

# **FIRE CHARACTERISTICS OF STEEL MEMBERS COATED WITH NANO-ENHANCED POLYMERS**

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## **ABSTRACT**

Applying a polymeric coating on steel members has been demonstrated to be an effective countermeasure for the threat of blast on building and other structures. The development of a blast-resistant coating for steel with good characteristics in a fire would provide buildings with protection against explosions and a fire following the blast, as well as against ordinary building fires. An important characteristic of this coating would be to provide a thermal barrier to heat, such that the temperature of the steel remains for as long as possible below temperatures at which its strength would be weakened. This paper presents a numerical evaluation of melting and burning of nano-enhanced polymeric coatings applied on steel members. Viscosity measurements were performed to obtain needed parameters for the simulations. Polyurea nanocomposite residues showed a minimum in viscosity with temperature, possibly caused by cross-linking and charring. Model results for the polyurea residue having the lowest minimum viscosity value showed that the coating remained attached to the steel sides, although there was some flow that led to the breaking off of a chunk of material from an overhang.

## **INTRODUCTION**

The development of a blast-resistant coating for structural members that also performs well in a fire would provide buildings with protection against explosions and a fire following the blast, as well as against ordinary building fires. An important characteristic of this coating would be to provide a thermal barrier to heat, such that the temperature of the steel remains for as long as possible below temperatures at which its strength would be weakened. Since the materials being considered for blast-resistant coatings are polymer-based, it is important to investigate their behavior in fire.

Fire continues to pose a threat to life safety and a burden to the economy within the United States. In 2009, NFPA reports that US public fire departments responded to 1,348,500 fires, resulting in 3010 civilian fire deaths, 17,050 injuries and \$12.5 billion in property losses [1]. This includes 480,500 fires in structures, with 78.5 % of these occurring in residences. Non-residential buildings accounted for 44,500 fires. Direct property losses do not include indirect losses, such as business interruption. The total cost of fire in the US, including economic losses, insurance coverage, career fire departments, building costs for fire protection, the value of donated time from volunteer firefighters, and the monetary equivalent for deaths and injuries due to fire has been estimated as 2.5 % of the US gross domestic product [2]. Fire represents one of the most severe environmental hazards. Among the forms of man-made or natural disasters (e.g. blast, earthquakes, hurricanes, drought), fire is a major loss factor; one that may accompany other disasters. Many recent reports and white papers have highlighted the numerous drawbacks in the

current approaches to structural fire protection and have called for research and training efforts to advance the state-of-the-art in structural fire protection. Structural fire safety is one of the key considerations in the design of built infrastructure. Until the 1990's, there were very few forums for structural fire engineers to exchange ideas and research results.

During a severe fire scenario, a beam or column flange will be subjected to high levels of heat flux. At sufficiently high temperatures, a blast-resistant polymer-based coating covering the steel component may soften and melt. This will cause the coating to lose strength and drip over the surface, leaving the beam or flange unprotected. In this paper, the thermal response of a steel structural component coated with a blast-resistant polyurea-based nanocomposite is studied using a computational model of melting and dripping behavior. The model includes conductive heat transfer through the polymeric layer and the steel. The flow behavior is based on measurements of viscosity after exposing the nanocomposite to the high heat fluxes encountered in a fire.

## VISCOSITY MEASUREMENTS

Viscosity tests were carried out on four specimens: neat polyurea (as a control), polyurea with polyhedral oligomeric silsesquioxane (POSS), polyurea with exfoliated graphene nanoplatelets (XGnP), and a fourth polyurea nanocomposite, labeled Type 4 in this report. Polyurea is a thermoset plastic that cures irreversibly into a solid through cross-linking. Unlike thermoplastics, a thermoset material will decompose under reheating before it reaches its melting temperature. Decomposition will change the properties of the polymer, and in the high temperatures of a fire the thermoset material may melt and flow as it decomposes. Its viscosity is therefore expected to be dependent on its thermal history. Thermoset plastics may also char or bubble in a fire.

Melting and dripping was observed for several coating materials during cone calorimeter experiments also carried out under this paper, demonstrating the appropriateness of investigating how this behavior might affect the effectiveness of the coating as a protective barrier.

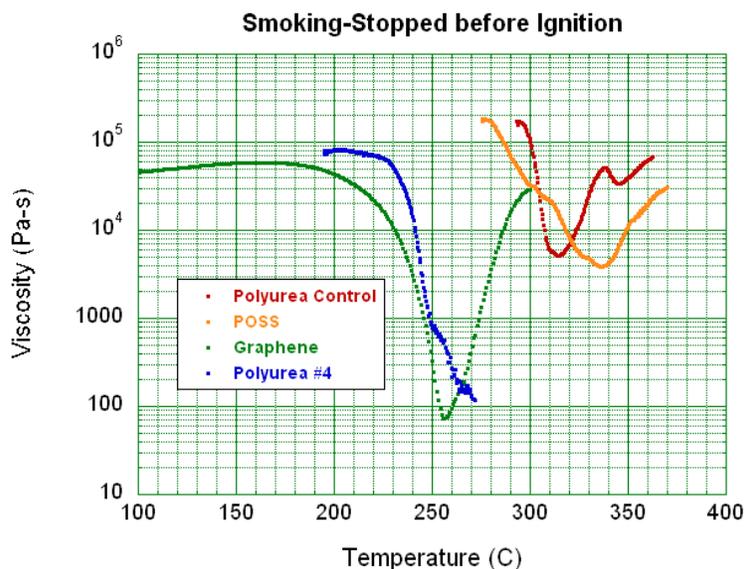
In a first attempt to measure the viscosity of the polyurea specimens in fire, a cone heater was used to heat the polyurea nanocomposites to the point of decomposition. A small amount of each of the samples was exposed to 40 kW/m<sup>2</sup>. This was done by placing the sample under the cone heater with the shutters closed (sample backside wrapped in foil sitting on top of a ceramic blanket on top of the load cell). Then the cone shutters were opened and the time at which the sample began to smoke heavily was measured. This point was selected as an indication that the material was close to ignition. At this point the shutters were closed, and immediately the sample was removed from the cone to try to preserve the material thermal history at that point. The times varied for the four polyurea samples, as shown in Table 1. This is suspected to be due in part to the sample color (which affects the absorption of radiation) and sample thickness.

<b>Specimen</b>	<b>Initial color</b>	<b>Time to heavy smoking (s)</b>
Polyurea control	Black	13
Polyurea + XGnP	Black	11
Polyurea + POSS	Tan-green	26
Polyurea Type 4	White	7

**Table 1.** Time at which heavy smoking begins for polyurea specimens exposed to heat flux of 40 kW/m<sup>2</sup>.

The two black polyurea samples (control and XGnP samples) were slightly deformed but did not look much different from their starting forms. The polyurea + POSS sample, which began as a tan-green color, had some discoloration (yellow/brown spots) but otherwise was unwarped and did not look much different from the starting material. The surface of polyurea Type 4 was somewhat degraded.

Rheology data collected for the materials using a parallel plate rheometer are shown in Figure 1. The results of this initial assessment were mixed. The control and polyurea + POSS samples did not soften enough to start the rheometry testing until 290 °C. At 360 °C the material was smoking and giving off a strong odor in the lab, so the experiments were stopped. The polyurea + XGnP sample was much softer, and it was possible to start collecting rheology data as low as 100 °C. However, it was a “completely decomposed and bubbly mess” by 300 °C.



**Figure 1.** Viscosity relationships with temperature for polyurea control, polyurea with POSS, polyurea with XGnP, and polyurea Type 4, after heating to the point of decomposition.

Three samples in this test reached a minimum viscosity at some temperature, after which the viscosity increased. This could be a result of either cross-linking and charring or bubbling (in which case the viscosity of the polymeric melt itself is no longer being measured). Note that the generation of multiple bubbles can cause the viscosity to either increase or decrease, depending on the capillary number and whether the bubbles deform or behave more as particles. The sample within the rheometer was not visible during testing, so it is not certain which physical phenomena were taking place. For the polyurea control, there is a second decrease in viscosity followed by a second increase. Rheometric measurements were not obtained for the fourth sample (polyurea Type 4) beyond 275 °C. Given its behavior in the second set of tests below, it is likely that this sample also undergoes an increase in viscosity at higher temperatures. The temperatures that the polymers will experience in a fire depend on the thermal properties of the polymer and the substrate as well as the radiative flux, but they can be expected to exceed 400 °C.

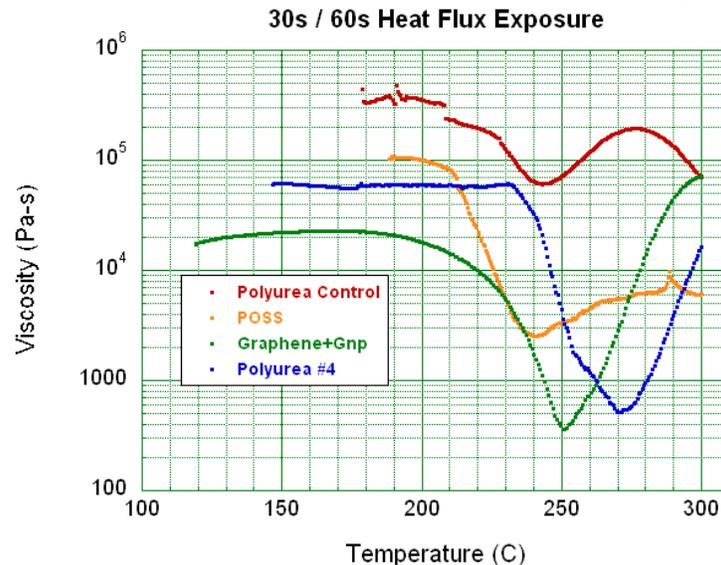
In the second set of tests, the four samples were exposed to additional heat damage by allowing the samples to remain for a longer time at the same heat flux level of 40 kW/m<sup>2</sup>. The intent was to allow the material to undergo significant decomposition for rheology testing. The results were as follows:

- Polyurea control: Exposed to 40 kW/m<sup>2</sup> heat flux for 30 seconds. Surface greatly degraded with lots of bubble and sink marks from popped bubbles.
- Polyurea + XGnP: Exposed to 40 kW/m<sup>2</sup> heat flux – sample auto-ignited at 30 seconds. Ran test again with new material and stopped at 20 seconds – surface greatly distorted and bubbled.
- Polyurea + POSS: Exposed to 40 kW/m<sup>2</sup> heat flux for 60 seconds. Material had begun to melt and liquefy – greatly degraded.
- Polyurea Type 4: Exposed to 40 kW/m<sup>2</sup> heat flux for 30 seconds. Surface greatly degraded (greenish-brown, lots of bubbling on surface)

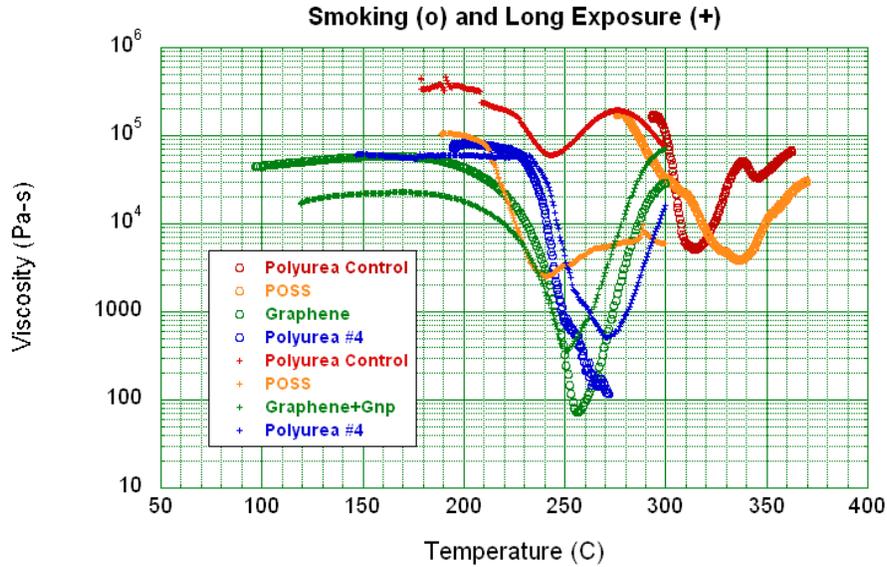
The polyurea + POSS sample was much thicker than the others. To get this thermally thick sample to degrade to the same extent as the other thinner samples, it was decided that exposure for a longer time period was necessary in order to achieve higher temperatures.

Figure 2 shows the viscosity relationships with temperature for the residues of the polyurea nanocomposites after the longer exposures of the second set of tests. All samples reach a minimum in viscosity followed by an increase due to cross-linking and/or bubbling. The polyurea control again underwent a second period of decreasing viscosity.

In Figure 3 all eight viscosity-temperature curves are plotted together to show the effect of exposing the polyurea samples to a heat flux for a longer period of time. In two cases (control and POSS), the viscosity decrease and minimum viscosity point occur at a much lower temperature after longer heat exposure. In at least three cases (POSS, graphene, and Type 4), the viscosity at low temperatures is smaller after longer exposure. In three cases (control, graphene, and Type 4), the minimum viscosity reached is higher for residues after longer exposures.



**Figure 2.** Viscosity relationships with temperature for polyurea control, polyurea with POSS, polyurea with XGnP, and polyurea Type 4, after heating for 20 s (graphene), for 30 s (control and Type 4) or for 60 s (POSS).

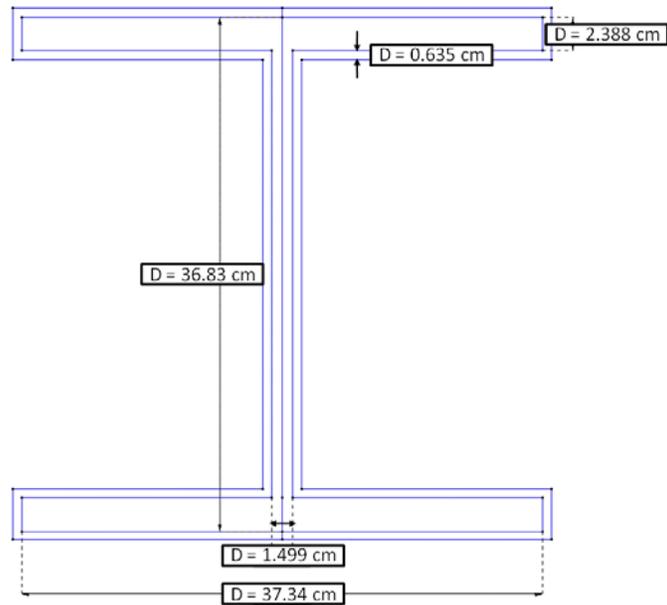


**Figure 3.** Viscosity relationships for four polyurea samples after heating to the point of decomposition (circles) and for longer exposures of 20 s, 30 s, or 60 s (points).

#### COMPUTATIONAL MODEL

The rate at which the polymer-based coating over a steel composite softens and flows upon exposure to a specified heat flux can be studied using the Particle Finite Element Method (PFEM) [3]. In this method, solid and fluid domains are defined within a finite element structure. During a single time step, each node becomes a particle that moves according to the individual forces acting upon it. The new boundaries of solid and fluid domains are defined, a new finite element mesh is created, and the continuum equations that apply to each domain are solved. This method has been used to study the melt flow behavior of polypropylene (PP) [4-6]. In addition to the thermal properties, the model requires viscosity data as a function of temperature to determine the melting and flow behavior of the polymer.

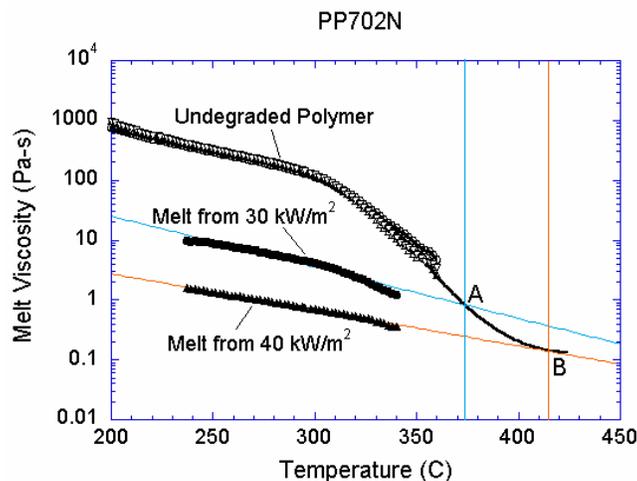
To model the heating of a steel beam or column covered by a blast-resistant coating that may melt and flow in a fire, the geometry was defined as shown in Figure 4. The dimensions are for a wide flange structural steel section of W14x120 with a ¼-inch (0.635-cm) thick polyurea nanocomposite coating. The initial finite element mesh is at least two elements thick in the areas of coating that are exposed to heat (and thus expected to drip), and the resolution is lower throughout the steel and the unheated sections of coating in order to lower the runtime, especially for 3D models. A heat flux of 35 kW/m<sup>2</sup> is applied to the heated surfaces.



**Figure 4.** Dimensions of steel beam and blast-resistant coating.

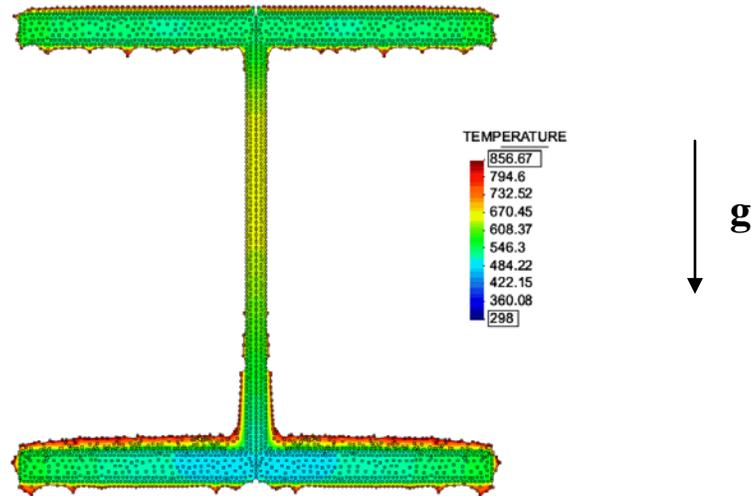
#### MODEL RESULTS FOR POLYPROPYLENE

The PFEM model was tested for this geometry using the properties of a variety of polypropylene, PP702N, used in previous work on melting and dripping behavior in fire [4-6]. The melt viscosity as a function of temperature for this polymer is shown in Figure 5, as measured by rheometry for undegraded PP702N and for the melt residue after being heated at 30 kW/m<sup>2</sup> and at 40 kW/m<sup>2</sup>. The relationship used in the model, shown by the black line, connects the curve for the undegraded polymer to points A and B extrapolated from the viscosity curve for each melt sample to the temperature at which the sample was formed. The result is an empirical viscosity-temperature curve that implicitly accounts for molecular weight changes. Other material properties for PP702N are density  $\rho = 900 \text{ kg/m}^3$ , thermal conductivity  $k = 0.25 \text{ W/m-K}$ , and specific heat  $c_p = 2400 \text{ J/kg-K}$ . The properties used for steel are  $\rho = 7850 \text{ kg/m}^3$ ,  $k = 46 \text{ W/m-K}$ , and  $c_p = 500 \text{ J/kg-K}$ .

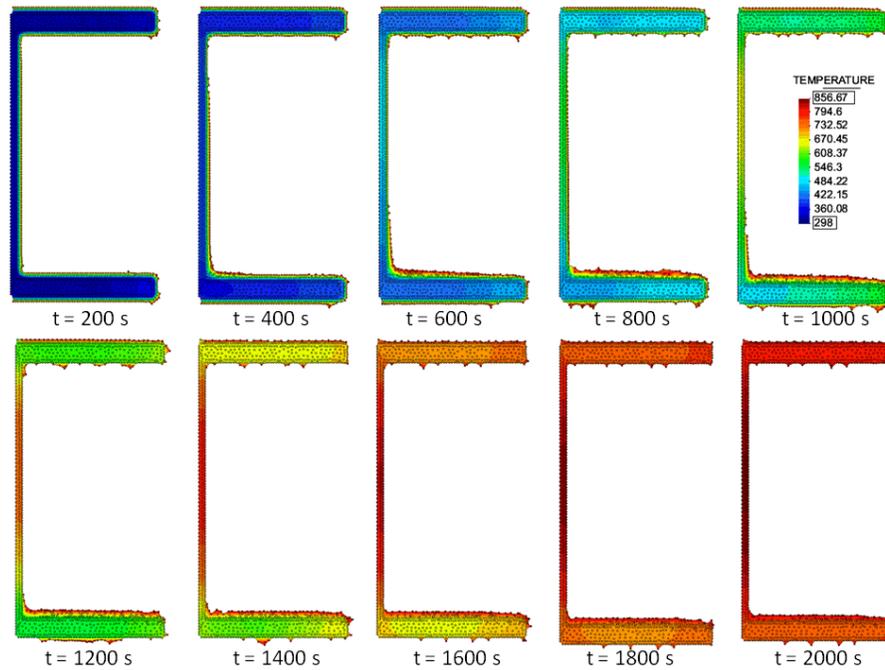


**Figure 5.** Viscosity relationship with temperature for PP702N, used in this study to set up and test model geometries.

Figure 6 shows a snapshot at time  $t=1000$  s of the temperature profile and location of the dripping polypropylene coating for a 2D beam exposed to  $40 \text{ kW/m}^2$  heat flux on all free surfaces. A time sequence showing the evolution of the temperatures and free surfaces with time is shown in Figure 7. This calculation has taken advantage of symmetry to cut the problem in half. Note that the temperature of the steel web rises rapidly as the coating drips down the web and leaves it exposed directly to the heat flux.



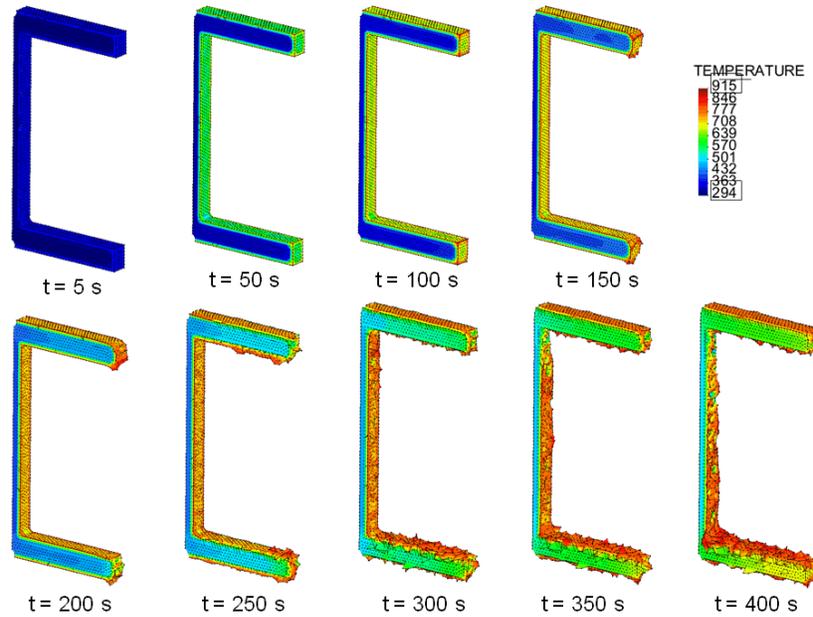
**Figure 6.** Temperature of beam at  $t = 1000$  s.



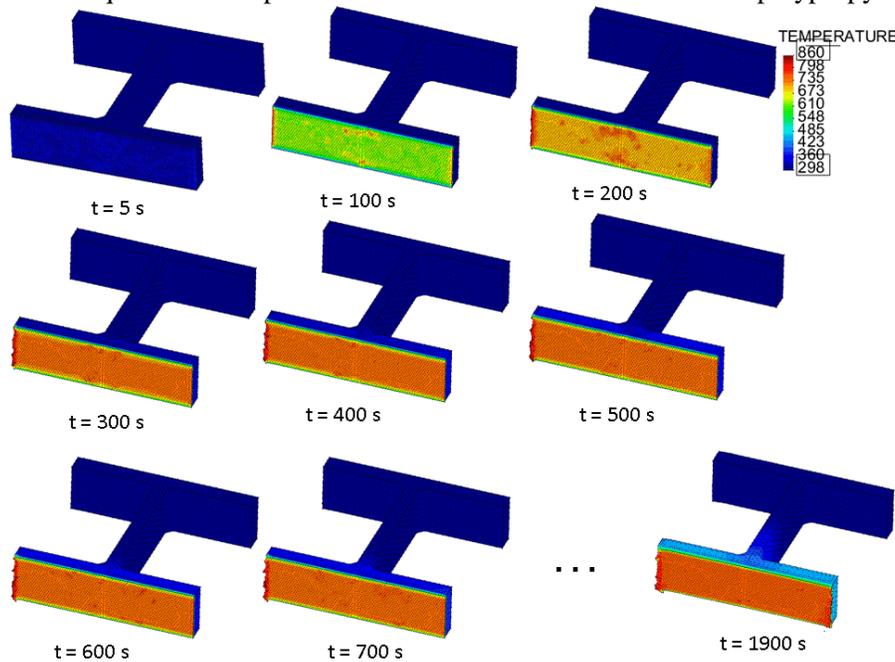
**Figure 7.** Time sequence of temperatures for a 2D steel beam coated with PP702N.

In Figure 8 the same problem is solved in three dimensions, with a narrow profile in the third dimension. Although the heat flux is applied only to the outer surfaces of the beam and not along the sides, heating occurs faster in this problem, indicating that edge effects are important.

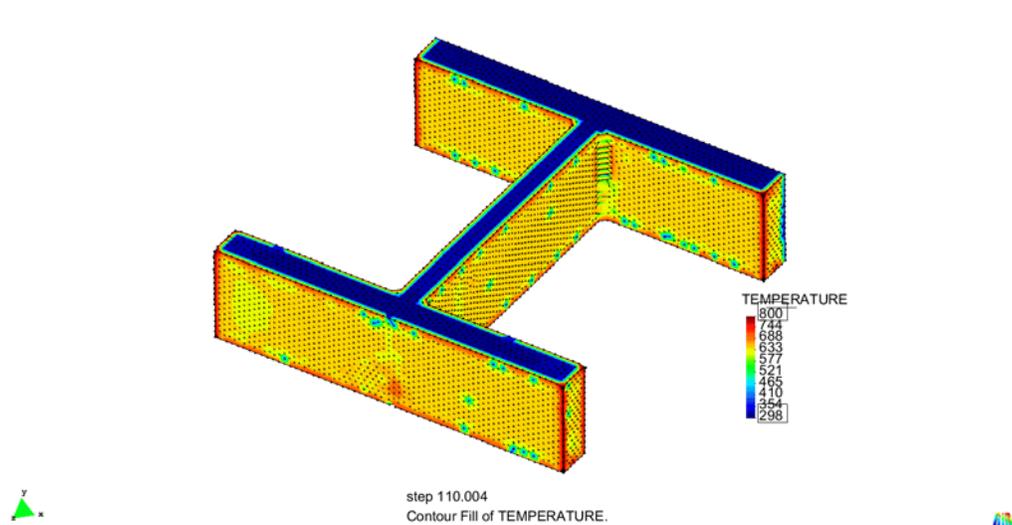
In Figure 9, the steel is in a column configuration, with only one face of the flange exposed to the fire. By time  $t=1900$  s, the steel under the heated coating is heating slowly, and the coating is gradually sliding down the face of the flange. Figure 10 shows a steel column with only one flange face protected from the fire. Because of the number of elements necessary to resolve the thin coating layer, runtimes for these 3D problems exceeded a week.



**Figure 8.** Time sequence of temperatures for a 3D steel beam coated with polypropylene.



**Figure 9.** Time sequence of temperatures for a 3D steel column coated with polypropylene and exposed on one flange face.



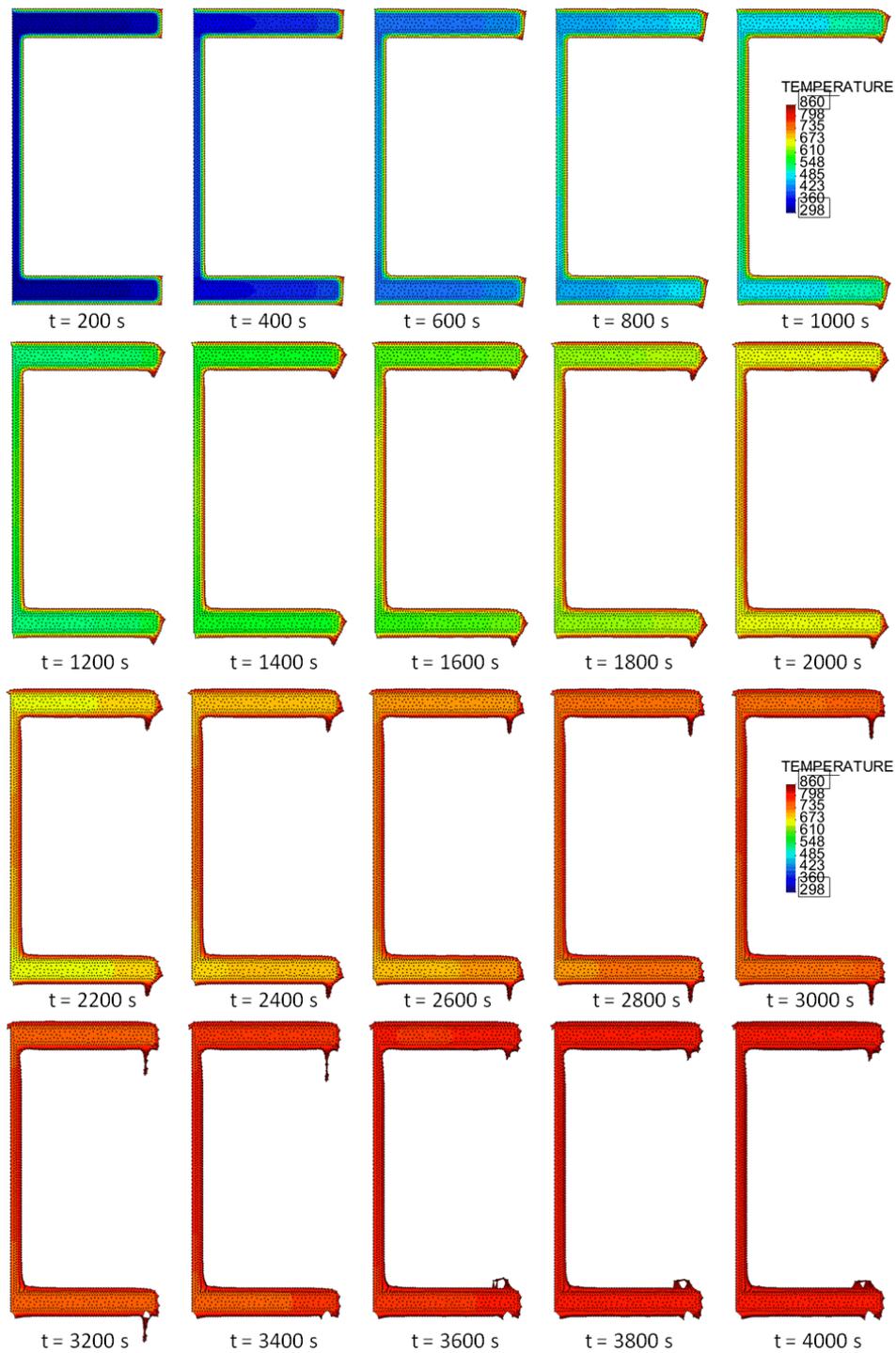
**Figure 10.** Temperatures for a 3D steel column coated with PP702N and exposed on every surface except one flange face.

#### MODEL RESULTS FOR POLYUREA NANOCOMPOSITE

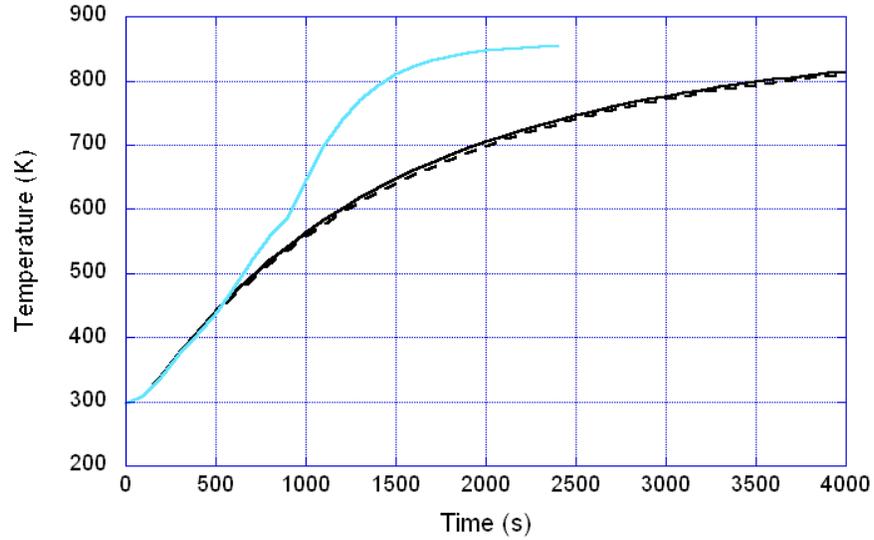
Comparing the viscosity plots of the polyurea nanocomposite residues in Figures 1-3 to the viscosity of the PP702N polymer in Figure 5, the minimum viscosity of the polyurea residues is found to be more than two orders of magnitude larger than that of the polypropylene. The increase in viscosity as the temperature increases past the minimum point, which can occur as low as 250 °C, raised the question of whether the coating would experience any flow at all during heating.

The polyurea nanocomposite with the lowest minimum viscosity, polyurea+graphene, was selected to study the effects of this viscosity behavior. A sequence showing the results from a heated 2D coated steel beam, in Figure 11, shows that, while little flow is observed over the vertical and horizontal faces, the coating near the overhang slips over the side to form a long piece of material that eventually breaks off and falls to the platform below. A comparison of Figure 11 with the results from PP702N in Figure 7 indicates that because the polyurea coating remains in place, the temperature of the steel beam remains cooler. In Figure 12 this is shown by comparing the temperature of the centerpoint of the steel for these two models as a function of time. As the PP702N coating drips off the vertical surface of the web and leaves it exposed, the temperature increases rapidly compared to the polyurea+graphene coating.

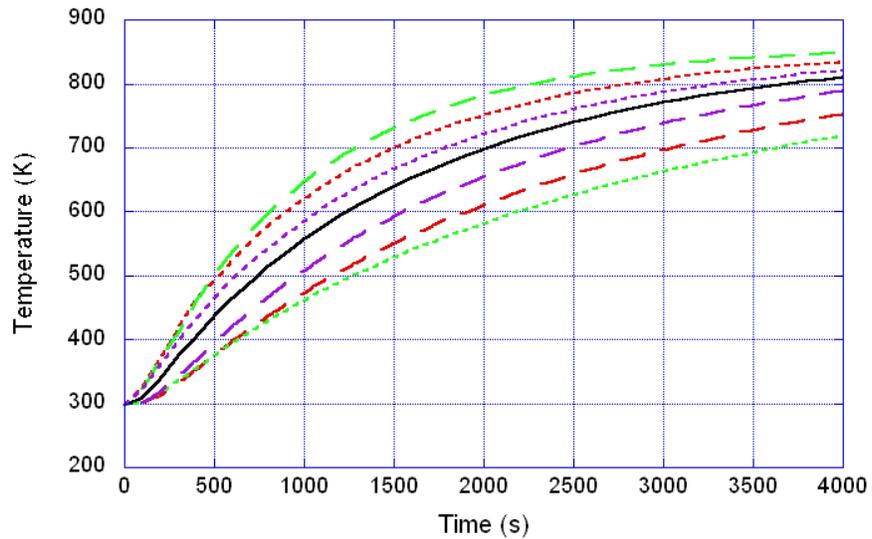
Measurements of the values of density, thermal conductivity, and specific heat were not obtained for the polyurea nanocomposite materials. Since the interest in this study was focused on the melting behavior, values of these parameters for polypropylene were used in the model. Figure 13 shows results of a brief sensitivity study for these material properties, which were each in turn doubled and halved in value.



**Figure 11.** Time sequence of temperatures for a 2D steel beam coated with polyurea with graphene nanocomposite, heated to the point of decomposition.



**Figure 12.** Temperature of steel at centerpoint for polyurea plus graphene at two levels of resolution (black, solid line is higher resolution) and for PP702N (blue).



**Figure 13.** Steel temperature at centerpoint for doubled (dashed lines) and halved (dotted lines) values of polymer density (purple), specific heat (red), and thermal conductivity (green).

## CONCLUSIONS

A model of the melting and dripping of thermoset polymeric coatings over steel was created, using viscosity measurements obtained by heating the coating material to and beyond the point of decomposition and measuring the rheometry of the residue. The model was set up and tested using a polypropylene material that is (relatively) well characterized. The polyurea nanocomposite residues showed a minimum in viscosity with temperature, possibly caused by cross-linking and charring. Model results for the polyurea residue having the lowest minimum viscosity value showed that the coating remained attached to the steel sides, although there was some flow that led to the breaking off of a chunk of material from an overhang.

This is the first attempt to model the melting and dripping of a polymeric coating covering an object, and the first model to look at the effects of the rheometry of thermoset materials. The paper highlights the challenge of obtaining viscosity measurements for polymeric materials exposed to fire and the need to develop appropriate test methods to characterize their behavior.

#### **ACKNOWLEDGEMENT**

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