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CHARACTERIZATION OF THE IGNITION BEHAVIOR OF POLYMERS COMMONLY USED IN THE AUTOMOTIVE INDUSTRY

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ABSTRACT

Ignition behavior of selected polymers, commonly used in the automotive industry, has been characterized by the maximum heat flux at which there is no ignition, defined as the *Critical Heat Flux, CHF,* and by a combination of thermo-physical properties, defined as the *Thermal Response Parameter (TRP)*. Polymers with high CHF and TRP values have high resistance to ignition.

The ignition temperatures of the polymers appear to be about 10 % higher than their decomposition temperatures. The TRP values calculated from the thermo-physical properties of the polymers (ignition temperature, density, heat capacity, and thermal conductivity) are about 33 % lower than the experimental TRP values obtained from the measured time-to-ignition at various external heat flux values. Inclusion of bond energies and chemical nature of vapors in the TRP formulation is suggested.

The CHF and TRP values of the selected polymers are comparable to the values for ordinary combustible materials, but are lower than the values for the highly thermally stable specialty polymers.

Key Words: polymers commonly used in the automotive industry, ignition resistance, thermal response, thermo-physical properties, thermally stable specialty polymers

INTRODUCTION

Several complementary research projects for studying different aspects of fires involving passenger vehicles and light trucks are being conducted at the General Motors (GM) R&D Center, at the Factory Mutual Research Corporation (FMRC), and at the National Institute of Standards and Technology (NIST). Large-scale vehicle bum tests for four types of vehicles (a passenger van, a utility sport vehicle, a front wheel drive vehicle, and a rear wheel drive vehicle) have been conducted. This paper presents the laboratory-scale experimental results on the ignition behavior of selected polymers, typical of parts of a 1996-model year passenger van. The selected polymers and

parts are listed in Table 1. The ignition behavior is characterized by the maximum heat flux at which there is no ignition, defined *as* the *Critical Heat Flux, CHF,* and by a combination of thermo-physical properties (ignition temperature, density, heat capacity, and thermal conductivity), defined as the *Thermal Response Parameter (TRP)*.

Ignition data from the laboratory-scale experiments combined with the data from the large-scale vehicle bum tests are found to be useful to assess the susceptibility of vehicles to post collision fires. In post collision fires, some of the polymer parts could be exposed to heat fluxes beyond the CHF values, if they are within or close to the path of a fire initiated external to the passenger compartment. There would be delayed involvement of polymer parts with higher CHF and TRP values (higher resistance to ignition).

EXPERIMENTAL

Compositions of the Selected Polymers

The compositions of most of the selected polymers were not known. Thus, a Nicole magnum-IR550 Fourier transform infrared spectrometer (FTIR) was used to identify the generic nature of the polymers and in some cases identify the type of additives used. The amounts of inorganic fillers used in the polymers were determined by thermal gravimetric analysis. Qualitative and semi-quantitative elemental analyses of the fillers were conducted by the X-ray fluorescence spectroscopy. In some instances, the filler types were identified from their crystalline structures (as determined by X-ray diffraction). The densities of the solid polymers were determined from the weights in air and in water. The measurement details and results are given in Ref. 1.

Decomposition Temperature

Thermal gravimetric analysis (TA-2 100 controller, TA Instruments, Inc) was utilized for the measurement of the polymer decomposition temperatures. A TA 2950 module operated in high-resolution mode where suppression of heating rate is automatically applied when degradation of the polymer proceeds at a fast rate. The heating rate was set at 50°C/minute, and the resolution factor was set at an intermediate value of 4. The sample was heated from room temperature to 980°C. The measurement details and results are given in Ref. 1.

Melting Point and Heat Capacity

Modulated Differential Scanning Calorimetry (TA 2920) was utilized for the measurement of these properties. Measurements were made in the temperature range of - 62°C to 270°C. Heating rate was set at 5°C/minute. The degree of modulation was set at ± 0.53 1°C, every 40 seconds. The measurement details and results are given in Ref. 1.

Critical Heat Flux and Thermal Response Parameter

CHF and TRP values were determined from the ignition data measured in the Flammability Apparatus, shown in Fig. 1. Rectangular (about 100 x 100-mm) or circular (about 99-mm in diameter) samples in horizontal configurations were used with thicknesses, d, listed in Table 1 in mm. Each sample was wrapped tightly by a 3-mm thick aluminum sheet, with edges covered by a 3-mm thick ceramic paper and placed inside a 3-mm thick aluminum dish. The sample was placed on top of a platform in the lower section of the Apparatus with sample surface coated black to reduce errors due to surface absorptivity differences. The ignition experiments were performed under natural airflow (no quartz tube). Heat flux to the top of the blackened surface of the sample was applied by four concentric, water and air-cooled, tungsten-quartz radiant heaters. A controller was used to apply power to the radiant heaters. A 10-mm long premixed ethylene-air pilot flame issuing from a 6-mm OD copper tube was used for igniting the vapor-air mixture
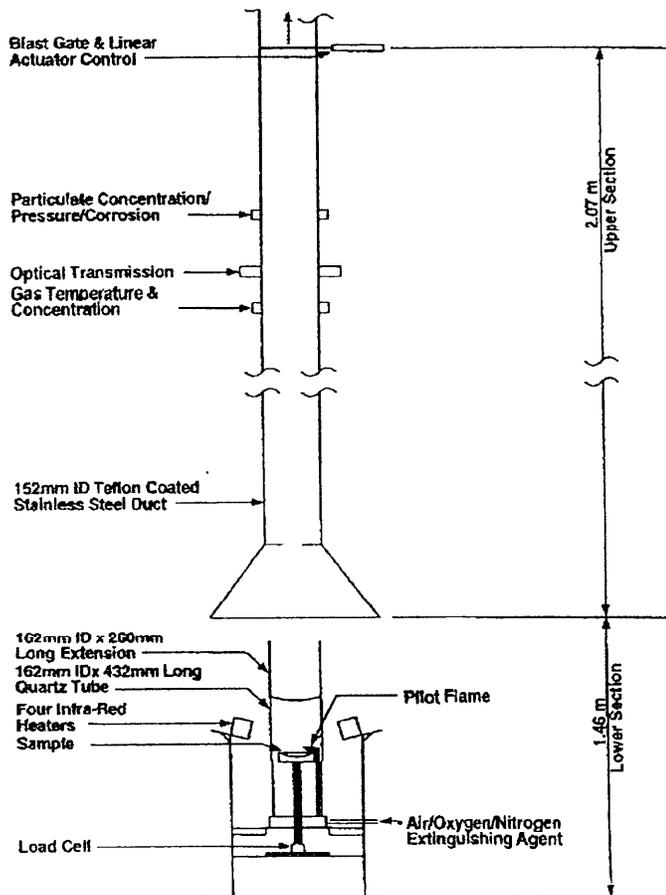
FIGURE 1. The Flammability Apparatus

In the experiments, times-to-ignition were measured at various external heat flux values in the range 10 to 60 kW/m². Measurement details and experimental data are given in Ref. 2.

RESULTS

Location of Parts in a Vehicle

Locations of various parts in a vehicle are shown in Fig. 2. The actual parts selected for the study are listed Table 1 (each part identified by vehicle access code {VAC} and component). The polymers used in manufacturing of the parts are also listed in table 1 along with their measured thermo-physical properties, i.e., thickness, d in mm; density, ρ in kg/m³; and heat capacity, c_p in kJ/kg-K and the values taken from the literature [3], i.e., thermal conductivity, k in kW/m-K. The calculated values of thermal diffusivity ($\alpha \approx k / \rho c_p$) are also listed in the table.

FRONT VIEW

Instrument
panel shelf

Air ducts

Hoodliner

Fender
Insulation

Firewall
insulation

Headlight
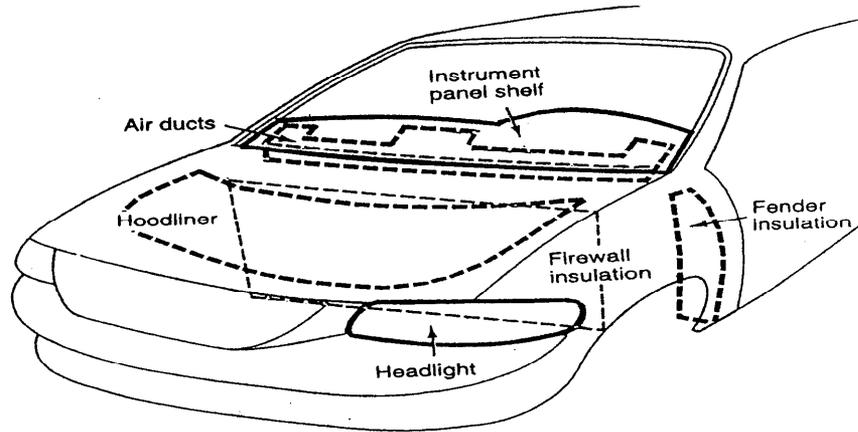
**TOP VIEW OF
ENGINE
COMPARTMENT**

Steering
column
boots

Grommet

Wire
harness
tube

HVAC unit

Windshield wiper tray

Hood to cowl
weatherstripping

Brakefluid
reservoir

Battery

Battery
casing

Resonator

SIDE VIEW

Headliner

Instrument
panel

Kick panel
insulation

Door lock contact

Wheel well
cover
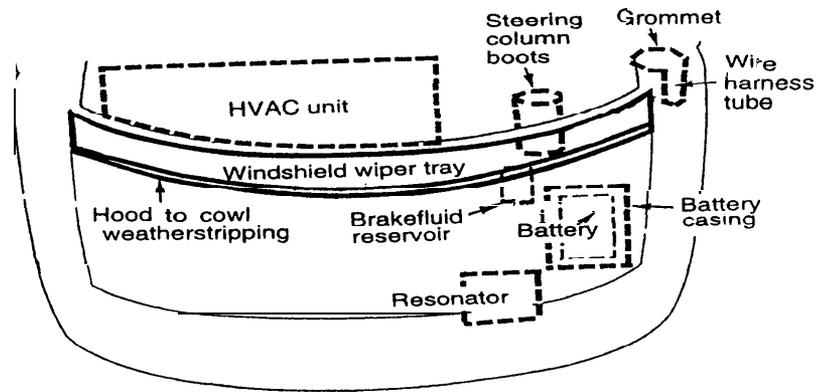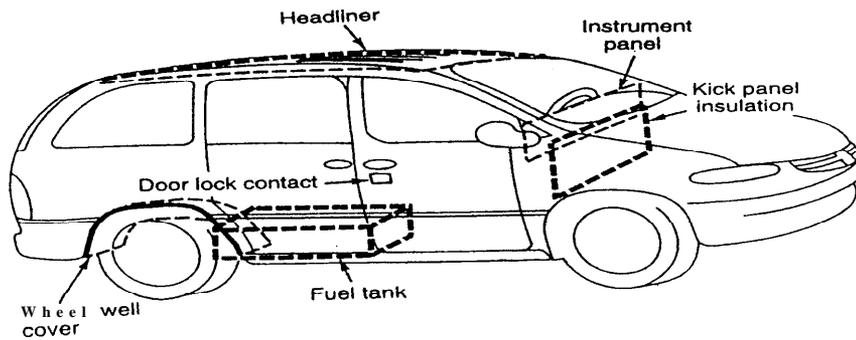
Fuel tank

Figure 2. Schematic Diagram showing Locations of Parts of a Passenger Vehicle.

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Table 1. Polymers Selected for the Study and Their Thermo-Physical Properties

VAC[a]	Component	Polymer[b]	d (mm)	$\rho \times 10^{-3}$ (kg/m³)	c_p (kJ/kg-K)	$k^c \times 10^3$ (kW/m-K)
201	Fuel tank	PE	6	0.94	2.147	0.42
208	Wheel well cover, fuel tank shield	PP	4	0.93	2.200	0.20
230	Battery cover	PP	5	0.90	2.216	0.20
256	Resonator structure	PP	5	1.06	2.082	0.20
611	Instrument panel shelf, main panel	PC	5	1.18	1.510	0.20
654	Instrument panel cover, exposed surface	PVC	5	1.20	1.374	0.21
676	HVAC unit, main housing, outer top	PP	5	NM	NM	0.20
732	Air ducts, large ducts	PP	5	1.04	1.934	0.20
743	Headliner, fabric-exposed surface	Nylon 6	13	0.12	2.192	0.24
788	Kick panel insulation backing	PVC	20	1.95	1.141	0.21
798	Headlight lens	PC	5	1.19	2.061	0.20
870	Hood liner face	PET	25	0.66	1.319	0.15
Ref	Polymethylmethacrylate	PMMA	25	1.19	2.090	0.27

a: Vehicle Access Code; **b**: PE: polyethylene; PP: polypropylene; PC: polycarbonate; PVC: poly (vinylchloride); PET: polyethyleneterephthalate; **c**: from Ref. 3; **Ref**: Reference polymer.

Ignition of Polymers

Under thermally thick experimental condition, the thermal penetration depth, δ, of a polymer sample is less than the actual thickness (**d**) of the sample, where $\delta \approx \sqrt{\alpha \, t}$ and t is the heat exposure time in seconds [4,5,6]. In this study, polymer sample thicknesses were selected such that the samples would satisfy the thermally thick conditions in the ignition experiments. Table 2 lists the values of **d** and δ for the polymer samples, where the values of δ is calculated from a and time-to-ignition (t_{ig}) measured in the experiment.

Data in Table 2 indicate that polymer samples with thickness ranges of 4 to 25-mm satisfy the thermally thick condition for external heat flux ≥ 30 kW/m². These samples are expected to satisfy the following relationship for the thermally thick condition [4,5,6], assuming that their behavior is similar to that of homogenous and inert materials and that temperature has a weak influence on the following combination of their thermo-physical properties

$$\sqrt{1/t_{ig}} = (\dot{q}_e'' - \dot{q}_{cr}'') / \Delta T_{ig} \sqrt{(\pi/4)(k \rho c_p)} \tag{1}$$

here $\dot{q}_e^{"}$ is the external heat flux (kW/m²), $\dot{q}_{cr}^{"}$ is CHF (kW/m²), and ΔT_{ig} is the ignition temperature above ambient (K). $\Delta T_{ig} \sqrt{(\pi/4)(k\rho c_p)}$ is used as the TRP formulation with units of kW-s$^{1/2}$/m².

Table 2. Thickness, Thermal Diffusivity, and Thermal Penetration Depth of Polymers

VAC[a]	Plastic	d (mm)	α (mm/s)	Calculated δ (mm) at Various External Heat Flux Values (kW/m²)									
				10	15	20	25	30	40	45	50	55	60
201	PE	6	0.21			7		5	4	4	3	3	3
208	PP	4	0.10			4		3	2		2		1
230	PP	5	0.10			5		3	2		2		2
256	PP	5	0.09		8	5		3	2		2		1
611	PC	5	0.11					4	3		2		2
654	PVC	5	0.13	10	4	3		2	2		2		1
676	PP	25	1.9			20		5	3		2		2
743	Nylon 6	13	0.91				7	6	4		3		3
788	PVC	20	0.09		4	3		2	2		1		1
798	PC	5	0.08					4	3		3		2
870	PET	25	0.17		4	3		1	1	1	1	1	1

Fig. 3 shows a plot for the ignition data of **polyethyleneterephthalate** (PET) as an example, where inverse of the square root of time-to-ignition is plotted against the net heat flux. PET data in Fig. 3 satisfy Eq.1 and thus inverse of the slope of the line is the TRP value.

The CHF value of 10 ± 1 kW/m² for PET is included in Fig 3 is related to heat losses due to convection and surface re-radiation. If one assumes that: 1) blackened polymer surface in the ignition experiment in the Flammability Apparatus behaves as a black body and 2) heat losses are mainly due to surface re-radiation, then CHF can be expressed as:
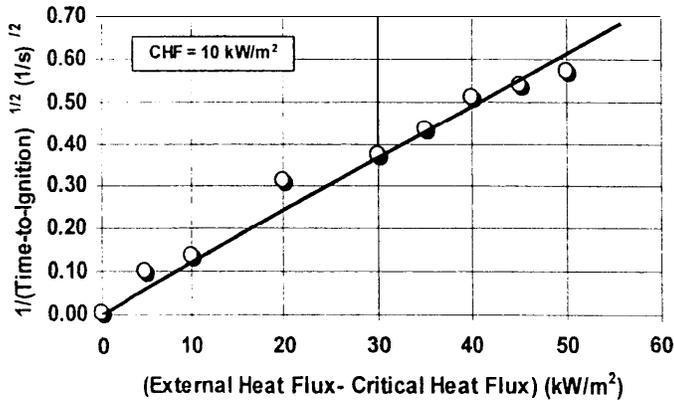
FIGURE 3. Time-to-Ignition Versus Net Heat Flux for Polyethyleneterephthalate, VAC 870

$$\dot{q}_{cr}^{"} \approx \sigma T_{ig}^4 \tag{2}$$

here, σ is the Boltzmann radiation constant (56.7 x 10^{-12} kW/m²-K⁴). For PMMA, used as a reference polymer, T_{ig} = 65 1 K [6]; decomposition temperature, T_d = 658 K [7]; CHF = 10 ± 1 kW/m² ($T_{ig} \approx$ 655 K from Eq. 2) [7]; TRP (calculated) = 259 kW-s$^{1/2}$/m²; TRP (experimental) = 274 kWs$^{1/2}$/m²,

which is 6 % higher than the calculated value; and TRP (experimental) = 296 $kWs^{1/2}/m^2$ from the literature data for time-to-ignition versus external heat flux [4], which is 12 % higher than the calculated value. It thus appears that the affect of temperature on the combination of physical properties for TRP formulation is self-compensating and convective cooling plays a minor role in ignition experiments in the Flammability Apparatus.

For PET, CHF = 10 kW/m^2, Tig ≈ 374 °C (from Eq. 2), T_d = 325 °C, TRP (experimental) = 174 $kWs^{1/2}/m^2$ (from the inverse of the slope in Fig 3) and TRP (calculated) = 113 $kW-s^{1/2}/m^2$ (from the thermo-physical properties in Table 1). These values are listed in Table 3. The values of T_{ig}, TRP (experimental) and TRP (calculated) for other selected polymers, obtained in a similar fashion, are also listed in Table 3. In the calculations a value of 20 °C was used for the ambient temperature. Measured values for percent inert and melting (T_m) and decomposition (T_d) temperatures are also listed in Table 3

Table 3. Thermal and Ignition Properties of Selected Polymers

VAC	Polymer	% Inert	CHF	Temperature (°C)			TRP(kW-s $^{1/2}$/m^2)^a	
				T_m (°C)	T_d (°C)	T_{ig}(°C)	Exp	Cal
201	PE	0.0	15	128	440	443	454	345
208	PP	2.2	15	166	429	443	288	240
230	PP	0.2	15	164	423	443	323	237
256	PP	20.4	15	164	430	443	277	208
611	PC	0.2	20	Amorphous	440	497	357	252
654	PVC	8.0	10	Amorphous	269	357	263	176
676	PP	N-M	15	Amorphous	NM	443	310	NM
732	PP	18.8	15	166	430	443	333	238
743	Nylon 6	1.4	20	221	497	497	154	106
788	PVC	52.9	10	Amorphous	255	374	215	214
798	PC	0.2	20	Amorphous	445	497	434	296
870	PET	1.3	10	245	325	374	174	113
Ref	PMMA	0.0	10	Amorphous	330	378	274	259

a: exp: experimental, cal: calculated; **NM:** not measured.

The calculated TRP values in Table 3 are about 33 % lower than the experimental values. The melting temperatures are about 56 % lower than the decomposition temperatures. The estimated ignition temperatures are about 10 % higher than the decomposition temperatures. Relationships between the melting, decomposition, and ignition temperatures are expected, as they are associated with the thermal stability of the polymers.

DISCUSSION

TRP consists of two components: 1) ignition temperature above ambient (ΔT_{ig}) and 2) combination of then-no-physical properties $[(\pi/4)(k\rho c_p)]^{1/2}$. The differences in the TRP values of the polymers thus could be due to differences in their thermal stability (ignition temperature and indirectly on the melting and decomposition temperatures) and/or due to differences in the thermo-physical properties.

In general, differences in the ΔT_{ig} values are associated with the differences in the generic nature of the polymers (bond dissociation energies), whereas the differences in the thermo-physical properties are associated with the differences in the nature of the fillers and variations of the properties with the temperature.

Ignition Temperature Differences

A thermally stable polymer has a high softening/melting temperature, high decomposition temperature, high bond dissociation energy, and high ignition temperature. Differences due to cyclic structures, crosslinking, ratio of branched to linear structures, and copolymerization are some of the factors for differences in the thermal stabilities of the polymers [3]. For example, there is a significant difference between the thermal stability of polyethylene, PE (CH_2-CH_2) and poly (tetrafluoroethylene), PTFE (CF_2-CF_2), due to strong C-F bonds. This difference between the thermal stability of PE and PTFE is reflected in the CHF values or the ignition temperatures of the two polymers listed in Table 3 and Table 4 respectively.

Differences in the CHF values or the ignition temperatures of the polymers examined in this study (Table 3) and of the specialty polymers (Table 4) indicate the differences in the thermal stability of these polymers. For the polymers examined in the study, the CHF values are in the range of 10 to 20 kW/m^2 (ignition temperature from 357 to 497 °C), whereas they are in the range of 25 to 50 kW/m^2 (ignition temperature range from 540 to 700 °C) for the specialty polymers. Although the polymers examined in this study and the specialty polymers differ significantly in their thermal stability, their combined thermo-physical properties in the TRP formulation are similar ($[(\pi/4)(k\rho c_p)]^{1/2}$ = 0.610 ± 0.19 and 0.570 ± 0.18 kW-s$^{1/2}$/m^2-K respectively). The TRP values for the polymers selected for the study (Table 3) and for the specialty polymers (Table 4), however, are significantly different, because of the differences in the ignition temperatures.

Thermo-Physical Property

Inorganic and organic materials as polymer fillers affect the thermo-physical properties and the TRP values, but have minor affect on the CHF or ΔT_{ig} values. The $[(\pi/4)(k\rho c_p)]^{1/2}$ values calculated from the thermo-physical properties for various polymers with varying types of fillers are listed in Table 5.

Table 4. Thermal and Ignition Properties of Specialty Polymers'

Polymer	Composition	CHF	T_{ig}	ρ x 10^{-3}	k x 10^3	c_p	TRP	
							Exp	Cal
Teflon®, PTFE	CF_2 50	700		2.18	0.25	1.0	654	444
Teflon@, FEP	$CF_{1.8}$ 50	700		2.15	0.25	1.2	680	484
Tefzel®, ETFE	CHF 25	540		1.70	0.23	0.9	481	273
Kel-F®, PCTFE	$CF_{1.5}Cl_{0.5}$ 30	580		2.11	0.22	0.9	460	321
Halar®, ECTFE	$CHF_{0.75}Cl_{0.25}$	38	613	1.69	0.15	1.0	450	265
Polysulfone	$CH_{0.81}O_{0.15}S_{0.04}$	30	580	1.24	0.28	1.3	469	333
PEEK	$CH_{0.62}O_{0.08}$	30	580	1.32	0.25	1.8	550	382
PVDF	CHF 40	643		1.70	0.13	1.3	506	296
PC	$CH_{0.88}O_{0.13}$ 30	580		1.20	0.21	1.2	455	273
Ultem®, PEI	$CH_{0.68}O_{0.14}N_{0.05}$ 25	540		1.27	0.22	1.4	435	288
CPVC	CHCl 40	643		1.50	0.22	0.9	435	301

a: from Refs. 3, 8, 9. Same units as in Table 1.

Table 5.Thermo-Physical Properties of Polymers With and Without the Fillers"

Polymer	Filler (%)	ρ x 10^{-3}	k x 10^3	c	$[(\pi/4)(k\rho c_p)]^{1/2}$
Polyester	0	1.13	0.29	1.7	0.66
	Glass (18-36)	1.48- 1.73	0.29	1.1-1.3	0.61-0.69
	0	1.13	0.23	1.7	0.59
Nylon6	Glass (33) 1.38		0.21	1.3	0.54
	Graphite (30)	NA	1.0	NA	NA
	0 1.1-1.4 0.17-0.2 1		1.1		0.40-0.50
Epoxy	Silica	1.6-2.0	0.42-0.82	0.84-1.1	0.58-1.28
	Aluminum	1.4-1.8	0.63-1.05	0.90-1.1	0.79-1.28
Polyphenylene	0	NA	0.29	NA	NA
Sulfide (PPS)	Graphite (30)	NA	0.28-0.75	NA	NA
	Glass (40)	NA	0.29	NA	NA
	0	NA	0.17-0.22	NA	NA
Polypropylene	Talc (40)	NA	0.32	NA	NA
(PP)	$CaCO_3$(40)	NA	0.29	NA	NA
	Glass (40)	NA	0.37	NA	NA
PTFE	0	NA	0.25	NA	NA
	Glass (25)	NA	0.33-0.41	NA	NA

a: from Ref. 3, 8,9. Units same as in Table 1. NA: not available,

The data in Table 5 indicate that the major affect of the filler type on $[(\pi/4)(k\rho c_p)]^{1/2}$ value appears to be due to increase in the density and in thermal conductivity. Silica and aluminum appear to have more affect on the k value rather than on the density. Nylon-filled with graphite also has a high k value. For fiber reinforced polyester, affect of k value on $[(\pi/4)(k\rho c_p)]^{1/2}$ is apparent from the data in Fig.' 4. For the same amounts of graphite, glass and kevlar fibers filled polyester, the TRP values increase with increase in the k value of the filler (k [graphite] >> k [glass] >> k [kevlar®]) (Handbook of Chemistry and Physics, 59th Edition, 1978-79).

Polymers with low k value fillers have little affect on the TRP values (PVC#788 52.9%; PP #256, 20.4%, and PP#732, 18.8 % (Table 3). The densities of these polymers are 1.95, 1.06, and 1.04 g/cm^3 respectively compared to the densities close to 0.9 for the unfilled polymers.
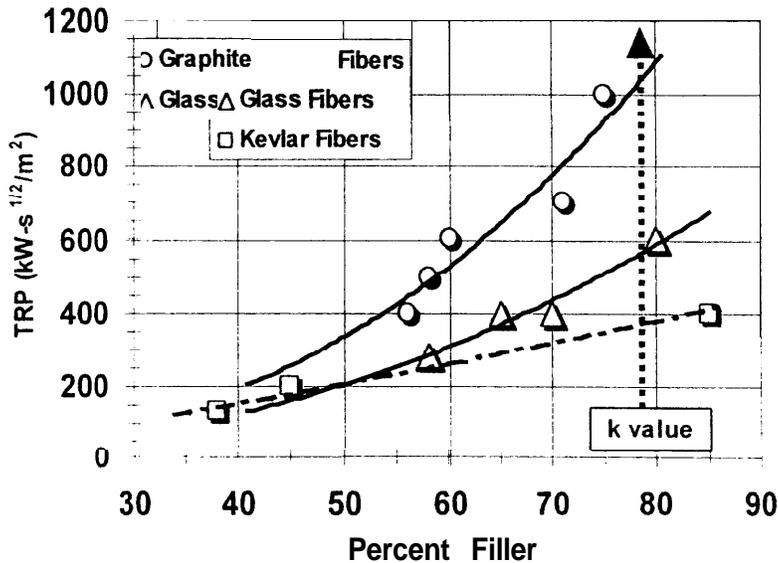
FIGURE 4. Experimental TRP Values for Fiber Reinforced Polyester

Experimental and Calculated TRP Values

The experimental and calculated TRP values from Tables 3 and 4 are plotted in Fig. 5. The calculated TRP values are 33 % lower than the experimental TRP values, suggesting that all the important factors have not been considered in the TRP formulation. The discrepancy between the calculated and experimental TRP values could be due to the reason that only T_{ig} value is used to account for the energies associated with chemical bonds that need to be broken and there is no accountability of the chemical nature of the vapors on ignition. The discrepancy between the experimental and calculated

FIGURE 5. Experimental Versus the Calculated TRP Values

TRP could also be due to the affect of temperature on the combination of thermo-physical properties in the TRP formulation, although the ignition data and then-no-physical properties of PMMA, used as the reference polymer, appear to indicate a minor effect.

SUMMARY

1) Time-to-ignition versus external heat flux relationship has been applied to examine the ignition behavior of selected polymers commonly used in the automotive industry;

2) The ignition behavior is examined on the basis of: a) maximum heat flux at which there is no ignition, defined *as* the *Critical Heat Flux (CHF)*, and b) combination of them-lo-physical properties (ignition temperature, density, heat capacity, and thermal conductivity), defined as the *Thermal Response Parameter (TRP)*.

3) In the CHF and TRP formulations, it is assumed that thermally thick conditions are applicable for sample sizes and experimental conditions used. It is also assumed that polymers behave as homogeneous and inert materials in the preignition period, the combination of thermo-physical properties in the TRP formulation are independent of temperature, and that heat losses by convective cooling is negligibly small compared to the surface re-radiation loss. The ignition data for the reference polymer, polymethylmethacrylate, suggest that these assumptions appear to be reasonable.

4) Higher CHF and TRP values enhance the resistance to ignition of a polymer. The CHF and TRP values of the polymers examined in the study are comparable to the values for the ordinary combustible materials but are significantly lower than the values for some thermally stable specialty polymers;

5) The TRP values calculated from the thermo-physical properties are about 33 % lower than the experimental TRP values, suggesting a need to account for factors such as energies associated with chemical bonds, affect of the chemical nature of the vapors on the ignition process and the affect of temperature on the combination of the thermo-physical properties in the TRP formulation;

6) The TRP values of the polymers are found to depend on thermal stability (expressed by the ignition temperature) and on the thermo-physical properties, especially thermal conductivity, although the affect of density could not be ruled out.

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