

## **Effect of Moisture on Ignition Time of Polymers**

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## LIST OF ACRONYMS & SYMBOLS

$\alpha$	Absorption coefficient ( $\text{m}^2/\text{kg}$ )
$\beta$	Heating rate (K/s)
$\varepsilon$	Surface emissivity
$\kappa$	Thermal conductivity (W/m-K)
$\rho$	Density ( $\text{kg}/\text{m}^3$ )
$\sigma$	Boltzmann radiation constant ( $5.7 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$ )
a	Absorptivity
b	Thickness (m)
c	Heat capacity (J/kg-K)
h	Heat transfer coefficient ( $\text{W}/\text{m}^2\text{K}$ )
$H_c$	Heat of combustion of the pyrolysis gases (J/g)
$m''_{cr}$	Critical mass flux ( $\text{kg}/\text{s}$ )
T	Temperature (C)
$T_{ign}$	Ignition temperature (C)
$T_{onset}$	Onset decomposition temperature (C)
$t_{ign}$	Time to ignition
$q''_{ext}$	External heat flux ( $\text{W}/\text{m}^2$ )
$q''_{net}$	Net heat flux ( $\text{W}/\text{m}^2$ )
CAS#	Chemical Abstract Services Registry Numbers
CHF	Critical heat flux ( $\text{W}/\text{m}^2$ )
HRR	Heat release rate ( $\text{W}/\text{m}^2$ )
MLR	Mass loss rate ( $\text{kg}/\text{m}^2\text{s}$ )
PA66	Polyhexamethyleneadipamide
PC	Polycarbonate
PEEK	Polyetheretherketone
PMMA	Polymethylmethacrylate
POM	Polyoxymethylene
PPSU	Polyphenylsulfone

## EXECUTIVE SUMMARY

A previous study of polyetheretherketone showed that the ignitability of this high-temperature engineering plastic is sensitive to the presence of absorbed moisture. The present research extends this work to include five other engineering plastics: polycarbonate, polyoxymethylene, polymethylmethacrylate, polyphenylsulfone, and polyhexamethylenedipamide. Separate batches of each polymer were equilibrated in hot water (80°C), 50% relative humidity at 20°C, or vacuum dried at 100°C and tested in a cone calorimeter at heat fluxes between 10–75 kW/m<sup>2</sup>. These hygrothermally conditioned samples were also examined by microscale combustion calorimetry to determine the effect of moisture on the thermal, decomposition, and combustion properties. It was found that absorbed moisture did not change the thermal decomposition or ignition temperatures significantly but was released as steam that formed microscopic surface bubbles at or above the softening (i.e., glass transition or melting) temperature of the polymer. The phase change from bound water to steam entrained in the polymer melt (i.e., foam) significantly reduced the ignition time as compared to dry samples. Attempts were made to account for the moisture-sensitive ignition delay in terms of thermal properties and chemical processes governing ignition and in a numerical thermokinetic pyrolysis model.

## INTRODUCTION

Studies show that moisture has a noticeable effect on the ignitability of combustible solids [1–3]. For wood [1], moisture increases the time to ignition ( $t_{ign}$ ) of thick samples as  $t_{ign} \propto (1+4w)^2$  (where  $w$  is the weight fraction of moisture in the sample), and thin samples as  $t_{ign} \propto (1+6w)$ . For polyetheretherketone (PEEK), a relatively hydrophobic, high-temperature engineering plastic [2 and 3], moisture decreases the time to ignition of thermally thin samples as  $t_{ign} \propto (1-68w)$ , a phenomenon that was attributed to the appearance of an optically and thermally distinct surface layer of water vapor bubbles that appeared at the melting temperature of the polymer [2]. This study is based on the observation that the effect of moisture on ignition time of thin samples of PEEK is approximately 10 times (68/6) greater than for wood and opposite in sign and PEEK films exhibit significant variability in tests of flame spread rate. It will determine whether variable ignitability associated with absorbed moisture is a general phenomenon in hydrocarbon polymers, and, if so, whether any of the various ignition criteria can account for this effect.

## BACKGROUND

Ignition is a critical phenomenon governed by the thermal and chemical properties of the solid polymer and the chemical composition and release rate of its thermal decomposition products (i.e., fuel gases). The coupled, time-dependent nature of condensed phase flaming combustion gives rise to a variety of proposed criteria for piloted ignition of solids [4 and 5]. These can be roughly divided into thermal (i.e., solid state) and chemical (i.e., gas phase) criteria.

Thermal theory of ignition: The thermal theory of ignition is based on the concept of a critical temperature for the solid at which piloted ignition occurs (i.e., an ignition temperature [ $T_{ign}$ ]). Physically, ignition temperature is the temperature at which thermal decomposition of the solid to gaseous fuel begins. An ignitability experiment is typically conducted in a cone calorimeter where the solid combustible plate sample is subjected to a constant irradiance at the front face. The rear face is insulated, and the time required to ignite the gases above the solid with an electric spark is measured. The time to ignition can be calculated from one-dimensional, unsteady heat transfer as the time required for the solid surface to reach ignition temperature. The transient energy balance for a thin combustible solid of thickness ( $b$ ), heat capacity ( $c$ ), and density ( $\rho$ ) in a cone calorimeter having convective heat transfer coefficient ( $h$ ) can be written in terms of the net heat flux ( $q''_{net}$ ) at the sample surface, the external heat flux ( $q''_{ext}$ ) from a radiant heater, the sample temperature ( $T$ ), and the initial/ambient temperature ( $T_0$ )

$$q''_{net} = aq''_{ext} - \left\{ \varepsilon\sigma(T^4 - T_0^4) + h(T - T_0) \right\} \approx aq''_{ext} - \bar{h}(T - T_0) \quad (1)$$

In equation 1,  $\sigma = 5.7 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$  is the Boltzmann radiation constant,  $a$  is the absorptivity of the sample,  $\varepsilon$  is its surface emissivity,  $T - T_0$  is the instantaneous difference between the sample and ambient (starting) temperature, and  $\bar{h}$  is an average heat transfer coefficient for radiant and convected energy in the cone calorimeter [4]. For a mean temperature,  $\bar{T} = (T_{ign} + T_0)/2$ ,

$$\bar{h} = h + \frac{\varepsilon\sigma(\bar{T}^4 - T_0^4)}{\bar{T} - T_0} \approx h + 5\varepsilon\sigma\bar{T}^3 \quad (2)$$

The approximation on the far right side of equation 2 represents less than 10% error in  $\bar{h}$  for normal ASTM E 1354 operating conditions in the cone calorimeter where  $h \approx 10 \text{ W/m}^2\text{-K}$ . For typical polymers,  $T_{ign} = 300^\circ\text{C} - 500^\circ\text{C}$  and  $a \approx \varepsilon \approx 1$ . In a cone calorimeter ignition experiment,  $\bar{h}$  is in the range 30–50  $\text{W/m}^2\text{-K}$ . The lumped, transient energy balance for a thermally thin sample with  $a = \varepsilon = 1$ , after substituting equation 1 for  $q''_{net}$ , is

$$\rho cb \frac{dT}{dt} = q''_{net} = q''_{ext} - \bar{h}(T - T_0) \quad (3)$$

The lumped analysis (see equation 3) is applicable if the Biot modulus is less than 10% of the effective temperature difference between the heating environment and the sample surface. For the radiant and convective boundary condition of the cone calorimeter (see equation 1), the criterion for a sample of thickness  $b$  to be thermally thin at  $q''_{ext}$  is

$$b \leq \frac{\kappa}{10\bar{h}} \left[ \frac{CHF}{q''_{ext} - CHF} \right] \quad (4)$$

In equation 4, the critical heat flux (CHF) for piloted ignition is  $CHF \leq q''_{ext}$ .

$$CHF = \varepsilon\sigma(T_{ign}^4 - T_0^4) + h(T_{ign} - T_0) = \bar{h}(T_{ign} - T_0) \quad (5)$$

For typical polymers,  $T_{ign} = 400^\circ\text{C} = 673\text{K}$ , so the overall heat transfer coefficient is  $\bar{h} \approx 40 \text{ kW/m}^2\text{-K}$ . Substituting these values in equation 4 with a typical polymer thermal conductivity,  $\kappa \approx 0.2 \text{ W/m-K}$ , shows that the 3 mm thick samples of this study will be thermally thin when  $q''_{ext} \leq 1.2 \text{ CHF}$  (i.e., only for external heat fluxes close to the critical value for ignition). Equation 4 also shows that as  $q''_{ext} \rightarrow \text{CHF}$ , samples of any thickness will be thermally thin.

Defining  $\theta = T - T_0$  and a thermal response time,  $\tau = \rho cb / \bar{h}$ , substituting into equation 3 and rearranging,

$$\frac{d\theta}{dt} + \frac{\theta}{\tau} = \frac{q''_{ext}}{\rho cb} \quad (6)$$

Equation 5 is solved using an integrating factor between the limits 0,  $t_{ign}$ , and  $T_0$ ,  $T_{ign}$ ,

$$T_{ign} - T_0 = \frac{q_{ext}''}{h} \left(1 - \exp(-t_{ign} / \tau)\right) \quad (7)$$

Combining equations 5 and 7 provides the relationship between the time to ignition and the external heat flux for a thermally thin sample,

$$t_{ign} = \frac{\rho cb}{h} \ln \left[ \frac{q_{ext}''}{q_{ext}'' - CHF} \right] = \frac{TCP}{CHF} \ln \left[ \frac{q_{ext}''}{q_{ext}'' - CHF} \right] \quad (8)$$

Where TCP is the thermal capacitance parameter,

$$TCP = \rho cb (T_{ign} - T_0) \quad (9)$$

At low heat flux, when  $q_{ext}'' \rightarrow CHF$  and  $t_{ign} \rightarrow \infty$ , a thick sample with an insulated rear face approaches a uniform temperature  $T \approx T_{ign}$  (i.e., it becomes thermally thin) so that equation 8 describes the time to ignition of thick samples in a cone calorimeter at external heat fluxes in the vicinity of the critical value. Conversely, at high heat fluxes, where  $q_{ext}'' \gg CHF$  and  $t_{ign} \rightarrow 0$ , even thin samples behave thermally like semi-infinite solids. Quintiere [6] has proposed an analog of equation 8 as a correlating function for  $t_{ign}$  of thermally thick samples or thin samples at high heat flux,

$$t_{ign}^{1/2} = \frac{TRP}{CHF} \ln \left[ \frac{q_{ext}''}{q_{ext}'' - CHF} \right] \quad (10)$$

Where TRP is called the thermal response parameter,

$$TRP = (T_{ign} - T_0) \sqrt{\frac{\pi}{4} \kappa \rho c} \quad (11)$$

Chemical theory of ignition: According to the chemical criterion for piloted ignition of solids, burning begins under a constant  $q_{ext}''$ , when the mass flux ( $m''$ ) is sufficient to maintain a flammable fuel-air mixture at a spark or pilot flame above the specimen. The ignition condition has also been expressed as a critical energy release rate, which is obtained by multiplying the critical mass flux ( $m_{cr}''$ ) by the heat of combustion of the pyrolysis (i.e., fuel) gases ( $H_c$ ), so that ignition occurs when the  $m''$  exceeds the  $m_{cr}''$  or the heat release rate (HRR) exceeds a critical value  $HRR_{ign}$ ,  $q_{cr}'' = H_c m_{cr}''$ . Using these criteria, the time to ignition is

$$t_{ign} = \text{Time at which } m'' \text{ first reaches } m_{cr}'' \text{ at constant } q_{ext}'' \quad (12)$$

$$= \text{Time at which } H_c m'' \text{ first reaches } HRR_{ign} \text{ at constant } q_{ext}'' \quad (13)$$

Both equations 12 and 13 are equivalent to reaching the lower flammability limit of a fuel-air mixture at the ignition source for a fixed test geometry and ventilation rate. Studies show that the HRR at ignition, unlike any of the other ignition criteria, is relatively independent of the type of solid fuel [4 and 7].

The independent variable in this study was the equilibrium moisture uptake of polymers, which was controlled by conditioning pure polymers at 100°C under vacuum (DRY); at 50% relative humidity at 20°C (RH50); and in 80°C water (WET). The dependent variable in these studies was the time to ignition, which is the time at which sustained burning is observed after the sample is irradiated at a constant heat flux at time  $t = 0$  in the presence of a spark igniter. The polymer properties governing thermal ignition in equations 7 and 8, as well as the processes governing chemical ignition in equations 12 and 13, were measured over a range of external heat flux in a fire cone calorimeter to determine the mechanism by which moisture affects the ignition delay.

## MATERIALS

The five polymers included in this study were: Polymethylmethacrylate (PMMA), Polyhexamethyleneadipamide (PA66), Polyoxymethylene (POM), Polycarbonate (PC), and Polyphenylsulfone (PPSU). They were additive-free (i.e., natural), commercial grade, obtained from various sources as large sheets (1m × 2m) and had a nominal thickness of 3 mm. Table 1 lists the polymers, their abbreviations, Chemical Abstract Services Registry Number (CAS#), glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and ignition temperature ( $T_{ign}$ ).

**Table 1. Polymers, Chemical Abstract Services Registry Number (CAS#), glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and literature values of ignition temperature ( $T_{ign}$ )**

Polymer	Abbreviation	CAS#	$T_g$ , °C	$T_m$ , °C	$T_{ign}$ , °C
Polymethylmethacrylate	PMMA	9011-14-7	114	N/A	317
Polyhexamethyleneadipamide	PA66	32131-17-2	50	260	456
Polyoxymethylene	POM	9002-81-7	-69	180	344
Polycarbonate	PC	24936-68-3	150	N/A	500
Polyphenylsulfone	PPSU	25608-64-4	219	N/A	575

Gases used for thermal analysis ( $N_2$ ,  $O_2$ ) and fire calorimetry ( $CH_4$ ) were high purity reagent grades obtained from local suppliers.

## METHODS

### Hygrothermal Conditioning

Specimens having dimensions of 100 mm x 100 mm were cut directly from the as-supplied sheets and exposed to three different environmental conditions. The first group, DRY, was held under vacuum at 100°C. The second group, WET, was immersed in distilled water at 80°C. The third group of specimens, RH50, was conditioned in a 50% relative humidity chamber at 20°C. Duplicate and triplicate specimens were periodically removed from the conditioning environments, lightly dried, and weighed to the nearest 0.01 g to determine the mass of water absorbed or desorbed during the hygrothermal conditioning.

### TGA Testing

Polymers created by stepwise reactions (e.g., polyesters and nylons) form H<sub>2</sub>O as a reaction product along with the polymer. Under certain circumstances of exposure to aqueous environments, the polymerization reaction can essentially be reversed and the polymer broken down. Also, exposure to elevated temperatures can break down high-molecular weight polymers. The polymers examined in this study were exposed to both hydrolysis and thermal degradation processes by placing the milligram-size samples into stainless steel containers along with distilled water. The containers were sealed and placed in the oven at various temperatures (165°C–265°C, depending on the transition temperature of the specific polymer) for a few hours. Polymer samples were removed from the containers and tested in a thermogravimetric analyzer (TGA, Mettler Toledo TGA/SDTA851) under nitrogen flow at 20 cm<sup>3</sup>/min at 10 K/min from 50°C–600°C. Some of the polymer samples appeared discolored (i.e., yellow) after the steam treatment. The results of TGA testing of steam treated samples were compared to the results of TGA testing of controlled samples (as-supplied sheets). No significant changes in weight loss of the samples as a function of temperature under isothermal conditions were determined. This signifies that samples were not chemically degraded by the presence of the water.

### Fire Testing

The time to ignition and heat released by burning polymers was measured using a fire calorimeter (Cone Calorimeter, Fire Testing Technology Limited) operating on the oxygen consumption principle according to a standard method [8]. Polymer specimens that had undergone hygrothermal conditioning were mounted horizontally using a specimen holder with the edge frame. The bottom and sides of each sample were wrapped with 20 μm thick aluminum foil. Specimens were exposed to a range of external heat fluxes from 10–75 kW/m<sup>2</sup> and the time to ignition, ignition temperature, and HRR during subsequent burning was recorded as a function of time. Two approaches were taken to measure surface temperature. A handheld thermocouple probe was used to measure the temperature of the top layer of a burning sample. An effort was made to hold the thermocouple bead as close as possible to the top surface of the sample. Temperature measurements were made up to, and a few seconds past, the observation of sustained flaming ignition. The ignition temperature was obtained by averaging the temperature readings. The second approach to measuring the ignition temperature was to attach a type K thermocouple to the polymer surface with a small piece of fiberglass tape. The temperature signal from the thermocouple was collected continuously throughout the heat release

measurement. Temperature measurements with an attached thermocouple yielded higher values than the handheld probe. Mass flux at the time of ignition was calculated from the mass flux in the cone data file after repeated Savitzky-Golay filtering to increase signal-to-noise ratio. This process is imprecise and the estimated mass flux and HRR at ignition are estimated to have errors of  $\pm 20\%$  and  $\pm 25\%$ , respectively, so differences of less than 50% in these values are probably not significant.

### Microscale Combustion Calorimetry

The onset decomposition temperature ( $T_{onset}$ ) is the temperature at which the HRR reaches 5% of the maximum value in a Microscale Combustion Calorimeter (MCC) at a heating rate of 1 K/s. The onset decomposition temperature, which approximates the ignition temperature in a fire calorimeter, was measured for all of the polymers in the study in accordance with the ASTM D 7309 Method A [9]. Tests were conducted on mg-size samples using nitrogen flowing at 80 cm<sup>3</sup>/min as a purge gas.

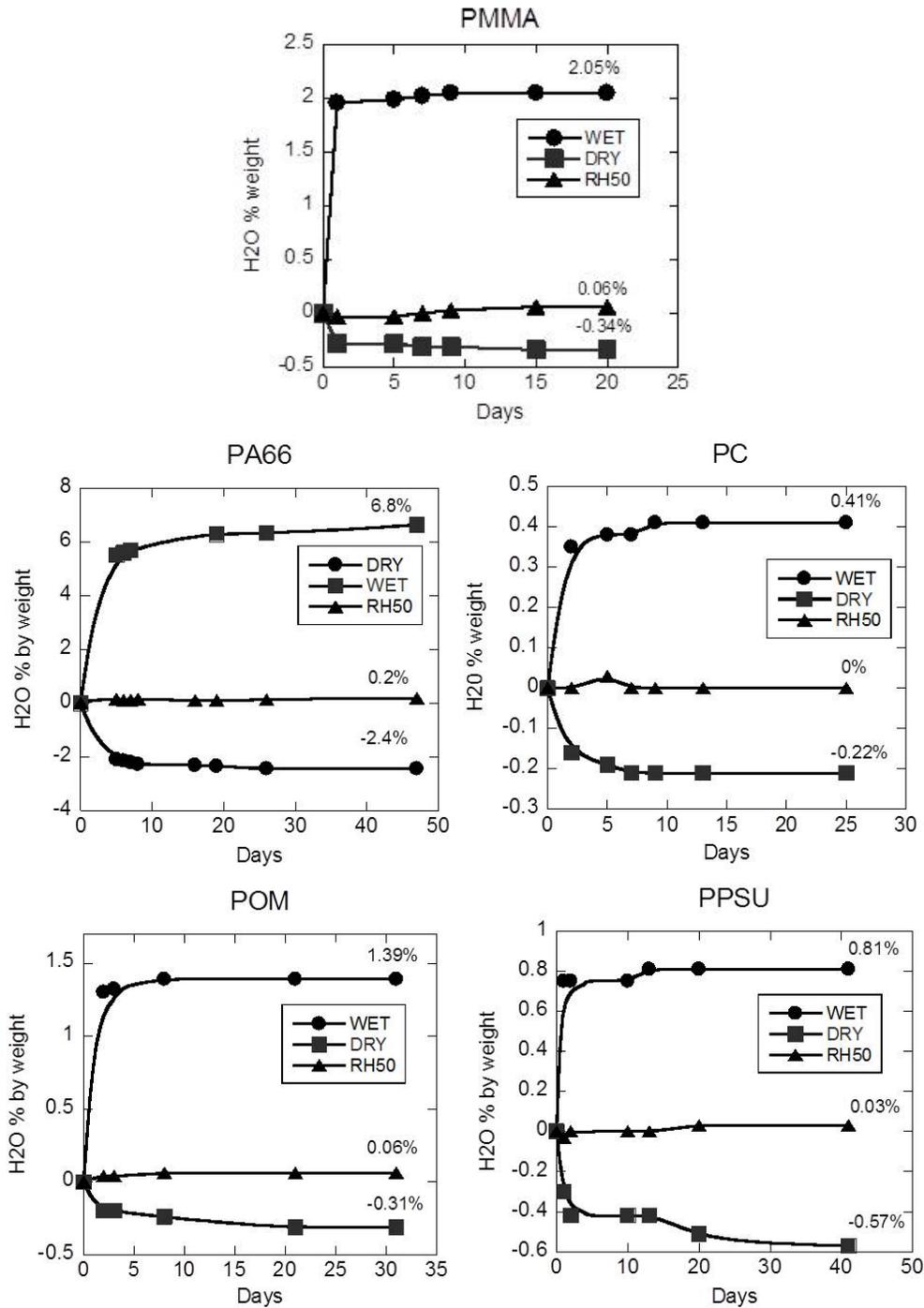
### Pyrolysis Modeling (ThermaKin)

Numerical modeling was performed using ThermaKin, a one-dimensional pyrolysis tool [10]. ThermaKin is a flexible computational framework that solves energy and mass conservation equations, which are formulated in terms of rectangular finite elements. A material is represented by a set of components, which may undergo chemical and physical interactions. In the ThermaKin model, the dry control polymer was represented by a single component, which was characterized by constant density (1,300 kg m<sup>-3</sup>), heat capacity (2,300 J kg<sup>-1</sup> K<sup>-1</sup>), thermal conductivity (0.24 W m<sup>-1</sup> K<sup>-1</sup>), reflectivity (0.05), absorption coefficient (1.5 m<sup>2</sup> kg<sup>-1</sup>), and gas transfer coefficient (2 x 10<sup>-5</sup> m<sup>2</sup> s<sup>-1</sup>). The polymer was specified to decompose via a first-order reaction, which was defined by the Arrhenius parameters,  $E = 1.98 \times 10^5$  J mol<sup>-1</sup>;  $A = 9.5 \times 10^{13}$  s<sup>-1</sup>; and the endothermic heat of reaction,  $H = 1.3 \times 10^6$  J kg<sup>-1</sup>. The property values and heat of reaction were average values for the set of polymers [11], and the Arrhenius parameters were those of PMMA. The polymer was assumed to produce no char. The one-dimensional objects that were used to model the cone experiments consisted of two layers. The top layer, which represented a polymer sample, had a thickness equal to initial sample thickness,  $b = 3 \times 10^{-3}$  m. The bottom layer was a perfect insulator parameterized to ensure no heat or mass transfer through the bottom boundary. The energy and mass conservation equations were solved by subdividing the object into 30 elements, which were 1 x 10<sup>-4</sup> m thick, and using a 0.005 second time step. Mass loss rate (MLR) histories were obtained by numerical differentiation of the object mass versus time data. In the simulations of the cone calorimetry tests, MLR was converted to HRR by multiplying it by measured effective heat of combustion. The ignition of the top layer surface was specified to occur when MLR exceeded 1 gm<sup>-2</sup>s<sup>-1</sup>, at which point convective cooling was turned off and a constant radiative heat flux of 15 kW m<sup>-2</sup> was added to the surface from the flame.

## RESULTS

### Hygrothermal Conditioning

Thermal and moisture (i.e., hygrothermal) equilibrium was obtained within a couple of weeks for all materials and conditioning regimes as shown by the weight change histories of the polymers in figure 1. For example, the WET PMMA samples increased 2.05% in weight compared to ambient starting weight, but the samples were no longer transparent, indicating physical changes induced by moisture (i.e., crazing). By comparison, the DRY PMMA samples lost 0.34% of their ambient starting weight. The moisture content of the WET PMMA specimens relative to the DRY state is  $2.05\% + 0.34\% = 2.39\%$ .

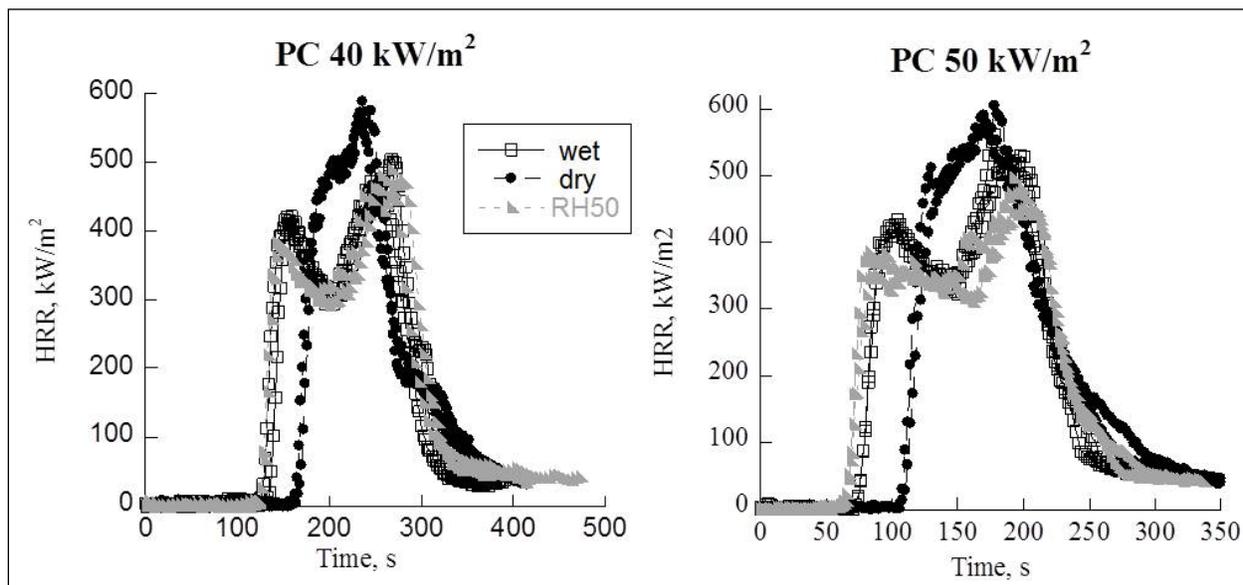


**Figure 1. Weight change histories of hygrothermally conditioned PMMA, PA66, PC, POM, and PPSU polymers**

The HRR Histories

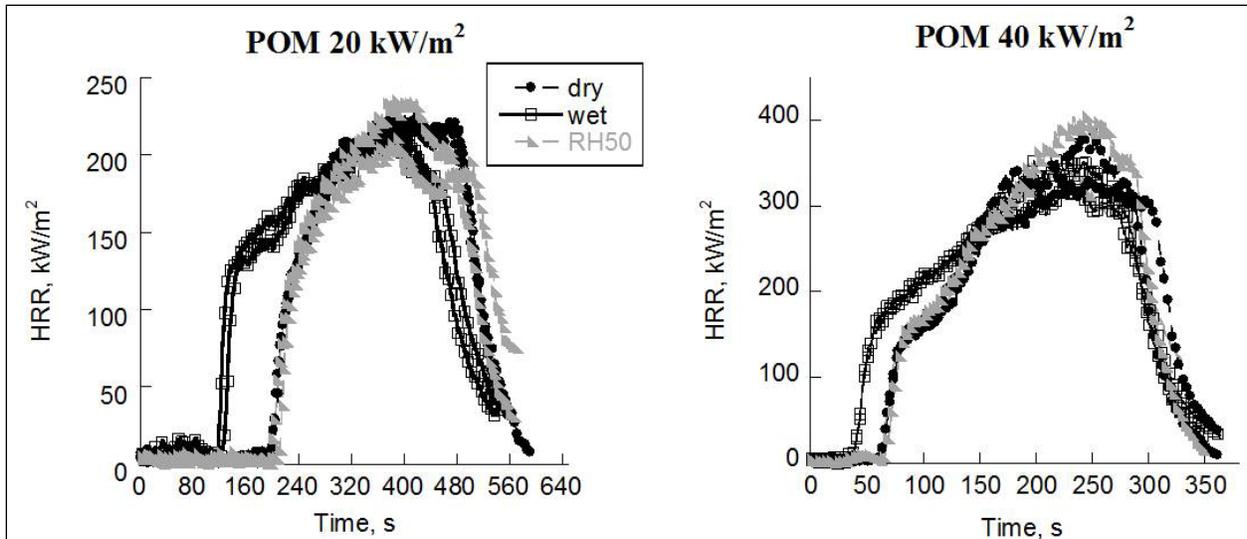
The PC is an amorphous polymer with a glass transition temperature of approximately 150°C. Total moisture content is 0.6%, the smallest amount for this study group of polymers. WET and

RH50 groups had almost identical times to ignition (with only a few seconds' difference) for most external heat fluxes (75, 50, and 40 kW m<sup>-2</sup>). DRY samples had significant delays in ignition times. The surfaces of the DRY samples prior to ignition were shiny and smooth; surfaces of the WET and RH50 samples were foamy. For PC, the presence of moisture (RH50 and WET samples) strongly correlates with premature ignition for the HRR histories at 40 and 50 kW/m<sup>2</sup> external heat fluxes, as shown in figure 2.



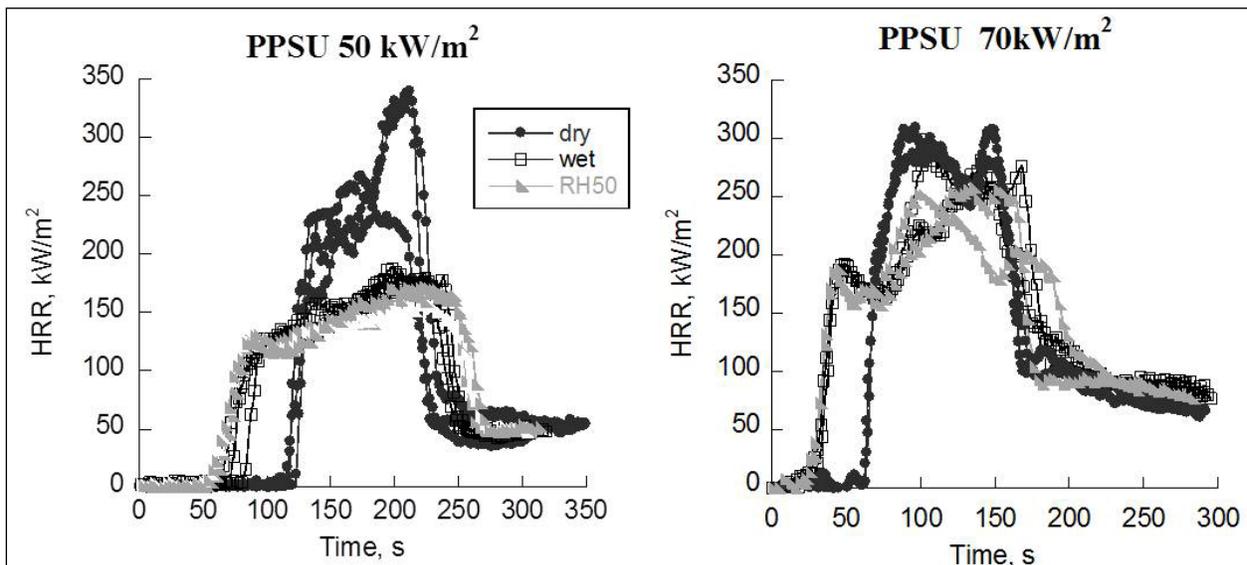
**Figure 2. Cone calorimetry data: the HRR histories for PC at 40 and 50 kW/m<sup>2</sup> external heat flux (note the large effect of moisture on the HRR history)**

The POM is a semi-crystalline polymer (43% crystalline) with a melting temperature of 180°C. Total moisture content was approximately 1.7% for WET samples. This polymer is different from the rest of the polymers in this study due to the fact that only WET samples produced micro bubbles on the surface. The RH50 samples had a reasonable amount of moisture inside (DRY samples lost 0.3% by weight) that was typical for the rest of the RH50 polymers in the group, but micro bubbles were not present for the POM RH50 polymers. One of the possible explanations is the viscosity of the sample. The ignition times of RH50 and DRY samples were very close, and WET samples had earlier ignition. Figure 3 shows HRR histories for POM at 20 and 40 kW/m<sup>2</sup> external heat flux, in which WET/RH50 samples ignited earlier than DRY ones.



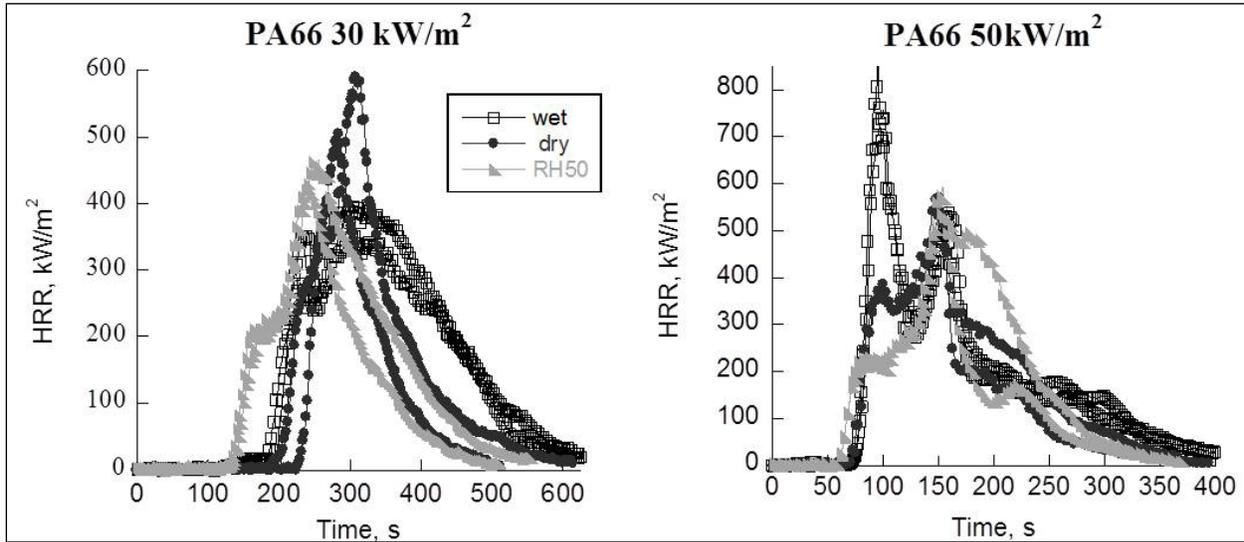
**Figure 3. Cone calorimetry data: The HRR histories for POM at 20 and 40 kW/m<sup>2</sup> external heat flux**

The PPSU is an amorphous polymer with a glass transition temperature of approximately 219°C. Total moisture content is 1.4% for WET samples. The WET and RH50 samples had close values for time to ignition for different external heat fluxes. The presence of moisture strongly correlates with premature ignition for this particular polymer. Figure 4 shows the HRR histories at 50 and 70 kW/m<sup>2</sup>, with ignition of WET samples occurring 40–100 seconds before DRY samples, depending on external heat flux.



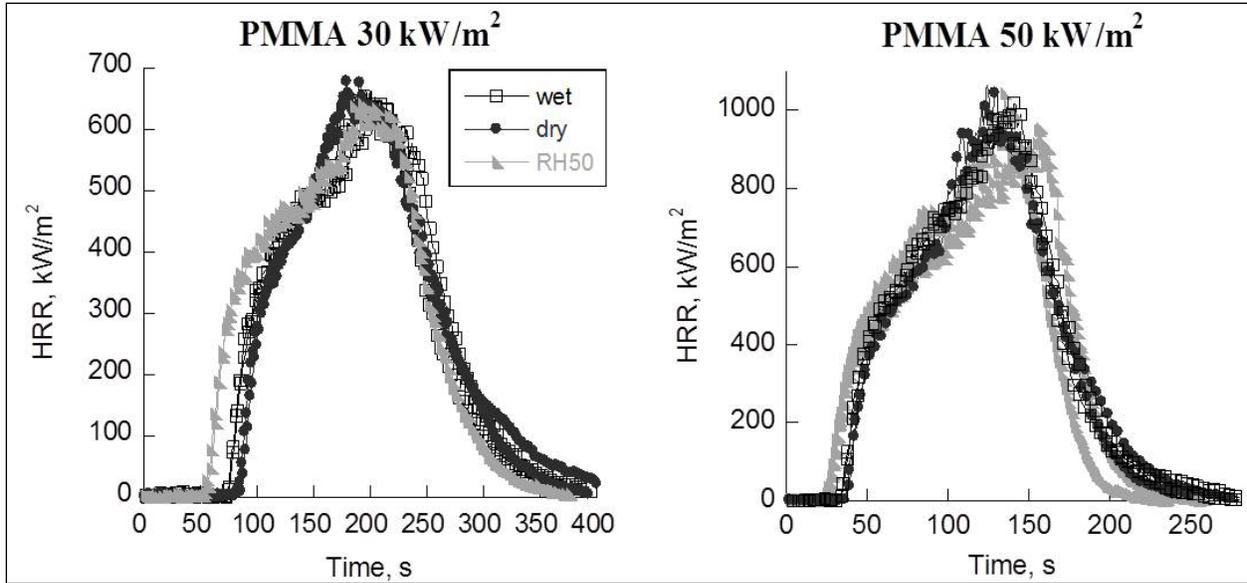
**Figure 4. Cone calorimetry data: the HRR histories for PPSU at 50 and 70 kW/m<sup>2</sup> external heat flux (note the large effect of moisture on the HRR history)**

The PA66 is a semi-crystalline polymer (29% crystalline) with a melting temperature of 260°C. Although WET samples have the largest amount of moisture (9.2% w/w) for this study group, only the RH50 ambient samples had premature ignition, as shown in figure 5. The WET and DRY samples had similar values for time to ignition but very different behavior. Bubbles, loud popping, and cracking sounds were observed for WET samples, whereas DRY samples had normal ignition.



**Figure 5. Cone calorimetry data: the HRR histories for PA66 at 30 and 50 kW/m<sup>2</sup> external heat flux (note the large effect of moisture on the HRR history)**

The PMMA is an amorphous polymer with a glass transition temperature of approximately 114°C. Total moisture content of WET samples is 2.4%. For PMMA, only the RH50 samples demonstrated premature ignition. Values for time to ignition for DRY and WET samples were similar. The WET and RH50 samples had bubbles on their surfaces prior to ignition; DRY samples had smooth and shiny surfaces. The WET samples had a different appearance after the conditioning process; they became whitish and cloudy instead of clear. Figure 6 shows HRR histories of PMMA at 30 and 50 kW/m<sup>2</sup> external heat flux, with a clear indication of the RH50 samples igniting 20–30 seconds before the WET or DRY samples.



**Figure 6. Cone calorimetry data: the HRR histories for PMMA at 30 and 50 kW/m<sup>2</sup> external heat flux**

### Ignition Times

Table 2 contains the average times to piloted ignition in the cone calorimeter for 3 mm thick samples of PMMA, POM, PA66, PC, and PPSU hydrothermally conditioned at three levels of moisture: WET, RH50, and DRY. The order of ignition in the last column of table 2 is the average rank order of ignition for each polymer expressed as a whole number.

**Table 2. Time to ignition in seconds vs. external heat flux for hygrothermally conditioned polymers**

		External Heat Flux, kW/m <sup>2</sup>								Ignition Order
		10	15/16	20	25	30	40	50	70/75	
PMMA	WET	532	212	150	—	72	—	33	17	2
	RH50	504	199	115	—	53	—	24	17	1
	DRY	1053	346	243	—	82	—	36	20	3
POM	WET	686	—	120	—	—	38	26	14	1
	RH50	853	—	203	—	—	65	39	20	2
	DRY	532	—	200	—	—	61	39	22	2
PA66	WET	—	792	445	—	190	130	78	37	2
	RH50	—	440	224	—	127	91	58	27	1
	DRY	—	631	502	—	205	120	74	35	2
PC	WET	—	—	—	524	249	128	70	25	2
	RH50	—	—	—	476	181	124	62	31	1
	DRY	—	—	—	491	350	162	105	49	3
PPSU	WET	—	—	—	—	421	107	50	17	1
	RH50	—	—	—	—	420	105	50	20	1
	DRY	—	—	—	—	520	201	115	63	2

### Visual Observations

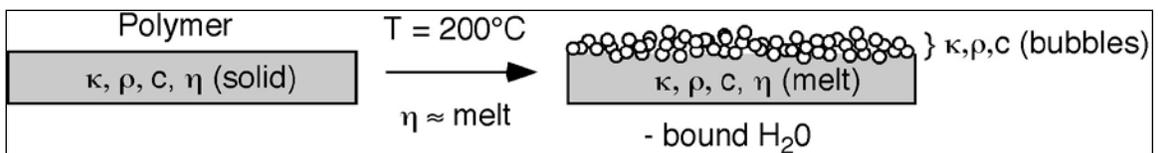
The physical behavior of samples during the heat-up period prior to ignition was recorded visually and photographically. In general, samples that contained moisture (RH50 or WET) exhibited vigorous bubbling on the surface, as shown in figure 7 for PC and figure 8 for PA66. Samples that were vacuum-dried exhibited smooth, clean surfaces with no surface bubbling, as shown on the left hand side of figure 7 for DRY PC. Bubbles usually formed on RH50 or WET samples at surface temperatures of 200°C–250°C, the range at which all of these polymers have softened ( $T_g$ ) or melted ( $T_m$ ), so that the viscosity ( $\eta$ ) is low enough to allow foaming during the release of bound water. Figure 9 is a schematic model of the 2-phase process of surface bubble formation used in the ThermaKin simulation, in which the full density solid polymer melts and then undergoes a phase change at 200°C–250°C to become a low-density material with thermal properties of polymer foam.



**Figure 7. Photographs of DRY and WET surfaces of PC prior to ignition**



**Figure 8. Photograph of surfaces of WET PA66 sample**



**Figure 9. Phenomenological MODEL of the surface morphology of moisture-containing polymers**

Effect of Moisture on Thermal and Chemical Parameters of Ignition

The sample temperatures at the onset of thermal decomposition measured in MCC were found to be independent of the moisture content, as shown in table 3. Table 3 also lists the measured surface temperature at ignition in the fire calorimeter tests. The temperatures at ignition in the fire calorimeter tests were difficult to measure and highly variable ( $\pm 20^{\circ}\text{C}$ ) but appear to be

relatively independent of the moisture content of the polymers. The CHF for piloted ignition was calculated for  $T_{onset}$  and  $T_{ign}$  using the surface energy balance of equation 14 for separate radiant and convective heat losses at ignition:

$$CHF = \varepsilon\sigma(T_{onset}^4 - T_0^4) + h(T_{onset} - T_0) \quad (14)$$

The surface emissivity was assumed to be that of the solid polymer in these calculations,  $\varepsilon = 0.9$ , and the convective coefficient in the cone calorimeter was  $h = 10 \text{ W m}^{-2} \text{ K}^{-1}$ . The presence (Y) or absence (N) of polymer foam prior to ignition is noted in the last column of table 3.

The thermal response time,  $\tau = \rho cb/\bar{h}$ , and CHF of the polymers at the three moisture levels were obtained experimentally by nonlinear least squares regression of equation 8 to the  $t_{ign}$  versus external neat flux data using  $\tau$  and CHF as adjustable parameters. The original data and best-fit curves are shown in figure 10, and the results of these curve fits are listed in the 4<sup>th</sup> and 5<sup>th</sup> columns of table 3 for WET, RH50, and DRY samples. The vertical separation of the points and curves in figure 10 shows that the ignition delay for polymers containing any water (i.e., the RH50 or WET samples) decreases by hundreds of seconds in the vicinity of the CHF and by 1–2 minutes at typical heat fluxes of 35–50 kW/m<sup>2</sup> used in regulatory and routine testing.

**Table 3. Parameters of thermal theory of ignition**

Polymer	Condition	H <sub>2</sub> O Content %, w/w	Thermal Response Time $\tau$ , Eq. (8) seconds	CHF Calculated, Eq. (8) kW/m <sup>2</sup>	$T_{onset}$ From MCC and Eq. (14) °C	CHF From MCC and Eq. (14) and ( $T_{onset}$ ), kW/m <sup>2</sup>	$T_{ign}$ From Cone and Eq. (5), °C	CHF From Cone and Eq. (5) kW/m <sup>2</sup>	Foam Observed $t < t_{ign}$ (Y/N)
PMMA	WET	2.4	219	9	345	10	335	10	Y
	RH50	0.4	181	9	343	10	332	10	Y
	DRY	0.0	312	10	348	10	348	10	N
PA66	WET	9.2	300	15	416	15	425	16	Y
	RH50	2.6	172	15	415	15	446	17	Y
	DRY	0.0	351	13	415	15	437	17	N
POM	WET	1.8	166	10	319	9	300	8	Y
	RH50	0.4	293	10	321	9	292	7	N
	DRY	0.0	374	8	321	9	283	7	N
PC	WET	0.6	138	24	492	21	448	18	Y
	RH50	0.2	106	25	494	21	436	17	Y
	DRY	0.0	222	22	497	22	466	19	N
PPSU	WET	1.4	60	30	541	27	491	22	Y
	RH50	0.6	61	30	542	27	490	22	Y
	DRY	0.0	136	29	544	27	503	23	N

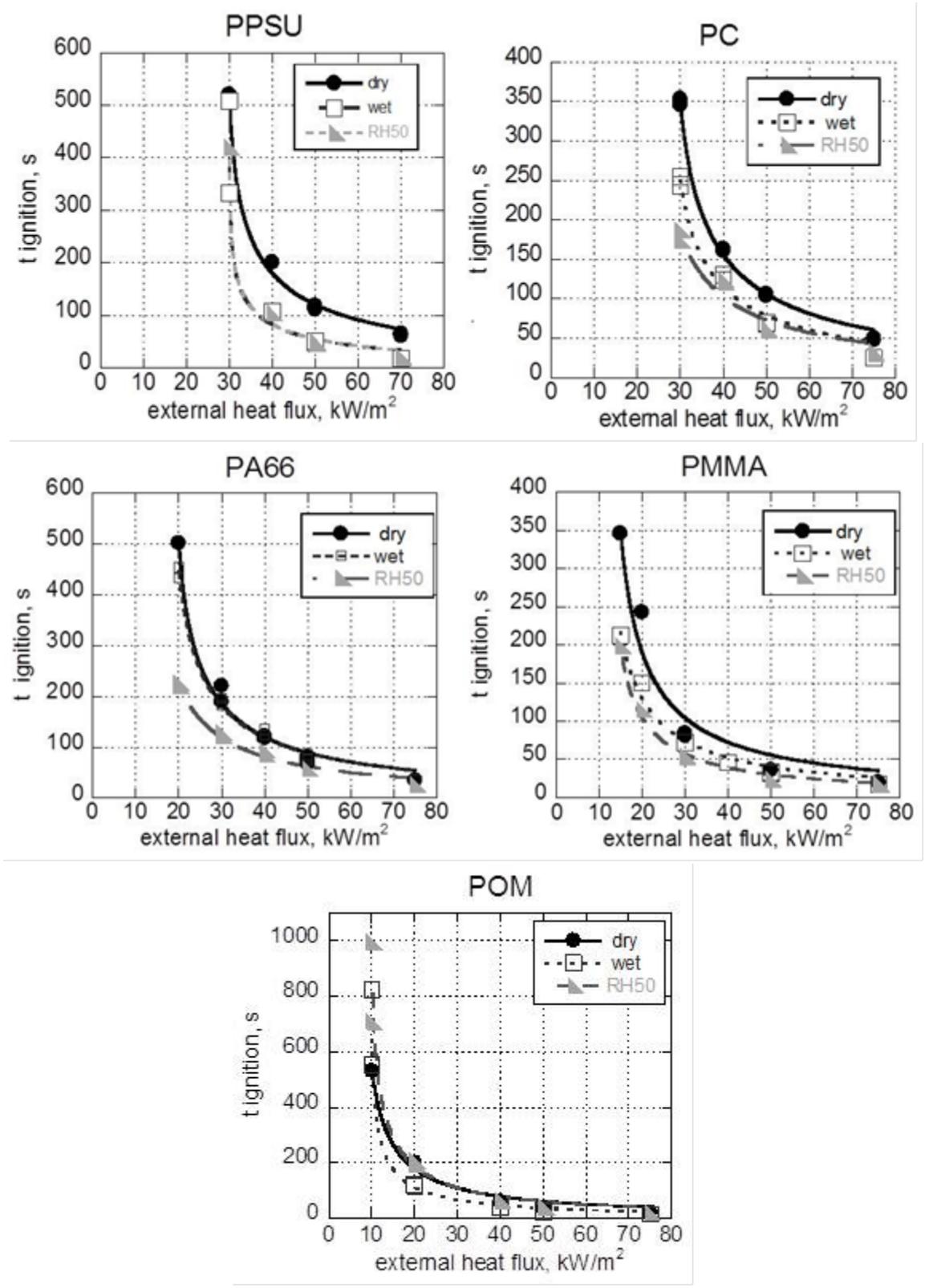


Figure 10. Time to ignition vs. external heat flux for hygrothermally conditioned polymers (solid circles are data; solid and dashed lines are fits of equation 1)

Table 3 showed that the CHF does not change significantly with water content, which is consistent with the observation that the onset decomposition temperature and ignition temperature do not change significantly for this range of moisture levels, as evidenced by calculated  $CHF_{onset}$  and  $CHF_{ign}$  in table 3 obtained from the corresponding measured temperatures and equation 14 and 5, respectively. However, the thermal response time,  $\tau = \rho cb / \bar{h}$ , decreases by approximately a factor of 2 when moisture is present compared to the value for DRY samples. Assuming the shorter response time is due primarily to a reduction in the sample density at ignition resulting from bubble formation, the effective density,  $\rho_{eff} = \tau \bar{h} / cb$ , was calculated for the three hygrothermal treatments using the  $\tau$  data in table 3, with  $\bar{h}$  estimated by equation 2 for  $T_{onset} = T_{ign}$  assuming typical polymer heat capacity at ignition,  $c(T_{ign}) = T_{ign}c_0/T_0 \approx 2500$  J/kg-K [7] for  $b = 3 \times 10^{-3}$  m. The results of these calculations are given in table 4. Only the DRY samples have effective densities at the time of ignition that are representative of the polymer densities listed in the second column of table 4 [7]. The WET and RH50 samples have significantly lower effective densities at ignition due to bubble formation, but these do not correlate with moisture content.

**Table 4. Effective density of hygrothermally conditioned samples at ignition**

Polymer	$\rho$ (kg/m <sup>3</sup> )	$\bar{T}$ (K)	$\bar{h}$ (W/m <sup>2</sup> -K)	WET	RH50	DRY
				Effective Density, $\rho_{eff}$ (kg/m <sup>3</sup> )		
PMMA	1175	454	27	788	652	1123
PA66	1140	488	33	1320	757	1544
POM	1420	438	24	531	938	1197
PC	1200	530	42	773	594	1243
PPSU	1320	549	47	470	480	1070

Table 5 contains the mass flux at ignition ( $m''_{ign}$ ), average effective heat of flaming combustion ( $H_c$ ), and HRR at ignition,  $HRR_{ign} = H_c m''_{ign}$ . Also in table 5 is the rank order of the experimental ignition times for each polymer from shortest (1) to longest (3). As seen in table 5, there is no significant systematic relationship between  $m''_{ign}$  or  $HRR_{ign}$  and the observed ignition order.

**Table 5. Parameters of the chemical theory ignition**

Polymer	Condition	H <sub>2</sub> O Content (% w/w)	Mass Flux at Ignition, $m''_{ign}$ (g/m <sup>2</sup> -s)	Heat of Combustion of Fuel Gases, $H_c$ (kJ/g)	Heat Release Rate at Ignition, $HRR_{ign}$ (kW/m <sup>2</sup> )	Rank Ordered Ignition Times
PMMA	WET	2.4	3.0±0.4	25.0	75	2
	RH50	0.4	2.1±0.3		53	1
	DRY	0.0	2.7±1.0		68	3
PA66	WET	9.2	4.2±0.6	28.4	119	2
	RH50	2.6	2.0±0.5		62	1
	DRY	0.0	1.1±0.4		31	2
POM	WET	1.8	1.8	14.0	25	1
	RH50	0.4	2.0		28	2
	DRY	0.0	2.1±0.7		29	2
PC	WET	0.6	3.3±1.0	26.6	88	2
	RH50	0.2	2.9±0.8		77	1
	DRY	0.0	3.8±0.4		101	3
PPSU	WET	1.4	1.8	22.1	40	1
	RH50	0.6	1.1±0.9		24	1
	DRY	0.0	4.8±0.4		106	2

### ThermaKin Simulations

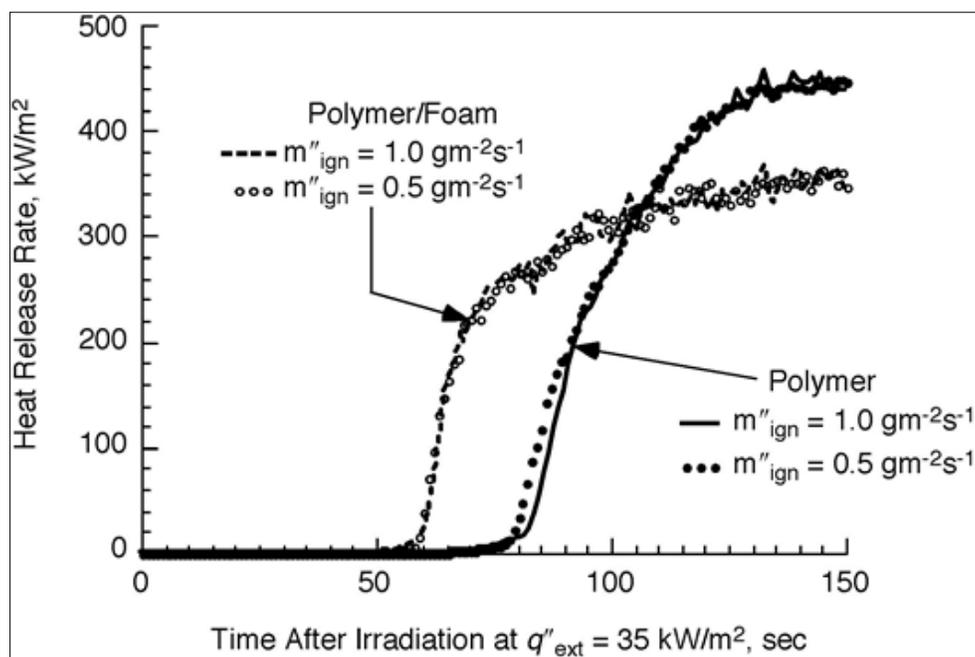
In the absence of any clear correlation between ignition delay and moisture content (see table 2) of homogeneous polymers using the thermal (see table 3) or chemical (see table 4) parameters, ThermaKin simulations were conducted to explore the possibility of a heterogeneous (2-phase) mechanism for premature ignition of water-containing polymers that was consistent with the visual observations of bubble formation just prior to ignition.

In the ThermaKin model, moisture-containing polymers would undergo a phase change from solid polymer to foamed polymer at 200°C, which is the average temperature at which surface bubbles appeared. The properties of the foamed polymer were obtained from the solid polymer properties when density was decreased by a factor of 2 (from 1300 kg m<sup>-3</sup> to 650 kg m<sup>-3</sup>), which is consistent with the  $pcb/\bar{h}$  results for the WET and DRY polymers in tables 3 and 4. Thermal conductivity was also decreased from  $\kappa = 0.24 \text{ W m}^{-1} \text{ K}^{-1}$  to  $\kappa = 0.04 \text{ W m}^{-1} \text{ K}^{-1}$  based on a series

model calculation for a 1/1 mixture of polymer and air, as per the decrease in density. Thermal decomposition parameters remained those of the full density polymer.

Additional calculations were performed to test the chemical criteria for ignition in which the critical mass flux at ignition was reduced by a factor of 2, from  $1 \text{ g m}^{-2} \text{ s}^{-1}$  to  $0.5 \text{ g m}^{-2} \text{ s}^{-1}$ .

External heat flux was set at  $q''_{ext} = 35 \text{ kW m}^{-2}$ . Figure 11 shows the results of these calculations for a standard polymer [11] decomposing via a foam intermediate, as shown in figure 9 (i.e., the 2-phase model). Ignition occurs 50 seconds earlier when a typical polymer generates a foamy layer prior to thermal decomposition. Figure 11 also shows that reducing the critical mass flux of a full density polymer (1-phase model) by a factor of 2 does not significantly change the time to ignition.



**Figure 11. ThermoKin simulations of HRR histories for WET and DRY samples (solid circles and solid line are single phase (polymer) model at two values of  $m''_{ign}$ . Open circles and dashed line are two-phase (polymer/foam) model at two values of  $m''_{ign}$ .)**

## CONCLUSIONS

The polymers examined in this study on the effect of moisture on ignition delay spanned a range of thermal stability, morphology, and chemical affinity for water, yet all of these heteroatom-containing polymers (O, N, S) could absorb small amounts of water (< 1 % w/w under ambient conditions) that led to premature ignition compared to DRY samples. Ignition of moisture-containing polymers occurred minutes earlier than the DRY polymers at external heat fluxes in the vicinity of the critical value (see table 2). At higher heat fluxes used for routine and regulatory fire testing ( $35\text{--}50 \text{ kW/m}^2$ ), samples that contained moisture ignited dozens of seconds earlier than their DRY counterparts. Although ignition delay did not strictly correlate

with the moisture content of polymers, the presence of water was always a prerequisite for premature ignition compared to DRY samples.

For the thermal theory of ignition, moisture did not affect the critical heat flux for ignition nor the ignition temperature of individual polymers. The explanation for premature ignition of moisture-containing polymers in the context of heat transfer was provided by numerical pyrolysis modeling using ThermaKin with a solid-to-foam phase change at 200°C to represent the release and entrainment of bound water in the molten polymer. The two-phase ThermaKin model qualitatively captured the premature ignition of moist samples using experimentally derived densities for the wet polymer foam. Reducing the critical mass flux or heat release rate for ignition of the full density polymer or foamed polymer had a negligible effect on the ignition delay calculated with ThermaKin, consistent with the experimental results. Based on the results of this study, standard hygrothermal conditioning procedures are highly recommended for tests of fire performance where repeatability and reproducibility are important.

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