

**THE PAST AND FUTURE OF PUBLIC FLAME  
RETARDANCY RESEARCH**

by

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# The Past and Future of Public Flame Retardancy Research<sup>ψ</sup>

## ABSTRACT

Public flame retardancy research at the National Institute of Standards and Technology (NIST) has had a long cooperative relationship with the Flame Retardant Chemicals Association (FRCA). Issues of fundamental and practical importance have been investigated, with a positive impact on public fire safety. This paper reviews some of these programs and interactions, with a focus on recent and planned consortia activities associated with mechanistic studies of new approaches to flame retarding commodity polymers.

## INTRODUCTION

Over the last few decades the Flame Retardant Chemicals Association (FRCA) and its member companies and the National Institute of Standards and Technology (NIST) [1] have participated in a variety of mutually beneficial collaborative, research interactions. These interactions continue today, and will presumably persist into the future. They include in depth personal communications, FRCA sponsored summer students, and FRCA member company funded Cooperative Research and Development Agreement (CRADA) projects (one-to-one or consortia).

Past interactions have included:

- 1) summer student research projects on: thermal degradation of cross-linked poly(methyl methacrylate) (PMMA) [2], molecular modeling of polymer flammability, development of tomographic-FTIR methods for combustion characterization [3], the survey of melamine, melamine phosphate and melamine borate as flame retardants (FR) for cyanate ester resins for aircraft composite applications [4], determination of the mass yield of smoke in real- and reduced-scale experiments, polymer melt rheometer, applied to the characterization of polypropylene, and non-burning, melt-flow experiments [5].
- 2) a project which compared flame retarded commercial polymer formulations to non-FR formulations; and demonstrated the importance of flame retardants and heat release rate in controlling time to incapacitation in room fire tests [6].
- 3) the New Flame Retardants Consortium, which determined the FR mechanism of silica [7].
- 4) the Flammability of Polymer-Clay Nanocomposites Consortium, which focused on determining the FR effects of nanocomposites [8].

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As of the writing of this manuscript two new NIST consortia are being organized. The first project will focus on development of high-throughput tools and screening methods for characterizing material flammability. This consortium is in the final stages of forming and will begin work in summer 2001. The second consortium will focus on determining the affect of the degree of flame retardancy of information technology housing materials on fire growth in full scale room fires. This paper will review highlights of these FR research projects, stressing the measurement technology and science that NIST developed to help FRCA member companies deliver innovation to the FR world market.

## **NIST FLAME RETARDANCY RESEARCH**

The field of flame retardancy is a dynamic one. Today important aspects of the flammability requirements for materials continue to change. The users of flame retardants (FR) and FR products demand, “environmentally friendly”, processing-stable, FRs that have a positive impact (or at least no negative impact) on physical properties; all of these demands must be met at, or below, current costs. Performance based codes, new flammability tests and the requirements of new FR markets (e.g. mattress), require that improved levels of understanding, better measurement tools and new approaches be developed by NIST.

## **NEW FLAME RETARDANTS CONSORTIUM**

Promising results from an internal NIST project prompted the formation of the New Flame Retardants Consortium in October 1997; namely, the discovery that silica gel and potassium carbonate reduced the peak heat release rate (HRR) of several commodity polymers. This new flame retardant approach was effective in polypropylene (PP), nylon 6,6, PMMA, cellulose, poly (vinylalcohol) (PVA), and to a lesser extent in polystyrene (PS) and poly (styrene-co-acrylonitrile) (SAN). The peak heat release rate was reduced by up to 68 %, with a mass fraction of 10 % [9] additives [10]. As part of our internal effort to determine the flame retardant mechanism, we first focused our efforts on characterizing the char structure, which resulted from burning poly (vinyl alcohol) with these additives. We found that the additives increased the (carbonaceous) char yield, but did not change the chemical structure of the char [11]. The New Flame Retardants Consortium’s goal was to determine the FR mechanism of silica in commodity polymers. The members were Nyacol Products, PQ Corporation, FMC Corporation, Sekisui America, and Akzo Nobel.

The approach of the program focused on the affects of silica material properties on polymer flammability. The results of this project were reported in a final report [7, 12] and the important aspects of this work are presented here [13].

The affect of silica morphology and  $K_2CO_3$  on the flammability and nitrogen-gasification of polypropylene (PP) was determined. A full factorial design-of-experiment(DOE) was used to evaluate three silica gel material properties: pore volume, **particle size** and surface silanol concentration. Table 1 shows **the** material properties for the silica gels used.

Pore Volume (cm <sup>3</sup> /g)	Particle Size (μm)	Pore Diameter (nm)	Surface Area (m <sup>2</sup> /g)	Silanol Concentration (mmol/g)	Heat Treatment (°C)
3.0	20	28	400	0.5	900
3.0	20	28	400	1.7	220
3.0	5	28	400	0.5	900
3.0	5	28	400	1.7	220
1.3	10	15	350	1.0	500
0.45	20	2.3	800	0.5	900
0.45	20	2.3	800	1.7	220
0.45	5	2.3	800	0.5	900
0.45	5	2.3	800	1.7	220

The Cone calorimeter data (flux:35 kW/m<sup>2</sup>, not shown) reveals that neither the silica gel particle size, nor the presence of K<sub>2</sub>CO<sub>3</sub> significantly changed the effect on HRR [14] that the silica gel inherently produces in PP. That is, each of these formulations reduces the HRR by about the same amount: about 50%. Figure 1, which shows peak HRR for combinations of silica gel pore volume and particle size, reveals that the formulations with silica gels with the highest pore volume (3 cm<sup>3</sup>/g) have a significantly lower flammability. It should be noted that no significant differences were observed in ignition times (42 s ± 10 s) for any of the formulations.

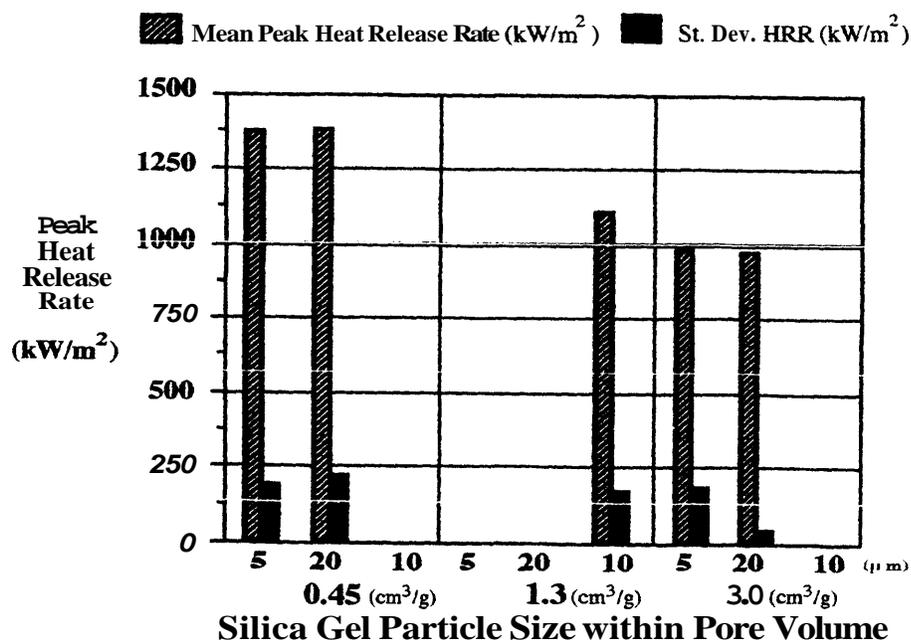


Figure 1. Peak HRR versus particle size and pore volume. Clearly, the 3.0 cm<sup>3</sup>/g pore volume has a strong influence on the reduction in HRR produced by the silica gels.

These data show that pore volume is, within experimental uncertainty, the primary factor in enhancing the fire retardant properties of silica gel in PP. The Cone Calorimetry data also shows that the high pore volume silica gel samples do not reduce flammability by changing the gas phase combustion processes, i.e., the carbon monoxide yield is unchanged (0.04 kg/kg

$\pm 0.001$  kg/kg) and the specific heat of combustion,  $H_c$ , is unchanged as the pore volume is varied (data not shown).

The silica gel appears to function by reducing the rate that fuel is fed into the gas phase. This can be seen by examining Figure 2, which shows the mass loss rate (MLR) data for the three different pore volumes studied. One possible explanation for this behavior is that the larger pore diameter of the high pore volume silica gels can accommodate the PP macromolecule, or its decomposition products. The radius of gyration of PP, in this molecular weight range, is  $\sim 70$  nm, when measured in solution [15], and may be somewhat smaller in the melt. The nominal average pore diameter of the high pore volume material is  $\sim 28$  nm. Since, there is a distribution of pore diameters it seems likely that a significant fraction of the pores might be able to fit a PP macromolecule, or its decomposition products; thereby trapping or delaying the loss of decomposition products from the condensed phase, and thus reducing the MLR.

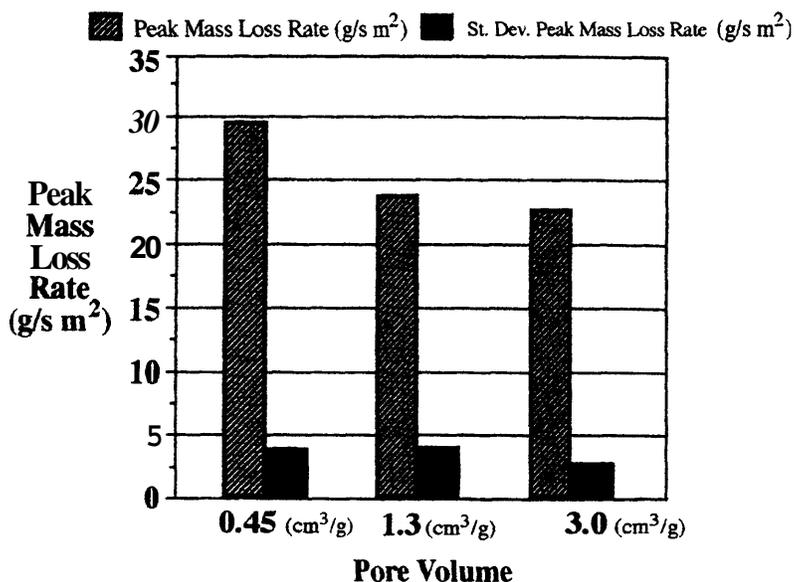


Figure 2. Mass loss rate data for the three different pore volumes studied.

In this phase of the flammability study of the FR properties of silica gel we observed an enhanced effectiveness of the silica gel. The reduction in peak HRR compared to pure PP or (PP with PP-g-MA) is 60 %, for the formulations with high pore volume silica gel. Figure 3 shows the HRR versus time plots for PP, PP/PP-g-MA with high pore volume ( $3.0 \text{ cm}^3/\text{g}$ ) silica gel and PP/PP-g-MA with the low pore volume ( $1.0 \text{ cm}^3/\text{g}$ ) silica gel, similar to that used in our original study [9]. These data show that the new (high pore volume) silica gel is 2 times as effective as the original low pore volume material.

To further explore the influence of silica material properties on silica FR-properties, we prepared silica/PP samples using fused silica, fumed silica, and a high pore volume ( $2.0 \text{ cm}^3/\text{g}$ ) silica gel.

Table 2 shows the material properties of the four types of silica used. These silicas are very different, specifically in terms of their particle morphology, surface area, and level of silanol functionality. Figure 4 shows representations of the silica types.

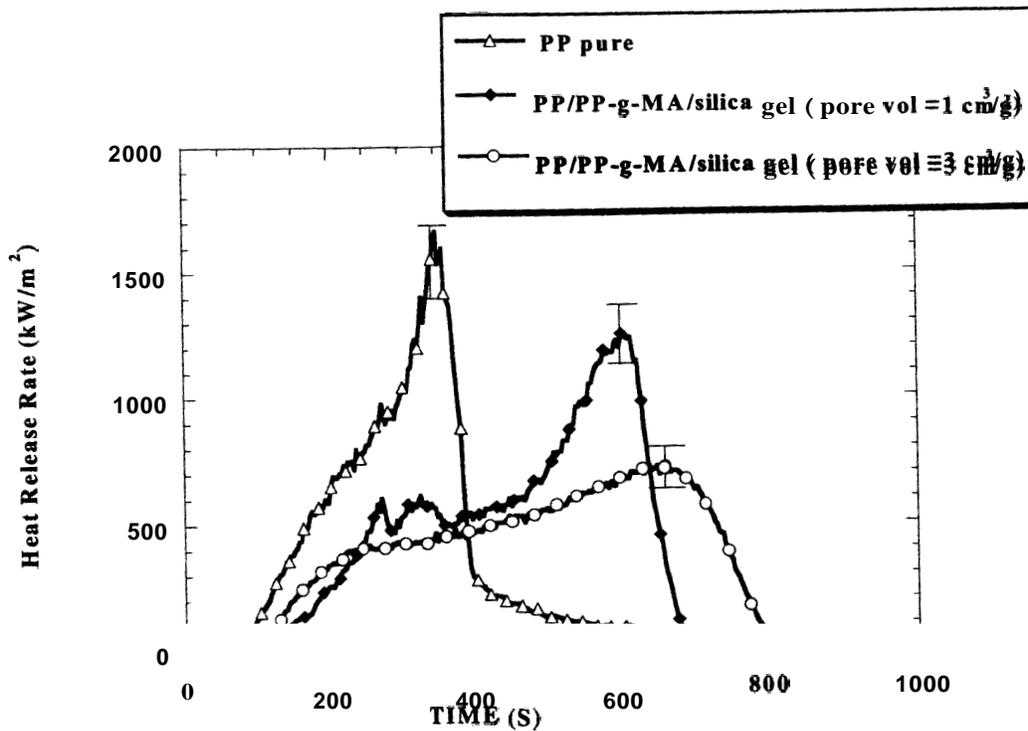


Figure 3. The HRR versus time plots for pure PP, PP/PP-g-MA (mass fraction 5%) with mass fraction 10% high pore volume ( $3.0 \text{ cm}^3/\text{g}$ ) silica gel, and PP/PP-g-MA (mass fraction 5%) with mass fraction 10% low pore volume ( $1.0 \text{ cm}^3/\text{g}$ ) silica gel.



Figure 4. Drawing of the morphologies for silica gel (left), fused silica (center), and fumed silica (right).

The Cone Calorimeter results revealed that the fused silica had only a moderate effect on the peak heat release rate of PP, and surprisingly, that hydrophilic fumed silica gives the same factor-of-3 reduction in peak heat release rate that large-pore silica gel produces. Since hydrophilic fumed silica has no pore structure an alternative mechanism must be operating. An alternative FR mechanism may be related to the well-known thickening effect hydrophilic fumed silica has on non-polar liquids [16]. When hydrophilic fumed silica is suspended in non-polar liquids an inter-particle hydrogen-bonding network forms: this silica network

as that of pure PP was observed. Scattered white powder was observed at the end of the test equal to the original silica mass. The digitized video images of the sample of PP with hydrophobic fumed silica (mass fraction 10%) are also not shown in Figure 6; however, the behavior was similar to that of the pure PP sample up to about 200 s. After 400 s, some solid islands were observed, and this pattern remained until the end of the test. Vigorous bubbling was observed between the islands. For the sample of PP with silica gel (mass fraction 10%) initial melting and bubbling phenomena were similar to the above three samples up to about 180 s, as seen in the left bottom picture in Figure 6. At about 180 s, the sample surface rapidly solidified and a crust-like layer formed. It appeared that this layer continued to thicken, as seen in the middle and right bottom images in Figure 6. The mass of the residue at the end of the test (800 s) appeared to be a rigid crust instead of a powder, and was about 9% of the original sample mass. No significant amount of carbonaceous char was formed by the addition of the silica gel. Behavior very similar to the PP/silica gel sample was also observed for the PP/hydrophilic fumed silica sample: except that the surface layer of the residue at the end of the test was very fluffy and white.

The measured mass loss rates from the gasification experiments of the five PP/silica samples (not shown here) decrease in the order: PP/fused silica > PP/hydrophobic fumed silica > PP/silica gel = PP/hydrophilic fumed silica.

From the visual observations of the gasification experiments it appears that the melt viscosity of PP is significantly enhanced by the addition of silica. Both silica gel and hydrophilic fumed silica show the same thickening behavior. For the hydrophilic fumed silica the thickening is due to the inter-particle hydrogen bonding shown in Figure 5; on the other hand, the thickening from silica gel can in part be due to this type of mechanism, but entanglement of the polymer in the large silica gel pores may also play a part in increasing the viscosity [18].

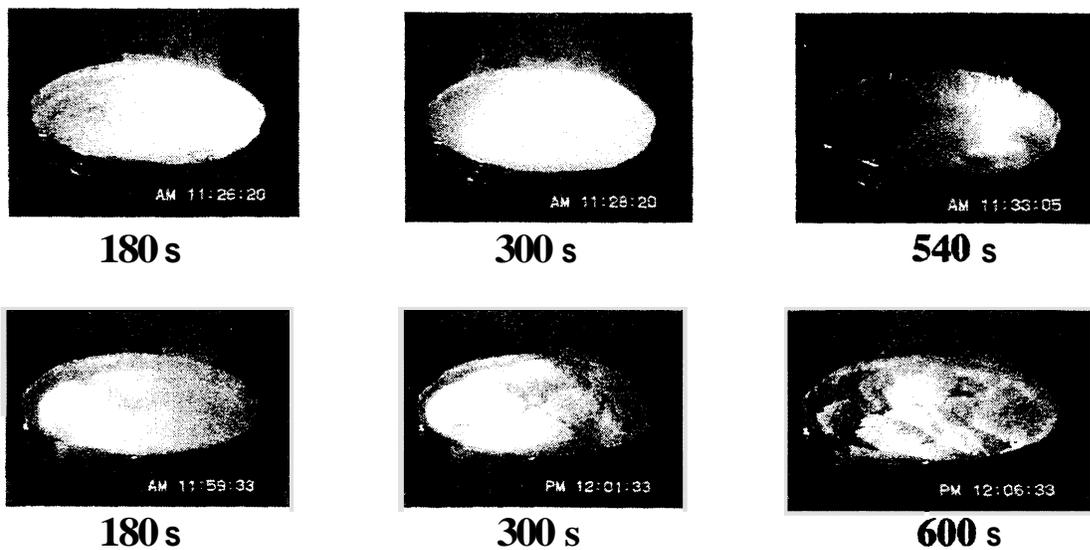


Figure 6. Digitized images of sample surface during gasification in  $N_2$  at  $40 \text{ kW/m}^2$ . Pure PP (Top row) ; PP with silica gel (mass fraction 10%) (bottom row).

From the results discussed here, and additional experiments performed by the consortium team, the following mechanism was proposed; *the silica gel( andfumed silica) frame retardant mechanism in PP appears to consists of two mechanisms: first, reduction in the transport rate of the thermal degradation products; and second, reduction in thermal diffusivity of the sample near the surface due to gradual accumulation of silica, which acts as a thermal insulation layer.*

## FLAMMABILITY OF POLYMER-CLAY NANOCOMPOSITES CONSORTIUM

Once again, the results of NIST internal research stirred interest in formation of a research consortium to investigate a new approach to reducing the flammability of polymers. The interest derived from the observation that “nanocomposites” (mica-type clays such as montmorillonite nano-dispersed in polymers) exhibit the unusual combination of reduced flammability, in the form of lower peak heat release rates [19,20,21,22], and improved physical properties [23]. In October of 1998 the Flammability of Polymer-Clay Nanocomposites Consortium formed to determine the FR mechanism of montmorillonite (MMT) clay dispersed in polymers at the nanometer-scale. The members of the consortium were: GE Company, 3M Corporation, Nanocor, Sekisui America, Great Lakes Chemical, PQ Corporation, Raychem, Southern Clay Products, the Air Force Research Laboratory (AFRL), and the Federal Aviation Administration (FAA).

The results of the first year of this project were reported in a 2000 NIST report [8] and a summary of the important aspects of this work are presented here. The results from the first year are summarized in Table 3. The flammability properties of nanocomposites prepared from PS, PP, nylon-6 (PA-6), and poly(ethylene-co-vinylacetate) (EVA) were characterized. The observed reductions in HRR are quite significant. However, the most important result from the first year’s work is the formation of a clay-reinforced carbonaceous char during combustion of nanocomposites. This is particularly significant for systems whose base resin normally produces little or no char when burned alone (PS, PPgMA, PA-6, and EVA). It appears from the gasification data (videos and mass loss data) that this clay-reinforced carbonaceous char is responsible for the reduced mass loss rates and hence the lower HRRs.

Table 3. Summary of results.

Result/Critical Experiment	EVA	PA-6	PS	Epoxy	PP
Peak HRR reduced by:	70 %	80 %	80 %	0 - 20 %	70 %
Shorter $t_{ign}$	no	yes	no	no	no
High initial HRR or MLR	yes	no	yes	yes	yes
Carbonaceous char formed	yes	yes	yes	no	yes
HRR of Intercalated vs. delaminated	-	equivalent	-	-	-
HRR of tethered vs. non-tethered	-	-	-	-	-
Effect of different clays on HRR	-	-	-	-	-
Effect of crosslinking on HRR	TBD	-	-	-	-
Effect of Mw on HRR	-	-	moderate	-	-
Effect of loading level on HRR	5 % max	10 % max	5 % max	TBD	5 % max
Effect of charring resin (PPO) on HRR	-	none	-	-	-

The HRR data for pure PS and the PS with alkylammonium treated montmorillonite (PS/AMMT) nanocomposites with 2 %, 5 %, and 10 % AMMT are shown in Figure 7. The reduction in peak HRR improves as the mass fraction of MMT increases. The additional improvement for the PS/AMMT nanocomposite with 10 % AMMT only occurs during the first 100s of the burn. This is typical of the result for other polymer nanocomposites we evaluated. A leveling off of improvement in flammability properties at 5 % is also a common result for many other properties (tensile strength, modulus, permeability, etc.) [24]. As impressive as the HRR data are for the PS system, the data most telling of the novelty of this approach, to flame retarding PS, comes from the gasification data taken on these samples. The MLR data from the gasification of PS/AMMT nanocomposites show the identical trends to those found in the HRR data from the Cone (see Figure 7). However, the digitized video images taken during the gasification of the low  $M_n$  PS/5 % AMMT nanocomposite show the most important effect of the nano-dispersed clay on the PS degradation; in contrast to the rapidly-boiling liquid layer observed for the pure PS, the PS/5 % AMMT sample appears to solidify and converts to a black solid residue very early in the experiment, at 90 s. Once this residue (char) forms, the MLR slows to 25 % of that for pure PS.

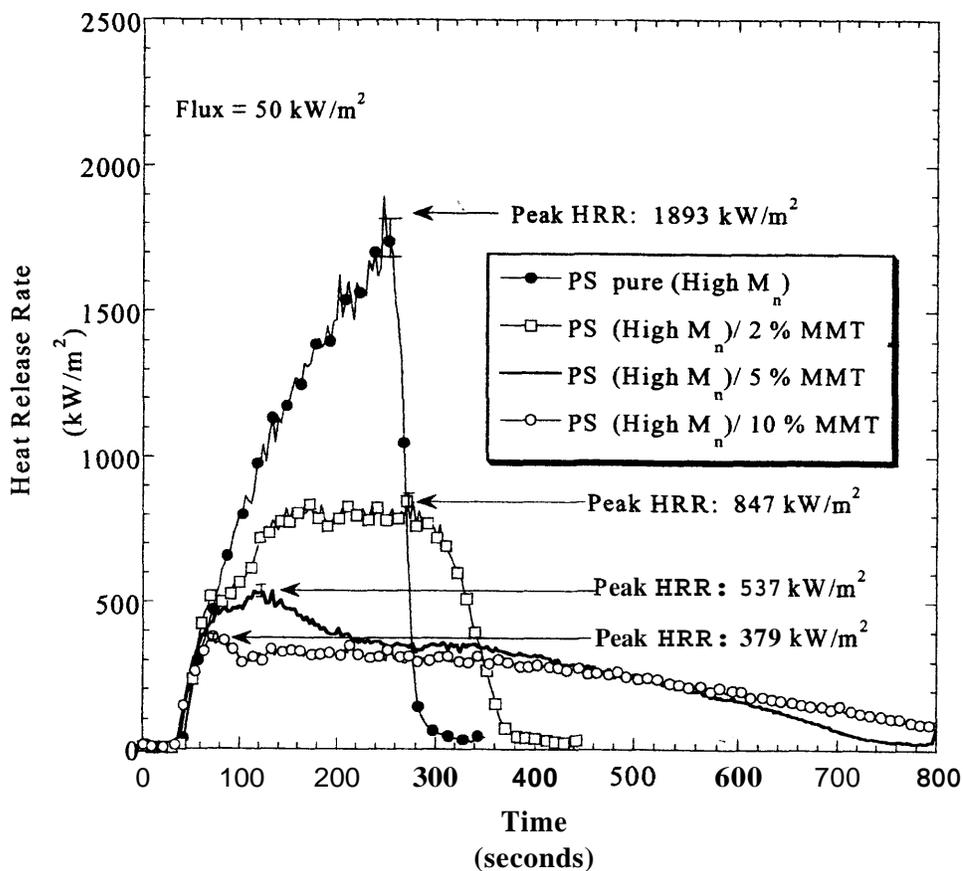


Figure 7. HRR plots for the pure high  $M_n$  PS, and the high  $M_n$  PS/ MMT nanocomposites with 2 %, 5 %, and 10% AMMT.

The data in Table 4 show that the MLR and residue yield are the only flammability parameters which are significantly affected by the presence of nano-dispersed MMT.

Table 4. Cone Calorimeter and Radiative Gasification data for PS/AMMT nanocomposites.

	Residue Yield <sup>a</sup> [%]	Peak HRR [kW/m <sup>2</sup> ]	Average Specific Ext. Area [m <sup>2</sup> /kg]	Average H <sub>C</sub> [MJ/kg]	Peak MLR (Cone) [g/s]	Peak MLR (Gasification) [g/s]
PS (High M <sub>n</sub> )	0.2 %	1870	1320	31	59	41
PS/5 % AMMT	4.9 %	540	1230	26	22	14
PS (Low M <sub>n</sub> )	0.3 %	1940	1300	31	63	42
PS/5 % AMMT	4.9 %	540	1650	29	19	13

Uncertainties for the data can be found in the experimental section of the full NIST report [8].

a: These are carbonaceous residue yields only, the silicate fraction has been subtracted out. All silicate is assumed to have survived the gasification, and the organic is assumed to have been volatilized completely. We assume also that the carbonaceous residue is solely derived from PS. The uncertainty in the carbonaceous residue yields are ± 0.5 % (one sigma).

The video images (Figure 8) and the gasification residue yield data (Table 5), for the PS/AMMT nanocomposites, show that the otherwise non-char forming PS is converted to a charring system by the nano-dispersed clay. This is significant because very few other additive flame retardants are capable of causing virgin PS (without a carbonific) to give carbonaceous char, especially at this low a loading and with such dramatic reduction in flammability.

Table 5. Carbonaceous char yields for PS/MMT nanocomposites.

Nanocomposite	Carbonaceous Char yield"
pure PS	0.2 %
PS/5 % AMMT	2.3 %
PS/10 % AMMT	3.3 %

a: These are carbonaceous residue yields only, the silicate fraction has been subtracted out.

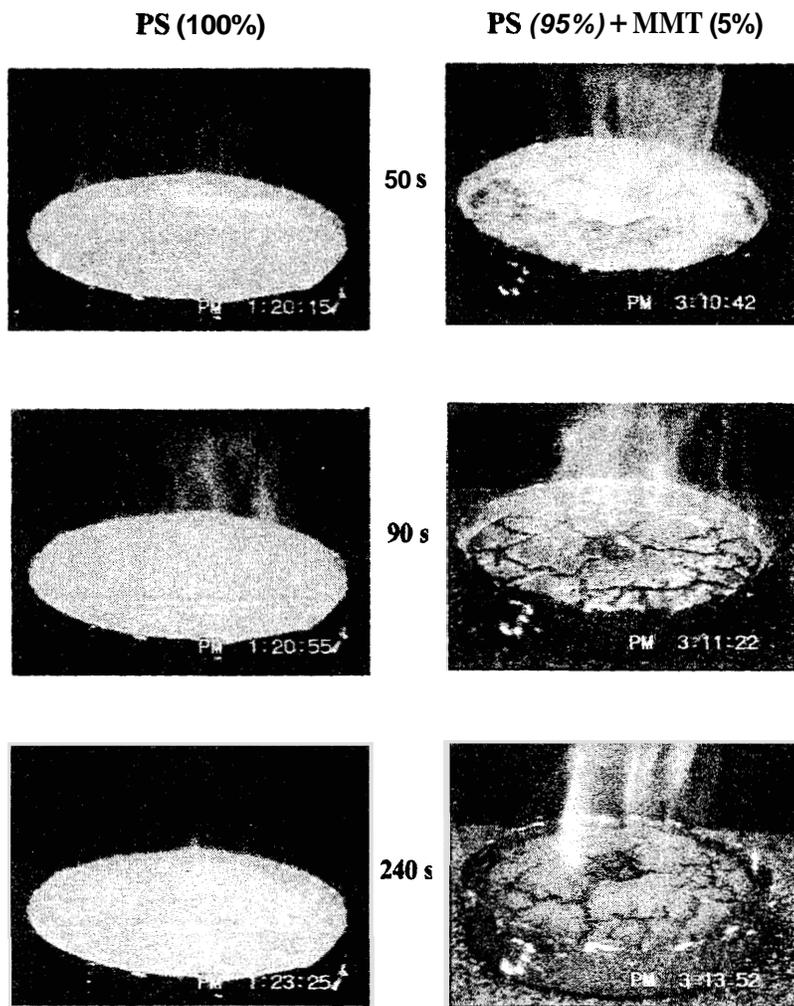


Figure 8. Digitized images from nitrogen gasification at a **flux** of 50 kW/m<sup>2</sup> of pure PS (low  $M_n$ ) and PS/5 % **AMMT** nanocomposite (low  $M_n$ ).

From the entirety of the data gathered during the first year of the consortium, we concluded that intercalated nanocomposites perform as well as delaminated nanocomposites. We were not able to determine if there is an effect of end-group tethering, due to the weak overall effect observed for the epoxy nanocomposites in general. We did not explore nanocomposites with different layered silicates (clays), *i.e.*, hectorite versus montmorillonite. We conclude that a small but significant effect on HRR may be due to the greater melt viscosity of the nanocomposites, but rheological measurements still need to be made to confirm this conclusion. In terms of the effect of loading level, the effectiveness of the nanocomposite approach to reducing HRR, in most cases, levels **off** at 5 % silicate loading. And finally, the use of a char-enhancer (PPO) did not decrease the flammability of the PA-6 nanocomposites, but other char-enhancing co-additives should be explored.

The most important aspect of the nanocomposite approach is the combined improvement in **both** flammability properties and physical properties. Nano-dispersed montmorillonite causes non-char forming polymers, such as polystyrene, to form char. The resulting residue is essentially a carbonaceous-silicate nanocomposite, where the clay enhances the insulating and

mass transport properties of the carbonaceous char and provides the flame retardant effect. A variety of issues remain to be addressed, some have been - in the second year of the consortium, however these results will not be for public release for one year; Other issues, such as processing stability, new characterization methods and new montmorillonite treatments, are being addressed within internal NIST programs [25].

## **NIST HIGH THROUGHPUT APPROACHES TO MATERIALS FLAMMABILITY RESEARCH**

A revolution in chemical knowledge discovery is underway. A paradigm shift from one-at-a-time experimentation to high throughput (HT) experimentation has already occurred in the pharmaceutical and chemical catalysis industries [26]. The time from inspiration to product launch has been cut from 20 years to 5 years [27]; this factor of *four* acceleration in time to market renders the old approaches nearly obsolete. Organizations that do not adopt these techniques will not be able to compete with those that do. HT methods allow R&D the opportunity to quantitatively explore multi-dimensional property space, conducting and characterizing thousands of experiments in as little as a day; it allows one to generate a data base of the results and build predictive models rapidly. Recently, we have initiated a program of research to develop HT methods for the formulation and flammability screening of multicomponent FR materials. We see the development and application of HT approaches as critical to the continued success of the FR industries. The purpose of this project is to promote communication and technology dissemination on HT methods and its applications to materials flammability research, to facilitate direct interactions, and the efficient transfer of this technology to US industry. A workshop was recently held at NIST and a research plan has been proposed to the prospective members. This proposal is summarized here.

The temperature of a hot object can be determined from the spectral characteristics of the radiant energy it emits. This information can be captured as a function of time and position using an imaging spectrometer. This capability to obtain temperature distributions,  $T(x,y,t)$ , from the analyses of infrared (IR) images may allow for high-throughput screening of materials flammability. In this project, experiments will be performed to determine the feasibility of using an IR camera to measure the temperatures of burning materials. The temperature measured at the underside of burning samples will be used as an indicator of flammability performance. The temperature at this location clearly depends on the thermal stability and insulating capacity of the material above it, including any char that forms on the surface of the sample. Since these properties correlate with flammability performance, we hypothesize that the most fire resistant materials will have the lowest temperatures.

The consortium project team will assemble, calibrate and demonstrate a prototype system consisting of a uniform radiant heat source and an IR camera capable of measuring the temperatures of burning polymer samples [Figure 9]. A test method for screening multiple samples for flammability performance will be developed and validated by correlating the

results with conventional measurements, such as cone calorimetry and UL-94. We anticipate that the technology developed in this project will be transferred to the participating members and provide them with a powerful tool for improving performance and reducing flammability of materials.

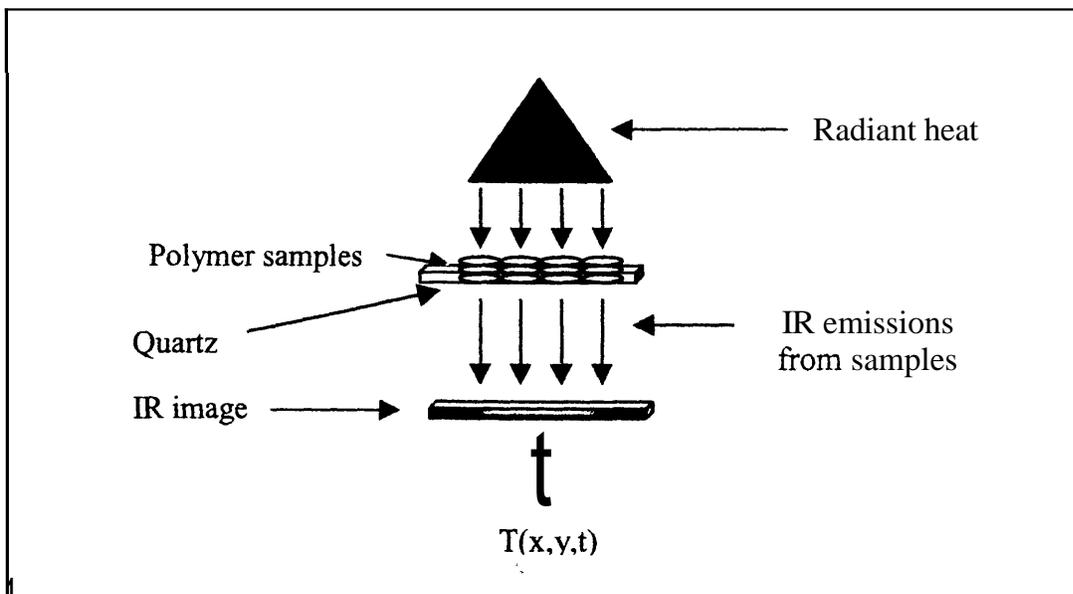


Figure 9. Schematic drawing of High Throughput flammability screening method.

## SUMMARY

A variety of new concepts, measurement tools, and FR approaches have been developed at NIST in partnership with the FRCA. The common theme which runs through each of the NIST programs is the focus on our mission: to provide measurement technology and science to help US industry compete in a cost effective, timely manner to the world markets. Future cooperation between FRCA and NIST must meet the challenges and opportunities posed by performance based codes, new flammability tests, requirements of new FR markets, and new materials.

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