NUMERICAL SIMULATION OF POLYMERIC MATERIALS IN UL 94 TEST: COMPETITION BETWEEN GASIFICATION AND MELT FLOW/DRIPPING

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ABSTRACT

The capability of the Particle Finite Element Method (PFEM, developed by CIMNE, the International Center for Numerical Methods in Engineering) to model the complex fire behaviour of polymers in the UL 94 scenario was investigated. For validation, a series of four PC/ABS blends were chosen, which covered different UL 94 classifications due to the competing effects of gasification, charring, flame inhibition and melt flow/dripping. The materials were characterized thoroughly; in particular, the impact of the additives bisphenol A bis(diphenyl phosphate) (BDP) and polytetrafluorethylene (PTFE) on the rheological properties was determined. The comparison of simulation and experiment showed that PFEM was able to reproduce the dripping and non-dripping behaviour of PC/ABS and PC/ABS+PTFE, respectively. Furthermore the simulated mass loss of this preliminary study agreed well with the experimental results, indicating that PFEM is a promising numerical tool for the simulation of polymers in the UL 94 scenario.

INTRODUCTION

In a fire, polymeric materials, in particular thermoplastics, easily exceed their melting temperature and tend to exhibit extensive melt flow and dripping. These effects can have different consequences for the fire. On the one hand, melt flow and/or dripping of burning material can lead to higher burning rates (e.g., due to larger surface area), additional pool fires on the ground, or enhanced downward flame spread. On the other hand, potential fuel can also be removed from the fire source by dripping or melt flow. Reducing the fuel involved in the actual fire can hinder ignition, slow down the fire growth or support extinction. The UL 94 test is a small-scale fire test where melt flow and dripping can both enhance and reduce the fire risks. The critical impact of dripping is considered in the UL 94 classification. Further, the test result is influenced mainly by heat transfer, gasification and combustion properties. The scope of this work is to analyse the capability of numerical simulation to model the complex fire behaviour of polymers in the UL 94 test, including dripping phenomena.

As validation, UL 94 experiments were conducted using four different materials based on a polymer blend of polycarbonate/acrylonitrile butadiene styrene (PC/ABS). Different additives lead to a variation of the fire behaviour in the UL 94 test [1]. The competing effects are gasification, charring, flame inhibition and melt flow/dripping, whose impact on the test performance is studied. Computational methods for the numerical simulation of fires typically discretize and solve the transport equations on a fixed grid. This prevents the calculation of large deformations or dripping. The increasing interest in so-called fluid-structure interaction (FSI) problems has led to the development of robust and efficient numerical methods for the analysis of engineering problems involving the interaction of fluids and structures. These methods account for large motions of the fluid free surface and the existence of fully or partially submerged bodies.

Early studies by Butler et al. have shown the potential of these methods when applied to fire problems [2-4]. In the present study the capability of the Particle Finite Element Method (PFEM), developed at CIMNE, to simulate the fire behaviour is analysed in the UL 94 scenario.

MATERIALS

Four bisphenol A polycarbonate/acrylonitrile-butadiene styrene (PC/ABS) blends were investigated with and without the flame retardant bisphenol A bis(diphenyl phosphate) (BDP) and polytetrafluorethylene (PTFE) as an anti-dripping agent. The materials with BDP contained 12.5 % mass fraction of the flame retardant. The materials with PTFE contained 0.9 % mass fraction of a masterbatch consisting of styrene-acrylonitrile (SAN) and PTFE in a ratio of 1:1. Four different materials were investigated: PC/ABS, PC/ABS+BDP, PC/ABS+PTFE and PC/ABS+BDP+PTFE [1]. The materials were provided by Bayer MaterialScience AG (Dormagen, Germany).*

EXPERIMENTAL

The flammability of the samples was investigated according to the Underwriters Laboratory test for the flammability of plastics (UL 94), IEC 60695-11-10. The dimensions of the specimens were $(125 \times 13 \times 3)$ mm and $(125 \times 13 \times 1.5)$ mm. Additional experiments were conducted in order to determine the mass loss of the samples. For this the sample holder was placed on a scale and the mass of the set-up was recorded during the test. Dripping material was caught before touching the scale and hence considered as material lost.

Thermal gravimetric analysis was conducted using a TGA/SDTA 851 from Mettler Toledo. The measurements were performed under nitrogen with a sample weight of 10 mg. Measurements for kinetic analysis were taken at heating rates of (1, 2, 5 and 10) K/min. Differential scanning calorimetry (DSC) was conducted with a DSC 7 from Perkin Elmer under a nitrogen atmosphere. The sample weight was between 2 and 4 mg, and the heating rate was 5 K/min.

For rheological investigations the rheometer Anton Paar Physica MCR301 was used, with plate-plate geometry, a plate gap of 1 mm and a plate diameter of 25 mm. Isothermal measurements were conducted at four temperatures (453 K, 473 K, 523 K and 573 K) in the frequency sweep mode. The frequency was varied between 100 Hz and 0.1 Hz and a small deformation (gamma = 1 %) was chosen. All measurements were taken in a nitrogen environment.

PFEM MODEL

The Particle Finite Element Method (PFEM) is a general formulation for analysis of fluid-structure interaction problems. The method was developed by the International Center for Numerical Methods in Engineering (CIMNE) in Barcelona, Spain. A general overview of the code is given in Oñate, et al. (2004) [5]. It has proved to be a powerful tool for the modelling and analysis of complex multidisciplinary problems in fluid and solid mechanics that involve large continuous deformations, coupled thermal effects, fragmentation and separation of fluid particles, and complicated conditions between different fluids or between fluids and solids [5-10].

PFEM combines particle-based techniques with the standard finite element method (FEM). The mesh used for solving the continuum equations with the FEM consists of nodes. These nodes are viewed as material points (particles). The key feature of PFEM is the use of an updated Lagrangian description to model the motion of nodes, which are tracked during the transient solution. According to their density, initial acceleration and velocity, and subject to the force of gravity, the nodes can move freely and can even separate from the main analysis domain, transporting their momentum and physical properties. Once the motion is applied, a robust and efficient remeshing algorithm connects the nodes into a finite element grid for solution of the state variables in the new configuration. The basic PFEM algorithm involves the following steps:

1) Definition of particles (with a given velocity, density, gravity, etc.), volume, boundary conditions and free surfaces.
2) Evaluation of the forces in the particles by solving the Navier-Stokes equations using the FEM. This requires generating the mesh, which is done using extended Delaunay tessellation [11].
3) Evaluation of the velocity and acceleration of each particle using the updated Lagrangian description.
4) Moving the particles and proceeding with 1).

Regarding the analysis of problems related to polymeric materials, additional submodels are applicable, as described in Ref. 4. In particular; the thermal decomposition of the materials is of major interest in simulating the fire behaviour of polymers. Additional terms in the conservation equations for mass and energy account for the mass loss due to gasification and the energy absorbed during gasification, respectively. The volumetric heat flux due to gasification is equal to the product of density, enthalpy of decomposition and the temperature-dependent volume variation. In the current version, thermal decomposition kinetics are expressed by a single-step, first-order Arrhenius equation.

MODEL SET-UP

The model used to simulate the UL 94 scenario was formulated in 2D and consisted of the rectangular sample positioned in the vertical direction. The sample dimensions were (120x12) mm and the sample consisted of 462 nodes and 790 three-noded triangular cells, respectively. The velocity of the nodes on the top side of the sample, where the sample is clamped, was fixed to zero. In the vertical UL 94 test, a flame produced by a Bunsen burner was applied to the sample twice, each time for a duration of 10 s. For simplification, the model concentrated on the samples' behaviour during and after the first ignition. The boundary condition regarding the heat flux to the sample was estimated according to the work of Hamins, Bundy and Dillon (2005) [12], who thoroughly characterized the heat flux of a candle flame. The maximum heat flux at the bottom of the sample was set to 100 kW/m² decreasing linearly in the upward direction to 0 kW/m² at the top. After 10 s when the Bunsen burner was removed, the boundary condition was changed to 75 kW/m² (estimated value) at the bottom according to a reduced flame size observed in the experiments.

In the simulations, it is assumed that the polymer melt flow behaves like an incompressible fluid. The parameter responsible for describing the phase change from solid to melt is the viscosity, which is expressed as a function of temperature. A quasi-rigid behaviour of the polymer object at room temperature is reproduced by setting the viscosity to a sufficiently high value so that the unheated polymer moves a negligible distance over the duration of the problem. As temperature increases in the thermoplastic object due to heat exposure, the viscosity decreases by several orders of magnitude as a function of temperature. This induces the melting and flow of the particles in the heated zone. Numerically, the temperature-dependent viscosity is implemented by the standard constitutive equation for an incompressible Newtonian fluid. Generally polymer melts do not exhibit a linear shear stress versus strain rate curve, and are known to behave like non-Newtonian fluids. But for higher temperatures and regarding a narrow range of shear rate like the ones experienced in the UL 94 test, the assumption of a Newtonian behaviour becomes plausible.[13]

BEHAVIOUR IN THE UL 94 TEST

In the UL 94 test of the 3 mm thick samples, PC/ABS and PC/ABS+BDP achieved a V-2 classification.[14] The specimen exhibited melt flow and dripping and the materials finally extinguished by dripping.[1] Dripping was the dominant behaviour for both materials, but was more pronounced in the PC/ABS+BDP sample. Figure 1 shows the UL 94 residues of 1.5 mm thick samples at the conclusion of the test. All samples were exposed 10 s plus 10 s to the flame, but burning lasted for different durations. Compared to the PC/ABS sample, the addition of the flame retardant and its plasticising behaviour accelerated the melt flow and dripping and self-extinction occurred earlier in the PC/ABS+BDP specimen.

Adding PTFE significantly influenced the UL 94 performance. The residue of the PC/ABS+PTFE sample is shown in Figure 1. With the addition of PTFE dripping did not occur. This characteristic was observed in all samples containing PTFE. PC/ABS+PTFE burned most completely in the vertical set-up. It achieved a HB classification due to its performance in the horizontal test configuration. Conversely, PC/ABS+BDP+PTFE achieved the highest classification of V-0. The sample extinguished immediately each time the burner was removed due to the synergistic effects of the flame retardant BDP and the anti-dripping agent PTFE.

Figure 1. Original specimen (I) and UL 94 residues of PC/ABS (II),
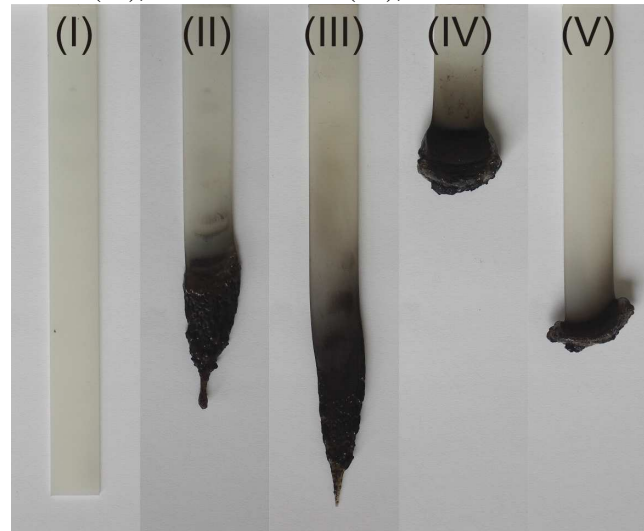PC/ABS+BDP (III), PC/ABS+PTFE (IV),and PC/ABS+BDP+PTFE (V)

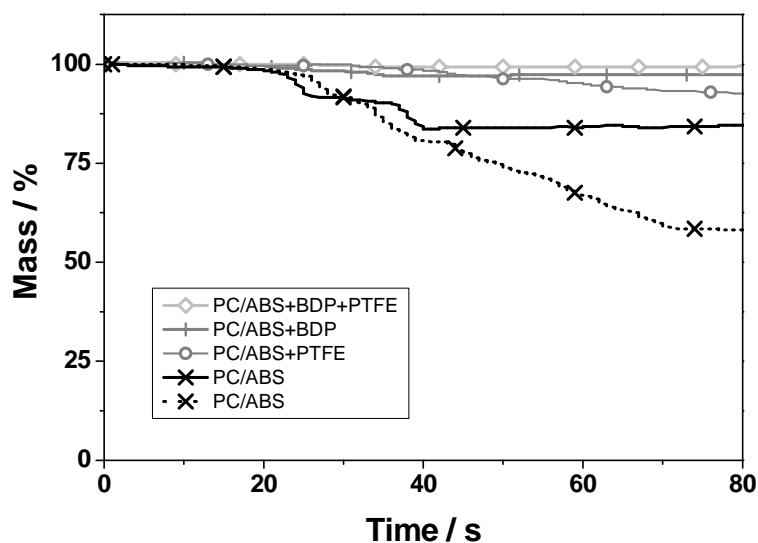Figure 2. Mass versus time of selected specimen in the UL 94 test

Figure 2 shows the mass versus the time of five selected samples tested in the UL 94 set-up as described above. The thickness of the samples was 1.5 mm. PC/ABS+BDP+PTFE (open rhombi) extinguished immediately and therefore almost no mass was lost. PC/ABS+BDP (plus sign) also extinguished shortly after the flame was applied, but through dripping of the burning polymer. Correspondingly, two small steps are present in the mass versus time curve, leading to a small but measurable mass loss. PC/ABS+PTFE (open circle) burned almost completely right after the flame was applied once. Mass is lost only through gasification. The mass loss rate is small but seems to be constant over time. In the case of PC/ABS, two different behaviours were observed. In most cases, after applying the flame for a short time burning and dripping appeared simultaneously until self-extinction took place due to considerable dripping. The corresponding mass characteristics for these cases are shown by the solid line (marked with X). The two major mass loss steps indicate the repeated sequence of applying the flame. For a few PC/ABS samples, the time of simultaneous burning and dripping was prolonged. The dotted line represents a specimen which burned/dripped for ~60 s before self-extinction occurred. During this time the mass loss rate was more or less constant.
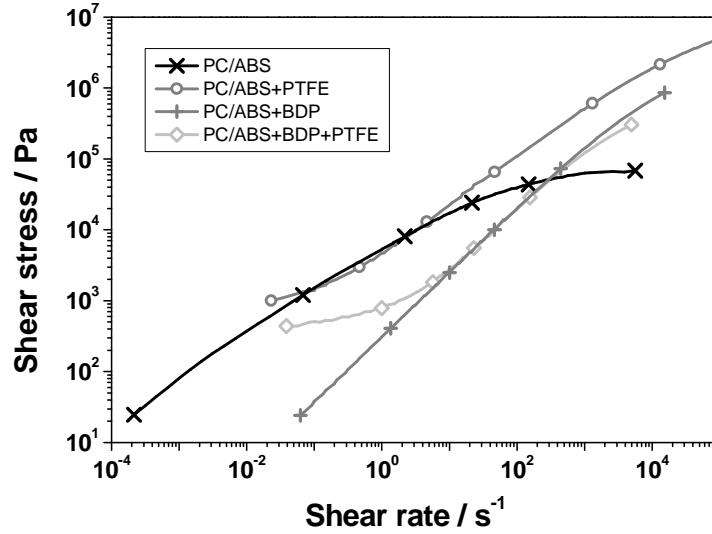
RHEOLOGICAL CHARACTERISTICS

Figure 3 shows the viscosity as a function of temperature measured at 10 Hz, as reported in a previous paper,[1] With the addition of BDP the viscosity is decreased by nearly an order of magnitude, demonstrating the pronounced plasticizing effect of BDP in PC/ABS. As shown above, when less than 1 % mass fraction PTFE is added, the UL 94 performance and the dripping behaviour change. The influence of PTFE on the viscosity measured versus temperature at 10 Hz is less obvious, but a slight increase at higher temperatures is indicated.

Figure 3. Viscosity as a function of temperature measured at 10 Hz in a plate-plate rheometer [1].
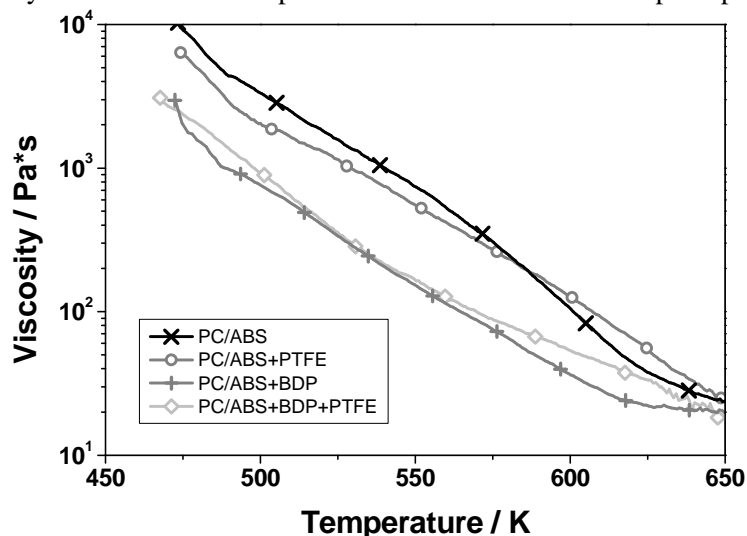
In Figure 4, the shear stress versus the shear rate of the materials is shown. The mastercurves with the reference temperature of 523 K were determined from isothermal measurements of the four materials. As Figure 3 and Figure 4 illustrate, PTFE does not compensate for the plasticizing effect of BDP, but works in a totally different way. For the analysis of dripping behaviour the region of low shear rates is of major interest.[13] In this region the addition of PTFE influences the curve shape considerably. Without PTFE the shear stress decreases with decreasing shear rates. The addition of PTFE leads to a flow limit, i.e. even at very low shear rates the sample shows a certain resistance to stresses. Translated to the material's behaviour in the UL 94 test, the flow limit of materials containing PTFE prevents the samples from dripping. In contrast, at elevated temperatures and in particular at low shear rates materials without PTFE cannot resist gravitational forces so that dripping takes place.

Figure 4. Mastercurves of shear stress versus shear rate with the reference temperature of 523 K

In Figures 3 and 4, the influence of the additives BDP and PTFE on the rheological properties of PC/ABS is explained and therewith the different dripping behaviour. The graphs in Figure 4 also indicate that the rheological characteristics are strongly dependent not only on temperature but also on shear rate. Furthermore other influencing factors exist, like molecular weight, homogeneity, porosity, charring etc. Hence, determining the proper viscosity relationship to use in the numerical simulations is challenging. The viscosity values presented in Figure 3 were not suitable for the simulation because of the high shear rate (10 Hz) applied.

INPUT PARAMETERS

Table 1 gives an overview of the input parameters used in PFEM to describe the material PC/ABS. The values for the density at room temperature were taken from the material data sheet of the commercial PC/ABS blend T65 from Bayer MaterialScience. The thermal conductivity and the specific heat capacity corresponding to the values for the melt were also obtained from the data sheet. Perfect emissivity was assumed as in Ref. 4. The focus of the simulation was on the competing effects of gasification and melt flow/dripping. The key parameters are the viscosity and the parameters describing the thermal decomposition, namely the Arrhenius coefficient, activation energy and heat of decomposition.

Table 1. Input parameters for PFEM simulations regarding the material properties of PC/ABS

| Parameter	Unit	PC/ABS
Density ρ	kg/m³	1130
Thermal conductivity k	W/(m*K)	0.15
Spec. heat capacity c_p	J/(kg*K)	1740
Emissivity ε	1	1.0
Activation energy E	J/kmol	21800
Arrhenius coefficient A	1/s	2×10^{10}
Heat of decomposition h_{dec}	kJ/kg	1050

The implementation of gasification effects in PFEM is based on a single-step first-order Arrhenius equation. The current PFEM version does not consider any kind of residue formation. Therefore the decomposition kinetics of the materials were evaluated from TGA measurements using the ASTM E698 approach, where only the data of the maximum mass loss rate are considered. Figure 5 shows the logarithm of the heating rate versus the reciprocal of the temperature at maximum mass loss (in 1000 K), indicating the practicability of the approach for the material system based on PC/ABS. The heat of gasification for

PC/ABS was determined with differential scanning calorimetry according to Ref. 15. Figure 6 shows the heat flow versus temperature. The shaded area indicates the decomposition region.

Figure 5. Evaluation of the decomposition kinetics of PC/ABS

Figure 6. Determining the heat of gasification of PC/ABS with DSC measurements
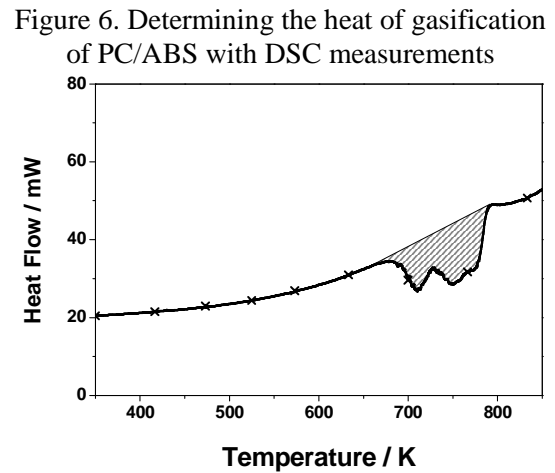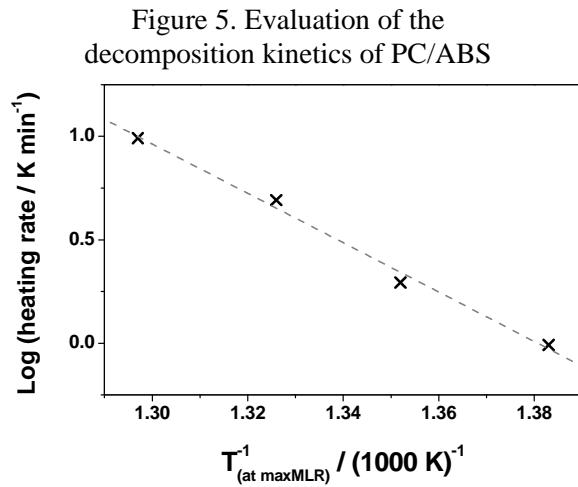
The temperature-dependent viscosity was determined from the isothermal frequency sweep measurements using the rheometer. Dripping is related to low shear rates, hence the viscosity values were taken at the lowest shear rate measured of 0.1 Hz. The highest temperature applied in the tests was 573 K to keep the material from decomposing, which begins at a decomposition temperature of 600 K. For PC/ABS, PC/ABS+BDP and PC/ABS+BDP+PTFE the viscosity values for higher temperatures were estimated based on the exponential fit of the isothermal measurements (473 K, 523 K and 573 K) at 0.1 Hz. In the case of PC/ABS+PTFE the curve was assumed to progress parallel to the curve of PV/ABS+BDP+PTFE. Figure 7 shows the data points at (453, 473, 523 and 573) K and the estimated characteristic for higher temperatures (lines).

Figure 7. Rheological characteristics at 4 different temperatures (points) and the exponential fits (lines) used for the simulations.
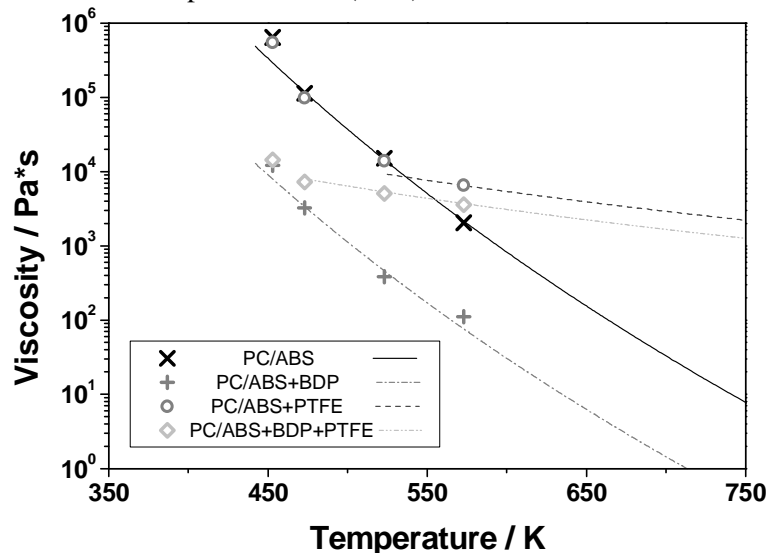
COMPARISON OF SIMULATION AND EXPERIMENT

For the simulations the boundary conditions regarding the heat flux to the sample were assumed to be constant over time. This simplification was based on the observations regarding the mass loss in the UL 94 test (Figure 2). The mass loss of PC/ABS+PTFE occurred due to gasification only and the mass loss rate was approximately constant. As a result, the heat flux was assumed to be constant, too, according to the general relation for steady burning as a function of the mass loss rate, external heat flux and the latent

heat of gasification.[16] The spatial profile of heat flux was assumed to be linear decreasing from the bottom to the top of the sample, as described above. For this initial study, these simplifications were applied in the absence of a submodel for gas phase combustion that is currently under development at CIMNE.

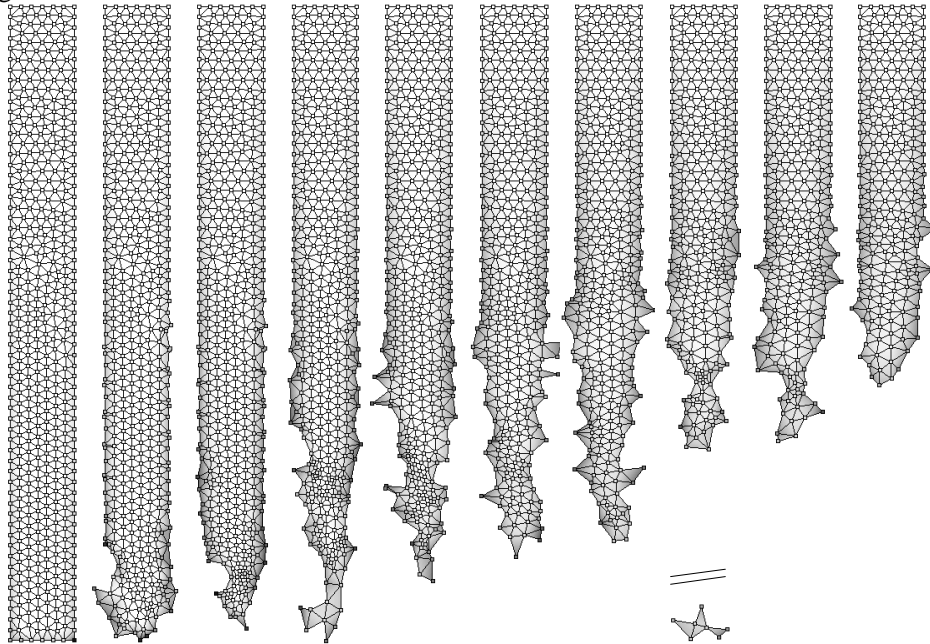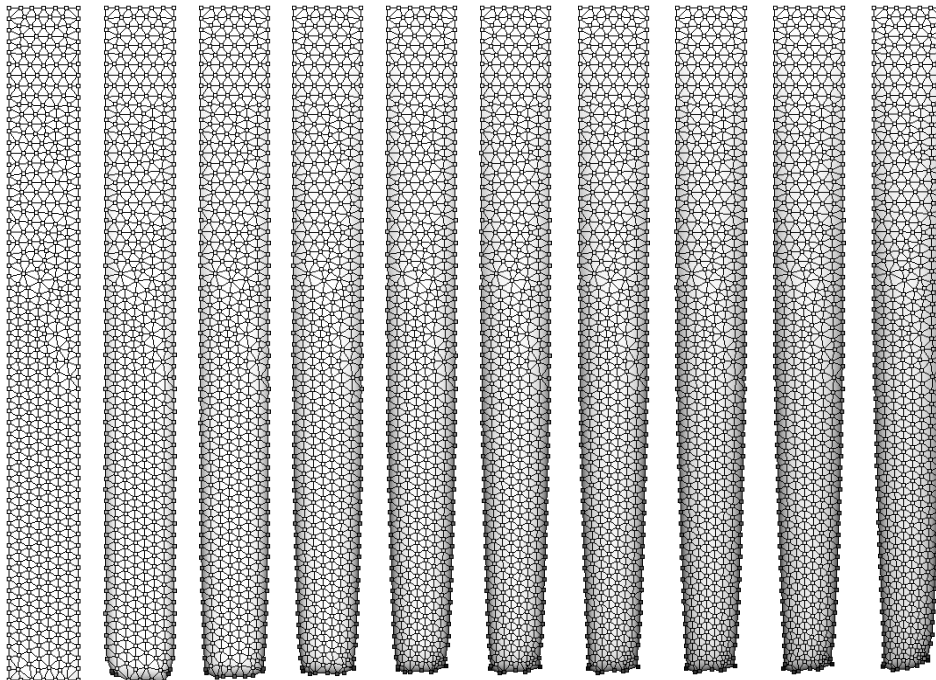Figure 8. Pictures of the simulation of PC/ABS in the UL 94 test between 0 and 90 s

Figure 9. Pictures of the simulation of PC/ABS+PTFE in the UL 94 test between 0 and 90 s

The temperatures in the simulations exceeded the decomposition temperatures of the materials (700 K to 800 K) within the first ten seconds. Thereafter, maximum temperatures at the surface were between 800 K and 900 K. The viscosity determined for PC/ABS did not lead to dripping in the simulations, despite the high temperatures. The viscosity of polymers is known to be dependent on molecular weight, which is reduced during decomposition. This effect was not considered in the viscosity measurements for this study.

Ohlemiller and Shields [13] observed a decrease of viscosity of about three orders of magnitude for PP and PS melts that had seen certain levels of radiative heat. Adjusting the viscosity according to these findings leads to improved results of the simulation, which is shown in Figure 8 for a PC/ABS sample. The pictures are taken every 10 s between 0 and 90 s. Figure 8 indicates that PFEM is able to model dripping in the UL 94 set-up, including a falling drop in the third frame from the right. However, in the case of PC/ABS improved methods for obtaining the material properties are needed in particular regarding the viscosity.

In Figure 9, the simulation of PC/ABS+PTFE is seen. Again the pictures are taken between 0 and 90 s at intervals of 10 s. The model predicts the influence of viscosity on the performance in the UL 94 set-up very well. As observed in the experiments of PC/ABS+PTFE, dripping is prevented. Even though additional effects like the contraction and charring of the materials have not been considered, PFEM was able to reproduce the basic influence of PTFE. Figure 10 shows the simulated mass over time of PC/ABS and PC/ABS+PTFE. The characteristics agree well with the measured data for both materials in Figure 2. Taking into account the complexity of the problem, the comparison of simulation and experiment indicates the potential of PFEM for modelling polymers in the UL 94 scenario.

Figure 10. Mass versus time of PC/ABS and PC/ABS+PTFE as simulated with PFEM
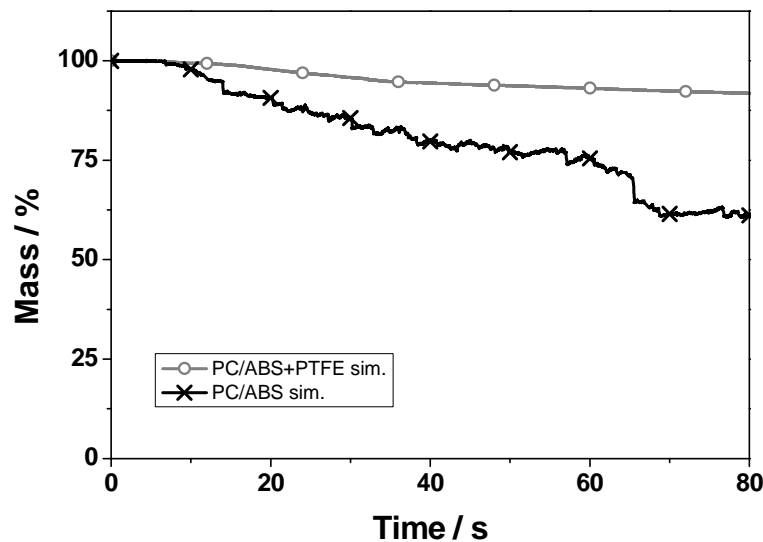
CONCLUSIONS

In this work the capability of the Particle Finite Element Method (PFEM), developed at CIMNE, to simulate the fire behaviour of a material system in the UL 94 scenario was analysed. The main focus was on the competing effects of gasification and melt flow/dripping. The material system covered different UL 94 classifications due to different dripping behaviour and combustion characteristics.

First the materials were characterized thoroughly, particularly with regard to the rheological properties. In the case of PC/ABS and PC/ABS+BDP the flame retardant decreased viscosity and caused more intensive dripping. The addition of less than 1 % mass fraction PTFE to PC/ABS and PC/ABS+BDP, respectively, led to a flow limit, which was shown to be responsible for the lack of dripping in the flammability test.

The comparison of simulation and experiment highlighted the potential of PFEM to model the complex behaviour of polymers in the UL 94 scenario. The influence of viscosity and flow limit on the dripping behaviour was reproduced. The effects of PTFE on viscosity prevented the sample from dripping. Furthermore the simulated mass loss agreed reasonably well with the experimental results, indicating the potential of PFEM to model polymer-related fire problems like the UL 94 scenario.

However, this work has highlighted some needs for further development of the PFEM model and for improved methods for obtaining the key material properties to successfully model the UL 94 test. Future

work will include:

- further improving the input data regarding the viscosity of the pyrolyzing melt,
- replacing the heat flux approximation by an implementation of a reasonable sub-model for the flame-associated mass loss and flame heat flux,
- reasonable implementation of flame inhibition (and charring),
- extending to a 3D geometry.

ACKNOWLEDGEMENTS

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