschaft.
3. Chang, W.-H.; Scriven, R. L.; Ross, R. B. In *Flame-Retardant Polymeric Materials*; Lewin, M.; Atlas, S. M.; Pearce, E. M., Eds.; Plenum Press, New York, NY, 1975; pp. 399-454.
4. Bertelli, G.; Locatelli, R.; Marchetti, E.; Camino, G.; Costa, L. In *Proc. of the Int'l. Symp. on Flame Retardants*; Beijing, China, 1-5 Nov. 1989; Yuxiang, O.; Minxiu, Z., Eds.; Intl. Acad. Publ.; pp. 191-198.
5. Bertelli, G.; Camino, G.; Goberti, P.; Marchetti, E.; Luda Di Cortemiglia, M. P.; Costa, L. In *Fire Safety Science - Proceedings of the Third International Symposium*; Edinburgh, Scotland, 8-12 July 1991; Cox, G.; Langford, B., Eds.; Elsevier Appl. Sci.: New York, NY, 1991; pp. 537-546.
6. Camino, G.; Luda, M. P.; Costa, L. In *Recent Advances in Flame Retardancy of Polymeric Materials*; Lewin, M., Ed.; Business Communications Co., Inc.: Norwalk, CT, 1993, Vol. 4; pp. 12-22.
7. Agunloye, F. F.; Stephenson, J. E.; Williams, C. M. In *Flame Retardants '94; 6th International Conference*; London, England, 26-27 Jan. 1994; Interscience Communications Ltd.: London, England, 1994; pp. 109-116.
8. Marchal, A.; Delobel, R.; Le Bras, M.; Leroy, J.-M.; Price, D. *Polym. Deg. & Stab.* **1994**, *44*, 263-272.
9. Camino, G.; Luda, M. P.; Costa, L. In *Fire and Polymers II; Materials and Tests*