A Numerical Model of Bubbling Thermoplastics

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Thermoplastic Materials in Fire
Microscopic Photographs of PMMA

Numerical Model

• 1-D Finite element model
  – Mass balance for gas and polymer
  – Energy balance

• Individual bubble dynamics
  – In 3-D
  – Sizes and locations of bubbles determine amount of gas in each element
  – Motion of bubbles determine velocities
Continuity Equations

• Polymer
\[
\frac{\partial}{\partial t} (\rho_p \phi_p) + \frac{\partial}{\partial z} (\rho_p \phi_p W_p) = -\rho_p \phi_p B e^{-E/RT}
\]

• Gas
\[
\frac{\partial}{\partial t} (\rho_g \phi_g) + \frac{\partial}{\partial z} (\rho_g \phi_g W_g) = +\rho_p \phi_p B e^{-E/RT}
\]

• Volume Fractions:
\[
\phi_p = \frac{V_p}{V} \quad \phi_g = \frac{V_g}{V}
\]
Energy Equation

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

where

\[ (\rho c_p)^* = \sum_k \rho_k \phi_k c_{p_k} \]

\[ W^* = \frac{\sum \rho_k \phi_k W_k}{\sum \rho_k \phi_k} \]

\[ k^* = (k_p)^{\phi_p} (k_g)^{\phi_g} \]
Bubble Model

- Nucleation
- Bubble growth
- Migration
- Coalescence
- Bursting
Bubble Nucleation

• Homogeneous vs. heterogeneous nucleation
  (Thermal fluctuations) (Impurities)

• Arrhenius function for nucleation rate $J$

$$J = MB \exp\left(-\frac{\Delta F_{cr}}{k_B T}\right)$$

• Elasticity
• Gas diffusivity through melt

• Rate easily varies by $9+$ orders of magnitude!
Secondary Nucleation

Yarin et al., AIChE J. 45:2590-2605 (1999)
Bubble Growth

• Models
  – Infinite domain; finite radius
  – Temperature gradients – radial
  – Dominant mechanism depends on size
    • Surface tension, inertia, evaporation
  – Diffusion-driven: $R \propto t^{1/2}$
  – Polymer melt: between Newtonian fluid and diffusion-driven growth

• Secondary nucleation
  – In strongly viscoelastic liquids
Bubble Migration

• Driven by gravity, temperature gradients (surface tension, viscosity dependence on T)

\[ U = -\frac{2(\rho_p - \rho_g) g R^2}{9 \mu} + \left[ 2 R \dot{R} \left( -\frac{d \ln \mu}{dT} \right) + \frac{R}{3 \mu} \left( -\frac{d \ln \sigma}{dT} \right) \right] \frac{\partial T}{\partial z} \]

• Wake effects
• Bubbles slow as approach surface
Approach to Interface

Bubble Velocity Nearing Interface

Coalescence and Bursting

• Stages:
  – Approach
  – Drainage of thin film
  – Rupture by surface instability - rapid

• Strongly dependent on presence of surfactants
  – Clean interface: ~ 1 ms
  – Surfactant: ~100 s

• Vaporization due to heating not considered
Thin-film Drainage

(a) Calculated shapes
Ca = 0.5, \lambda = 5.0

(b) Calculated shapes
Ca = 1.0, \lambda = 0.02

Hartland (1967b)
Ca = 0.507, \lambda = 4.76

Hartland (1969)
Ca = 1.037, \lambda = 0.021
Bursting

• Gases released by sample
  – Determines the mass loss rate
  – Heat release rate of fire
• Long-lasting bubbles may form insulating layer
Bubble Model

\[ \Delta t_{\text{drain}} \]

\[ \dot{m} \]

\[ \Delta poly_{\text{elem}} \rightarrow \Delta gas_{\text{elem}} \]

\[ \Delta gas_{\text{elem}} \leftarrow \Delta poly_{\text{elem}} \]
Numerical Model

- Bubbles t=114.25
- Temperature Profile t=114.25
- All Bubbles t=114.5
- Remaining Bubbles t=114.5
- Temperature Profile t=114.5

Δt

Determine physical properties of elements, Calculate temperatures
Gasification, Bubble growth and migration
Subtract burst bubbles
Determine physical properties of elements, Calculate temperatures
Effects of Bursting Delay in PP

Drainage time = 0 sec

0.01 sec
Effect of Bursting Delay on Sample Thickness vs. Time

Drainage times = 0, 0.01 seconds
Temperature vs Time for Sample Surfaces

Drainage times = 0 (orange), 0.01 (green) seconds
Nucleation Model
PP vs. PMMA
Other Bubble Effects

- Radiation
  - Internal transmission
  - Scattering
- Oxygen entrainment
- Distortion of surface geometry
Conclusions

• Bubbling behavior in thermoplastic materials exposed to fire is highly complex
  – First principle modeling has a long way to go

• Because of insulating layer and direct impact on mass loss rate, bubble behavior at surface is critical
  – Bursting, coalescence, nucleation, approach to interface
  – Need to include radiation effects