

EFFECTS OF THE GENERIC NATURE OF POLYMERS ON THEIR FIRE BEHAVIOR

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ABSTRACT

Fire behavior of four aliphatic and two aromatic C, H, O, N, S, and Cl atom containing polymers has been examined. Experiments were performed in three ASTM E 2058 Fire Propagation Apparatuses. The differences in the ignition behavior of polymers were found to be mainly due to differences in the ignition temperature. Chemical effects appear to contribute about 25 % towards the ignition resistance of the polymers. For thermoplastics, formation of polymer melt and its burning as a pool fire was found to increase the fire intensity by factors of two to four. The combustion efficiency and generation efficiency of CO₂ were found to decrease and the generation efficiencies of CO and smoke were found to increase by changes in the generic nature of the polymers (aliphatic to aromatic to halogenated). About four times as much carbon atoms in the polymers converted to smoke than converted to CO. Large-scale fire propagation behavior of polymers was characterized by a Fire Propagation Index (**FPI**). The **FPI** values of melting type thermoplastics (showing rapid-fire propagation behavior) were high, whereas they were low for the engineered charring type and halogenated polymers (showing either slow or decelerating fire propagation behavior).

KEYWORDS: flammability, fire properties, ignition, combustion, and fire propagation

INTRODUCTION

Polymers are macromolecular organic materials manufactured by the modification of natural products or by synthesis from suitable intermediates. The number of basic polymers is large, the list is growing, and variations and modifications to these basic polymers, and co-polymers are quite large. Almost all the polymers consist of hydrogen, oxygen, nitrogen, sulfur, chlorine, fluorine, and silicone atoms bonded alone or in combination with other atoms to the polymer backbone of carbon atoms with different types of chemical bonding. Polymers can be predominantly crystalline, amorphous or a combination of both the natures. In predominantly crystalline polymers, chains are packed together more efficiently and tightly than in the amorphous polymers [1]. Polymers with higher crystallinity have higher thermal stability than amorphous polymers. All these differences are reflected in wide variations in the fire behavior of polymers.

In our study, we have attempted to examine the differences in the fire behavior of polymers because of variations in their generic nature and physical and chemical properties. Four aliphatic and two aromatic polymers with H, O, N, S, and Cl atoms bonded to the polymer backbone of C atoms were examined. Independent experiments

were performed in the three ASTM E 2058 Fire Propagation Apparatuses [2], one at INERIS, one at FM Global Research (FMR) and one at FM Approvals.

EXPERIMENTAL

POLYMERS USED IN THE STUDY

The following polymers were examined as sheets from original resins, without any additives, except those used for processing:

1. Polyoxymethylene, POM (aliphatic: C, H, O atoms, M_{mono} : 29 g/mole, melting type);
2. Poly(methylmethacrylate), PMMA (aliphatic: C, H, O atoms; M_{mono} : 100 g/mole, melting type);
3. Nylon 6,6 (aliphatic: C, H, O, N atoms; M_{mono} : 226 g/mole, melting type);
4. Poly(vinylchloride), PVC, rigid (aliphatic: C, H, Cl atoms; M_{mono} : 62 g/mole, charring type),
5. Polycarbonate, PC (aromatic: C, H, O atoms; M_{mono} : 238 g/mole, charring type);
6. Polysulfone, PSF (aromatic: C, H, O, S atoms; M_{mono} : 442 g/mole, charring type).

The measured elemental composition and net heat of complete combustion are listed in Table 1. The data indicate that the resins are relatively pure with negligible amounts of impurities or additives. Additional information on the polymer samples, data analysis and experimental facilities are described in Ref [3]. For the analysis of experimental results, these data along with the literature data listed in Table 2 were used.

Table 1: Measured Elemental Composition and Net Heat of Complete Combustion of Polymers

Polymer	Elemental Composition (% Weight)						ΔH_T MJ/kg
	C	H	O	N	S	Cl	
POM	41.40	6.91	51.40	0.15	< 0.04	< 0.02	15.7
PMMA	60.10	8.56	32.14	<0.1	<0.04	<0.02	24.8
Nylon 6,6	61.86	10.25	17.82	11.98	<0.02	<0.02	29.2
PVC (rigid)	38.90	4.77	4.33	< 0.1	0.36	49.00	19.3
PC	75.70	5.50	18.40	< 0.1	< 0.04	< 0.02	29.9
PSF	72.90	4.82	14.39	< 0.1	8.2	0.02	30.4

Table 2: Thermophysical Properties of Polymers from the Literature^a

Polymers	$k \times 10^3$ (kW/m-K)	$p \times 10^{-3}$ (kg/m ³)	c (kJ/kg-K)	$\Delta H_{\text{ch}}/\Delta H_{\text{g}}$ (MJ/MJ)
POM	0.28	1.42	1.46	6
PMMA	0.18	1.19	1.47	17
Nylon 6,6	0.23	1.14	1.70	12
PVC (rigid)	0.25	1.38	1.41	2
PC	0.21	1.20	1.17	7
PSF	0.28	1.24	1.30	5

a: data are taken from Refs. 1,4,5,6,7, 8 and 9.

APPARATUS, EXPERIMENTS, AND MEASUREMENTS

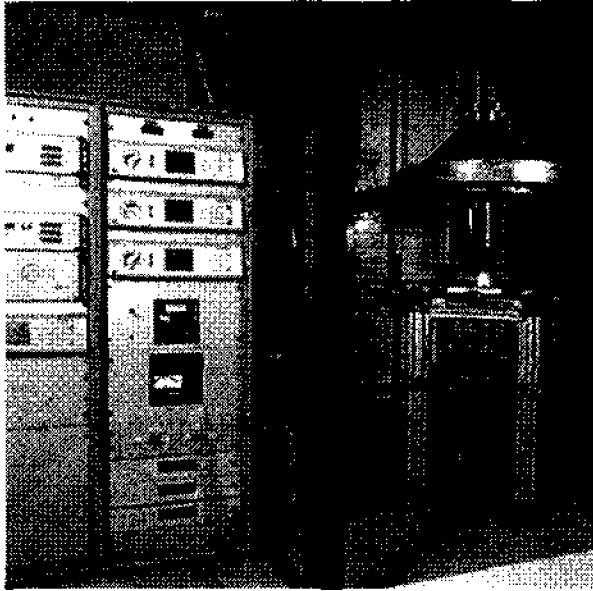


Figure 1. ASTM E 2058 Apparatus at INERIS [2]

One of the three ASTM E 2058 Fire Propagation Apparatuses used in this study is shown in Fig. 1. Three types of experiments were performed: 1) ignition, 2) combustion, and 3) fire propagation. For ignition and combustion experiments, 100-mm square and 10-mm thick horizontal sheets were used. The sample surface was painted black. For fire propagation experiments, 300-mm long, 100-mm wide and 10-mm thick vertical sheets were used. The sides and back of all the samples were tightly covered with ceramic paper and aluminum foil as described in the ASTM E 2058 standard. Cross wires across the surfaces were used for all the samples, because some of the samples expanded when exposed to external heat flux due to charring.

Ignition experiments were performed under quiescent normal airflow condition with a small pilot flame close to the surface. The entire sample surface was exposed to external heat flux in the range of 10 to 60 kW/m². Combustion experiments were performed under co-normal airflow rate of 158-mm/s (volumetric flow rate of 2.9 x 10⁻³ m³/s) with entire surface exposed to 50 kW/m² of external heat flux. The fire propagation experiments were performed in 40 % oxygen concentration in the co-air-oxygen mixture flowing at a rate of 158-mm/s (volumetric flow rate of 2.9 x 10⁻³ m³/s). Only the 120-mm bottom part of the sample was exposed to 50 kW/m² of external heat flux in the presence of a pilot flame in the fire propagation experiments.

In the ignition experiments, ignition-time was measured as a function of the external heat flux. In the combustion and fire propagation experiments, measurements were made for the release rates of polymers vapors, heat, and products.

IGNITION

In the experiments, ignition-time, defined as the appearance of a sustained flame, was measured visually by a stopwatch. The measured ignition-time at each flux from the three laboratories varied between 3 to 15 % of the average value for the non-charring and non-expanding POM, PMMA, and nylon and between 4 to 31% of the average value for the charring and expanding PC, PSF, and PVC. The variations were higher at lower heat fluxes than for heat fluxes > 30 kW/m², where the variations were only between 3 to 10% of the average value for all the polymers, a range used to obtain the ignition properties of the polymers.

The ignition-time and external heat flux relationship shown in Fig. 2 for POM is very similar for all the polymers and has been analyzed using the following well known relationship for thermally thick conditions [10]:

$$1/t_{ig}^{1/2} = (\dot{q}_e'' - \dot{q}_{cr}'') / (T_{ig} - T_a) \sqrt{k\rho c} \quad (1)$$

The term $(T_{ig} - T_a)\sqrt{k\rho c}$ is defined as the *Thermal Response Parameter (TRP)* of the polymer [8]. \dot{q}_{cr}'' is the minimum heat flux at or below there is no sustained ignition, which is about 10 kW/m² in Fig. 2. The TRP value is derived from the inverse of the slope in the range of $\dot{q}_e'' > 30$ kW/m². \dot{q}_{cr}'' and TRP values derived in this fashion are listed in Table 3.

The TRP values from the three laboratories vary between 6 to 11% of the average value. There is no variation in the \dot{q}_{cr}'' values. The values are lower for the aliphatic polymers compared to the aromatic and aliphatic halogenated polymers.

Data in Table 3 and for many polymers listed in the literature [1,4,5,6,7] show that the $\sqrt{k\rho c}$ component of TRP is approximately constant with an average value of 0.72 ± 19 %. The differences in the TRP values in Table 3 thus are mainly due to the differences in the T_{ig} values. This is supported by the estimated¹ $\sqrt{k\rho c}$ values also listed in Table 3, which are very similar to the calculated $\sqrt{k\rho c}$ values. The T_{ig} values of polymers depend on the chemical bond dissociation energies and generic nature of the polymer vapor in addition to thermal effects [9,11]. For ordinary polymers, $T_{ig} \ll T_v$ or decomposition temperature (T_d), which supports the influence of the bond dissociation energy on the ignition behavior [9,11]. For high temperature and highly halogenated advanced engineered polymers, $T_{ig} \gg T_v/T_d$ suggesting the influence of both bond dissociation energy as well as of the generic nature of the polymer vapors [9,11].

It is estimated that chemical factors contribute to some 25 % in the TRP value [9].

It is, therefore, necessary to account for factors such as energies associated with chemical bonds and chemical nature of the vapors in addition to thermal effects to describe the ignition behavior of polymers.

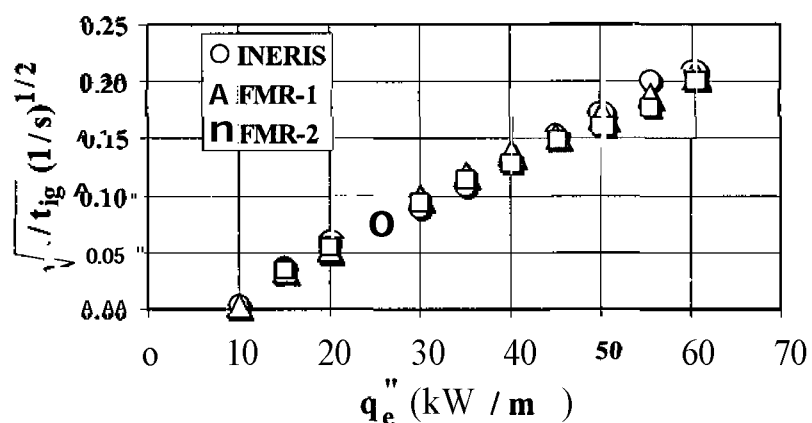


Figure 2. Ignition-time versus external heat flux (Eq. 1) from the ignition data for POM measured in the ASTM E 2058 apparatuses. FMR: FM Global Research.

¹ The $\sqrt{k\rho c}$ values of polymers were estimated from the expression: $\sqrt{k\rho c} = TRP / \{(\dot{q}_{cr}'')^{0.25} \times 364\} - 293$, where it is assumed that heat losses are mainly due to surface reradiation, polymer surface acts as a black body and the ambient temperature is 20 °C.

COMBUSTION

In the experiments, release rates of polymer vapors, heat, and fire products were determined². In the experiments at 50 kW/m², the 10-mm thick melting type polymers (POM, PMMA, and nylon) burned as liquid pool fires, whereas the 10-mm thick charring type polymers (PVC, PC, and PSF) burned as solid polymers. Thus, the data for POM, PMMA, and nylon are for the combustion of polymer melts whereas the data for PVC, PC, and PSF are for the combustion of solid polymers.

Table 3. Ignition Properties of Polymers

Polymer	Lab	TRP (kW-s ^{1/2} /m ²)	\dot{q}_{cr}'' (kW/m ²)	$(k\rho c)^{1/2}$ (kw-s ^{1/2} /m ² -K)	
				From Table 2	Estimated
POM (aliphatic C,H,O atoms)	INERIS	238	10	0.76	0.67
	FMR-1	286			0.81
	FMR-2	294			0.83
	Average	204 ± 11%		Average	0.77
PMMA (aliphatic C,H,O atoms)	INERIS	200	10	0.56	0.56
	FMR-1	196			0.55
	FMR-2	217			0.61
	Average	204 ± 6%		Average	0.58
Nylon 6,6 (aliphatic C,H,O,N atoms)	INERIS	263	15	0.67	0.62
	FMR-1	244			0.58
	FMR-2	278			0.66
	Average	262 ± 6 %		Average	0.62
PC (aromatic C,H,O atoms)	INERIS	323	25	0.54	0.62
	FMR-1	313			0.60
	Average	318		Average	0.61
PSF (aromatic C,H,O,S atoms)	INERIS	333	30	0.67	0.60
	FMR-1	357			0.64
	FMR-2	313			0.56
	Average	334 ± 7%		Average	0.60
PVC (aliphatic C,H,Cl atoms)	INERIS	333	15	0.70	0.79
	FMR-1	357			0.85
	FMR-2	385			0.91
	Average	358 ± 7%		Average	0.85

The polymer vapors, heat and product release rate profiles and steady state (maximum) values from the three laboratories were in excellent agreement, such as shown by the data in Fig. 3 for the heat release profiles for POM and by the steady state data in Table 4^{3,4}.

² For heat release rate from the Oxygen Consumption and Carbon Dioxide Generation Calorimetries, net heat of complete combustion per unit mass of oxygen consumed and CO and CO₂ generated were obtained from the data in Table 1.

³ *Combustion efficiency* (χ) is defined as the ratio of the chemical (actual) heat of combustion to the net heat of complete combustion [8].

Release Rates of Polymer Vapors, Heat, and Products

For the combustion experiments at $\dot{q}_e'' = 50 \text{ kW/m}^2$, the release rates of polymer vapors, heat, and products can be expressed as:

$$\dot{m}'' = (\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') / \Delta H_g \quad (2)$$

$$Q_{ch} = (\Delta H_{ch} / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') = \chi(\Delta H_T / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') \quad (3)$$

$$\dot{G}_j'' = (y_j / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') = f_j(\Psi_j / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_{rr}'') \quad (4)$$

In the combustion experiments, flames were completely lifted off the surface due to high release rate of polymer vapors. Under this condition, \dot{q}_f'' value can be assumed negligibly small and \dot{m}'' values can be predicted from $\Delta H_{ch}/\Delta H_g$ and \dot{q}_{rr}'' values. Assuming $\dot{q}_f'' = 0$, the predicted \dot{m}'' values for ordinary polymers are in the range of about 20 to $30 \times 10^{-3} \text{ kg/m}^2\text{-s}$ for $\dot{q}_e'' = 50 \text{ kW/m}^2$. The measured range of \dot{m}'' values in

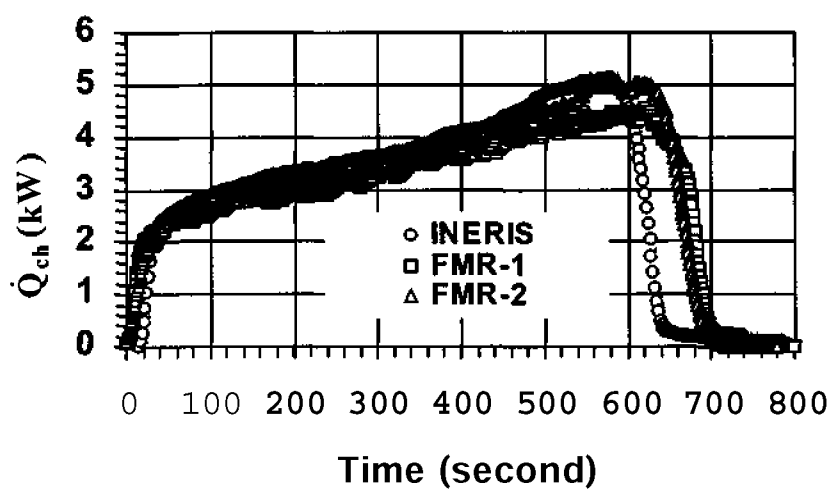


Figure 3. Heat release rate in the combustion of POM in normal air at 50 kW/m^2 in the ASTM E 2058 apparatuses.

Table 4 for the three charring type polymers (PVC, PC, and PSF) is similar to the predicted range. The measured range for \dot{m}'' values for melting type polymers (POM, PMMA, and nylon), however, is significantly higher than the predicted range for the solid polymers, but similar to that for the generic similar liquids. For example, the predicted \dot{m}'' values are $50, 55, 93 \times 10^{-3} \text{ kg/m}^2\text{-s}$ for methanol, hexadecane, and butanol respectively at 50 kW/m^2 [12].

The measured range of \dot{m}'' values for the melting type polymers (POM, PMMA, and nylon) are similar to the predicted \dot{m}'' range at 50 kW/m^2 for generically similar liquids. These observations suggest that formation, flow, and burning of polymer melt as liquid pool fires are critical stages in fires in thermoplastics (thickness $\leq 10\text{-mm}$ for $\dot{q}_e'' > 50 \text{ kW/m}^2$). The importance of these behaviors was also found critical in large-scale fires of 3 to 5-mm thick polymer parts of a minivan [13].

⁴ *Generation efficiency* (f_j) of a product is defined as the ratio of the yield of the product to its maximum possible stoichiometric yield based on its elemental composition [8]. For example for the calculation of the maximum possible stoichiometric yield of CO, it is assumed that in the combustion all the carbon atoms in the polymer are completely converted to only CO.

Combustion Efficiency and Generation Efficiency of Products

Data in Table 4 and Figs. 4 and 5 indicate that $\chi \ll f_{CO_2}$, that these two parameters are inversely proportional to f_{CO} and f_{sm} and that there is a linear relationship between f_{CO} and f_{sm} . The data also show that % and f_{CO_2} decrease and f_{CO} and f_{sm} increase as the generic nature of the polymers changes from aliphatic to aromatic to halogenated.

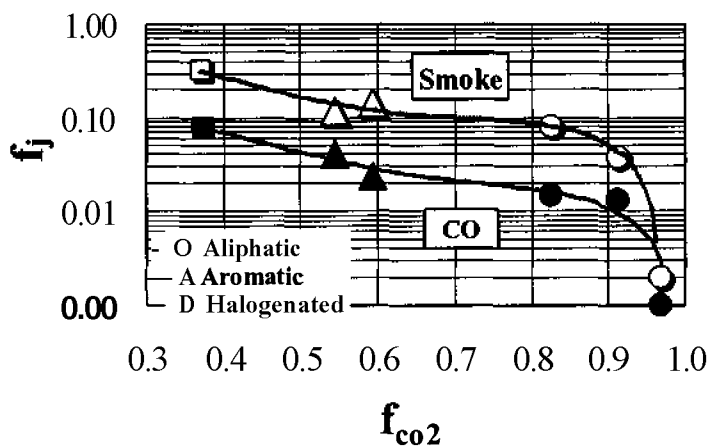


Figure 4. Generation efficiencies of CO and smoke versus CO_2 efficiency for the well-ventilated combustion of polymers.

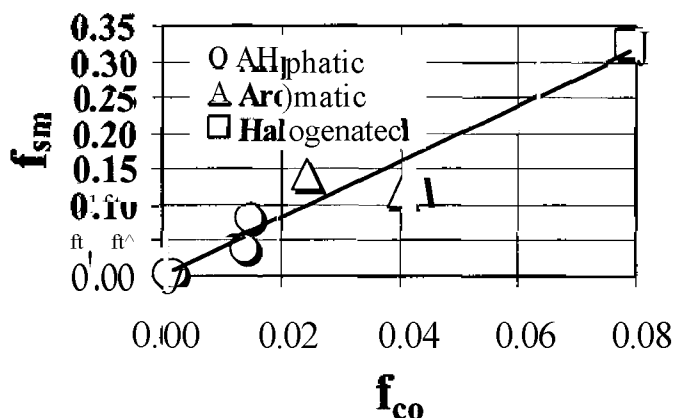


Figure 5. Generation efficiency of smoke versus CO efficiency for the well-ventilated combustion of polymers.

rapid for POM and PMMA, but was slow for PVC, PC, and PSF. Fire propagation experiments could not be performed for nylon 6,6 due to rapid melting. The heat and product release rate profiles during fire propagation, from the three laboratories, were in excellent agreement, as shown in Fig. 6 for PMMA.

For examining the upward fire propagation behavior of polymers, theoretical expression for the flame spread velocity [10,15] was utilized. With an assumption that the forward heat transfer from the leading edge of the flame is proportional to $(\dot{Q}/w)^n$, flame spread theories [15] suggest the following expression for the upward fire propagation velocity:

$$v^{1/2} \propto (\dot{Q}_r/w)^n / (T_{ig} - T_a)(k\rho c_p)^{1/2} \quad (5)$$

About four times as much carbon atoms are converted to smoke compared to the conversion to CO. Molecular weight of the monomer appears to have a stronger effect on the χ , f_{CO} , and f_{sm} values than the generic nature of the atoms in the structure. The implications of variations in the χ , f_{CO_2} , f_{CO} and f_{sm} values are reflected in the expressions for the release rates of heat and products in Eqs. 3 and 4.

FIRE PROPAGATION

Vertical fire propagation experiments were performed in 40 % oxygen concentration, with bottom 30 % of length exposed to 50 kW/m^2 in the presence of a pilot flame. The 40 % oxygen concentration simulates flame radiative heat flux transferred to the surface in large-scale fires [14]. The fire propagation experiments thus are simulation of large-scale upward fire propagation.

In the experiments release rates of heat and products during upward fire propagation and initial and final weight of the sample were measured. Fire propagation was very

Table 4. Release rates of Polymer Vapors and Heat, Heat of Combustion and Yields of Products in the Combustion of Polymers

Polymer	Lab	$\dot{m}'' \times 10^3$ kg/m ² -s	\dot{Q}_{ch}'' MW/m ²	ΔH_{ch} MJ/kg	Yield kg/kg		
					CO	CO ₂	Sm
POM aliphatic: C, H, O M= 29 g/mole	INERIS	52	0.75	15.1	0.002	1.46	0.001
	FMR-1	39	0.59	15.2	0.001	1.47	0.001
	FMR-2	43	0.66	15.4	0.001	1.49	0.001
	Average	44	0.67	15.2	0.001	1.47	0.001
	<i>Combustion Efficiency</i>			<i>0.97</i>			
	<i>Generation Efficiency</i>				<i>0.001</i>	<i>0.969</i>	<i>0.002</i>
PMMA aliphatic: C, H, O atoms M = 100 g/mole	INERIS	84	1.81 ^a	21.6 ^a	0.050 ^a	1.94 ^a	0.022 ^a
	FMR-1	80	1.83	23.0	0.012	2.02	0.030
	FMR-2	78	1.80	23.2	0.024	2.03	0.022
	Average	81	1.82	22.8	0.018	2.00	0.025
	<i>Combustion Efficiency</i>			<i>0.92</i>			
	<i>Generation Efficiency</i>				<i>0.013</i>	<i>0.912</i>	<i>0.038</i>
Nylon 6,6 aliphatic: C,H,O,N atoms M — 226 g/mole	INERIS	46	1.21	23.8	0.026	2.04	0.037
	FMR-1	56	1.53	24.0	0.017	2.06	0.058
	FMR-2	54	1.54	25.0	0.029	2.14	b
	Average	52	1.43	24.3	0.024	2.08	0.048
	<i>Combustion Efficiency</i>			<i>0.83</i>			
	<i>Generation Efficiency</i>				<i>0.015</i>	<i>0.825</i>	<i>0.080</i>
PVC aliphatic: C,H,C1 atoms M = 62 g/mole	INERIS	20	0.16	7.9	0.086	0.551	0.094
	FMR-1	21	0.17	8.2	0.071	0.570	0.128
	FMR-2	28	0.20	7.8	0.091	0.520	0.116
	Average	23	0.18	8.0	0.083	0.55	0.113
	<i>Combustion Efficiency</i>			<i>0.42</i>			
	<i>Generation Efficiency</i>				<i>0.079</i>	<i>0.372</i>	<i>0.323</i>
PC aromatic: C,H,O atoms M = 238 g/mole	INERIS	23	0.43	18.9	0.046	1.73	0.117
	FMR-1	31	0.51	17.1	0.032	1.57	0.146
	FMR-2	28	0.49	18.3	0.049	1.67	0.086
	Average	27	0.48	18.1	0.042	1.66	0.116
	<i>Combustion Efficiency</i>			<i>0.60</i>			
	<i>Generation Efficiency</i>				<i>0.024</i>	<i>0.594</i>	<i>0.142</i>
PSF aromatic: C,H,O,S atoms M = 442 g/mole	INERIS	20	0.44	17.2	0.045	1.59	0.098
	FMR-1	20	0.45	17.2	0.079	1.59	0.079
	FMR-2	22	0.39	16.5	0.085	1.52	0.085
	Average	21	0.43	17.0	0.070	1.57	0.087
	<i>Combustion Efficiency</i>			<i>0.56</i>			
	<i>Generation Efficiency</i>				<i>0.040</i>	<i>0.543</i>	<i>0.119</i>

a: slightly under-ventilated conditions due to extremely high burning rate at 50 kW/m². CO is unusually high and heat release rate, heat of combustion, and CO₂ and smoke yields are low; b: data not recorded properly.

Based on the correlation between small-scale and large-scale upward fire propagation experiments, Eq 5 is modified as follows [16,17]:

$$v^{1/2} * [(\chi_r / \chi_{ch}) \dot{Q}_{ch} / w]^{1/3} / (T_{ig} - T_a)(k\rho c_p)^{1/2} \quad (6)$$

Multiplying Eq. 6 by 1000 and assuming $\chi_r/\chi_{ch} \approx 0.42$, a *Fire Propagation Index (FPI)* has been defined to describe the large-scale vertical fire propagation behaviors of polymers based on small-scale test measurements [8,9,17]:

$$FPI = 1000 \left(\frac{(0.42 \dot{Q}_{ch} / w)^{1/3}}{(T_{ig} - T_a)(k\rho c_p)^{1/2}} \right) = 750 (Q_{ch} / w)^{1/3} / (T_{ig} - T_a)(k\rho c)^{1/2} \quad (7)$$

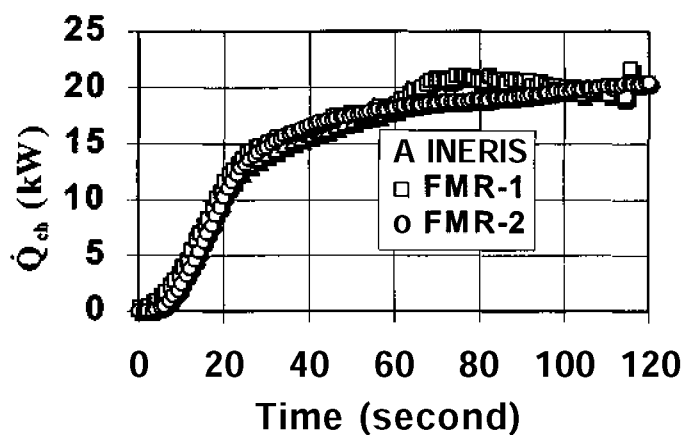


Figure 6. Heat release rate profile for the upward fire propagation at 40 % oxygen concentration for PMMA.

The \dot{Q}_{ch} values from the fire propagation experiments and the $(T_{ig} - T_a)\sqrt{k\rho c}$ values, defined as **TRP**, from the ignition experiments are used in Eq. 7 to calculate the **FPI** values. Based on the visual observations in small-scale and large-scale fire propagation experiments, the following behaviors have been observed [8,9, 16,17]:

- 1) For $FPI < 6$: flames are close to extinction conditions and fire propagation is limited to the ignition zone (area where surface is exposed to external heat flux in the presence of a pilot flame);
- 2) For $6 < FPI \leq 10$: fire propagation is decelerating and stops short of the sample length;
- 3) For $10 < FPI \leq 20$: there is fire propagation beyond the ignition zone;
- 4) For $FPI > 20$: fire propagation beyond the ignition zone is very rapid.

Excellent correlation has been found between the **FPI** values from the small-scale and large-scale tests [8,9,17]. The **FPI** concept thus has been adopted for the acceptance of polymers in the clean rooms of the semi-conductor industry by FM Approvals and Underwriters Laboratories (UL) [18,19], and for electrical cables and conveyor belts by FM Approvals [20,21]. Thus, we have also used the **FPI** concept in this study to describe the fire propagation behaviors of the selected polymers.

Since there is an excellent agreement between the three laboratories for the heat release rate profiles and **TRP** values, **FPI** values from the three laboratories also show excellent agreement as indicated in Fig. 7.

The **FPI** value of PMMA (23) suggest rapid propagation that is confirmed by the data from the large-scale parallel tests [9,17] and many large-scale vertical wall fires [22,23,24]. The **FPI** value for POM is 13 for which fire propagation was observed to be rapid. For char forming polymers (PC and PSF) and halogenated polymer (PVC), the

The **FPI** values were in the range of 6.9 to 8.4, for which fire propagation was observed to be either slow or decelerating. Thus, all the factors that influence the

variations in the ignition and combustion behaviors of polymers are also responsible for the differences in the fire propagation behavior.

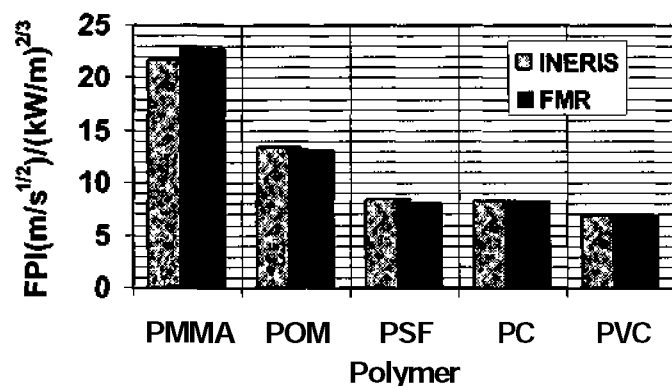


Figure 7. Fire Propagation Indices for Polymers.

SUMMARY

- 1) Under similar experimental conditions, differences in the ignition, combustion, and fire propagation behaviors of polymers are found to be influenced by the generic nature and molecular weight of the monomer;
- 2) Ignition temperature appears to be the main factor affecting differences in the ignition

behavior of polymers. The $\sqrt{k\rho c}$ values are weakly dependent on the generic nature of the polymers. About 25 % of the ignition resistance is due to differences in the generic nature of the polymers;

- 3) The combustion efficiency and generation efficiency of CO_2 decrease and the generation efficiencies of CO and smoke increase as the generic nature of polymers changes from aliphatic to aromatic to halogenated. The combustion efficiency and generation efficiencies of products are closely related. A direct linear relationship is found between the generation efficiencies of CO and smoke, whereas an inverse non-linear relationship is found between the generation efficiency of CO_2 and that of CO and smoke;
- 4) About four times of the carbon atoms in the polymer are converted to smoke than to CO ;
- 5) Generation rate of vapors for polymers that burn as solids is well predicted from the heat of gasification and surface reradiation loss at high external heat flux values where flame heat flux is negligibly small. The generation rate of vapors for polymers that burn as liquid pool fires however is under-predicted, suggesting that heat of gasification values for liquids rather than that of solid polymers need to be used.
- 6) Large-scale fire propagation behavior of polymers is well characterized by a Fire Propagation Index (FPI). Melting type ordinary thermoplastics have high FPI values and have been observed to have rapid-fire propagation. The FPI values for the engineered charring type and halogenated polymers are low and have been observed to have either slow or decelerating fire propagation beyond the ignition zone.

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NOMENCLATURE

- c Heat capacity (kJ/kg-K)
 f_j Generation efficiency of product j
 \dot{G}_j Generation rate of product j per unit polymer surface area ($\text{kg/m}^2\text{-s}$)

ΔH_i	Heat of combustion of the polymer (MJ/kg)
ΔH_g	Heat of gasification of the polymer (MJ/kg)
k	Thermal conductivity (W/m-K);
\dot{m}''	Release rate of polymer vapors per unit polymer surface area ($\text{kg/m}^2\text{-s}$)
M_{mono}	Molecular weight of the monomer (g/mole)
q''	Heat flux per unit polymer surface area (kW/m^2)
\dot{Q}_{ch}''	Chemical heat release rate per unit polymer surface area (kW/m^2)
t_{ig}	Ignition-time (s)
T	Temperature ($^{\circ}\text{C}$)
V	Upward fire propagation velocity (m/s)
W	Sample width (m)
y_j	Yield of product j (g/g)
<i>Greek</i>	
χ	Combustion efficiency
ρ	Density (kg/m^3)
<i>Subscripts</i>	
a	Ambient
ch	Chemical
cr	Critical
d	Decomposition
e	External
rr	Re-radiation
T	Total or Complete
V	Vaporization

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